Cruise Report

RV Pelagia May 28 – June 15, 2016
Nynashamn, Sweden – Texel, the Netherlands
64PE411

Baltic Sea

Caroline Slomp (Chief Scientist)
with contributions from participants

Universiteit Utrecht

Koninklijk Nederlands Instituut voor Zeeonderzoek

NWO
Nederlandse Organisatie voor Wetenschappelijk Onderzoek

Table of Contents **page number**

Appendices

Photo cover: Lander retrieval at Bornholm

1. Introduction and participants

This cruise forms part of the Vici Project "Response of the Iron Biogeochemical Cycle on Continental Shelves to Seawater Deoxygenation" funded by the Netherlands Organisation for Scientific Research (NWO). The project involves partners in the Netherlands (Utrecht University, UU and the Royal Netherlands Institute for Sea Research; NIOZ; Texel and Yerseke), the United States (Rutgers University) and Sweden (Lund University) and has links with the BONUS project COCOA.

Specific goals of this cruise:

This aim of this cruise is to gain insight into the mechanisms and rates of iron release from sediments in the Baltic Sea and the lateral transport of iron (and other trace metals) from sediments in shallower areas to the adjacent anoxic basin.

GEOTRACES

The Fe Baltic cruise has been endorsed as a GEOTRACES process study and will follow International GEOTRACES protocols relating to intercalibration, methodology and data management.
http://www.geotraces.org/science/intercalibration/945-intercalibration-procedures
http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf

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Cruise blog: geoblog.weebly.com/expedition-baltic-sea-2016

Collaborators
outside the Netherlands:

THE STATE UNIVERSITY OF NEW JERSEY
RUTGERS

LUND
UNIVERSITY

Table 1. Baltic Fe cruise-participants and their contact information and activities.

Name & affiliation	Contact information	Main activity
1. Caroline Slomp, UU	c.p.slomp@uu.nl	Chief scientist
2. Mathilde Hagens, UU	m.hagens@uu.nl	Water column sampling, water column alkalinity, DIC, pH
3. Wytze Lenstra, UU	W.K.Lenstra@uu.nl	CH4, flux incubations, sulfate reduction
4. Martijn Hermans, UU	M.Hermans@uu.nl	Micro-electrodes, porewater alkalinity
5.Niels van Helmond, Lund University, Sweden/UU	n.vanhelmond@uu.nl	CH_4, sulfate reduction, porewater, sediment collection
6. Matthias Egger	m.j.Egger@uu.nl	Porewater (centri-fugation, rhizons), sediment collection incl. resin embedding
7. Marie Seguret, UU	M.J.M.Seguret@uu.nl	Water column sampling, in-situ pumps
8. Rob Witbaard, NIOZ	Rob.Witbaard@nioz.nl	Landers, macrofauna (incl. whole core incubations)
9 Liz Robertson, Lund University, Sweden	elizabeth.k.robertson@googlemail.com	Sediment N-dynamics sediment collection
10. Silke Severmann Rutgers University, USA	silke@marine.rutgers.edu	Water column sampling, in-situ pumps, rhizon sampling for isotopes
11. Amy Anderson, Rutgers University, USA	anderson@marine.rutgers.edu	Water column sampling, in-situ pumps, rhizon sampling for isotopes
12. Silvia Hidalgo Martinez NIOZ-Yerseke	Silvia.Hidalgo@nioz.nl	Microbiology, DNA/RNA samples, Fe reduction
13. Ruud Groenewegen, NIOZ	Ruud.Groenewegen@nioz.nl	Landers, CTD, electronics
14. Sharyn Ossebaar, NIOZ	Sharyn.Ossebaar@nioz.nl	Nutrient analyses, sampling from Niskins
15. Jan van Ooyen, NIOZ	Jan.van.Ooijen@nioz.nl	Nutrient analyses, sampling from Niskins
16. Lorendz Boom, NIOZ	Lorendz.Boom@nioz.nl	Sediment coring, CTD, landers
17. Santiago Gonzalez, NIOZ	Santiago.Gonzalez@nioz.nl	Radio-isotopes, sediment collection, DOC sampling

Figure 1: The crew and scientists of the Baltic Fe expedition

2. Cruise Track and overview of activities

A total of 23 stations were visited in 16 days. See Figure 2 for cruise track and Tables 2 and 3 for coordinates, date of sampling and activities.

Overview of sample collection and primary responsible:

1. **UltraClean CTD** (MTE, Marie, Silke, Mathilde, Amy)
   - Sensor data for temperature, salinity, oxygen, transmissivity, fluorescence
   - Collection of water samples
     - total number of water samples: ca. 700
     - Collection of samples for alkalinity (Mathilde)
     - Collection of samples for nutrients (NH_4, NO_3, NO_2, PO_4, silica, sulfide and DIC for UU, ICP-OES for UU (Jan van Ooijen/Sharyn Ossebaar, NIOZ)
     - Collection of samples for DOC (Santiago)
     - Collection of water and particulate samples in clean container:
       - Total Fe and other (unfiltered sample)
       - Dissolved Fe (<0.2 um filter)
       - Truly Dissolved Fe (<0.02 um filter)
       - Suspended material > 0.2 um
       - Suspended material 0.2> and >0.02 um (selected sites, + dissolved for comparison,)
       - Samples for isotopes (U, Cr) (Silke, Amy)

2. **In-situ pumping** to collect suspended material at selected sites for mineralogical, geochemical and isotope analyses (Marie, Silke, Mathilde, Amy)
   - Four pumps, 3 with one filter (NIOZ), 1 with a dual filter (UU)
   - 7 deployments of 4 pumps (3 NIOZ, 1 UU), i.e. 28 water depths. Note: 1 depolyment for Silke at station F80 and one deployment at station BY5 with only Quartz filters.

3. **Lander and other flux incubations**:
   - sediment cores: total flux (oxic, anoxic) and Br- (Wytze)
   - seafloor: landers (Rob, Ruud), 11 sites

4. **Sieving** for macrofauna (Rob, Wytze)

5. **Porewater and sediment collection**:
   - multicore slicing in glovebox and centrifugation, subsampling (Matthias, Niels)
   - separate core for NO3 profile (Niels)
   - CH4 core (Wytze)
   - rhizon sampling, selected sites (for DOC or nutrients/ICP-OES; Mathilde, Niels)
   - frozen core + photograph (Niels)
   - 2 cores for microelectrode profiling (Martijn), one of these sliced oxic for DNA/RNA (Silvia) with remaining sediment stored as well (for 210Pb and other analyses).
   - sediment cores for whole storage and experiments (selected sites, Martijn, Niels)
   - core for DNA/RNA methane oxidizers (selected sites; Silvia, Martijn)
   - resin embedding for mineral analyses reoxidized sediments (selected sites Matthias)
6. N cycling (Liz)
7. Water column alkalinity titrations, pH, DIC (Mathilde)
8. DOC sampling water column and sediment (selected stations; Mathilde)
9. Alkalinity titrations porewater (Martijn)
10. Sulfate reduction measurements (Niels, Wytze)
11. Fe reduction measurements two sites (Silvia, Martijn, Wytze)

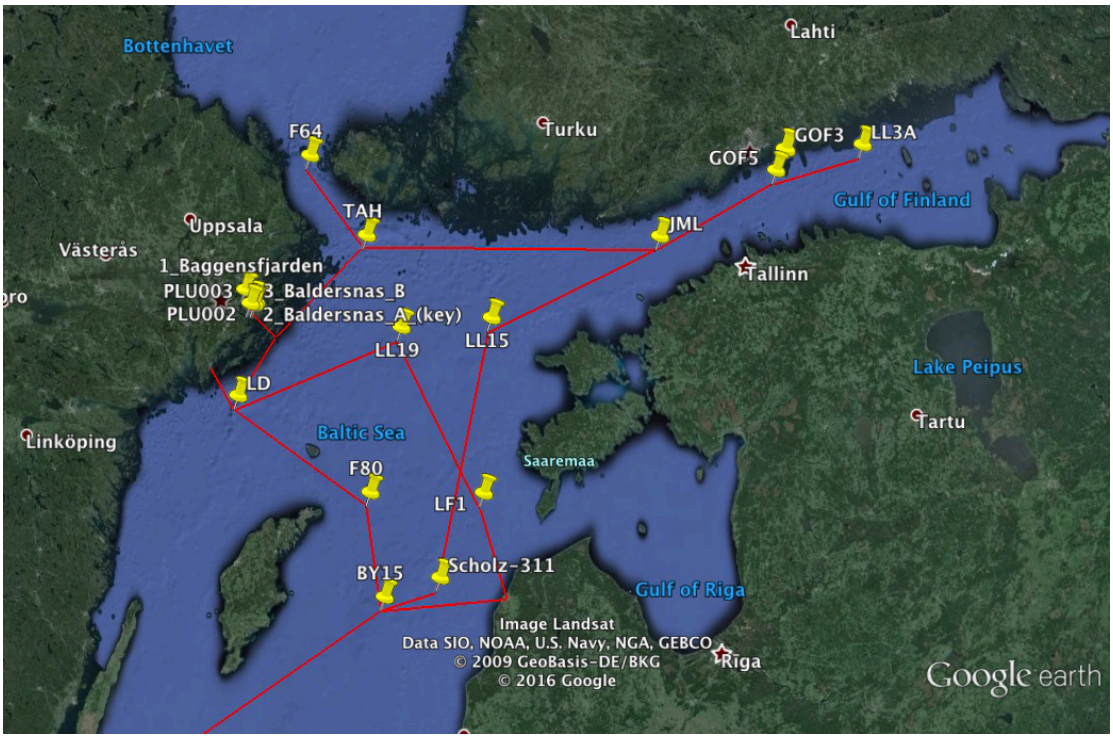

Figure 2a. Map with stations in the northern Baltic Sea with the cruise track.

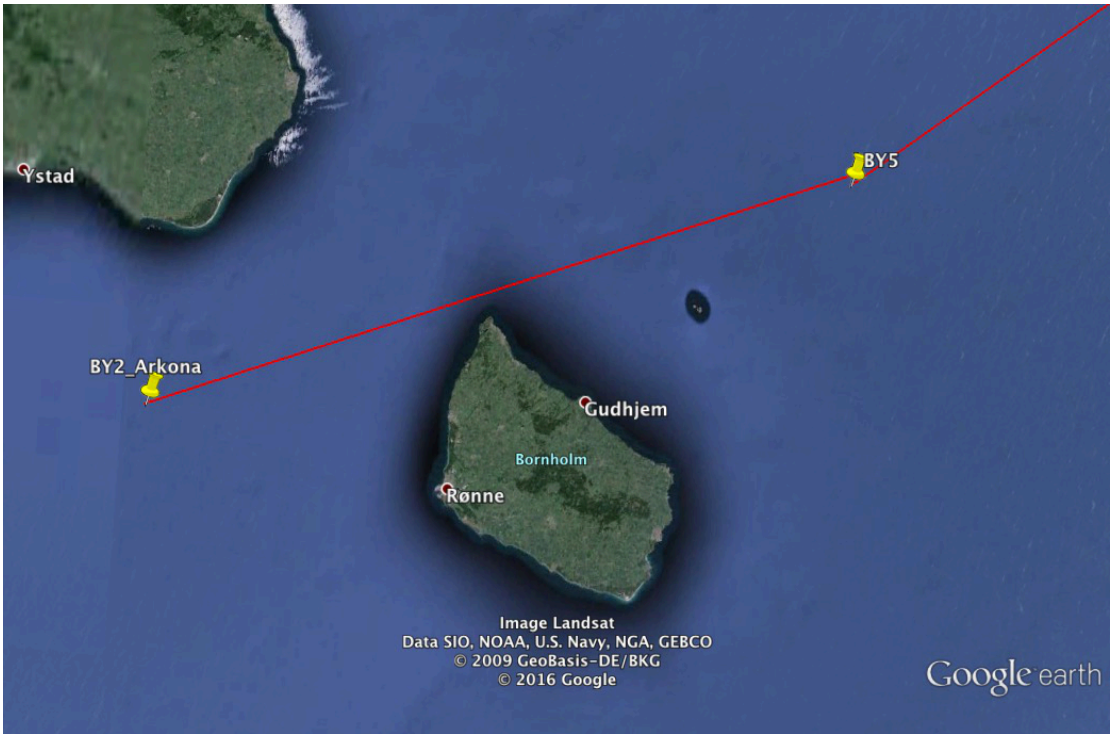

Figure 2b. Map with stations in the southern Baltic Sea and cruise track.

Table 2. Sample sites, coordinates and water depths

Sample sites Baltic cruise 2016			position N	position E	National	water
Our code	Old codes	Area	deg min	deg min	waters	depth (m)
Fe Baltic -x	**Stockholm sites**					
1	PLU15_005	Baggensfjarden	59°18.55'	18°19.41'	Sweden	40
2	PLU15_003	Estaviken	59 13.185'	18 23.674'	Sweden	68
*2	-	Ingarofjarden (Baldersnas)	59°13.33'	18°27.01'	Sweden	40
3	PLU15_002	Ingarofjarden (Baldersnas)	59°13.33'	18°27.02'	Sweden	37
	Aland Sea					
4	F64	Solovjeva	60°10.90'	19°08.80'	Finland	290
5	TAH**	Tröskeln Ålands Hav	59°36.0'	19°56.91'	Finland	74
	Gulf of Finland					
7	JML	Gulf of Finland	59°34.92'	23°37.50'	Finland	80
9	GOF5	Gulf of Finland	59°57.10'	25°11.02'	Finland	65
10	LL3A***	Gulf of Finland	60°4.43'	26°18.30'	Finland	60
15	GOF3	Gulf of Finland	60 4.43'	25 19.42'	Finland	55
	N. and E. of Gotland					
12	LL15	East Gotland	59°6.59'	21°26.90'	Estonia	135
13	LF1	LF Transect 1 oxic	57°58.95'	21°16.84'	Estonia	67
16	Scholz 311	East Gotland oxic	57°26.49′	20°43.49′	Latvia	65
	Euxinic basins					
17	LL19	Northern Gotland	58°52.84'	20°18.65'	Sweden	173
18	F80	Faro Deep	58°00.0'	19°53.8'	Sweden	194
19	BY15	Gotland Basin	57°19.20'	20°3.00'	Latvia	237
20	IODP-LD	Landsort Deep	58°37.34′	18°15.25′	Sweden	451
	Hypoxic southern basins					
21	BY2	Arkona	54°58.504'	14°05.937'	Sweden	47
22	IODP-BY5	Bornholm	55°28.09′	15°28.63′	Denmark	87

Note:
* site PLU003: wrong coordinates from SGU; could not be sampled
** site TAH was in the middle of a shipping lane and its location was changed slightly
*** site LL3a could not be sampled because of a cable; new coordinates as close as possible to old site

Figure 3. The Pelagia in the harbor of Nynashamn.

Table 3. Overview of activities at each station (CTD, MC) and deployments of instruments (lander, 4 pumps) where relevant, including day and date of sampling. Where more multicores were taken than were used (because they were e.g. too full, not full enough or failed) the total number of deployments is included in brackets. *: coordinates in SGU report of July 4, 2015 incorrect; PLU_003 site 2 not sampled. Qtz = quartz. (+): successful lander.

Day	station	UC CTD	Standard CTD	MC casts	In-situ pumps	Lander	Casino St. no.
1 (28/5)	20 (LD)	1	-	0 (3)	-	-	1
2 (29/5)	17 (LL19)	1	-	3 (6)	4	1 (+)	2
3 (30/5)	13 (LF1)	1	-	5 (7)	4	1 (+)	3
5 (1/6)	19 (BY15)	1	-	2 (3)	-	1 (+/-)	4
5 (1/6)	14 (BY15a) 18 (F80)	-	-	1	- 4 (qtz)	- -	5 6
6 (2/6)	18 (F80) 20 (LD)	1	-	1 (1) 1 (1)	4 -	1 (-) -	6 7
7 (3/6)	2* 1 (PLU005) 2 (PLU003)	1 1 -	- - -	4 (8) - -	- - -	- 1 (-) -	8 9/12 10
8 (4/6)	3 (PLU002) 5 (TAH)	- 1	1 -	5 (6) -	- -	- -	11 13
9 (5/6)	4 (F64)	1	-	2 (4)	4	-	14
10 (6/6)	9 (GOF5) 15 (GOF3)	1 -	1 1	4 (5) 1 (3)	- -	2 (+) -	15, 17 16
11 (7/6)	10 (LL3A)	1	1	5 (7)	4	2 (+)	18
12 (8/6)	7 (JML)	1	1	4 (5)	4	-	19
12 (8/6)	12(LL15)	1	-	-	-	-	20
13 (9/6)	16(Sch-311) BY15b BY15c BY15d 16 (Sch-311)	1 - - - -	1 1 1 1 -	5 (8) 1 (3) 1 (2) 1 -	- - - -	2 (+) - - - 2 (+)	21 22 23 24 25
14 (10/6)	19(BY15)	-	-	-	4	-	26
15 (11/6)	22(Bornholm)	1	1	4 (4)	4 4 (qtz)	2 (+)	27
16 (12/6)	21 (Arkona)	1	1	5 (5)	4	2 (+)	28

3. Day-to-day activities (narrative)

Day 1 – Saturday May 28

All cruise participants arrived in Nynamshamn on **Friday May 27** and boarded the ship on the morning of **Saturday May 28**. The ship left the harbor at 14.30. There was a safety drill at 16.00h. The first station (Station 20; Landsort Deep) was reached at 16.30h.

Figure 4. Safety drill on first day on board.

Ultraclean CTD
Deployment of the CTD at station 20 began at ca. 15.20h. Bottles were closed according to the CTD sample list (Appendix I). The CTD was on deck around 16.42 and was directly transferred to the clean container where sampling began as soon as possible.

Multicores
Three multicore casts were taken at this station between 19.45h and 21.00h. All deployments were unsuccessful because the cores were too full.

Transit to station 17, LL19 (Northern Gotland); 164 m

Day 2 – Sunday May 29

Lander deployment
One lander (TROLL) was deployed at 8.18h at 0.5 nm to the NE of the sample location.

Ultraclean CTD
Deployment of the CTD began at ca. 8.48h and was completed at 9.47h. 24 bottles were closed according to the CTD sample list (Appendix I) and were subsequently sampled in the clean container.

In-situ pumping
4 McClane pumps (3 single filter, 1 dual filter) were deployed at depths of 10, 70, 90 and 140 m for 2h (pumping did not last longer than ca. 70 min. The deployment was completed at 13.11h

Multicores

Six multicore casts were taken at this station (between 13.30h and 16:45h). The first cast (12 x 10 cm) was successful. Of the next 5 casts with the second multicorer (8 x 6 cm and 4 x 10 cm) only three were successful.

