ELISABETH MANN BORGESE - Berichte

MnION cruise

Cruise No. EMB276

17.09.2021 – 29.09.2021
Rostock (Germany) Rostock (Germany)

Maren Voss, Christian Burmeister, Keji Cheng, Kaja Gentsch, Colleen Hansel, Vera Hübner, Anne Köhler, Martin Kolbe, Chad Ostrander, William Pardise, Heide Schulz-Vogt, Lina Taenzer,

Chief Scientist: Maren Voss

Leibniz Institute for Baltic Sea Research, Warnemünde, IOW
2021

Table of Contents

1 Cruise Summary

1.1 Summary in English

During EMB276 cruise the biogeochemistry of the water column with special focus on the redox zone was investigated at a total of seven stations in the eastern Gotland Sea and the Faroe Deep. For this purpose, profiles were made with the CTD and the pump CTD and samples were taken for trace metals, manganese, iodine, oxygen and nitrogen. A novel system to measure reactive oxygen was integrated into the CTD on board and tested for the first time in the suboxic and anoxic regions of the water column. Successful high-resolution nutrient and sensor profiles were recorded with the pump CTD. These data will allow for the first time new insights into the coupling of Mn with other elemental cycles such as nitrogen, sulfur and trace metals.

1.2 Zusammenfassung

Während EMB276 Reise würde an insgesamt sieben Stationen die Biogeochemie der Wassersäule mit besonderem Fokus auf die Redoxzone untersucht in der östlichen Gotlandsee und dem Farötief. Hierzu wurden Profile mit der CTD und der Pump CTD gemacht und Proben für Spurenmetalle, Mangan, Jod, Sauerstoff und Stickstoff genommen. Ein neuartiges System zu Messung reaktiven Sauerstoffs würde in die CTD an Bord integriert und das erste Mal in der suboxischen und anoxischen Bereich der Wassersäule getestet. Erfolgreich wurden hochaufgelöste Nährstoff und Sensorprofile mit der Pump CTD aufgenommen. Diese Daten werden es erstmals neue Einblicke in die Kopplung von Mn mit anderen Elementkreisläufen wie Stickstoff, Schwefel und Spurenmetallen erlauben.

2 Participants

2.1 Principal Investigators

Name	Institution
Voss, Maren, Prof.	IOW
Schulz-Vogt, Heide, Prof.	IOW
Hansell, Colleen, Prof.	WHOI

2.2 Scientific Party

Name	Discipline	Institution
Christian Burmeister	Biological Oceanography	IOW
Keyi Cheng	Geochemistry	Univ. Mich.
Kaja Gentsch	Biological Oceanography	IOW
Vera Hübner	Technician	MPI-Bremen
Anne Koehler	Marine Geology	IOW
Martin Kolbe	Physical Oceanography	IOW
Chadlin Miles Ostrander	Geochemistry	WHOI

William Pardis	Engineer	WHOI
Heide Schulz-Vogt	Biological Oceanography	IOW
Lina Taenzer	Geochemistry	WHOI
Maren Voss	Biological Oceanography	IOW
Colleen Hansel Wankel	Geochemistry	WHOI

2.3 Participating Institutions

IOW	Leibniz Institute for Baltic Sea Research, Germany
MPI-Bremen	Max Planck Institute for Marine Microbiology, Bremen
WHOI	Woods Hole Oceanographic Institution, USA
Univ. Mich.	Michigan State University, USA

3 Research Program

3.1 Description of the Work Area

The Gotland Basin located in the central Baltic Sea is the largest deep Basin with a maximum depth of 248meters (Fig. 3.1). Since numerous rivers enter the Baltic Sea from the east and south the surface salinity is only between 7-8psu. The surface waters are usually well mixed and warm so that they become separated from below by a thermocline below which cold and oxic winter water is found. At depth however, higher salinities of up to 12psu are typically found and reflect the inflow of saline water from the North Sea that became diluted on its way with brackish water. A pronounced interface between the winter water and the anoxic bottom water is therefore observed around 80-100 experiencing euxinic conditions towards the bottom. The interface is characterized by interleaving waters causing highly variable oxygen concentrations in a 10 to 20 m thick layer (Fig. 5.1). Other Basins like the Farö Deep (Fig. 5.2) or the Landsort slightly differ such that the water seems to be more stagnant experiencing less interleaving. Nutrients in surface waters are high in spring but during autumn mostly still at detection limit while regeneration of sinking particles in the cold water layer leads to increasing nitrate and phosphate concentrations. Nitrate in particular is decreasing rapidly where it is used as electron acceptor in suboxic waters and usually not detectable in euxinic waters where ammonium increases continuously towards the bottom.

.