Lander retrieval
The lander was retrieved at 19.41h

Transit to station 13 (LF1), st. 3 began at 19.44h

Day 3 – Monday May 30

Lander deployment
One lander (TROLL) was deployed at 8.05h at 0.5 nm from the location.

Ultraclean CTD
Deployment of the CTD began at ca.8.20h and was completed at ca 9h.. 24 bottles were closed according to the CTD sample list (Appendix I) and were subsequently sampled in the clean container.

In-situ pumping
4 McClane pumps (3 single filter, 1 dual filter) were deployed at depths of 10, 17, 30 and 55 m for 2h. The deployment began at 10h and was completed at 12h.

Multicores
Seven multicore casts were taken at this station between 13h and 15.30h. The first two were not full enough. The next 5 were used (3 from the 12 x 10 cm MC, 2 from the other multicorer.

Figure 5. Living isopod found at site LF1.

Lander retrieval
Recovery of the lander began at 19.30h. Because the rope got stuck under the ship, the recovery of the lander was delayed until ca. 21h.

In the evening and night, slow transit (3.5 knots) in the direction of Ventspils for removal of the rope underneath the ship.

Day 4 – Tuesday May 31

Anchor position outside harbour of Ventspils followed by transit into harbour, no sampling. A diver removed the rope and we left the harbor at ca. 19.30h.

Figure 6. The diver that removed the rope.

Day 5 – Wednesday June 1

Lander deployment

A lander was deployed at ca. 0.15h at 0.5 nm from station 19 (BY15).

Ultraclean CTD

An attempt was made to take an ultraclean CTD cast, but there was no contact with the instrument. The housing of the electrical system was filled with water and it had to be repaired. This took ca. 2 hours

Multicores

The ship moved to a new position 1 nm downstream from the main station BY15 and two multicores were taken successfully (after one failure because the cores were too full).

Ultraclean CTD

The ultraclean CTD was deployed from 11.30 to 12.45h.

Lander retrieval

The lander was retrieved between 13.45 and 14.15. One chamber did not close, one was filled with sediment but a third had a perfect sample.

Transit to station 14 (BY15a)

Because the oxygen was so low at BY15, we took one more multicore in the area. However, this core was also pitch black at the surface and the microsensor profile showed that there was no oxygen in the bottom water.

Transit to station 18 - F80. Four in-situ pumps were deployed at

Day 6 – Thursday June 2

The in-situ pumps (with quartz filters) were taken out at station F80 at 7 am. The lander was retrieved between 8 and 8.30h. Unfortunately, all chambers were filled completely with mud and there was mud in the syringes.

Ultraclean CTD & in-situ pumping
At 8.45h the ultraclean CTD deployment began. It was completed one hour later and in-situ pumping began and lasted until 13h.

Multicore cast
One multicore cast was taken successfully.

Transit to station 20, Landsort Deep. New attempt to multicore this location. One multicore was too full. Two gemax cores were attempted, one did not close, the second was too full. No multicores from this site.

Day 7 – Friday June 3

Entry of Stockholm Archipelago.

Figure 7. View from the ship, Stockholm Archipelago

Arrival at station 2* (wrong station PLU003 because of wrong coordinates from SGU).

Ultraclean CTD & multicore cast
The ultraclean CTD was deployed from 9.30 to 10h. The water depth was not 68 m as should be the case for PLU003 according to the SGU report. A sediment core was taken and was found to be different from the sediment sampled in July 4, 2015 (more oxic).

Transit to station 1, Baggensfjarden, PLU005.

Ultraclean CTD & multicore casts
The ultraclean CTD was deployed from 12h to 12.30h. Three multicores were taken (12 x 10 cm), of which the first failed and two were sampled. Four additional multicore casts were taken with the second multicorer and the last two were successful and were sampled. The ship moved position slightly and a fifth multicore cast was taken at 35 m depth. This multicore cast was unsuccessful (nearly empty core liners).

Lander deployment

A lander was deployed at ca. 16h.

Transit
Transit to station 2A, Estaviken (water depth 68 m), the real station PLU003. Arrival at 17.30h. Visit of coast guard. Permission for sampling in Swedish water debated. Sampling halted until 21.15h; permission for sampling at this site granted and then withdrawn. Permission for sampling at other sites confirmed.

Transit to station 3 (PLU_002).

Day 8 – Saturday June 4

CTD
Sampling began at 8h, with a standard CTD to check the CTD profile of the previous day. The profiles were indeed similar.

Multicoring
Six multicore casts were taken. The cores of the first and second cast (10 cm cores) were not full enough. Eight cores from the third cast were fine (four were empty). The fourth to sixth cast were taken with the second multicorer (8 x 6 cm, 4 x 10 cm). Multicoring ended at 10h.

Transit, lander retrieval and transit
The lander was retrieved at site 1 (Baggenfjarden) at 11.15 after a brief transit.
Transit to station 5 (TAH). Arrival at 19.45h.

Ultraclean CTD at station TAH. The position was changed slightly because of the location in shipping lane. Completion of sampling at 20.25h.

Transit to station 4 (F64)

Day 9 – Sunday June 5

Ultraclean CTD
Sampling at F64 began at 8h with an Ultraclean CTD. The water was oxygenated to the seafloor as expected and there was also a high turbidity in the deep water, as reported in earlier studies. The Ultraclean CTD was on deck at 9.05h.

In-situ pumping
The four in-situ pumps were deployed at depths of 10, 30, 40 and 50 m from 9.45 to 10.45h.

Multicores
Four multicore casts were taken with the multicorer with 8 x 6 cm and 4 x 10 cm cores. The first and third multicore cast failed. The cores were distributed as detailed in the appendix. This was an unusual site with grey clay underlying a thin brown sediment layer. There were many Mn nodules between a depth of ca. 1 and 4 cm. This suggests a very low sedimentation rate. The transit to station 9, GOF5, began at 12.30h.

Day 10 – Monday June 6

Multicore and lander deployment

A first multicore cast as a test was taken at 9h. The sediment was black, with a grey-brown surface layer and light grey sediments at depth. Based on the weights of the multicorer, it was decided to keep the settings of the lander the way they were. Both landers were deployed at 10h.

Ultraclean CTD
The ultraclean CTD was deployed as soon as possible afterwards. A strikingly low beam transmission was observed near the bottom and the filters at depth had a dark color.

Standard CTD with optode
The standard CTD was deployed with an optode connected to the bottom sensor to obtain a complete profile of oxygen near the bottom.

Multicore
Five multicore casts were done, with the first two being fine (12 x 10 cm), a failure of the first one of the other type (8 x 6 cm, 4 x 10 cm), and two additional successful ones.

Transit
Transit to site GOF3 (station 15). This site is located at 60 m depth in an area that overall is shallower.

Standard CTD with optode
A deployment of the standard CTD with the optode was performed and an oxygen concentration (in the lowest CTD-sensor reading) of 112 uM was determined.

Multicore
Three multicore casts were done with the first one being too full, the second one (60 m) being fine but with the sediment having overall the same appearance as GOF5. After moving the ship to a location with a water depth of 55m, a final multicore was taken. This one was sampled down to a depth of 10 cm. At this site, there was oxygen in the bottom water and there were abundant macrofauna.

Transit and retrieval of lander
There was a short transit back to site GOF5 and the landers were retrieved between 19.30 and 20.00h

Transit to site LL3a began around 20h.

Day 11 Tuesday June 7

Because there was a cable at the original location selected for sampling, the position of the station was altered and was moved to the south (60 2.04' N; 26 19.21'E) The water depth in this area was ca. 64 m, i.e. slightly shallower than the original station (which has a water depth of 68 m).

Multicore and lander deployment
A first multicore cast as a test was taken at 8h. The sediment was mostly black, with a grey-brown and orange surface layer and light grey sediments at depth. White mats of Beggiatoa were visible. Based on the weights of the multicorer (3 weights on top), it was decided to keep the settings of the lander the way they were. There was quite some suspended matter in

the overlying water in the core, suggesting material in the surface sediment that was very easily resuspended. Both landers were deployed by 9.10h.

Ultraclean CTD
The ultraclean CTD was deployed around 9.25h. The water depth was 60 m. Based on the CTD profiles (incl. low beam transmission at depth), it was decided to deploy the in-situ pumps at 10, 20, 35 and 50 m.

Standard CTD with optode
A deployment of the standard CTD with the optode was performed. An oxygen concentration (in the lowest CTD-sensor reading) of 16 uM was determined.

Multicores
Seven multicore casts were taken. The first cast (12 x 10 cm) was too full (2 x 5 weights), but the second and third were fine. The cores were distributed as described in the appendix. Four additional casts with the other multicorer were taken. The first one was too full, but the next three were fine. Because one core was lost during removal from the corer, an additional (third) cast with this multicorer was performed. There were some minor differences from core to core in the sediment material at the surface (brown layer more or less visible, more/less black at the top, more/less Beggiatoa.

In-situ pumps
The in-situ pumps were deployed after lunch and the pumps ran from 13.30h to 14.30h. The bottom filter contained a lot of colored material.

Lander retrieval
The two landers were retrieved after dinner at 19.30h.

Transit to station 7, JML, began directly after retrieval.

Day 12 Wednesday June 8

Ultraclean CTD
The ultraclean CTD was deployed at 8h (total water depth from CTD: 77 m). The CTD was completed at 7.45h.

In-situ pumps
The in-situ pumps were deployed from 9.15 to 10.30h (75 minutes of pumping) at water depths of 10, 40, 55 and 70m. The filter of 55 m was very brown.

Multicores
The two first multicore casts (12 x 10 cm) were successful and yielded cores full of highly laminated sediments with a fluff layer on top. The first multicore cast with the other corer (8 x 6 cm, 4 x 10 cm) failed, but the next two were successful.

Standard CTD with optode
The standard CTD was deployed with the optode to test the performance of the optode relative to the oxygen sensor on the CTD.

Transit to site 12 (LL15) began at ca. 12.30h.

Arrival at site 12 (LL15) at 20.30h.

Ultraclean CTD
An ultraclean CTD was deployed at this site (water depth of 135 m). The CTD was completed ca. one hour later.

Transit to site 16, Scholz 311, began at ca. 21.30h.

Day 13 Thursday June 9

The ship arrived at site 16, Scholz 311, at ca. 7h.

Multicore and lander deployment
The ship was moved to 0.5 nm from the main site. A quick multicore cast was taken at 8h to assess the sediment composition. This was firm enough for the lander deployments. The two landers were deployed successfully.

Figure 8. Dead isopod in a multicore at site Scholz-311.

Ultraclean CTD and standard CTD
The ultraclean CTD was deployed from 8.45 to 9.40h. The standard CTD with optode was deployed from 9.40h to ca. 10h.

Multicoring
Multicoring commenced at 10h. The first multicore (12 x 10 cm) was not full enough but one core was used by Martijn for micro-profiling. The next two multi-core casts were successful. The multicorer was switched and five casts were taken of which the second and fifth were successful. In one of the cores there was a dead isopod (Sarduria) on the sediment surface. Three additional multicore casts were taken in the BY15 area (BY15b, c, d).

Day 14 Friday June 10

In-situ pumping
The 4 in-situ pumps were deployed at station 19 (BY15) from 8.30h to 10.30h at depths of 220, 200, 175 and 85m. Pumping was successful (several hundreds of liters for each pump).

Transit to station 21 (Bornholm; BY5) began directly after retrieval of the pumps.

Day 15 Saturday June 11

Arrival at station 22 (Bornholm; BY5) at ca. 6.30h.

Multicore and Lander deployment
The first multicorer was on deck at 8.10h. This was again a test core for the lander deployment. Both landers were deployed between 8.15h and 8.45h. The first lander was deployed without a rope, because it broke when the lander was at the water line. The second lander was deployed with a string of buoys.

Ultraclean CTD and standard CTD with optode
The ultraclean CTD was deployed at 9.15h. and was on deck again at 9.45h. The standard CTD with the optode was then deployed from 10h to 10.15h.

Multicores
Four multicores were deployed as planned.

In-situ pumping
In-situ pumping (2h) began at 12.15h and ended at 14.15h (4 pumps). A second deployment of all 4 pumps with quartz filters was then performed from 15.30h to 19h.

Lander retrieval
Both landers were retrieved between 19.30 and 20.30h.

Transit to station 21 (Arkona) from 20h onwards

Day 16 Sunday June 12

The ship arrived at Arkona at around 6h.

Lander deployment
Both landers were deployed between 8h and 8.30h.

Ultraclean CTD and standard CTD with optode
The ultraclean CTD was deployed at 8.50h and was on deck again at 9.15h. The standard CTD with the optode was then deployed until 9.40h.

Multicores
Five multicore casts were taken.

In-situ pumping
In-situ pumps were deployed at depths of 10, 20, 30 and 40 m for 2h.

Dredging
Because a shell was found on deck, there was dredging in the afternoon to obtain samples of Arctica Islandica for Rob. Living samples were found.

Lander retrieval
Both landers were retrieved by 19.25h.

End of sampling. Transit to Texel began at 19.30h. Passage through Kieler Canal from ca. 9h-ca. 16.30h. Arrival at Texel at ca. 16h on Tuesday June 14.

4. NUTRIENTS – Fe VICI Baltic Cruise 64PE411 on R.V. Pelagia, June 2016

Jan van Ooijen[1] and Sharyn Ossebaar[1]
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Summary
Nutrients were analysed in a thermostated lab containers equipped with a QuAAtro Gas Segmented Continuous Flow Analyser, measuring approximately 3700 samples during the cruise for the different parameters for CTD, porewater, lander and incubations experiment samples. Measurements were made simultaneously on three channels for Ammonium, Nitrite, and Nitrate with Nitrite together. In the other lab container, Dissolved Inorganic Carbon (DIC) and Sulphide samples were each separately measured. Samples for Phosphate and Silicate were also taken and will be stored in a refrigerator until further analysis back at the NIOZ, The Netherlands. All measurements were calibrated with standards diluted in low nutrient seawater (LNSW) in the salinity range of the stations of the Baltic Sea ranging from 18 - 5 ‰ to ensure that analysis remained within the same ionic strength.

Equipment and Methods
Sample Handling
The seawater samples were collected in 60ml high-density polyethylene syringes with a three way valve from the Niskin bottles of the CTD Rosette. The syringes with a three way valve were first rinsed three times with a small amount of the sample taken directly from the CTD-rosette bottles before being completely filled. After sampling on deck, the samples were processed immediately in the lab container; samples were filtered over 0.2µm and instantly sub-sampled into two vials made out of high density polyethylene, also known as 'pony-vials. The NH4 and NO3 plus NO2, DIC and HS- samples were measured in the lab container usually within 24 hours of sub sampling. Samples were stored in a refrigerator at 4°C and prior to analysis, all samples were brought to lab temperature in about one to two hours. To avoid gas exchange and evaporation during the runs with NH4, DIC or HS- analyses, all vials including the calibration standards were covered with 'parafilm' under tension before being placed into the auto-sampler, so that the sharpened sample needle easily penetrated through the film leaving only a small hole. The QuAAtro uses an LED instead of a lamp as a light source as it is not affected by the movement of the ship giving a stable reading and a sampler rate of 60 samples per hour was used. Calibration standards were diluted from stock solutions of the different nutrients in 0.2µm filtered LNSW diluted with de-ionised water to obtain approximately the same salinity as the samples and were freshly prepared every day. This diluted LNSW was also used as the baseline water for the analysis in between the samples. The LNSW is surface seawater depleted of most nutrients. Each run of the system had a correlation coefficient of at least 0.9999 for 10 calibration points, but typical 1.0000 for linear chemistry. The samples were measured from the lowest to the highest concentration in order to keep carry-over effects as small as possible, i.e. from surface to deep waters. Concentrations were recorded in 'µmol per liter' (µM/L) at an average container temperature of 21.8°C. During the cruise, a freshly diluted mixed nutrient standard, containing silicate, phosphate and nitrate (a so-called nutrient cocktail), was measured in every run. The cocktail sample was used as a guide to monitor the performance of the standards.

Pore-water from sediment cores was collected under anoxic conditions in glove bags under nitrogen atmosphere and sub sampled for H2S, DIC, N, PO4 and Si. For the PO4 pore-water samples, an extra addition of 5µl 5N HCl per 1ml of sample was added to compensate for high DIC background levels, expected up to 25mM DIC, to keep the pH in between 1 and 2

to prevent any form of iron-phosphate precipitates. Sulfide samples were diluted using a dilution factor of 4 made with anoxic demineralised water containing 8ml 1N NaOH/L. DIC samples were also diluted using a dilution factor of 10 with anoxic demineralised water containing 12g NaCl/L, this ensuring that the samples remained with the same ionic strength as deep water of the Baltic Sea.

Analytical Methods
The colorimetric methods used are as follows:

Ammonium (NH_4) reacts with phenol and sodiumhypochlorite at pH 10.5 to form an indo-phenolblue complex. Citrate is used as a buffer and complexant for calcium and magnesium at this pH. The blue color is measured at 630nm (Koroleff, 1969 and optimized by W. Helder and R. de Vries, 1979).

Nitrate plus Nitrite (NO_3+NO_2) is mixed with an imidazol buffer at pH 7.5 and reduced by a copperized cadmium column to Nitrite. The Nitrite is diazotated with sulphanylamide and naphtylethylene-diamine to a pink colored complex and measured at 550nm. Nitrate is calculated by subtracting the Nitrite value of the Nitrite channel from the 'NO3+NO2' value. (Grasshoff et al, 1983).

Nitrite (NO_2) is diazotated with sulphanylamide and naphtylethylene-diamine to form a pink colored complex and measured at 550nm. (Grasshoff et al, 1983).

Dissolved Inorganic Carbon (DIC):
Samples are acidified online after being oxidised by H_2O_2 to prevent H_2S being released before entering the silicon dialyser whereby the formed CO_2 is dialysed to a secondary flow. This secondary flow contains a slightly alkaline phenolphthalein solution giving a pink colour. The more CO_2 that is dialysed, the lower the pH and therefore some discolouration of the pink reagent is observed. This decolouring is measured at 520nm and is an inverse chemistry spectrophotometer method described by Stoll, Bakker, Nobbe and Haesse, 2001.

H_2S:
To keep the samples in the S_2^- form under alkaline conditions, a small aliquot of NaOH is added. The Hydrogen Sulfide in the sample reacts with para-aminodimethylaniline and ferric chloride to yield methylene blue which is measured at 660nm as described by Grasshof, K., 1969.

Back at the NIOZ, The Netherlands;

Silicate (Si) reacts with ammonium molybdate to a yellow complex and after reduction with ascorbic acid, the obtained blue silica-molybdenum complex is measured at 820nm. Oxalic acid is added to prevent formation of the blue phosphate-molybdenum complex (Strickland & Parsons, 1968).