3.2 Aims of the Cruise

The overall goal of the research program is to define the distribution and underlying redox cycling pathways that govern the speciation of Mn, and to identify the subsequent coupling of Mn with the cycling of oxygen, iodine, and nitrogen. We want to interrogate the cycling of Mn within the Baltic Sea and predict that reactive Mn, as Mn(III)-L and Mn oxide particles, is a primary control on the redox landscape of Mn-rich stratified waters, particularly at redox boundaries and within the suboxic zone. Recent methodological and technological advances now allow for unprecedented potential in characterizing the composition of Mn within solution and particles via high sensitivity spectrophotometric methods and synchrotron-based spectroscopy, respectively. Combining these advances with new sensors for measuring ROS *in situ* and natural abundance and tracer-level isotopic analyses will provide new windows into the coupling of Mn with other elemental cycles like nitrogen, sulfur and trace metals.

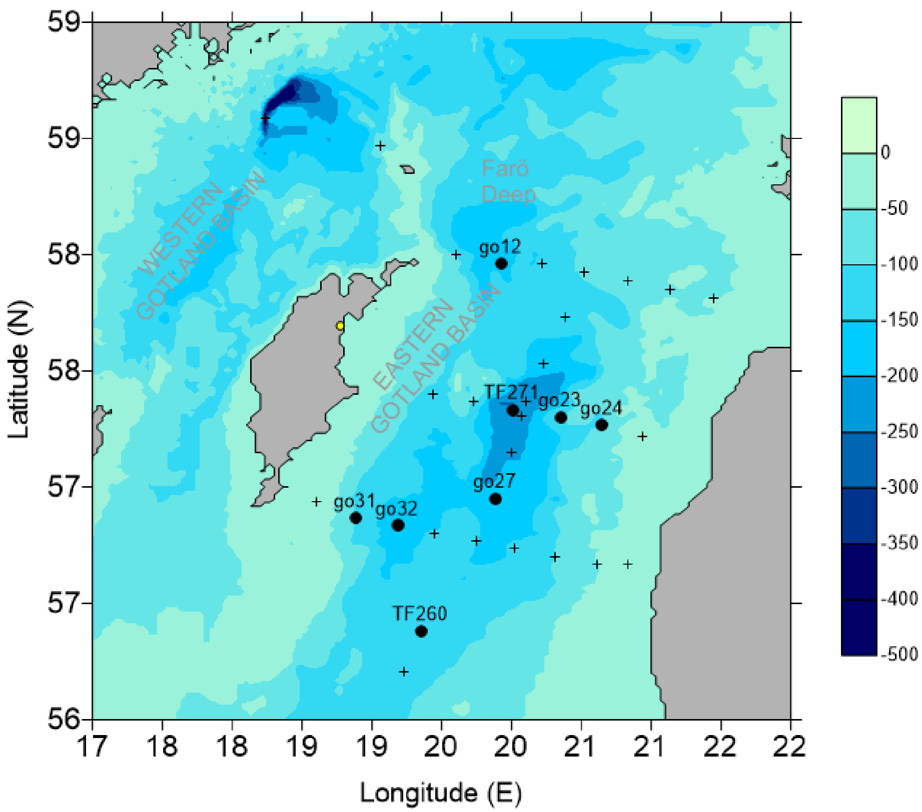

Fig. 3.1 Station map showing the entire station grid as suggested in the application (+) and the stations that were actually accomplished during the cruise (•). The yellow dot shows Slite on Gotland.

3.3 Agenda of the Cruise

Like in the ship time proposal we divided our work for this first research cruise to the Baltic Sea into two major task.

Task 1: At all stations we will delineate overall geochemical structure of the redoxcline by determining profiles of ROS, Mn, I and N. A standard rosette will first be deployed to determine the temperature, dissolved oxygen, and salinity profiles via the CTD package. A microsensor array provided and operated by collaborator de Beer (MPI) and Heide Schulz-Vogt (IOW) will also be deployed to collect data on pH, H_2S, N_2O, H_2, H_2O_2, redox, and a high sensitivity O_2 STOX sensor for low level O_2 detection (~1 nM).

The CTD and microsensor data will provide the overall geochemical structure of the redoxcline. Considering the dynamic conditions within the Baltic Sea, the depth and magnitude of the suboxic zone can vary spatially and temporally (see (Dellwig et al., 2012; Dellwig et al., 2018). The Mn, I, and N profile will be defined by collecting water at 8-10 depths spanning redox boundaries through the redoxcline, including the oxic, suboxic, and anoxic zones, defined by the CTD and microsensor data. Water will be analyzed for dissolved Mn speciation (Mn(II),