Ortho-Phosphate (PO_4) reacts with ammonium molybdate at pH 1.0, and potassium antimonyltartrate is used as a catalyst. The yellow phosphate-molybdenum complex is

reduced by ascorbic acid and forms a blue reduced molybdophosphate-complex which is measured at 880nm (Murphy & Riley, 1962).

Calibration and Standards

Nutrient primary stock standards were prepared at the NIOZ as follows;
Phosphate (PO_4): by weighing Potassium dihydrogen phosphate in a calibrated volumetric PP flask to make 1mM PO_4 stock solution.
Ammonium (NH_4): by weighing Ammonium Chloride in a calibrated volumetric PP flask to make 1mM NH_4 stock solution.
Nitrate (NO_3): by weighing Potassium nitrate in a calibrated volumetric PP flask set to make a 10mM NO_3 stock solution.
Nitrite (NO_2): by weighing Sodium nitrite in a calibrated volumetric PP flask set to make a 0.5mM NO_2 stock solution.
Silicate: by weighing Na_2SiF_6 in a calibrated volumetric PP flask to 19.84mM Si stock solution.
DIC: by weighing Na_2CO_3 stock in a calibrated volumetric PP flask set to make a 200mM stock solution.
S_2^- : by weighing Na_2S in 0.5N NaOH set to make a 50mM Sulphide stock solution.

All standards were stored at room temperature in a 100% humidified box. The calibration standards were prepared daily by diluting the separate stock standards, using three electronic pipettes, into four 100ml PMP volumetric flasks (calibrated at the NIOZ) filled with diluted LNSW. The blank values of the diluted LNSW were measured onboard and added to the calibration values to get the absolute nutrient values.

Statistics
Quality Control
Our standards have already been proven by inter-calibration exercises from ICES and Quasimeme, and over the past years the RMNS exercise organised by MRI, Japan, concluded them to be within the best obtainable limits to the mean of the better laboratories.
To gain some accuracy, the Cocktail standard which contains PO4, NO3 and Si has been monitored since 1997, showing between run reproducibility better than 1.5% , but typically 0.7% of its average value. The following values were obtained from the cocktail which was diluted 100 times in a calibrated PP volumetric flask, being measured in every run onboard.

	Average value	S.D.	N	Dilution Factor
PO4	0.899 uM	0.009uM	42	250
NO3	13.701 uM	0.285uM	42	250

Although our cocktail standard is measured in every run and its value remained stable for all nutrient measurements during the cruise, it is vitally important to get a certified nutrient reference material, like the standard seawater for salinity that is directly for use, in order to obtain real accuracy to give better comparison between labs and cruises.

Mean Detection Limits

The method detection limit was calculated during the cruise using the standard deviation of ten samples containing 2% of the highest standard used for the calibration curve and multiplied with the student's value for n=10, thus being 2.82. (M.D.L = Std Dev of 10 samples x 2.82)

	µM/l	Used measuring ranges µM/l:
PO4	0.011	2.0
NH4	0.007	5.0
NO3+NO2	0.005	15.5
NO2	0.002	0.5
HS-	0.178	400

Further Remarks

It is suggested that through diluting the samples by means of electronic pipettes, one for the sample and one for the dilution water, a small error of maximum 1.0% could be introduced. The reported pore-water results took into account the dilution steps that were made in the glovebag prior to analysis for HS- and DIC.

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5. Water column sampling incl. ultraclean CTD

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[1]Utrecht University, [2]Rutgers University

Sampling of the water column was carried out by using an ultra-clean trace metal conductivity-temperature-depth (CTD) sampler consisting of an all-titanium frame with 24 sample bottles of 24 L each made of PVDF plastic (abbreviated uc CTD, made at NIOZ), arranged as two rows of twelve bottles (Figure 17).

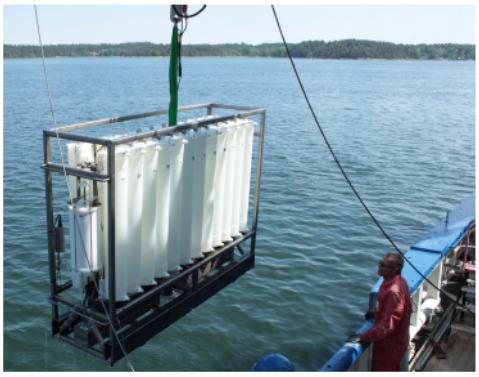
a)  b) 

Figure 9. a) uc CTD being retrieved at the Stockholm archipelago, b) uc CTD placed back into the clean CTD container.

A Kley France winch was used to deploy the uc CTD to deep waters by a 17.7 mm diameter Kevlar hydrowire with seven independent internal signal/conductor cables (Cousin Trestec S.A.). Sampling of the uc CTD occurred in a class 100 clean-room container specially designed to get the uc CTD in and out rapidly to avoid contamination. The container was also equipped with an anti-room separating the main part of the container of the outside by a plexiglass door to keep dust and other sources of contamination outside. Moreover the designed container allowed simultaneous sampling of 12 bottles covering both sides of the uc CTD. To prevent contamination and to keep the uc CTD safe and secure, the uc CTD was at all times placed inside the clean air container (meeting class 100 clean-room specifications) when not in use during casts.

The water column structure of Station 1 to 22 was analysed and 24 samples were in general taken with the uc CTD or with a 5 m resolution. Three categories of stations were identified: oxic: stations 1,2, 4, 5,13 and 21; anoxic: 7, 10, 12 and 20 (also sulfidic), 16, 17, 18, 19 (also sulfidic) and hypoxic: station 9, 10. Special emphasis was put on the transition zone between oxic and sulfidic waters ('redoxcline'), which is prominent in the Baltic Sea basin. In this transition zone, water was collected at 5 m intervals. In addition, several samples below and above the redoxcline were collected. Anoxic samples were collected following the Black Sea cruise procedure, explained in the "Collection of trace metals" paragraph below. The sensors on the uc CTD collected continuous profiles of key physicochemical water column properties: conductivity, temperature, fluorescence, beam transmission and dissolved O_2, the latter with a Seabird oxygen electrode. The water collected in the uc CTD bottles at various depths was immediately sampled for trace metal analysis but also sampled and analyzed on-board for alkalinity, dissolved inorganic carbon (DIC) and pH along with NH_4^+, NO_2^-, PO_4^{3-} (analysed later in the lab) and HS^- with Quattro gas-segmented continuous flow analyzers.

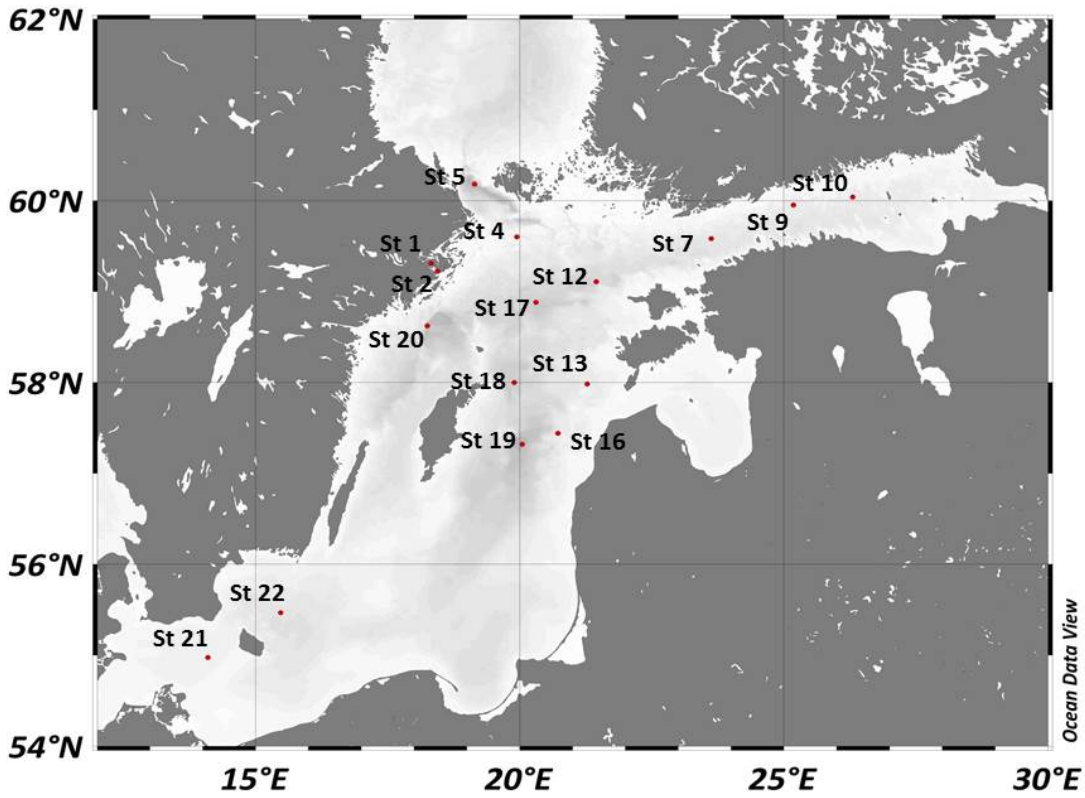


Figure 10. Baltic Sea and the different uc CTD stations.

Description of the uc CTD

To avoid contamination, the frame of the uc CTD was made of titanium and all the electronic pressure housings and other parts were made of titanium or clean plastics like Teflon, PVDF or POM. Prior to a cast the frame was prepared inside that container and transported to the CTD-launching spot using a custom made aluminum pallet and a long bedded forklift. After the cast the uc CTD was immediately returned to the clean air container to avoid contamination of the equipment with grease, rust or smoke particles from the ship. After closing of the container the air treatment system started to clean the air using HEPA-filters (meeting class 100 clean-room specifications after 15 minutes). The electronic CTD sensor system consisted of a SBE9plus underwater unit, a SBE11plusV2 deck unit, a NIOZ developed multivalve bottle-controller, a SBE3plus thermometer, a SBE4 conductivity sensor, a SBE5T under water pump, a SBE43 dissolved oxygen sensor, a Chelsea Aquatracka MKIII fluorometer, a Wetlabs C-Star transmissiometer (25 cm, deep, red) and a Satlantic PAR-sensor for underwater-PAR. Due to the butterfly-type closure on both ends of the bottle the opening was maximized resulting in an excellent flow-through. Opening and closing of the bottles were controlled by a hydraulic system. For bottom-detection a Benthos PSA-916 altimeter was installed.

Collection for trace metals

Before sampling, the uc CTD and container were thoroughly rinsed with freshwater as handling of the uc CTD by the crew members could have introduced dust/dirt into the container and the nutrient sample collection could have compromised the quality of the Teflon valves on the bottles.

Unfiltered, filtered samples were collected in acid washed Low Density PolyEthylene (LDPE) bottles (overnight at 60 °C 1 % Decon bath, overnight 60 °C 10 % HCl reagent grade

and 0.1 % HCl baths, stored in 0.1 % HCl). LDPE tubing was acid washed following the same procedure as for the LDPE bottles (overnight at 60 °C 1 % Decon bath, overnight 60 °C 10 % HCl reagent grade and 0.1 % HCl baths).Polycarbonate 47 mm filter holders were cleaned as follow: plastic parts (holder, connectors and valves) were placed for one week in cold 1 % Decon bath and cold 10 % HCl reagent grade for a week for the plastic parts, o-rings were placed overnight in cold 0.1 % HCl reagent grade bath. All filters were acid washed following the GEOTRACES cookbook: 10 % in distilled hydrochloric acid at 60 °C overnight and stored in MilliQ water.
The bottles of the uc CTD were over-pressured (9 psi) resulting in a flow of sample water into the gas lines of the CTD on a few occasions at the beginning of the cruise. It was therefore decided to sample for unfiltered first and start the 0.2 µm filtration with pressure. Each sample bottle was rinsed with the sample to collect using the following procedure: shaking for a few seconds, pouring of the seawater into the cap, rinsing of the threads of the cap and bottle. This procedure was repeated three times before collection.

Total and dissolved samples were acidified on board to pH 1.8 with distilled hydrochloric acid prepared at the home laboratory in Utrecht.

Procedure for oxic sample on the uc CTD:
For oxic water, the sample collection involved a simple set up, LDPE and C-Flex tubing and the filter holder.
- Unfiltered samples were directly collected from the uc CTD bottles using a LDPE tubing, 10 cm long to avoid contact with the titanium frame.
- 0.2 µm dissolved samples were directly filtered from the uc CTD bottles under nitrogen pressure using 0.2 µm Sartobran 300 cartridges (Sartorius, Figure 11). The cartridge was rinsed with at least 0.5 L of sample and the 60 mL bottle was filled up to the shoulder.
- 0.02 µm dissolved samples were directly processed from the uc CTD bottles under nitrogen pressure using Virosart cartridges (Sartorius, Figure 19). The cartridge was rinsed with at least 1 L of sample and the 60 mL bottle was filled up to the shoulder.

a) b)

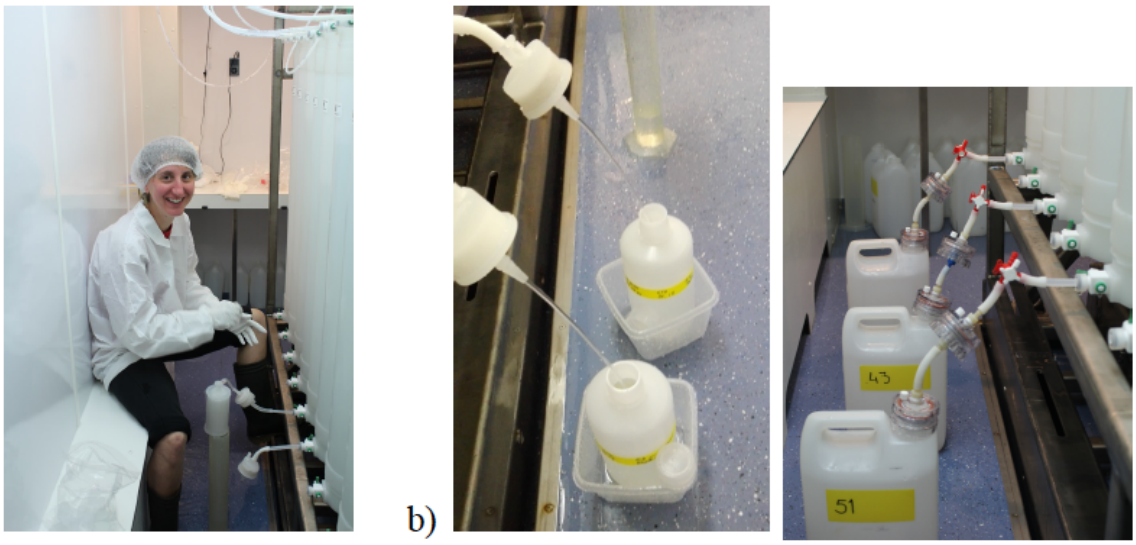


Figure 11. a) Marie setting up the 0.02 µm connected to 0.2 µm filter, b) filtration on 0.2 µm for chromium and uranium, c) 0.02 µm particulate material collected using in series 0.2 µm and 0.02 µm filters.

- 0.2 µm particulate samples were directly processed from the uc CTD under nitrogen pressure using 47 mm 0.2 µm Supor membrane filter placed in filter holder attached to the

bottle by a LDPE tubing and Tygon/C-flex tubing. The filtered seawater was collected in 5 L jerrycan for volume measurements. Once the collection was finished, the filter was taken to the HEPA in the lab container, vacuumed to remove any excess of seawater (about 12 mL) and placed in a Petri slide to be stored at - 20 °C. In the meantime, the volume of seawater passed through the filter was recorded.
- 0.02 µm particulate samples were directly processed from the uc CTD under nitrogen pressure using an assembly of two 47 mm filter holders connected by a Tygon tubing. 0.2 µm Supor membrane filter was placed in the first filter holder and 0.02 µm Supor membrane filter was placed in the second filter holder, collecting the size fraction between 0.2 and 0.02 µm and also avoiding immediate clogging of the 0.02 µm filter. Once the collection was finished, the filter was taken to the HEPA in the lab container, vacuumed to remove any excess of seawater (about 12 mL) and placed in a Petri slide to be stored at - 20 °C. In the meantime, the volume of seawater passed through the filter was recorded.
- Some requirements needed to be addressed to obtain the GEOTRACES process study label: surface, intermediate and deep waters were sampled in duplicate, filtered on 0.2 µm. Bottles of 250 mL were collected and will be sent to various laboratories for intercomparison.

<u>Anoxic sample collection procedure on the uc CTD:</u>
For anoxic water, the set up involved LDPE and C-Flex tubing, filter holders and two three-way valves for the 0.2 µm filtration and two filter holders and a three way valve for the 0.02 µm filtration.
- Unfiltered samples were directly collected from the uc CTD bottles using a LDPE tubing, 10 cm long to avoid contact with the titanium frame.
- 0.2 µm dissolved samples were directly filtered from the uc CTD bottles under nitrogen pressure using 0.2 µm Sartobran 300 cartridges (Sartorius). The cartridge was rinsed with at least 0.5 L of sample and the 60 mL bottle was filled up to the shoulder.
- 0.02 µm dissolved samples were directly processed from the uc CTD bottles under nitrogen pressure using Virosart cartridges (Sartorius). The cartridge was rinsed with at least 1 L of sample and the 60 mL bottle was filled up to the shoulder.
- 0.2 µm particulate samples were directly processed from the uc CTD under nitrogen pressure using 47 mm 0.2 µm Supor membrane filter placed in filter holder attached to the bottle by a LDPE tubing and Tygon/C-flex tubing. The filtered seawater was collected in 5 L jerrycan for volume measurements. Once the collection was finished, a sequence of actions was followed, first the valve below the filter holder was closed then the top valve was closed, the uc CTD valve was closed and finally the N_2 valve closed. The filter holders with filter were transferred to an N_2-purged glovebag in a cold room (10 °C for deep stations and 17 °C for shallow stations). The filter holders were set upright and both valves removed and the filter vacuumed to remove any excess of seawater. In most cases, the filter holder needed to be opened and closed again to release water from the head space in the top part of the filter holder. The filters were then placed in a Petri slide and placed in a geochemical sampling bag and sealed with N_2. The bag was then stored at -20 °C. In the meantime, volume of seawater passed through the filter was recorded.
- 0.02 µm particulate samples were directly processed from the uc CTD under nitrogen pressure using an assembly of two 47 mm filter holders connected by a Tygon tubing, a three way valve was placed above the 0.2 µm filter holder. 0.2 µm Supor membrane filter was placed in the first filter holder and 0.02 µm Supor membrane filter was placed in the second filter holder. Once the collection was finished, a plug was placed on the connector below the 0.02 µm filter holder, the top valve closed, the uc CTD valve closed and finally the gas line closed. The whole setup was then taken to the HEPA in the lab container, vacuumed to

remove any excess of seawater (about 12 mL) and placed in a Petri slide to be stored at - 20 °C. In the meantime, volume of seawater passed through the filter was recorded.

a)  b) 

Figure 12. Filtration setup for the 0.2 um filtration and b) processing of the anoxic 0.2 µm filter by Amy.

Sample collection was divided as follow:
- Universiteit Utrecht: Total and dissolved Iron (Fe) and other trace metals were collected: duplicates of 60 mL unfiltered seawater for total concentrations, duplicates of 60 mL seawater filtered on 0.2 µm and duplicates of 60 mL seawater filtered on 0.02 µm for dissolved iron and metals. Particulate material was also collected on 0.2 µm and 0.02 µm for spectrophotometry analyses at the Synchroton (ESRF Grenoble) and for total elemental concentrations using total digestion.
- Rutgers University: Water samples for total and dissolved Chromium (Cr) and Uranium (U) and Fe isotopes were collected: 500 mL of unfiltered seawater for total concentrations and 1 L of 0.2 µm filtered seawater for dissolved concentrations.

6. **Water column profiles**

Amy Anderson[1] and Marie Séguret [2]
[1] Rutgers University [2] Utrecht University

On the following pages the plots that were produced on board the Pelagia for samples collected with the ultraclean CTD system are shown. The results are presented in the order that they were sampled between 28 May and 12 June 2016.

For each station, up to three different plots are presented. The first set is from measurements by the CTD. The figure includes 5 subplots showing temperature (° Celsius), salinity, density sigma-theta (kg/m^3), beam transmission (%), and oxygen (umol/L). The downcast is plotted.

In the second plot, nutrient data from CTD water samples are represented. For these plots the order is ammonia (NH_4^+), nitrate and nitrite combined (NO_3 + NO_2), nitrite only (NO_2), dissolved inorganic carbon (DIC), and lastly, hydrogen sulfide (HS^-). Not all stations were measured for HS^- due to the oxygenated conditions.

For the final plot, filters of the particulates were collected from the bottles on the CTD. The filters were 0.2 um mesh size supor filters. Between 1-5 L of water was filtered. Not all water sample stations were sampled for particulates due to time constraints.

All stations with nutrient profiles were sampled with the ultra clean CTD. The conventional CTD was used to test out sites prior to sampling with the multicorer or lander. The CTD plots were made and are also included below when there was no ultra clean CTD cast at a station. Unless noted, the ultra clean CTD was used.

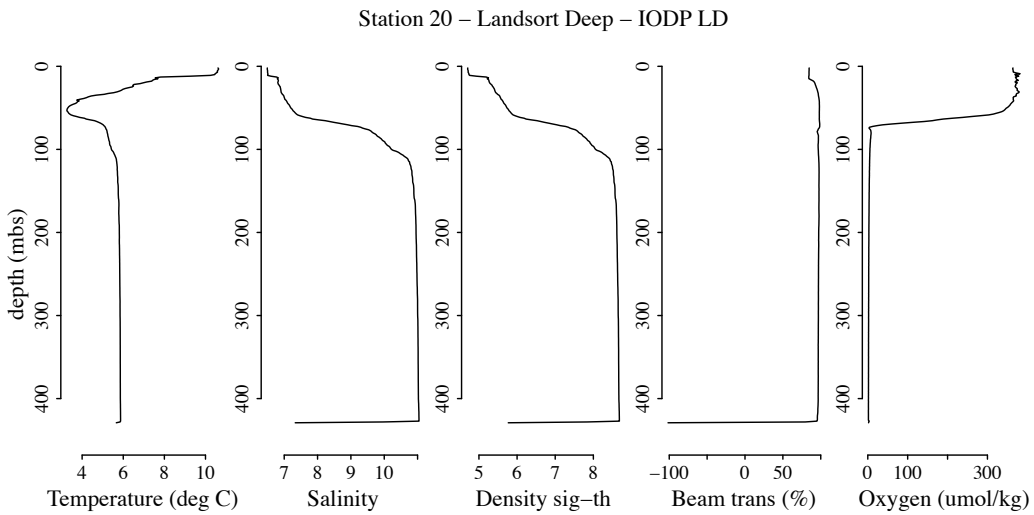


Figure 13. Water column profiles, all stations

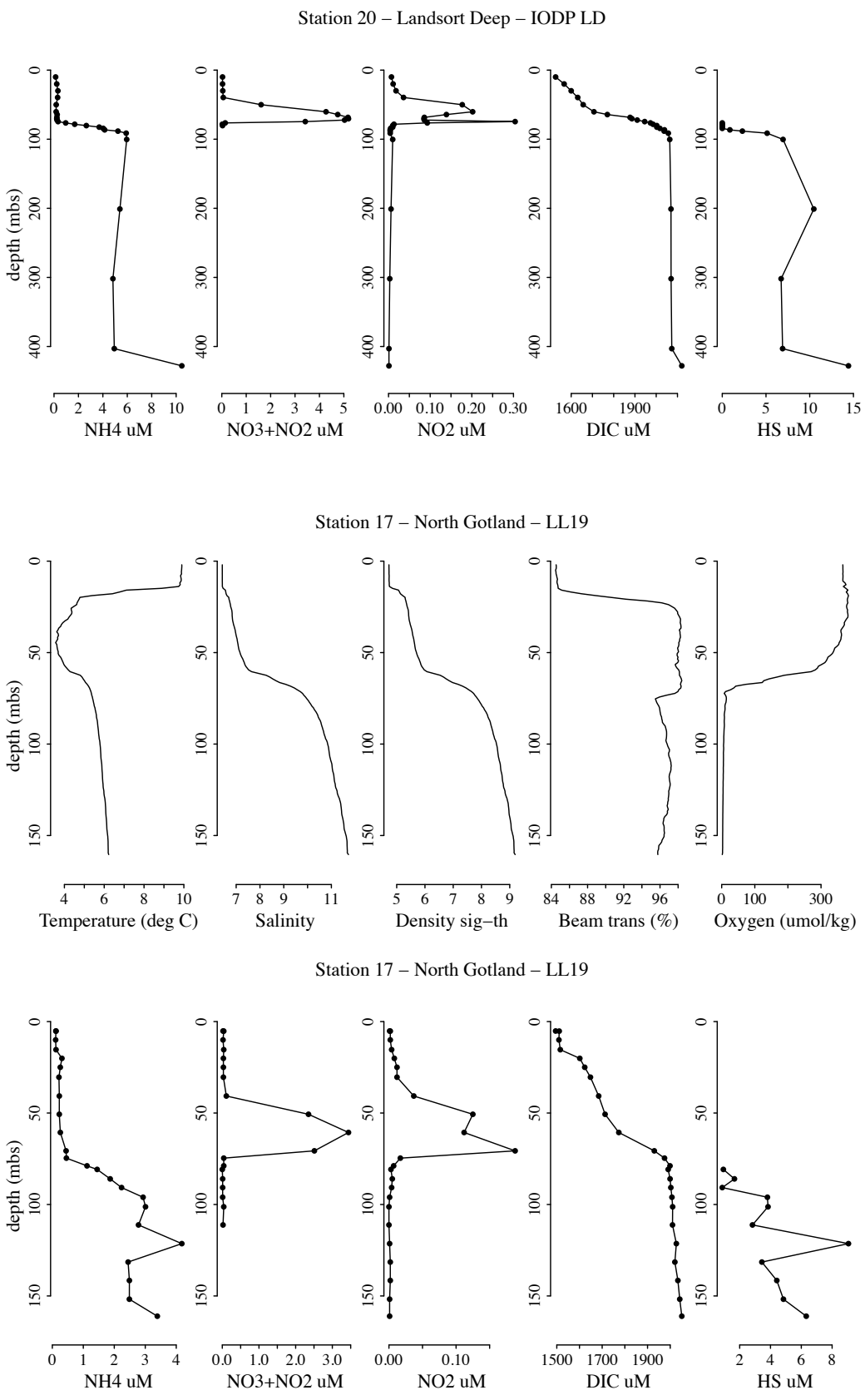
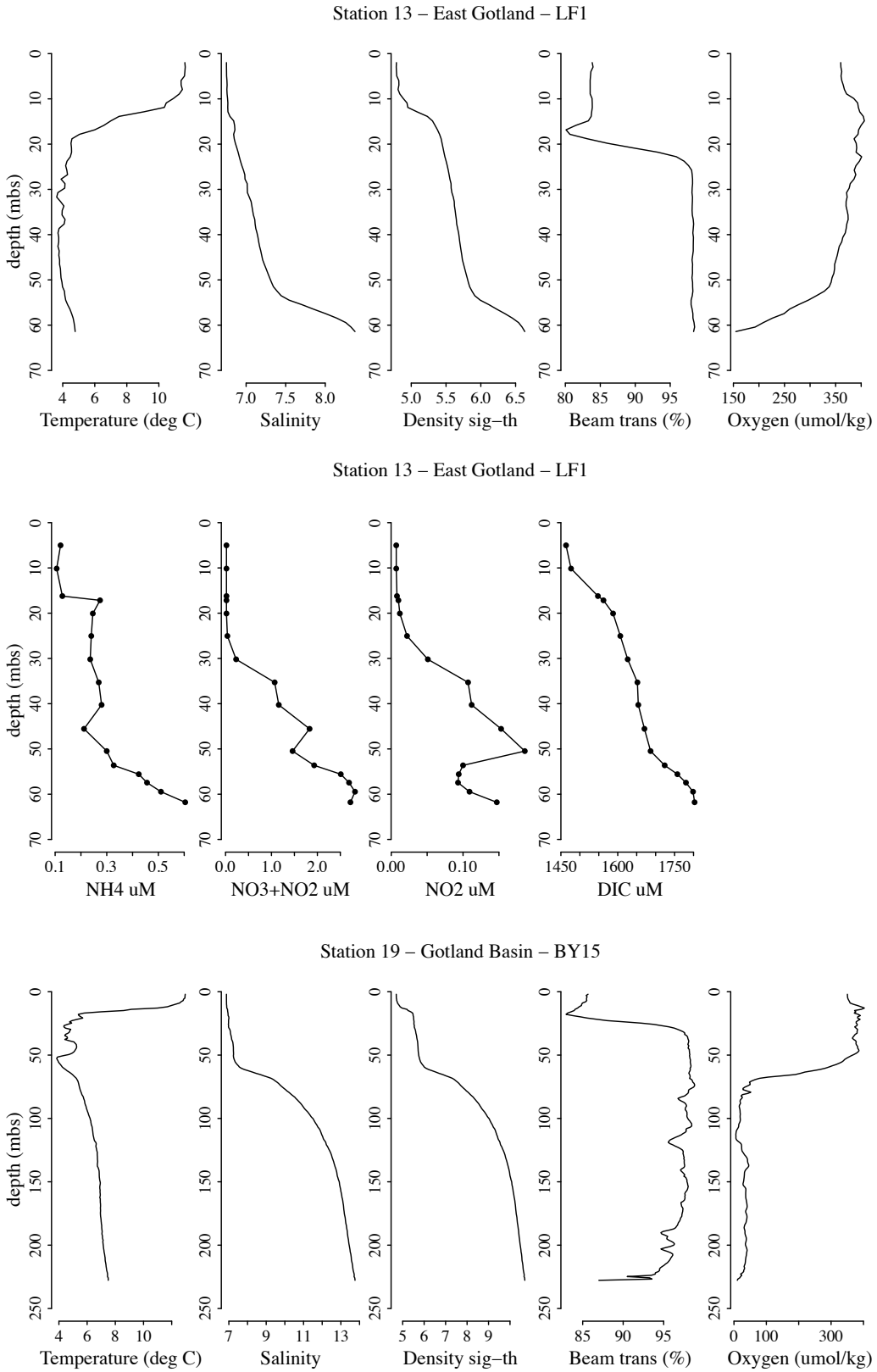


Figure 13 (continued)



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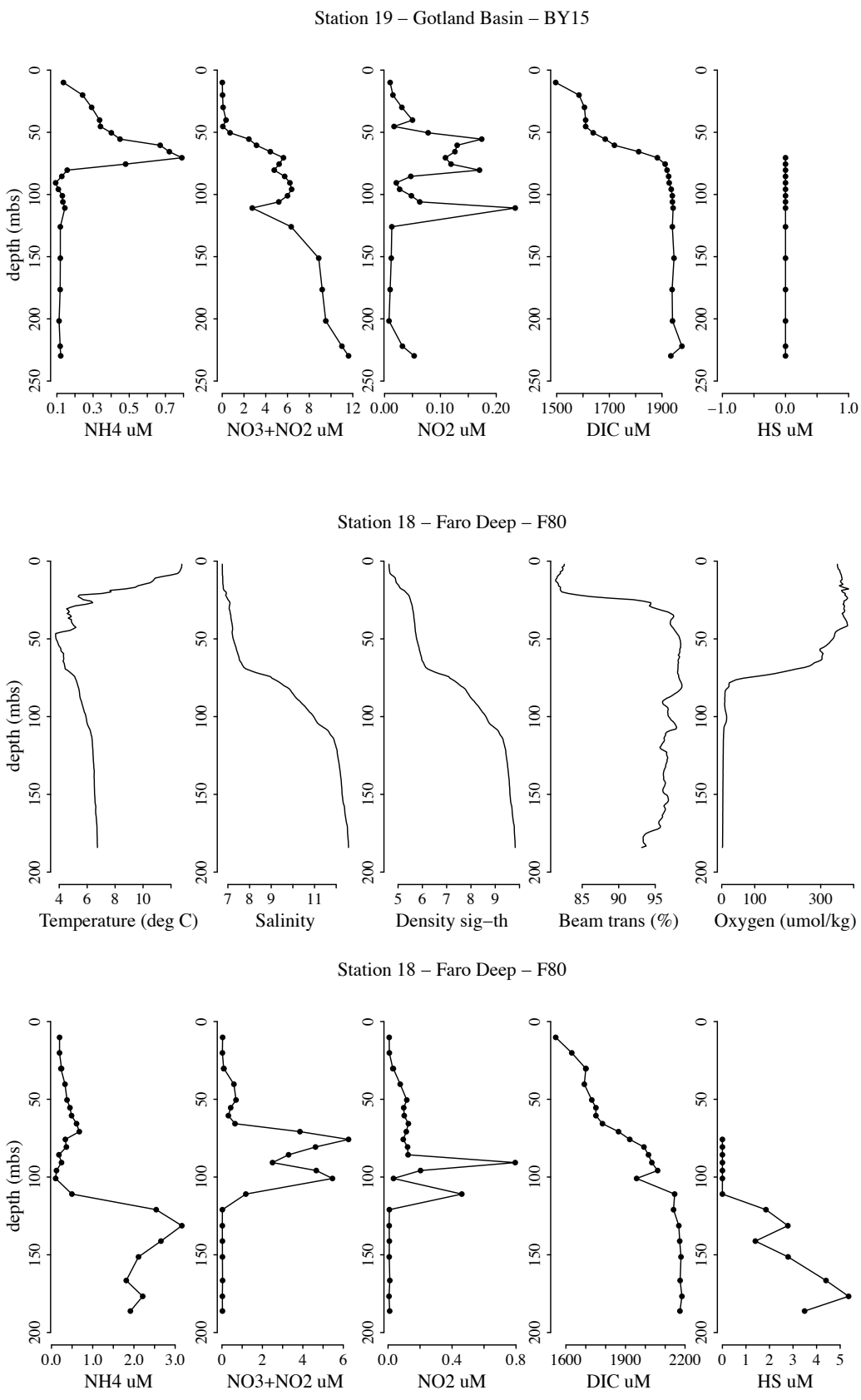

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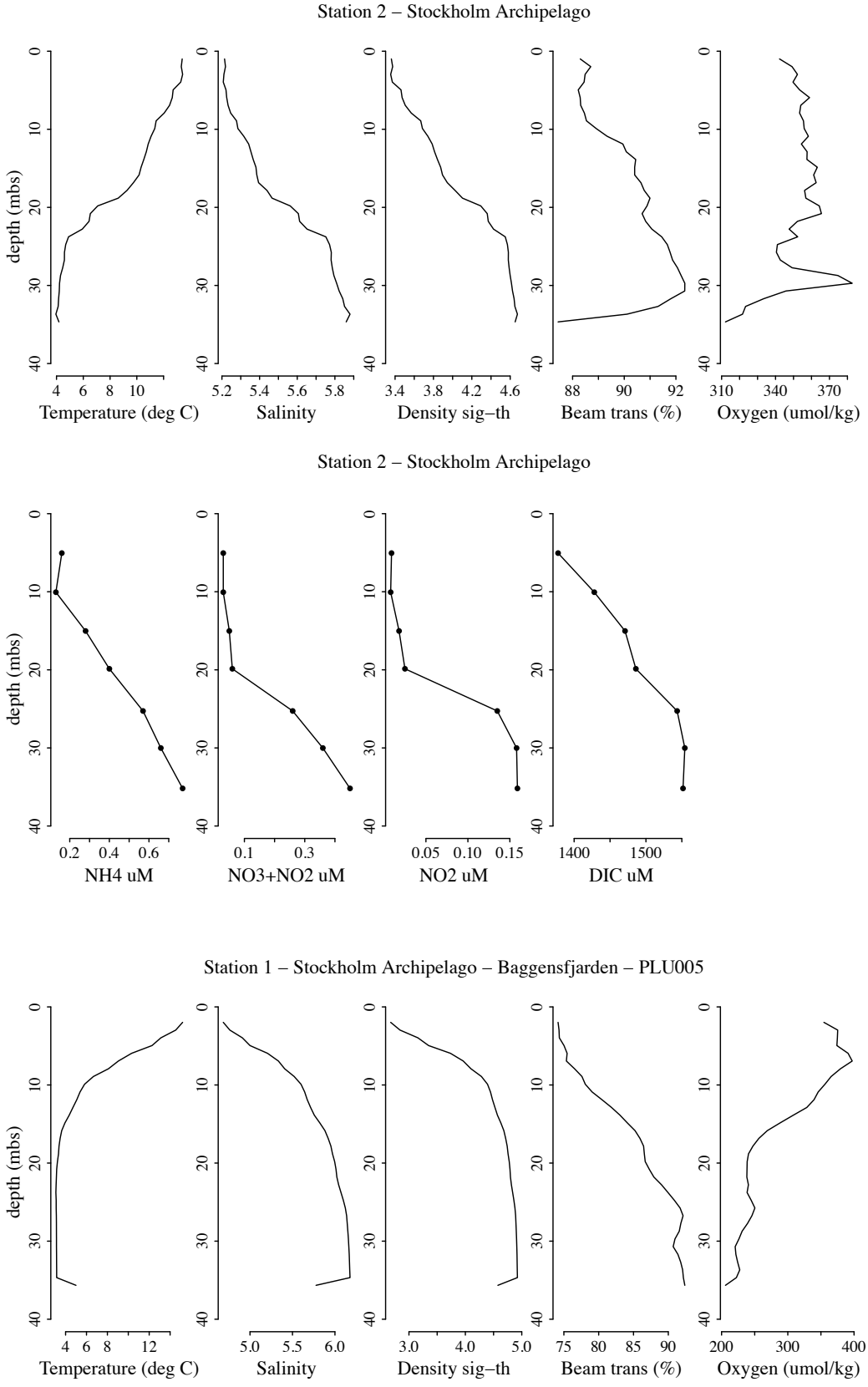