Mn(III)-L, and total dissolved Mn) using a recently established porphyrin method (Madison et al., 2011; Madison et al., 2013; Oldham et al., 2017a,b,c). Higher water volumes will also be filtered to collect particles for Mn oxide (MnOx) quantification using the Mn (III,IV)-specific colorimetric probe Leucoberbelin Blue (LBB) (see Oldham et al., 2017). Samples for dissolved nitrogen species including nitrate, nitrite, and ammonium, will be filtered, frozen and measured at WHOI and/or IOW. Filtered samples will also be analyzed shipboard for IO_3^- and total iodine (IO_3^- + I^- + DOI) concentrations using conventional spectrophotometric methods (Jickells et al., 1988). Filtered, frozen samples will be measured at MSU via ICP-MS for IO_3^-, I^-, and DOI individually following chromatographic separation (Hou et al., 2001).
Due to the short lifetime of superoxide (<30s), concentrations will be measured *in situ* using a novel submersible chemiluminescent sensor (SOLARIS) recently developed in the Hansel lab (NSF OTIC 1736332, co-PI Wankel). This instrument will be integrated into the rosette for real-time data collection, and calibrated as described previously (see Diaz et al., 2013).
Task 2: At all stations, we will obtain particles for later detailed particulate P, trace element and Mn oxide characterization. We will investigate the role of Mn oxides in the (ad)sorption and shuttling of trace metals and phosphorus (P) within and out of the suboxic zone. Based on previous Mn oxide profiles defined via LBB (Task 1), higher volume particle samples will be collected at 5-7 depths spanning the MnOx particle maxima for identification and quantification of Mn oxide associated trace elements (Köhler) and P (Schulz-Vogt), and also spectroscopic characterization of the Mn oxides (Hansel). Based on Schulz-Vogt's recent discovery that magnetotactic bacteria store and transport polyphosphate within the Black Sea (Schulz-Vogt et al., 2019), particles will also be collected spanning the P peak as observed via the pump-CTD in-line analyzer. Water will be collected using the standard CTD rosette or pump-CTD, filtered (0.4 um polycarbonate filters), rinsed with MQ water, and frozen for later characterization via a combination of ICP-OES, fluorescence and scanning electron microscopy, and X-ray absorption spectroscopy (Dellwig et al., 2012; Learman et al., 2011; Schulz-Vogt et al., 2019).

4 Narrative of the Cruise

It was planned to leave Rostock at Friday, the 17th of September in the morning. However, due to a strong storm in the central Gotland Basin it didn't make sense as we would have had to weather a day on site without being able to deploy any equipment. We therefore left Rostock port a day later, 18th September at 8 o'clock and still had to steam against waves so that we could only reach a ships speed of 5-6 kn, sometimes only 3 kn. Nevertheless, the engineers worked on the integration of the new Solaris system to the pump-CTD (PCTD) system for a day before they decided to attach it to the normal CTD with the wave compensating winch. After 48 hours of steaming, in the morning of September 20th, we deployed the first CTD with the Solaris System attached successfully at the station go31, the shake down station. At the first real sampling station, go32 we lowered the CTD as slowly as possible for testing, and included stops for extra calibration. After that the PCTD came into operation with a lowering speed of 1cm s^{-1}. Still the waves of more than one meter height prevented a good profile and it was decided to increase the speed to 2cm s^{-1} to achieve a consistent peak resolution throughout the water column. Several different microsensors measuring nanomolar oxygen, hydrogen sulfide, pH and the autoanalyser were integrated in the flow from the PCTD. The pH sensor in particular worked very well and will add important information for the interpretation of the other sensor readings. Since the deployment lasted far past dinner time we used the chance to recover the system during change of watch around midnight.

The next morning, Sept. 21st, we continued working on station go 27 situated in the middle of the eastern Gotland Basin with a water depth of 175 meters. Several CTDs were deployed to get enough water for everyone to do measurements of nitrification rates, trace metals, transcriptomics and other biogeochemical variables. The PCTD deployment started at the base of the euphotic zone down to anoxic waters (130m) but not the bottom. Several people collected water for the analysis of stable nitrogen isotopes in nitrate, nitrite, ammonium and trace metal concentrations. The classical Gotland Deep stations, TF 271, was our focus on the next day and we started at 6 o´clock with the CTD deployments another pump cast and the multicorer. We found an interesting profile with numerous ups and downs between 80 and 110m depth and before the water remained anoxic which is a typical feature for this station (Fig. 5.1). Everything worked well and everybody was extremely busy that day with the processing of water and sediment samples. Porewaters were also retrieved for nutrient analysis and ammonium isotopes.

Upcoming bad weather required again some adaptation of our sampling plan since high wind speeds and waves would prevent further sampling beyond Thursday, September 23rd midday. Instead of completing the transect across the deepest part of the eastern Gotland Basin we went to the Farö Deep located in the north and started work as early as 5 o´clock in the morning. The mixed layer depth was the same as at previous stations but oxygen concentrations declined rapidly around 80m depth and waters stayed anoxic towards the bottom (Fig. 5.2). We made another quick PCTD cast and collected water for the usual trace metal profile and other variables before we headed off to a safe harbor in Slite on the island of Gotland where we sought shelter from the very strong storm. Heavy rain came down too when we docked at the port near the cement factory. Unfortunately, the weather not only kept us on Friday but also all of Saturday in the harbor. Waves were again almost 2m high the open Baltic Sea with no prospect of work.

Saturday evening, we finally left harbor and continued our work along the transect across the central Gotland Basin on Sunday early morning at 5:30 at station go 24. The bright weather allowed us to deploy the MUC and we found clay sediment with only a small layer of organic debris on top as expected for this shallow station. As second station we went to go 23 and completed several CTD casts plus the PCTD as this was again a station with a pronounced redoxzone. Our final station was TF 260 at the southern end of the Basin on our last working day, September 27th. Everything went very well there too but our full schedule with sample request kept us busy until diner time.