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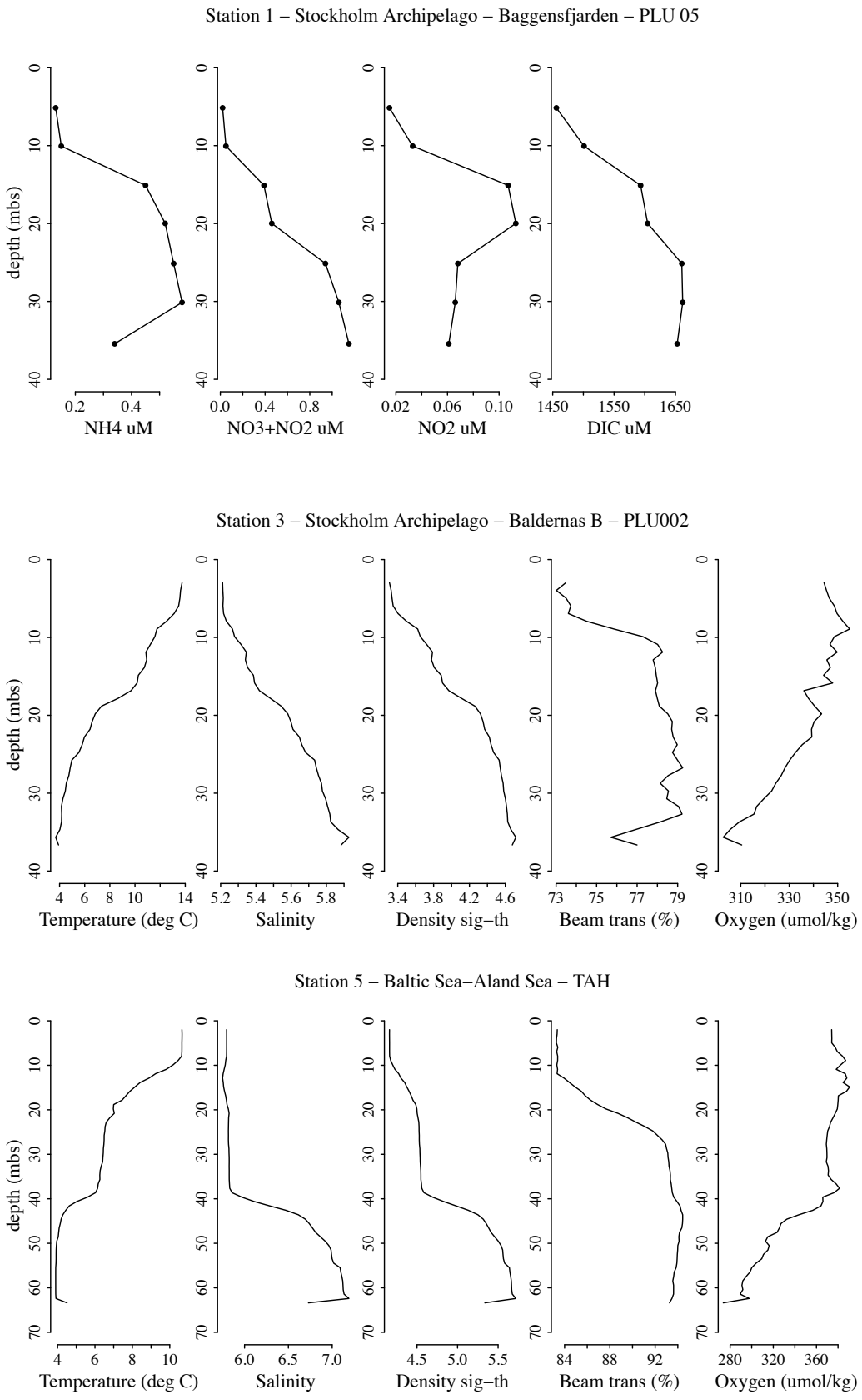
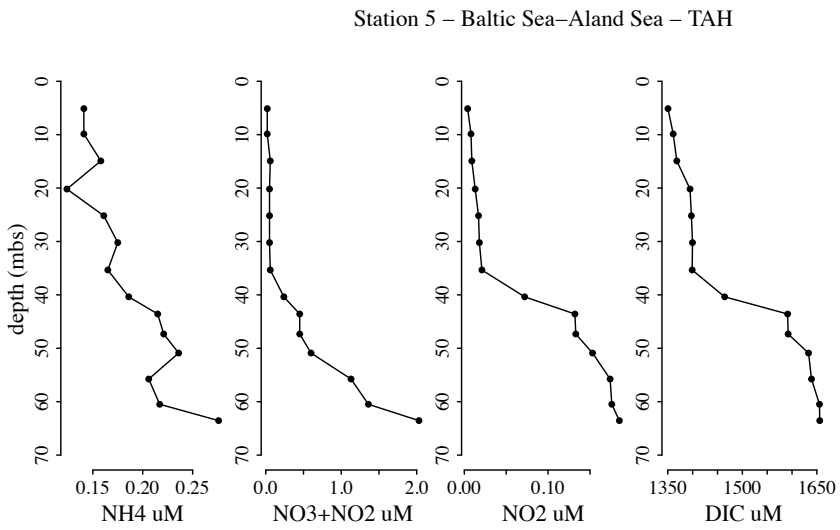
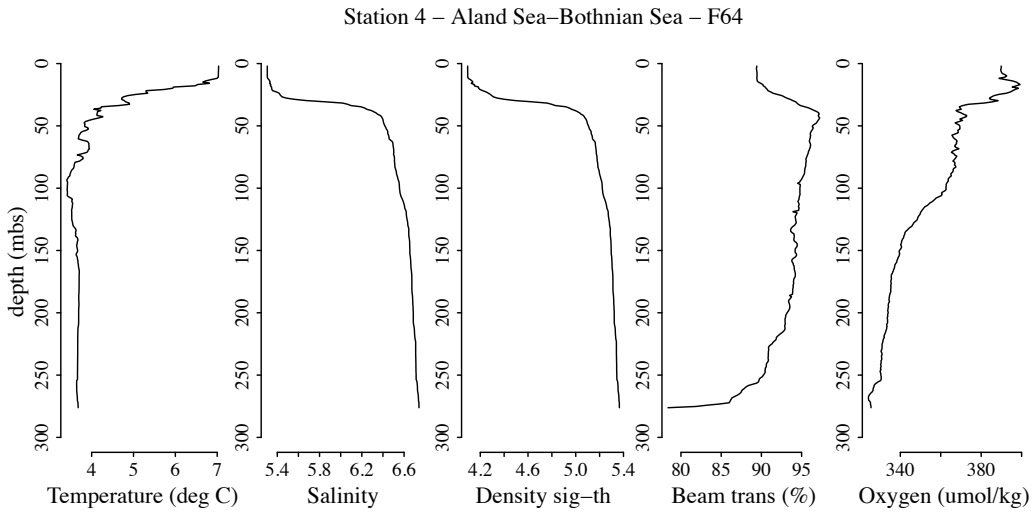
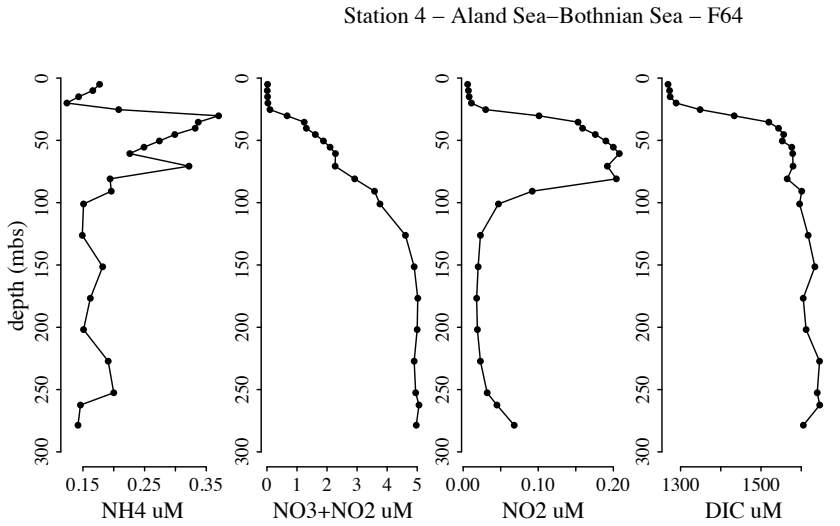


Figure 13 (continued)







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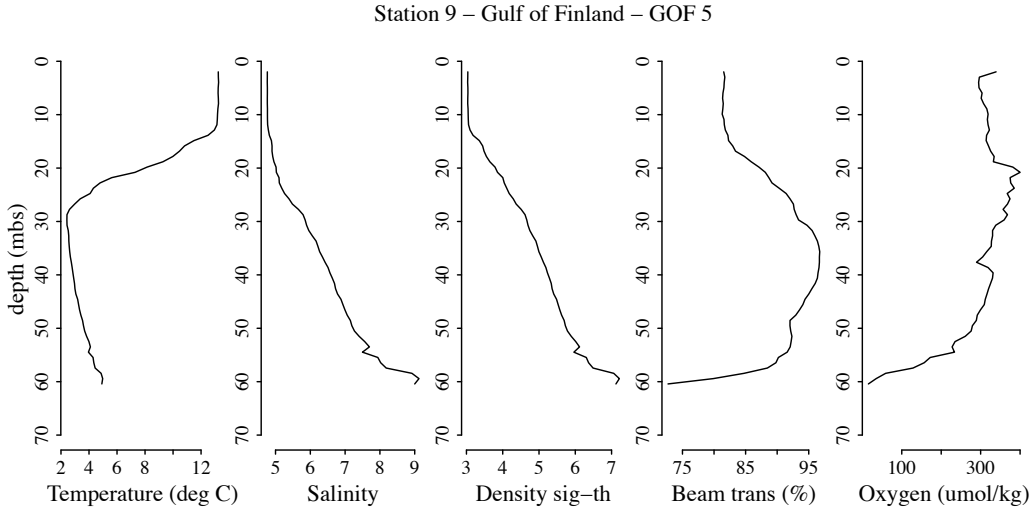

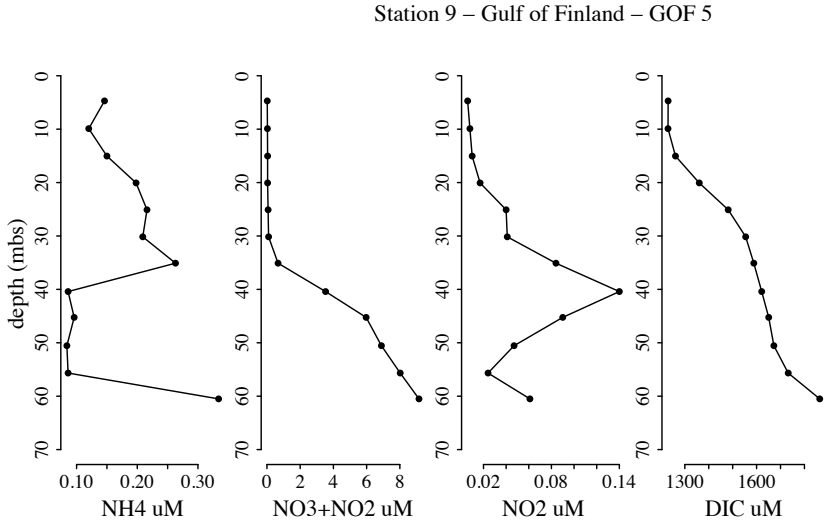

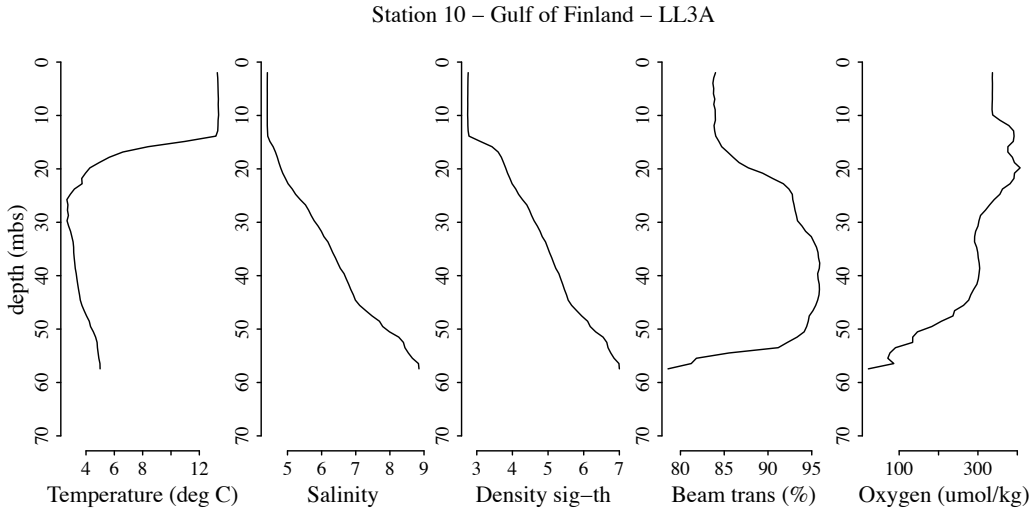

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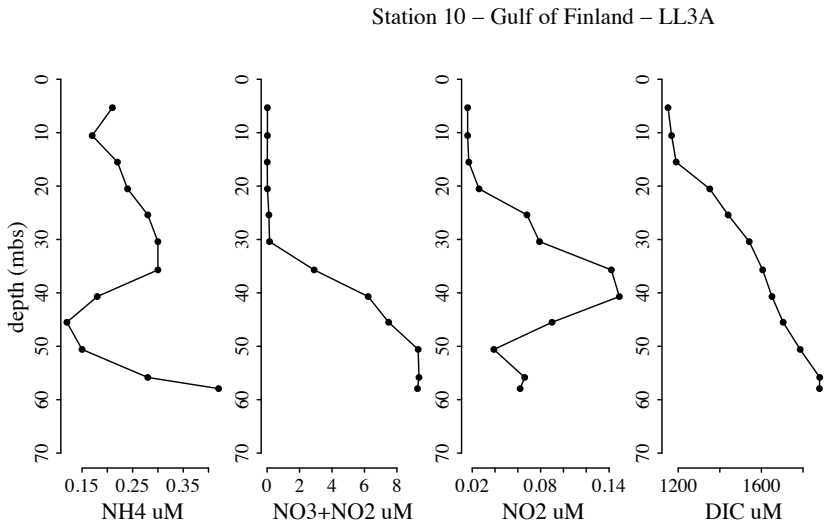

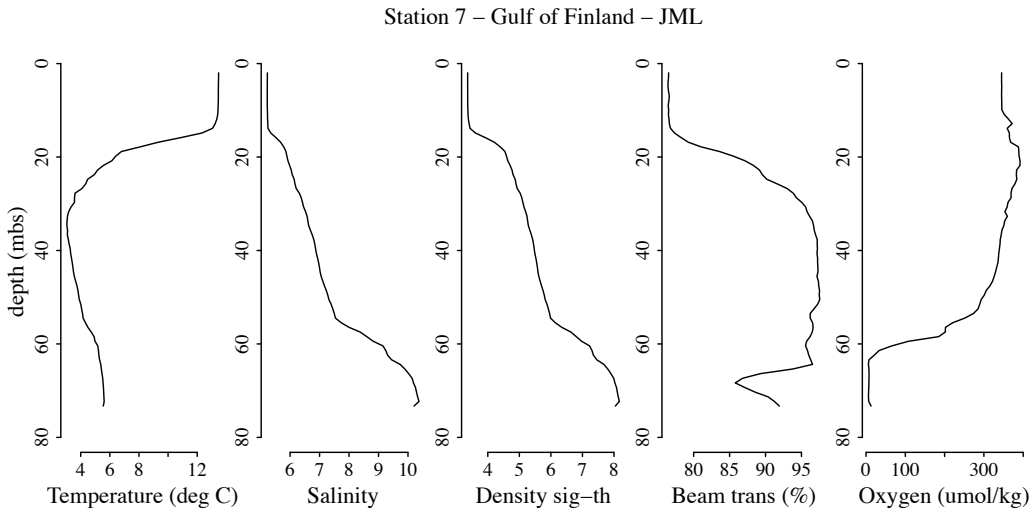

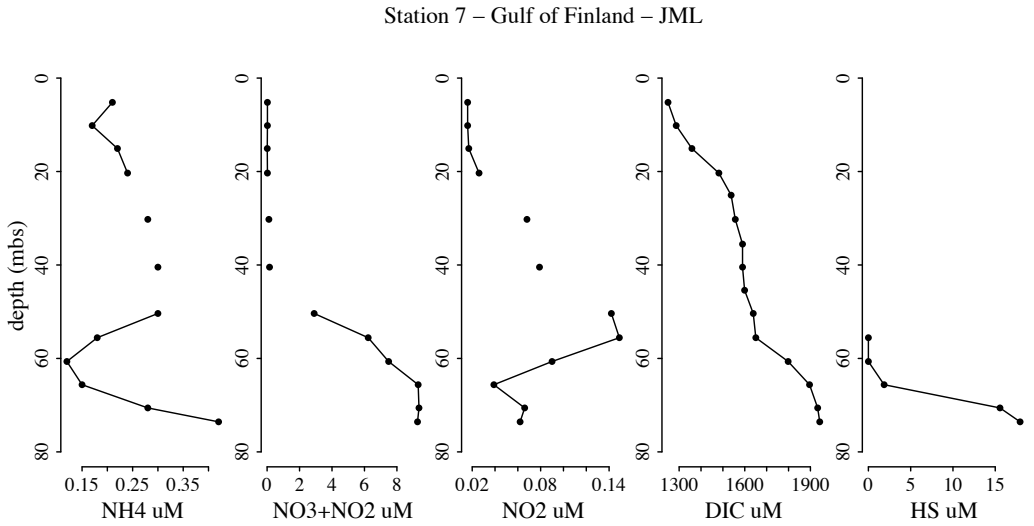

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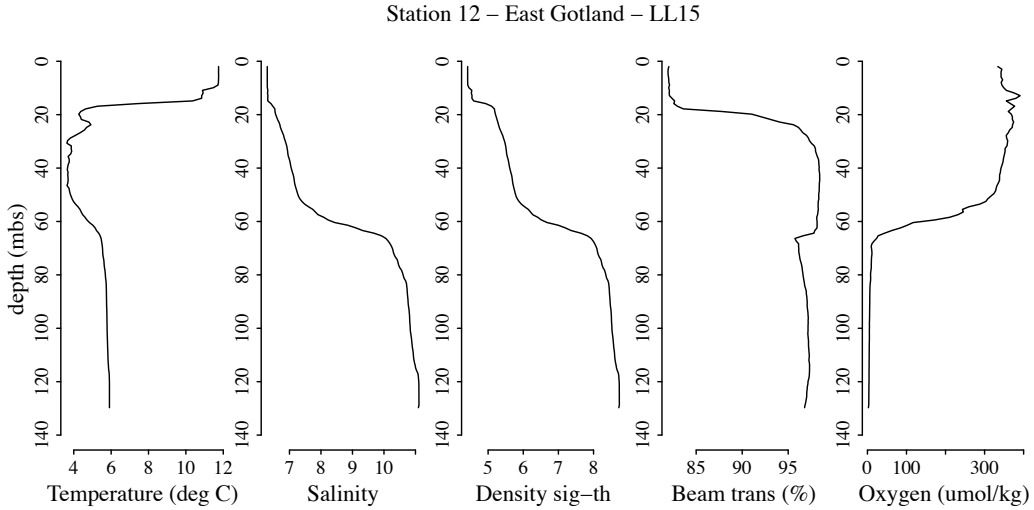

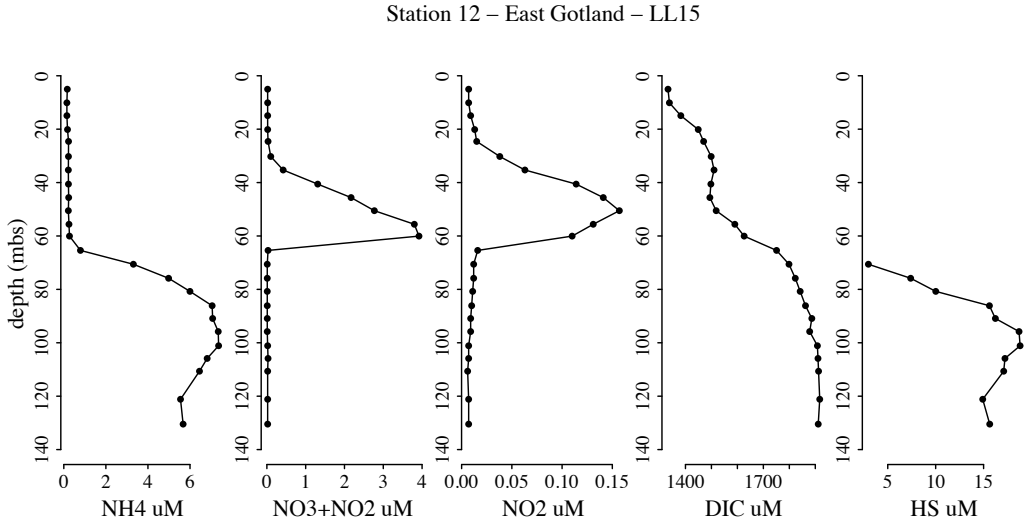

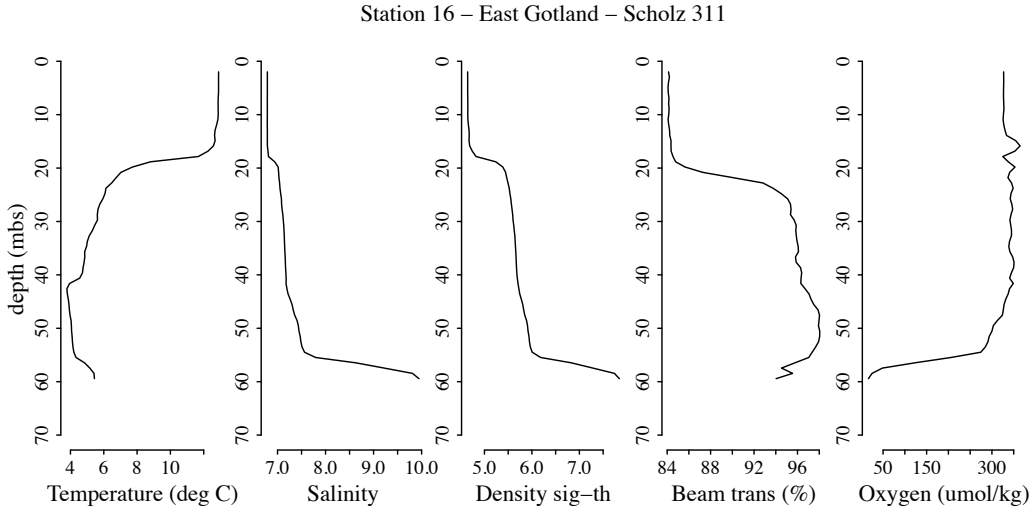

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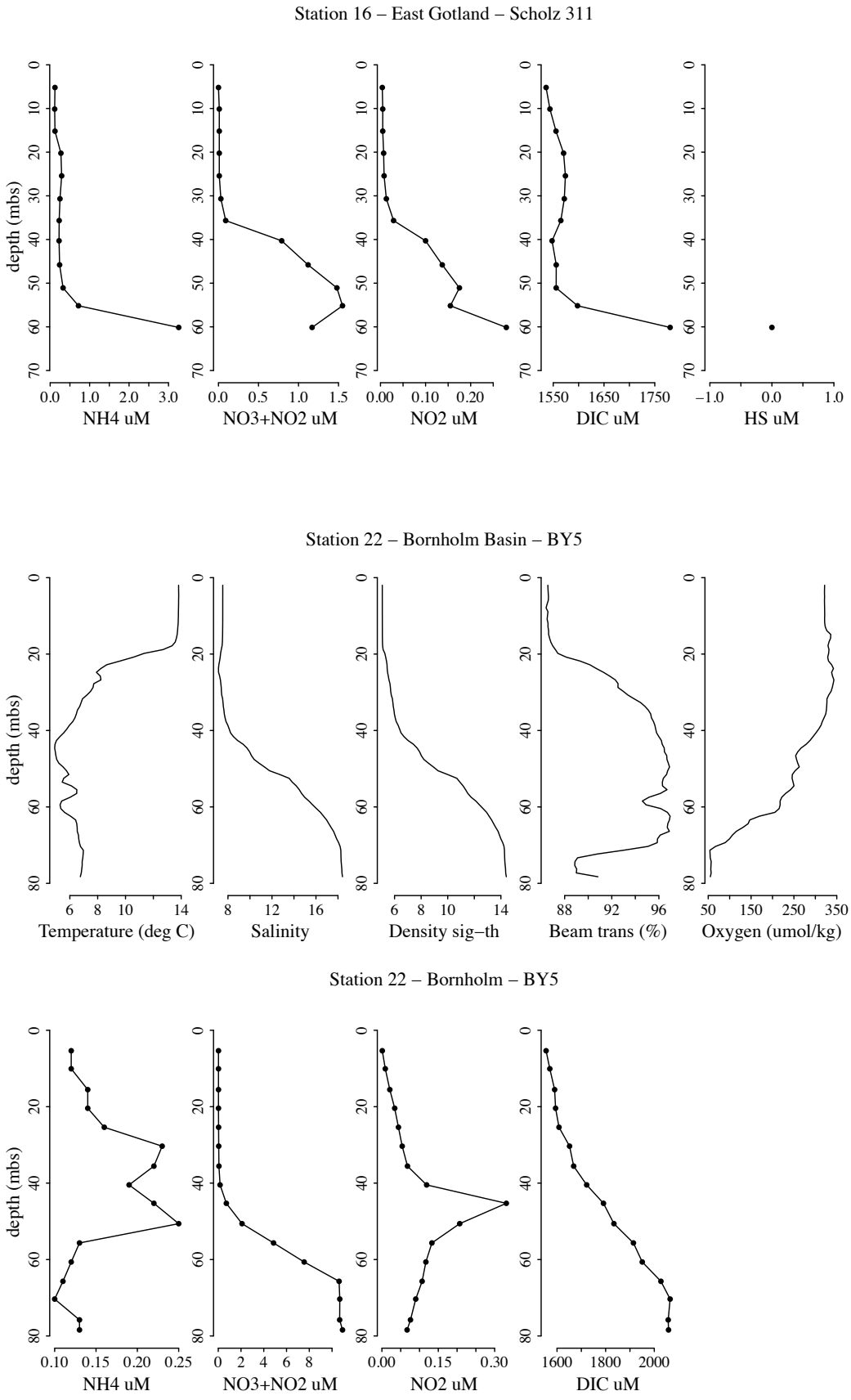

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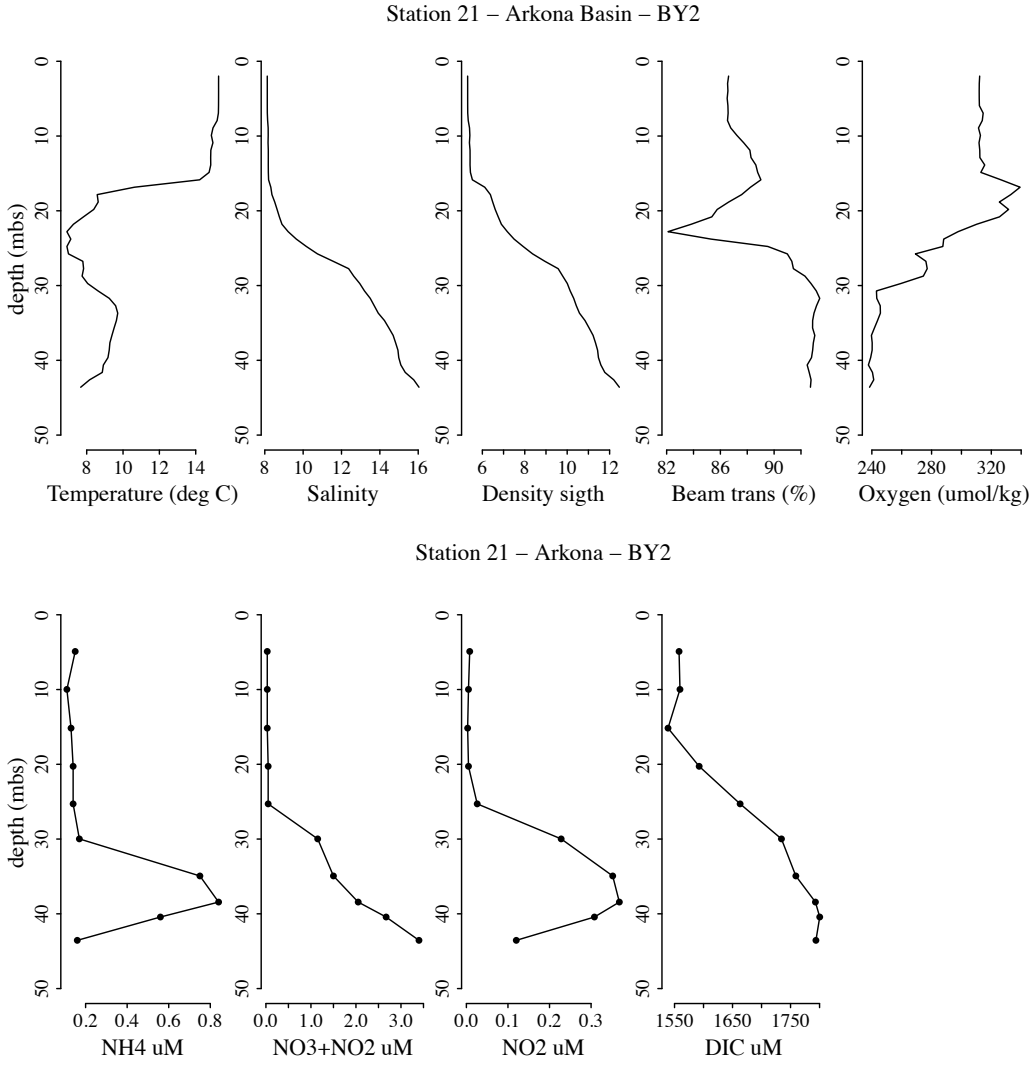


Figure 13 (continued)

7. Water column carbonate system parameters, Mathilde Hagens (UU)

a) Dissolved inorganic carbon (DIC) measurements using the AIRICA

The AIRICA (Automated Infra - Red Inorganic Carbon Analyser, designed and built by Dr. L. Mintrop, Marine Analytics and Data, Kiel, Germany) is a machine that has recently been acquired by NIOZ (AIRICA #25). It uses a high precision syringe pump to deliver an exact amount of sample (in this case 2.1 mL) to a stripper. CO_2 is liberated from the sample by acidification with 8.5% H_3PO_4 and is transported by a stream of carrier gas. After some drying steps, the carrier gas passes through a LICOR non-dispersive IR gas analyser, where the CO_2 concentration in the gas is measured. The integration of the resulting peak is directly proportional to the amount of CO_2 extracted from the sample. This measurement is repeated four times; the measurement most deviating from the mean is discarded.

At every CTD station, water samples were collected from every unique depth (the exact bottle numbers are the same as for DOC and nutrient sampling and can be found in their data tables) into ~500 mL borosilicate glass sample bottles with plastic caps, using Tygon tubing. These bottles were stored at 25°C in the dark until analysis, which usually took place within 12 hours of sampling. Throughout the cruise, duplicate samples were taken and some samples were measured twice to confirm the precision and reproducibility of our results.

b) DIC and total alkalinity (TA) measurements using the VINDTA

Sampling and analysis for DIC and TA broadly followed the standard operating procedures outlined by Dickson et al. (2007). Sampling occurred as described under a); samples were measured on the AIRICA first before being measured on the VINDTA.

All analyses were performed on a VINDTA 3C (Versatile INstrument for the Determination of Total Alkalinity, designed and built by Dr. L. Mintrop). Samples were measured on VINDTA #14, which is slightly modified from the original VINDTA. That is, the peristaltic sample pump was replaced with an overpressure system (~0.5 bar overpressure) and a 1 m long (though coiled) 1/8" stainless steel counterflow heat exchanger that was placed between the sampling line and the circulation circuit. This setup allows for the rapid, convenient and bubble-free loading of the pipettes with the water sample of 25ºC (± 0.1ºC), irrespective of the samples' initial temperature.

Certified reference material (CRM, Batch #154) obtained from Dr. Andrew Dickson at Scripps Institute of Oceanography (San Diego, California) was used for calibration purposes and quality control for both DIC and TA.

DIC was determined by coulometric titration. An automated extraction line takes a ~20 mL subsample which is subsequently purged of CO_2 in a stripping chamber containing ~1 mL of ~8.5% phosphoric acid (H_3PO_4). A stream of nitrogen carries the CO_2 gas into a coulometric titration cell via a Peltier cooler (condenser) and acid trap in order to remove any water. For stations with anoxic bottom-waters, an additional $AgNO_3$ scrubber was placed in between the stripper and the cooler to remove any H_2S from the samples. In these cases, the DIC titration time was increased from 11 to 13 minutes. The CO_2 reacts with the cathode solution in the cell to form hydroxyethylcarbamic acid, which is then titrated with hydroxide ions (OH^-) generated by the coulometer. The counts of the coulometer are then integrated over the duration of the titration to obtain the total amount of carbon titrated.

Determinations of total alkalinity (TA) were performed by acid titration that combines aspects from both the commonly used 'closed cell' method and the 'open cell' method, with a few adaptions to the standard VINDTA settings. First, instead of rinsing the alkalinity titration cell from below, a shower-head was installed which allowed for a faster and more thorough rinsing. Moreover, acid was added in aliquots of 0.15 mL up to a total of 4.2 mL, with an initial aliquot of 0.6 or 0.3 mL depending on the salinity and expected alkalinity. A 10 L batch of acid of ~0.1 M and salinity 12 was prepared to be used by the VINDTA.

c) Water-column pH

This method is based on SOP6b outlined by Dickson et al. (2007). At all CTD stations except station 1 (Baggensfjarden) and at selected depths, water samples were collected from the Niskin bottle into ~10 cm long optical glass spectrophotometric cells with two ports and Teflon stoppers. Upon return in the container, the exterior of the cell was carefully cleaned and dried before placing in a designated holder at 25°C in the dark until analysis, which took place within a few hours after sampling.

At the start of a measurement, the cell blank was determined at three wavelengths: 730 nm (a non-absorbing wavelength for the *m*-cresol purple dye) and two wavelengths corresponding to the absorption maxima of the base (I^{2-}) and acid (HI^{-}) forms of the dye (578 and 434 nm, respectively). This determination was repeated until the change with the previous blank determination was stable. Then, one of the cell caps was removed and 150 µL of concentrated (~2 mM) dye was carefully added deeply into the cell, ensuring no bubbles were added. The stopper was placed back and the cell swirled to fully mix the dye and sample. Then, the cell was placed back in the spectrophotometer in the same position as before and its absorbance was measured 3-5 times. For best results, the absorbance values should be between 0.4 and 1.0; considering the wide range of pH values in the Baltic Sea this criterion was however not always met.

Results for pH (on the total scale and at 25ºC) were calculated using the following equation:

$$pH = pK_2 + \log_{10}\left(\frac{A_1/A_2 - \varepsilon_1(HI^-)/\varepsilon_2(HI^-)}{\varepsilon_1(I^{2-})/\varepsilon_2(HI^-) - (A_1/A_2)\varepsilon_2(I^{2-})/\varepsilon_2(HI^-)}\right)$$

where pK_2 is the acid dissociation constant for the species HI^- (in mol/kg-soln) and A_1 and A_2 are the corrected absorbance values measured at the wavelengths corresponding to the absorbance maxima of the base (I^{2-}) and acid (HI^-) forms, respectively. The various extinction coefficient terms ε correspond to values measured for the specified species (*m*-cresol purple) at wavelengths 1 (578 nm) and 2 (434 nm), respectively:

$$\varepsilon_1(HI^-)/\varepsilon_2(HI^-) = 0.00691$$

$$\varepsilon_1(I^{2-})/\varepsilon_2(HI^-) = 2.2220$$

$$\varepsilon_2(I^{2-})/\varepsilon_2(HI^-) = 0.1331$$

The equilibrium constant K_2 is a function of temperature (T, in Kelvin) and salinity (S) and is determined by Clayton and Byrne (1993):

$$pK_2 = \frac{1245.69}{T} + 3.8275 + 0.00211(35 - S)$$

d) Water-column carbonate ion (CO_3^{2-}) concentration

This method is based on a relatively new method developed by Byrne et al (2008), using the equation as modified by Patsavas et al (2015), and measures CO_3^{2-} concentration based on its complexation with lead (Pb). As the Patsavas et al. (2015) equation has only been validated for

salinities of 18 and higher, it did not have priority in our sampling scheme. If time permitted, samples were taken from the 500 mL borosilicate bottles after AIRICA and VINDTA analysis at selected depths. These samples were collected into the same spectrophotometric cells as for pH analysis; they were however first filtered over 0.2 µm using either Acrodisc or SY25NN filters.