We headed back to Rostock with strong waves from west to northwest so that the ship was shaking heavily the entire night. On Tuesday work was finalized in the labs and packing and cleaning started. Everybody on board was satisfied with the achievements since we got the minimum amount of work done to generate – after all he analytical work - a first comprehensive idea about the element cycles of manganese, iodine, sulfur, oxygen and nitrogen and on the interlinked microbial processes in the redoxzone. The fact that we were not allowed to sample water in the Landsort Deep remained the only disappointment since we expected it to differ in processes and element cycles from the eastern Gotland Basin.

5 Preliminary Results

5.1.1 System Overview and Data Processing

CTD data had been processed into cnv.-files for the downcasts and besides the data were provided in second intervals for the down and up casts so that they could be merged with Solaris data. The data evaluation including the calibration of the Solaris system will take month to a year and will done at WHOI. The PCTD data were already aligned with microsensor and nutrient data. All basic CTD data will soon be provided through IOWs repository (see below).

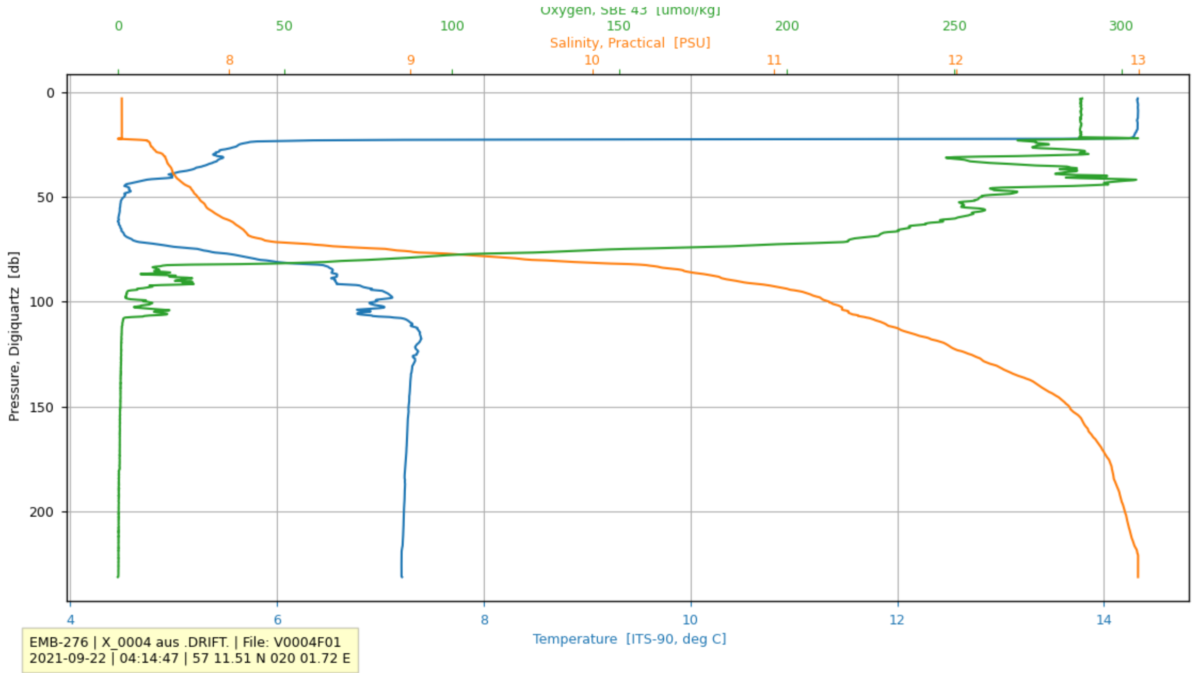

Fig. 5.1 Oxygen (green), Salinity (yellow), and temperature (blue) profile of station TF271 with typical variability of oxygen concentrations around 100m depth

5.2 Water Sampling with CTD/Rosette

5.2.1 CTD Measurements

(M. Kolbe, IOW)

The CTD onboard the EMB is a SBE9/11Plus model, operated on a heave compensated winch and equipped with dual, pumped circuits incorporating temperature (SBE3), conductivity (SBE4), oxygen (SBE43) sensors and pumps (SBE5T). Additional single sensors are Wetlabs ECO FLNTU providing optical measurement for backscattering, turbidity, and chlorophyll-a, a PAR/SPAR system from Biospherical Instruments Inc. and an altimeter for bottom range. Essential for water sampling in the Baltic, the CTD rosette is fitted with HYDRO-BIOS free flow water samplers on a SBE32 water sampler.
For close-range measurements at the sea floor the CTD features a downward facing video camera, spotlights and lasers to visually evaluate distance between device and sea floor. The supply with 24V DC power and a DSL data-uplink is carried out via Sea & Sun Telemetry System. On the additional RS232 ports the SOLARIS system was successfully integrated.

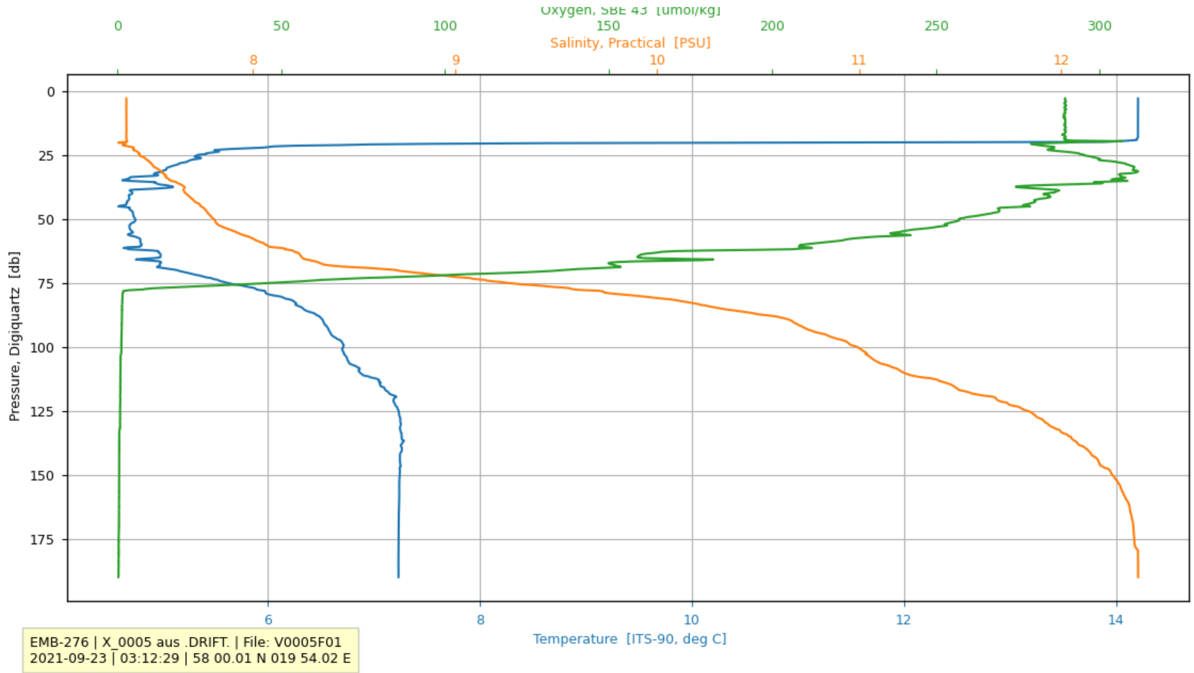

Fig. 5.2 Oxygen (green), Salinity (yellow), and temperature (blue) profile of station go12, Farö Deep, where no variability of oxygen concentrations is observed.

5.2.2 PCTD Measurements and microsensors

(H. Schulz-Vogt, IOW)

The pumped CTD is comprised of the same features as the CTD described above in chapter 5.2.1 "CTD Measurements". In addition, a 3 phase powered pump transports water through a special 680m long cable and slip ring to supply a constant water flow rate of max 4.5L/min on deck. Run by an electric winch (McArtney) the system can be heaved and veered at speeds as slow as 1cm/s.

The pump CTD delivers the water directly into the laboratory with a time delay of less than 7 minutes. As oxygen is measured at the head of the CTD and in the laboratory these two profiles are used for the alignment of the parameters measured at the head and in the laboratory. In the laboratory the line is split between an array of microsensors and the autoanalyzer. In this cruise we used microsensors for oxygen sulfide and pH with a 1 sec. resolution (appoximately 1 cm). First attempts to use a newly devolved H_2O_2 sensors gave some promising results. The autoanalyzer measures nitrate, nitrite, ammonia, phosphate and silicate in 30 sec. intervals resulting in aresolution of approximately 30 cm. All data obtained in the laboratory will be aligned using a time stamp.

5.2.3 Solaris System

(C. Hansel, L. Taenzer, W. Pardis WHOI)

SOLARIS is designed for the continuous in situ measurement of superoxide in seawater. The 24Vdc power and RS232 data interface of SOLARIS was integrated on the Borgese's inboard heave compensated CTD using a Sea and Sun TMS/DSL modem for real time data telemetry and control of the instrument. It was mechanically fixed to the CTD carousel (replacing the space of 4 bottles) with a custom bracket constructed of aluminum. SOLARIS was used to capture depth profiles during one or more CTD casts at seven different stations. In situ calibrations were done regularly during casts to characterize the sensor response under specific temperature and pressure conditions.

5.2.4 Nitrification

(M. Voss, K. Gentsch, WHOI)

At every station nitrification rates were measured in 3-4 depth of the water column focusing on the redoxzone. Water was carefully withdrawn from water bottles and immediately treated with labelled substrate. Also a time series incubation was accomplished at TF 260. We used the ^{15}N labelled ammonium addition and after 5hours of incubation collected the filtrate as well as a filter after the incubation. Furthermore, water from four PCTD casts was taken at selected depth from oxic nitrate rich waters into the anoxic and ammonium rich water. These samples will hopefully show the impact of combined nitrification and denitrification on the natural abundance of stable nitrogen isotopes in that layer.