Then, the exterior of the cell was carefully cleaned and dried before placing in a designated holder at 25°C in the dark until analysis, which took place quickly as samples had already been in the climate-controlled container for a while.

At the start of a measurement, the cell blank was determined at two wavelengths: 250 and 234 nm. This determination was repeated until the change with the previous blank determination was stable. Then, one of the cell caps was removed and 20 µL of 0.022 mM lead perchlorate ($Pb(ClO_4)_2$) solution was carefully added deeply into the cell, ensuring no bubbles were added. The stopper was placed back and the cell swirled to fully mix the dye and sample. Then, the cell was placed back in the spectrophotometer in the same position as before and its absorbance was measured 3-5 times.

Results were calculated using the following equation:

$$R = \frac{250^A}{234^A} = \frac{250^\varepsilon Pb + 250^\varepsilon PbCO_3 CO_3 \beta_1 [CO_3^{2-}]_T}{234^\varepsilon Pb + 234^\varepsilon PbCO_3 CO_3 \beta_1 [CO_3^{2-}]_T}$$

It was found that this equation did not produce any result below salinities of ~14.

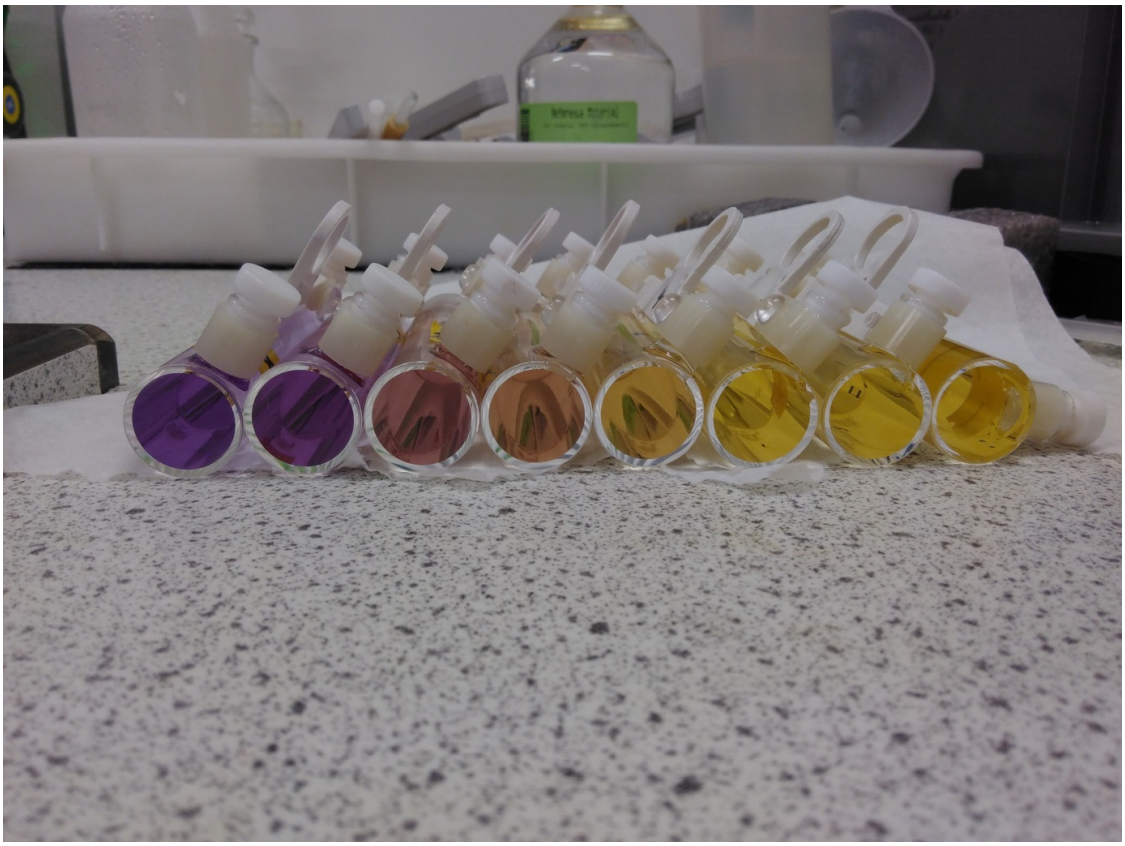


Figure 14 Example of a pH gradient from surface (left, high pH) to bottom (right, low pH) at station 7 (JML)

8. Dissolved organic carbon (DOC)
Mathilde Hagens (UU), Santiago Gonzalez (NIOZ)

Samples for water-column DOC were collected at each CTD station at every unique depth. At stations 2 (Baldersnas), 1 (Baggensfjarden), 22 (Bornholm) and 21 (Arkona basin), replicates were sampled for quality control. At stations 20 (Landsort Deep) and 17 (LL19), ca. 30 mL of water was drawn from the CTD bottle into 40 mL pre-combusted glass ampoules and in the container filtered over 0.7 µm GF/F Whatman syringe filters into pre-combusted, amber-coloured glass ampoules. At the other stations, ca. 30 mL of water was directly drawn from the CTD bottle into a syringe and filtered over 0.7 µm GF/F Whatman syringe filters into pre-combusted, amber-coloured glass ampoules. After sampling, samples were acidified with 5-6 drops of 37% HCl. The ampoules were then flame-sealed and stored at 4°C until analysis.

Moreover, at stations 18 (F80), 1 (Baggensfjarden) and 21 (Arkona basin) samples for porewater DOC were collected using rhizons. At each station, 15 different depths were sampled (see below). At Arkona basin an additional bottom-water sample was collected. Rhizons were inserted a few hours after core retrieval. Porewater was drawn via the rhizon into 20 mL syringes and ca. 10 mL was directly transferred into 50 mL pre-combusted, amber-coloured glass vials. The samples were then acidified with a few drops of 37% HCl and stored at 4°C until analysis.

Table 4: Depths of rhizon sampling for porewater DOC

St. 18 – F80		St. 1 – Baggensfjarden		St. 21 – Arkona basin	
Number	Depth (cm)	Number	Depth (cm)	Number	Depth (cm)
1	1	1	1	1	1
2	2	2	2	2	2
3	3	3	3	3	3
4	4	4	4	4	4
5	5	5	5	5	5
6	7	6	7	6	7
7	9	7	9	7	9
8	11	8	11	8	11
9	13	9	13	9	14
10	15	10	15	10	18
11	18	11	19	11	21
12	21	12	23	12	24
13	27	13	27	13	27
14	30	14	31	14	30
15	33	15	35	15	33
				0	bottom-water

9. In-situ pump sampling

Silke Severmann, Rutgers University, Ruud Groenewegen, NIOZ, Caroline Slomp, Utrecht University,

In situ pumping was performed at nine sites, with multiple casts at two stations (11 casts total). Four McClane pumps were used (3 x WTS-LV; 1 x WTS LV-Dual Filter). Each pump was programmed before deployment to pump between 60 and 240 minutes, and pumping typically started 15 min after pumps had reached target depth. For all except the first cast the initial flow volume was set to 6 L/min, and the minimum flow volume to 3 or 4 L/min. The Dual Filter pump was monted in a CTD frame and always deployed as the bottom pump of the cast. Pumps were either deployed before multicoring or at a distance of 1 nm from the mutlicoring site. Care was taken not to dump sediments over the side during pumping. Material was collected on polyethersulfone filters (Pall Supor, 0.8 µm poresize, 142mm diameter) with 55 µm prefilter, except for the Dual Filter pump, which was used without prefilter to allow overlying water to be retained in the filter baffle. For two duplicate casts quartz filters (Whatman QMA) with a nominal poresize of 1 µm were used without prefilters to collect large volume samples for metal isotope analysis.

The filters were collected immediately after the pumps were retrieved. For deployment in anoxic water the two filterheads from the Dual Filter pump were transferred immediately into a glovebag to retrieve the filter under anaerobic conditions. Previous tests have shown that the water that is retained in the baffle is the water from the original pump depth, i.e. it is not exchange during pump retriaval through the oxic upper water column. This allows the filters to remain anoxic.

The filters were photographed from above, placed in a petri-dish and packed in plastic bags (oxic samples) or aluminum bags (anoxic samples, handled in a glovebag, flushed with nitrogen) bags and stored at -20 C. All pump data were compiled in spreadsheet, an abbreviated version is included in this report (se Appendix II).

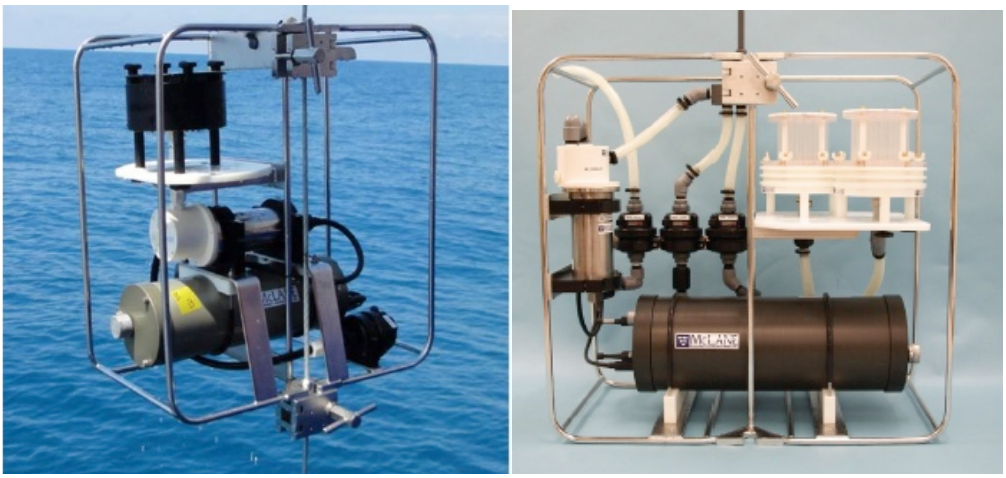


Figure 15: McClane pumps: Left: WTS-LV, Right: WTS-LV-DF

8. Micro-electrode profiling, Martijn Hermans, Utrecht University

High resolution depth profiling was performed with microelectrodes for O_2 (50-µm), H_2S (50-µm) and pH (100-µm) on multicores. These microelectrodes were connected to a four-channel Microsensor Multimeter (Unisense A/S). Calibrations for the sensors were performed daily prior to retrieving the multicores on deck.

O_2 calibration

The O_2 sensor was calibrated in artificial seawater with a similar salinity as the station that was measured that day by using the calibration chamber (Unisense A/S, Denmark). The first calibration point was made in air-saturated seawater (100% saturation) by vigorously pumping air in the calibration chamber with an aquarium pump. The second calibration point was made by flushing the calibration chamber with nitrogen for 10 minutes.

H_2S calibration

The H_2S sensor is light sensitive, since the electrolyte in the sensor gets photo-degraded by high light intensities, resulting in a false high background signal compared to the signal in the dark. Therefore, all calibrations were done in a dark room. Na_2S standards were used for a 5 point calibration (0, 0.59, 1.47, 2.94 and 5.88 µM). The Na_2S stock solution (≈ 0,01M ΣH_2S) was prepared anoxically by dissolving ~0,24 g Na_2S x 9 H_2O in 100mL of N_2-flushed water and subsequent storage in a nitrogen purged glovebox. Since the H_2S (50-µm) sensor detects the partial pressure of H_2S gas, which is only a fraction of ΣH2S, the calibration was performed quickly in N_2-flushed acidified seawater (pH ~3.5) to ensure there was no introduction of oxygen and that all ΣH_2S was available as H_2S.

pH calibration

Calibrations for pH were performed with three NIST (pH 4, 7 and 10) buffers (Hach) and a TRIS buffer to correct for salinity effects. The pH is reported on the total scale**.**

Measurements

After retrieval of the multicores on deck, one multicore was installed in the chemical lab within 5 minutes for high resolution depth profiling. Another multicore was stored in a climate room and was measured several hours later. Since the micro sensors have a limited length, the sediment in the multicores was pushed up with rubber stoppers. This ensured that the sediment almost reached the top of the multicore with 5 cm overlying water. Complete stagnation of overlying water was prevented by movements of the ship. The multicores were placed on an aluminium crate and attached to the laboratory table with a gas cylinder clamp and straps.

For stepwise movement (50-µm for 0-2.5 cm and 100-µm for 2.5-7.0 cm) the microsensors were installed in a 2D micromanipulator (Unisense A.S., Denmark). The micromanipulator was controlled by the SensorTrace Suite Profiling (v.2.2.100) software (Unisense A/S, Denmark).

The table below gives an overview of the different sites that were selected for high resolution depth profiling. The table also indicates the amount of cores and the replicate measurements per core that were measured. Stations F64 (Solovjeva) and Scholz311 were only measured once due to the fact that the sediment of F64 was enriched with manganese nodules and the top layer of Scholz-311 was enriched with shells. Replicate measurements were thus avoided to prevent the electrodes from breaking.

Table 5. Overview of sites selected for high resolution depth profiling of oxygen, sulfide and pH in the sediment

Station nr.	Old codes	Name of site	Date	Cores	Replicates per core
	Stockholm sites				
1	PLU15_005	Baggensfjarden	3-6-2016	1	3
2	PLU15_003	Baldernas A (3)	3-6-2016	1	2
3	PLU15_002	Baldernas B (2)	4-6-2016	2	3
	Aland Sea				
4	F64	Solovjeva	5-6-2016	1	1
	Gulf of Finland				
7	JML	Gulf of Finland 1	8-6-2016	1	3
9	GOF5	Gulf of Finland 3	6-6-2016	2	3
15	GOF5	Gulf of Finland 3	6-6-2016	2	3
10	LL3A	Gulf of Finland 4	7-6-2016	1	3
	N. and E. of Gotland				
13	LF1	LF Transect 1 oxic	30-5-2016	1	3
16	Scholz	East Gotland oxic	9-6-2016	1	1
	Euxinic basins				
17	LL19	Northern Gotland	29-5-2016	1	3
18	F80	Faro Deep	2-6-2016	1	3
19	BY15	Gotland Basin	1-6-2016	1	3
14	BY15A	Gotland Basin	9-6-2016	1	3
	BY15B	Gotland Basin	9-6-2016	1	2
	BY15C	Gotland Basin	9-6-2016	1	2
	BY15D	Gotland Basin	9-6-2016	1	2
21	BY2	Arkona	12-6-2016	2	3
22	IODP-BY5	Bornholm	11-6-2016	2	3

The table below shows the bottom water salinity and oxygen concentrations for the different sites. These bottom water oxygen concentrations were calculated based on the salinity and temperature and the oxygen electrode signal. The Stockholm and Aland Sea site(s) all contained oxygen at concentratsions >100 µM. There was a large gradient in bottom water oxygen in the Gulf of Finland with concentrations varying from 0 to 64 µM. Oxygen concentrations in the overlying water in the cores ranged from 7-40 µM, except for Faro Deep where the overlygin water in the cores was fully anoxic. At Bornholm, the water column was saturated with oxygen. However, the bottom water oxygen concentration was only ~ 18 µM at this site.

Table 6. Bottom water salinity and oxygen at the various sites. We note that at some

Station nr.	Old codes	Name of site	Salinity (‰)	O_2 (µM)
	Stockholm sites			
1	PLU15_005	Baggensfjarden	7.6	110
2	PLU15_003	Baldernas A (3)	5.9	143
3	PLU15_002	Baldernas B (2)	5.9	152
	Aland Sea			
4	F64	Solovjeva	6.7	175
	Gulf of Finland			
7	JML	Gulf of Finland	10.7	0
9	GOF5	Gulf of Finland	9.4	9
15	GOF3	Gulf of Finland	8.4	64
10	LL3A	Gulf of Finland	8.9	4
	N. and E. of Gotland			
13	LF1	LF Transect 1 oxic	8.4	69
16	Scholz	East Gotland oxic	10.1	3.3
	Euxinic basins			
17	LL19	Northern Gotland	11.7	19
18	F80	Faro Deep	12.6	0.00
19	BY15	Gotland Basin	13.8	9.5
14	BY15A	Gotland Basin	13.8	6.8
	BY15B	Gotland Basin	9.8	9.3
	BY15C	Gotland Basin	12.1	40
	BY15D	Gotland Basin	12.7	21
	Hypoxic southern basins			
21	BY2	Arkona	16.5	82
22	IODP-BY5	Bornholm	18.4	18

The figure below show the high resolution depth profiles of oxygen, H2S and pH for station 13. The oxygen penetration into the sediment at this site is ca. 2-3 mm (green line). The sulphide (red line) is spatially separated from the oxygen at station 13. The pH maximum could be related to the presence and activity of Beggiatoa.

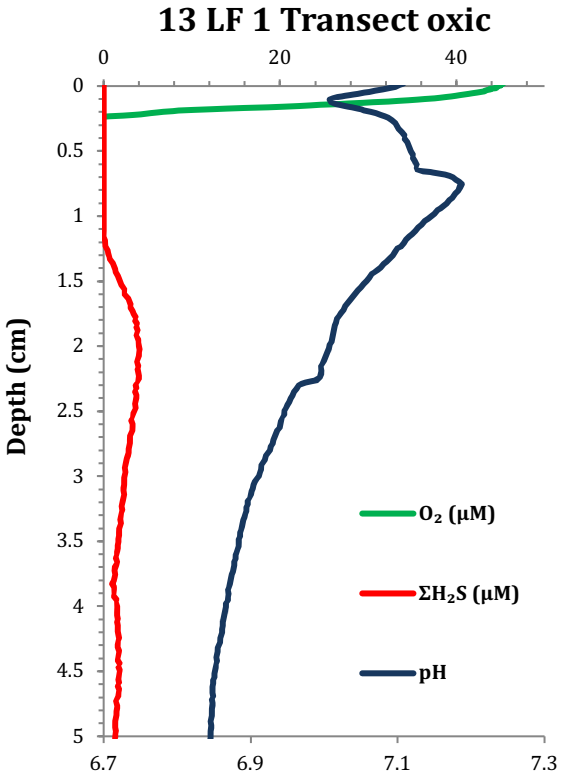


Figure 16. Micro-electrode profiles of oxygen, H2S and pH for station 13 (LF1)

9. Porewater collection

Matthias Egger, Niels van Helmond, Wytze Lenstra (UU) and Silke Severmann (Rutgers Univ.)