5.2.5 Trace metals and Iodine samples

(C. Hansel, WHOI, A. Köhler, IOW)

Samples were collected throughout the water column to quantify and speciate Mn and thallium (Tl) (a trace metal that (ad)sorbs to Mn oxides) within the dissolved and particulate phase. Waters were extracted directly from rosette bottles using a peristaltic pump through a Sterivex filter apparatus (0.2 um pore size) into sample bottles. Filtered waters were either unacidified (Mn) or acidified (Tl) for later analysis. Sterivex filters were evacuated and frozen at -20C. Three Sterivex were collected at each depth, one each for (1) Mn oxide quantification via the Leucoberbelin Blue assay, (2) acid dissolution and trace metal quantification via ICP-MS, and (3) metal oxidation state and mineralogy via synchrotron-based X-ray absorption spectroscopy (XAS) at the Stanford Synchrotron Radiation Lightsource (SSRL). Additionally, 10L of water were filtered through Whatman filters for Tl isotope analysis.

Samples for iodine measurement were collected from niskin bottles accompanied with Mn and Tl samples. Around 50 – 125ml samples were filtered through a Sterivex filters and stored in 50ml centrifuge tubes or 125ml Nalgene bottles. 2.5ml of each sample was collected and measured iodate concentration using a spectrophotometer on board. The rest of the filtered samples were stored at -20C to keep iodine speciation stable. The frozen samples are for chromatography separation and ICP-MS measurement for iodide concentration at Michigan State University. Eight seawater samples, either filtered or unfiltered, were collected from TF271 and TF260 stations for assessing in situ bio/abio reduction of iodate. Some filtered samples at surface

or oxycline from stations go12_Faro, go24, go23 and TF260 were analyzed with 1000nM potassium iodate standard addition in order to verify abiotic in situ reduction in oxygenated surface layers.
From the normal CTD at three sites nine depth were selected and samples for H_2S analysis, metals and filtered samples taken. Moreover, samples in high resolution analysis of Mn-react., H_2S and also metals were withdrawn from the PCTD from the same three station, go12, g27, and TF 271. All these will be analysed in the lab of O. Dellwig at IOW.

5.2.6 Sediments

(M. Voss, IOW, C. Ostrander, WHOI)

The MUC was deployed twice at the euxinic station TF271 and at the oxic station go24. At both stations pore water was retrieved with rhizons.
Sediment slices were collected to characterize the Tl isotope composition within the sediment. Sediment aliquots were also taken for metal (Mn, Tl, Fe) speciation – oxidation state and coordination environment (ie, mineralogy) – via near-edge x-ray absorption (XAS: both XANES and EXAFS) at SSRL.

5.3 Expected Results

- Nitrification rates will allow us to estimate the potential for denitrification and reactive nitrogen loss to combat eutrophication of the Baltic Sea.
- SOLARIS was used to capture the first depth profile measurements of superoxide in the Baltic Sea. We expect that this data will provide an initial understanding of how ROS dynamics differ between oxic and anoxic conditions in the ocean, and may facilitate the identification and characterization of biotic and abiotic superoxide production pathways. Considering the capacity of ROS (both superoxide and hydrogen peroxide) to mediate the redox cycling of Mn (and other metals), we expect to see a positive correlation between increased superoxide levels and Mn(III)-ligand complexes and Mn oxide concentrations. Given also the propensity for Tl to sorb to and fractionate at Mn oxide surfaces, we expect to see clear fractionation signals in response to Mn oxide maxima and with specific Mn oxide mineral phases known to induce isotopic fractionation. These elemental distributions will help inform future targeted experiments into the underlying reactions.
- Metal profiles will be generated for a detailed understanding of redox processes for these elements and provide important context for the other Mn species measured at WHOI and S-compounds.

6 Ship's Meteorological Station

Not applicable

7 Station List

7.1 Overall Station List

Station No.		Date	Gear	Time	Latitude	Longitude	Water Depth	Remarks/ Recovery
EMB	**IOW**	**2021**		**[UTC]**	**[°N]**	**[°W]**	**[m]**	
EMB276_1-1	go 31	20.09.	CTD	06:31:31	56°51,9039'	018°52,8345'	110.6	Shake down
EMB276_1-2	go 31	20.09.	PCTD	08:02:51	56°51,9591'	018°52,9043'	111.3	Shake down
EMB276_2-1	go 32	20.09.	CTD	12:56:21	56°50,0011'	019°10,9560'	164.2	
EMB276_2-2	go 32	20.09.	CTD	15:03:37	56°50,0241'	019°10,9748'	164.2	
EMB276_2-3	go 32	20.09.	PCTD	16:45:32	56°50,0041'	019°10,9697'	164.0	
EMB276_3-1	go 27	21.09.	CTD	06:15:16	56°56,9790'	019°52,9137'	177.1	
EMB276_3-2	go 27	21.09.	CTD	08:45:23	56°56,9394'	019°52,9715'	177.1	
EMB276_3-3	go 27	21.09.	CTD	10:12:25	56°57,0069'	019°52,9947'	176.7	
EMB276_3-4	go 27	21.09.	CTD	10:24:48	56°57,0245'	019°52,9920'	177.1	
EMB276_3-5	go 27	21.09.	CTD	12:24:23	56°56,9991'	019°52,9889'	177.1	
EMB276_3-6	go 27	21.09.	PCTD	12:54:10	56°56,9985'	019°52,9812'	177.1	
EMB276_4-1	TF 271	22.09.	CTD	04:07:21	57°11,5062'	020°01,7706'	238.1	
EMB276_4-2	TF 271	22.09.	CTD	06:09:10	57°11,5146'	020°01,7702'	237.9	
EMB276_4-3	TF 271	22.09.	PCTD	07:14:56	57°11,5228'	020°01,8148'	237.3	
EMB276_4-4	TF 271	22.09.	MUC	12:08:25	57°11,5492'	020°01,8063'	238.6	
EMB276_4-5	TF 271	22.09.	CTD	13:04:50	57°12,0176'	020°01,7961'	238.7	
EMB276_4-6	TF 271	22.09.	CTD	14:00:01	57°12,0299'	020°01,8202'	240	
EMB276_4-7	TF 271	22.09.	CTD	14:50:15	57°12,0378'	020°01,8765'	239.4	
EMB276_4-8	TF 271	22.09.	CTD	17:30:27	57°12,0041'	020°01,8575'	238.6	
EMB276_4-9	TF 271	22.09.	CTD	18:24:52	57°12,1667'	020°02,0151'	240	
EMB276_5-1	go 12 - Farö	23.09.	CTD	03:05:54	58°00,0157'	019°54,0234'	195.6	
EMB276_5-2	go 12 - Farö	23.09.	PCTD	04:49:40	58°00,0045'	019°54,0398'	195.7	
EMB276_5-3	go 12 - Farö	23.09.	CTD	04:56:30	58°00,0081'	019°54,0308'	195.7	
EMB276_5-4	go 12 - Farö	23.09.	CTD	07:35:14	58°00,0134'	019°54,0140'	195.6	
EMB276_5-5	go 12 - Farö	23.09.	CTD	08:18:01	58°00,0377'	019°53,9814'	195.4	
EMB276_6-1	go 24	26.09.	CTD	03:34:46	57°15,9981'	020°39,0777'	71.8	
EMB276_6-2	go 24	26.09.	CTD	04:45:04	57°16,0549'	020°39,0080'	71.1	
EMB276_6-3	go 24	26.09.	MUC	05:40:04	57°15,9934'	020°38,9961'	72.5	
EMB276_6-4	go 24	26.09.	MUC	06:03:34	57°15,9906'	020°39,0397'	72	
EMB276_7-1	go 23	26.09.	CTD	08:00:25	57°18,0345'	020°21,0143'	187.9	
EMB276_7-2	go 23	26.09.	CTD	09:00:26	57°18,0163'	020°21,0294'	187.3	
EMB276_7-3	go 23	26.09.	CTD	10:02:50	57°17,9993'	020°20,9715'	187.8	
EMB276_7-4	go 23	26.09.	CTD	11:05:36	57°18,0041'	020°21,0229'	187.1	
EMB276_7-5	go 23	26.09.	PCTD	11:28:28	57°18,0051'	020°20,9750'	187.1	
EMB276_7-6	go 23	26.09.	CTD	11:59:49	57°17,9975'	020°20,9979'	187.1	
EMB276_7-7	go 23	26.09.	CTD	12:51:51	57°18,0085'	020°21,0240'	187.1	
EMB276_7-8	go 23	26.09.	CTD	17:50:02	57°18,0102'	020°20,9967'	187.1	
EMB276_8-1	TF 260	27.09.	CTD	04:02:47	56°38,0203'	019°34,9891'	144.3	
EMB276_8-2	TF 260	27.09.	CTD	05:31:18	56°38,0027'	019°35,0094'	144.3	
EMB276_8-3	TF 260	27.09.	PCTD	06:49:30	56°38,0281'	019°35,0573'	144.3	
EMB276_8-4	TF 260	27.09.	CTD	07:14:23	56°38,0256'	019°34,9875'	144.3	
EMB276_8-5	TF 260	27.09.	CTD	11:57:14	56°38,0078'	019°34,9994'	144.3	
EMB276_8-6	TF 260	27.09.	CTD	12:58:07	56°38,0078'	019°35,0076'	144.3	

7.2 Profile Station List

Not applicable

7.3 Sample Station List

Samples were collected at all station listed under 7.1, in detail the following was done:
Water from the CTD was filtered for metal analysis, used for nitrification experiments and for calibrations of the newly developed SOLARIS system.
PCTD water was used for microsensor and nutrient measurements.
Sediment cores from the MUC were used for porewater extraction and sediments for Tl analysis.

8 Data and Sample Storage and Availability

The CTD data as such are of high quality and will be uploaded to ODIN data base. In compliance with the requirements of the National Science Foundation (NSF, USA), data will be uploaded to the NSF data repository managed by the Biological and Chemical Oceanography Data Management Office (BCO-DMO). Data archived with BCO-DMO are publicly available and easily searchable.
All data will also be shared via conference proceedings and publications, with raw data provided as supplementary materials.
All data will also be archived with the PIs and made available to interested parties upon request.

Table 8.1 Overview of data availability

Type	Database	Available	Free Access	Contact
hydrography		Date	Date	E-Mail
raw data CTD	ODIN	March 22	March 23	Martin.kolbe@io-warnemuende.de
Nutrient data	ODIN			
Metal, iodine data	BCO-DMO	Sept 22, 2022	Sept 22, 2022	chansel@whoi.edu
Superoxide data	BCO-DMO	Sept 22, 2022	Sept 22, 2022	chansel@whoi.edu
Microbial rates	-	Sept 22 2022	Dec 22, 2022	Maren.voss@io-warnemuende.de

9 Acknowledgements

We acknowledge the great support and help through the captain and crew of the Elisabeth Mann Borgese. Without the experience and support of Susanne Schöne with demanding custom issues the cruise could not have happened.

10 References

Dellwig, O., Schnetger, B., Brumsack, H.-J., Grossart, H.-P. and Umlauf, L. (2012) Dissolved reactive managese at pelagic redoxclines (part II): Hydrodynamic conditions for accumulation. Journal of Marine Systems 90, 31-41.

Dellwig, O., Schnetger, B., Meyer, D., Pollehne, F., Häusler, K. and Arz, H.W. (2018) Impact of the major Baltic inflow in 2014 on manganese cycling in the Gotland Deep (Baltic Sea). Frontiers in Mar. Sci. 5, 248.

Diaz, J., Hansel, C.M., Voelker, B.M., Mendes, C.M., Andeer, P.F. and Zhang, T. (2013) Widespread production of extracellular superoxide by marine heterotrophic bacteria. Science 340, 1223-1226.

Hou, X., Dahlgaard, H., & Nielsen, S. P. (2001). Chemical speciation analysis of 129I in seawater anda preliminary investigation to use it as a tracer for geochemical cycle study of stableiodine. Marine Chemistry, *74*, 145-155

Jickells, T. D., Boyd, S. S., & Knap, A. H. (1988). Iodine cycling in the Sargasso Sea and the Bermuda inshore waters. Marine Chemistry, *24*, 61-82.

Learman, D.R., Wankel, S.D., Webb, S.M., Martinez, N., Madden, A.S. and Hansel, C.M. (2011) Coupled biotic-abiotic Mn(II) oxidation pathway mediates the formation and structural evolution of biogenic Mn oxides. Geochim. Cosmochim. Acta 75, 6048-6063.

Madison, A.S., Tebo, B.M. and Luther III, G.W. (2011) Simultaneous determination of soluble manganse(III), manganese(II) and total manganese in natural (pore)waters. Talanta 84, 374-381.

Madison, A.S., Tebo, B.M., Mucci, A., Sundby, B. and Luther III, G.W. (2013) Abundant porewater Mn(III) is a major component of the sedimentary redox system. Science 341, 875-878.

Oldham, V.E., Jones, M., Tebo, B.M. and Luther III, G.W. (2017a) Oxidative and reductive processes contributing to manganese cycling at oxic-anoxic interfaces. Mar. Chem. 195, 122-128.

Oldham, V.E., Miller, M.T., Jensen, L.T. and Luther III, G.W. (2017b) Revisiting Mn and Fe removal in humic rich estuaries. Geochim. Cosmochim. Acta 209, 267-283.

Oldham, V.E., Mucci, A., Tebo, B.M. and Luther III, G.W. (2017c) Soluble Mn(III)–L complexes are abundant in oxygenated waters and stabilized by humic ligands. Geochim. Cosmochim. Acta 199, 238-246.

Schulz-Vogt, H.N., Pollehne, F., Jürgens, K., Arz, H.W., Beier, S., Bahlo, R., Dellwig, O., Henkel, J.V., Herlemann, D.P.R., Krüger, S., Leipe, T. and Schott, T. (2019) Effect of large magnetotactic bacteria with polyphosphate inclusions on the phosphate profile of the suboxic zone Black Sea. ISME J.

11 Abbreviations

MUC Multicorer

PCTD Pump CTD (conductivity, temperature, depth)

BCO-DMO Biological and Chemical Oceanography Data Management Office

XAS or XANES near-edge x-ray absorption

EXAFS near-edge x-ray absorption

SSRL Stanford Synchrotron Radiation Lightsource

12 Appendices

12.1 Selected Pictures of of Shipboard Operations

Pore water sampling

Water is withdrawn from the CTD with the Solaris System integrated