Pore waters were extracted from multicores for analysis of dissolved inorganic constituents. In combination with solid-phase analyses, these data will be used to assess the rates of diagenetic reactions in the sediments, and vertical fluxes of dissolved constituents between the sediments and the water column.

Sediment slicing and pore water sampling

Ten cm diameter multicores were recovered with an Oktopus multicoring apparatus (www.oktopus-mari-tech.de). Twelve cores were recovered per cast. Each core contained 30-60 cm of sediment, plus overlying water. The weighting system of the multicore was adjusted at each site to achieve optimum sediment recovery.

On deck, one core from each cast was stoppered at the top and base and transported to a temperature-controlled container (temperature set to match bottom water in situ temperature, 3-7 °C). Duplicate bottom water samples were extracted using 20 mL syringes positioned in the overlying water ~10 cm from the sediment surface. The filled syringes were transferred directly to a nitrogen-filled glovebox for later subsampling. The remaining water was drained from the core until ~2 cm of overlying water was left, and the core was inserted vertically into a nitrogen-filled glovebox inside the temperature-controlled container. The last overlying water was removed with a syringe and the core was sliced according to a general scheme:

Table 7. Sediment slicing intervals

Interval	Resolution
0–2 cm	0.5 cm
2–10 cm	1 cm
10–20 cm	2 cm
20 cm–core base	4 cm

Note that for site 15 (GOF 3) and BY15 A, only the first 10 cm were sampled. Furthermore, at sites BY15 B, C and D, only the upper 5 cm were sliced.

Each slice was divided between a pre-weighed 15 mL glass vial (for water content and solid phase analyses) and 50 mL centrifuge tubes (for pore water analyses). The glass vials were stored in gas-tight aluminum-laminate bags, which were heat-sealed and frozen at -20°C. The centrifuge tubes were centrifuged at 4500 rpm for 25 min. This yielded >10 mL pore water for most samples. After centrifugation, the tubes were returned to the glovebox and filtered through 0.45 µm Nylon filters into a 15 mL centrifuge tube labeled 'PW Bulk'. The bottom water sample was processed in the same way. From the bulk sample, subsamples were taken for a range of onboard and laboratory analyses. Subsampling for HS and alkalinity was performed immediately after filtration of a sample. All other subsampling was performed within 3 hours. 0.2-µm ME sub samples were taken at site 2, 13, 16, 21 and 22, while 0.02-µm ME sub samples were only taken for selected samples (12 in total) at site 21. At site 21, an additional core was sampled for pore water using rhizons (total of 15 samples, including bottom water).

An additional core was sliced under oxic conditions for the upper 5-10 cm and pore water was filtered through 0.8/0.2 µm Acrodisc filters after centrifugation and analyzed for NO3/NO2 to

evaluate the potential N contamination of the 0.45 µm Nylon filters. At sites 2, 9, 10, 13, 15, 16, 21 and 22, rhizon cores were taken and analyzed for pore water Fe2+ using the ferrozine method. These samples were stored for isotope analyses (Fe, U and Cr).

Table 8. Pore water sub sampling and analysis scheme.

Analysis	Vol. (mL)	Vial	Treatment	Code	Method	Storage
HS	0.5	Glass vial	1.5 mL of 8 mM NaOH	HS	Onboard AA	4°C
PO_4, Silica	1	Pony vial	4 µl 5 M HCl	PO4, Si	Onboard AA	4°C
DIC	0.5	Glass vial	4.5 mL 25 g/L NaCl	DIC	Onboard	4°C
NH_4, NO_3, NO_2	0.5 (from bulk)	15 mL greiner	None	Bulk	Onboard AA	4°C until analysis, then - 20°C
Alkalinity	1.2 (or 2 x 0.6)	IC vials	None	ALK	Onboard titration	4°C
S, Fe, Mn, TM*, major elements	2-3	15 mL greiner & 8 mL nalgene	10 µl suprapur 30% HCl per mL	ME ME_0.2 ME_0.02	ICP-OES ICP-MS (UU)	4°C
SO_4, Cl	0.15	IC vial	None	IC	Ion chrom. (UU)	4°C
Mn^{3+}	0.5	Pony vial	None	Mn(III)	UU	-80°C

* Trace metals. For selected stations, the 0.45 µm was further filtered through 0.2 µm and 0.02 µm. See Table 10.

Table 9. Pore water sub sampling and analysis scheme.

Station	Date	HS	PO_4, Si	DIC	NH_4	Alk	ME	ME 0.2	ME 0.02	SO_4, Cl	Mn^{3+}	CH_4
17 (LL19)	29-05-16	√	√	√	√	√	√			√	√	√
13 (LF1)	30-05-16	√	√	√	√	√	√	√		√	√	√
19 (BY15)	01-06-16	√	√	√	√	√	√			√	√	√
BY15A	01-06-16	√	√	√	√	√	√			√	√	
BY15B	09-06-16	√	√	√	√	√	√			√	√	
BY15C	09-06-16	√	√	√	√	√	√			√	√	
BY15D	09-06-16	√	√	√	√	√	√			√	√	
18 (F80)	02-06-16	√	√	√	√	√	√			√	√	√
1 (PLU_005)	03-06-16	√	√	√	√	√	√			√	√	√
2 (PLU_002)	04-06-16	√	√	√	√	√	√	√		√	√	√
4 (F64)	05-06-16	√	√	√	√	√	√			√	√	√
9 (GOF 5)	06-06-16	√	√	√	√	√	√			√	√	√
15 (GOF 3)	06-06-16	√	√	√	√	√	√			√	√	√
10 (LF3)	07-06-16	√	√	√	√	√	√			√	√	√
7 (JML)	08-06-16	√	√	√	√	√	√			√	√	√
16 (Scholz311)	09-06-16	√	√	√	√	√	√	√		√	√	√
22 (BY5)	11-06-16	√	√	√	√	√	√	√		√	√	√
21 (BY2)	12-06-16	√	√	√	√	√	√	√	√	√	√	√
rhizon		√	√	√	√	√	√			√	√	

Multicore methane sampling

For sampling pore water methane in the multicores, one core from each cast was pre-drilled with 2 cm diameter holes (two rows of 10 cm resolution holes on opposing sides of the tube, offset by 5 cm). The holes were taped with electrical tape prior to coring. Upon recovery, the core was immediately stoppered and removed from the multicorer. On deck, the taped holes were cut open with a Stanley knife and a 10 mL cutoff syringe was inserted horizontally to extract precisely 10 mL sediment. This was transferred directly to a 65 mL glass bottle pre-filled with saturated NaCl solution. The solution was topped up after addition of the sample

and a rubber stopper was inserted, ensuring that no air bubbles entered the bottle. A screw cap was then applied and the bottle was stored upside-down. The samples will be transported back to Utrecht, where 10 mL nitrogen headspace will be injected prior to analysis for methane (gas chromatography).

Sub-cores for resin embedding

Sub-cores (~ 7cm length) were taken at sites 1, 7, 9, 15, 17 and 19 using cut-off 15 mL centrifuge tubes and stored in 50 mL centrifuge tubes filled with oxygen-free acetone. These cores will be processed as described in detail in *Jilbert and Slomp (2013; GCA)* and *Egger et al. (2015; GCA)*. Discrete samples were taken around the sub-core in 0.5 cm intervals and stored in 50 mL centrifuge tubes at -20°C.

Example of results

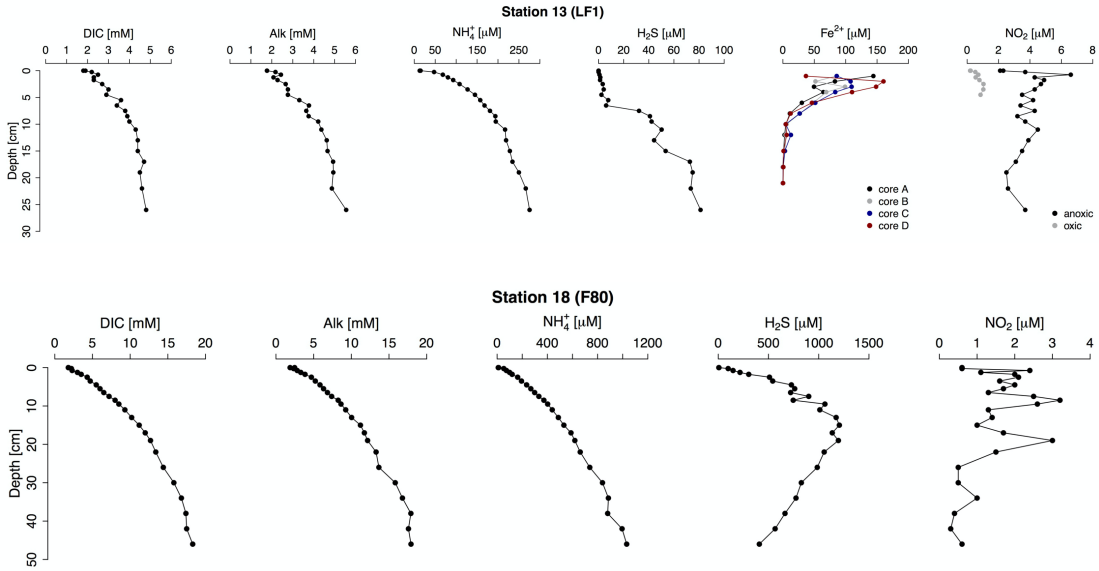


Figure 17. Porewater profiles of DIC, alkalinity, NH4, H2S and NOx as measured on board. At stations where rhizon samples were taken, Fe2+ profiles are also included.

12. Sediment collection and description; Niels van Helmond

12.1 Multicores sliced for 210Pb dating

One MC per station was sliced for 210Pb dating. The core was sliced using the hydraulic core extruding device onboard the *RV Pelagia*. After draining of the overlying water the core was sliced according to the following general scheme:

Table 10. Sediment slicing intervals

Interval (cm)	Resolution (cm)
0-2	0.5
2-10	1
10-20	2
20-core base	4

Storing of frozen cores

Every day one MC was sealed with rubber stoppers at the base and the top and placed vertically in a freezer for a minimum of 24 hours at -20°C. The next day the core was rinsed with hot water to let it thaw slightly, when the sediments started to move the entire core was removed from the liner after which it was rinsed for a photograph. After photographing, the core was placed in a plastic bag, which was compressed to get rid of oxygen. Finally this plastic bag was placed in an aluminum bag flushed and filled with N2 gas, and stored again in a freezer at -20°C.

Oxic slicing for pore water NOx

For most stations (with exception of the anoxic/euxinic sites) a core was sliced using the hydraulic core extruding device onboard the *RV Pelagia*. After the extraction of two bottom water samples the overlying water was drained of and the core was sliced according to the following general scheme:

Table 11. Sediment slicing intervals

Interval (cm)	Resolution (cm)
0-2	0.5
3-5	1

For the sites where relatively high bottom water oxygen concentrations where measured (i.e., St. 3 - PLU_002; St. 4 – F64; St. 16 – Scholz 311; St. 21 – BY2; St. 22 – BY5) the following scheme was used:

Table 12. Sediment slicing intervals

Interval (cm)	Resolution (cm)
0-4	0.5
4-10	1

Pore waters were filtered through 0.8/0.2 µm Acrodisc filters after centrifugation. From station 9 (GOF5) onwards filters were pre-cleaned through washing with 5 ml of milliQ and 1 to 3 ml of sample, because of the suspicion of NO_3 contamination by the filters.

12.2 Core descriptions

Sunday 29th of May: Station 17 – LL19 (164 mbss)
The retrieved sediment package is about 40 cm thick. The top layer of a few mm's consists of brown-greyish fluffy material, with some (~1-3 mm) orange/reddish organisms. The top 9 cm is composed of mm-scale laminations alternating between pitch black to whitish grey and brownish (mostly in the upper 2-3 cm) layers. From about 9 cm the sediments become more sticky and from 10 cm onwards sediments start to become clayey. The color changes from merely black to grey. From 15 cm onwards the sediments become rice waffle like, resulting from CH4 degassing. In the lower 10 cm the color becomes lighter grey, while the texture of the material does not change.

Monday 30th of May: Station 13 – LF1 (67 mbss)
The retrieved sediment package is about 30 cm thick. The top layer of a few mm's consists of brown-reddish sediments, followed by a few mm thick black layer. The following couple of cm's are composed of grey-brownish sediments with some black patches every now and then. From 4 cm onwards the sediments become really sticky and the color becomes more greyish. Between ~6 and 10 cm the grey color becomes much darker. Below this darker layer the sediments become lighter again and lower in the core, i.e. below 20 cm, the sediment becomes much drier.

Wednesday 1st of June: Station 19 – BY15 (237 mbss)
The retrieved sediment package is about 45 cm thick. The top consits of a white-greyish mat that overlays black "soupy" sediment, which comprises the top 7 cm of the core. A first fine grey layer is observed around 7 cm. From there on the sediments become a little sticky. Although the top ~20 cm generally remains black, more and more grey layers, ranging from a few mm's to a cm start to appear. Between 20 and 24 cm the general color of the sediments becomes grey, alternated by some black bands, which become more dominant towards the base of the core.

Wednesday 1st of June: Station 14 – BY15a (200 mbss)
The retrieved sediment package is about 40 cm thick. Despite its geographical location close to St. 19 (BY15) the lithology is rather different. The sediment surface consists of black fluffy and soupy sediments. The top 8 cm is composed of mm-scale laminations alternating between pitch black to whitish grey and brownish layers, very much comparable to the top sediments at St. 17 (LL19). Below these generally black laminated sediments are stickier grey sediments, which become lighter with depth. The lower 5 cm of the core are darker and more grey-brownish again.

Thursday 2nd of June: Station 18 – F80 (193 mbss)
The length of the core is close to 50 cm. The sediment surface consists of grey-brownish fluffy material. The top of the sediments consist of black, very liquid sediments, with some grey and brown material in the top 2-3 cm. With depth the water content decreases (i.e. less soupy), while the dark blackish color remains dominant in the top 20 cm. Around 20 cm two ~1 cm thick grey layers appear. After another 2 cm of generally black material, the sediments become dark greyish, and remain so until the bottom of the core. In general the lithology at St. 18 (F80) is similar to the lithology observed for St. 19 (BY15).

Friday 3rd of June: Station 1 – PLU_005 (35 mbss)
The length of the core is about 45 cm. The sediment surface and the top 5 mm of the core consist of brown fluffy material. Followed by generally black laminated material, interrupted by a lighter (greyish) layer around 3 cm. From 18 cm onwards the sediments become more greyish (still dark) and a little stickier, while the sediments remain laminated. Down core the laminations become more clear, showing distinct color differences, e.g. dark grey and blackish. At the bottom of the core some grass like material.

Saturday 4th of June: Station 3 – PLU_002 (40 mbss)
The length of the core is about 45 cm. The first 2 cm consists of red-brownish sediments, followed by 3 cm of grey to brownish sediments, interrupted by a few mm thick layer of black material, between 2 and 3 cm. Some worms are found in the upper part. After 5 cm the sediments become pitch black, which they remain till about 35 cm. Afterwards sediments become more sticky and the color becomes much lighter, i.e. greyish.

Sunday 5th of June: Station 4 – F64 (275 mbss)
The length of the core is just below 30 cm. The first 1.5-2 cm consist of dark reddish to brownish clay. The rest of the core consists of light grey, very sticky even "fatty" presumably glacial clay. The entire greyish clay section seems to be laminated. During coring and afterwards during slicing a distinct layer of Manganese-nodules was found, which seemed to be concentrated between 1 and 2 cm, right at the transition from the dark reddish sediments to the light grey clay.

Figure. 18. Mn nodules from site F64

Monday 6th of June: Station 9 – GOF5 (64 mbss)
The length of the core is just over 50 cm. The sediment surface is covered by a mat of white to greyish material. The top 5 mm consists of dark brown sediments followed by a few mm thick more orange to reddish layer, which is followed by a few mm's of somewhat greyish material. Below these top layers the sediments become darker and from 2 cm onwards sediments are very dark grey to black. Between 20 and 25 cm sediments are clearly laminated (alternation of grey and black layers) after which there is a clear transition to grey-brownish, sticky mud. Around 45 cm the mud becomes lighter grey and less sticky.

Monday 6th of June: Station 15 – GOF3 (55 mbss)
The length of the core is around 40 cm. The first few mm's consist of brown-greyish fluffy material, followed by a black layer of similar thickness. The following 3-4 cm consists of brown to greyish material with some black material in between. From 4 cm onwards the sediments become pitch-black. A few centimeters below this transition to black sediments, fine scale (1 mm >) grey laminations are recognized in the generally black mud. After 25 cm the

sediments become dark grey instead of black, while the lower ~5 cm's are composed of light grey muds.

Tuesday 7th of June: Station 10 – LL3A (68 mbss)
The length of the core was close to 50 cm. The surface sediments are covered by a mat of fluffy white material. The top cm of sediment consists of a very liquid soup of black and brown material, followed by a few mm red to orange layer, which seems to be underlain by a mm of greyish material. Some worms are found in the upper 7 cm. Up to 35 cm the sediments consist of generally black to darkish grey muds, with some subtle color changes. Subsequently sediments become more dark greyish, after which they become lighter grey towards the bottom of the core.

Wednesday 8th of June: Station 7 – JML (80 mbss)
The length of the core was close to 40 cm. The surface sediments (top 1 cm) consists of black to brownish fluffy/soupy material, followed by ~20 cm of finely laminated (1 mm > to a couple of mm's) sediment. While the sediment is generally dark grey and brownish, many fine-scale laminations consisting of light grey to whitish and black material. Below 20 cm the sediments become dark grey, while the laminations have disappeared. Furthermore the sediments have become stickier. Subsequently some rice waffle like structures are observed, which likely result from CH4 degassing.

Thursday 9th of June: Station 16 – Scholz 311 (65 mbss)
The core had a length of just over 30 cm. Multiple syphons are sticking out of the sediment surface (up to five syphons were counted in one MC). The top 4 cm consists of generally brown sediments. The first 5 mm seem to be a little lighter brown, followed by darker brown coarser sediment (silt to fine sand), which are already sticky and continue to a depth of around 4 cm. From 4 cm onwards sediments become darker and the brown color fades out and is replaced by a dark grey color, to even blackish color, which forms a distinct layer of ~2cm between 7 and 9 cm. In the lower part of this dark band the first worm is encountered. For the remainder of the core the color is lighter again, generally grey-brownish, with some darker layers.

Saturday 11th of June: Station BY5 – (87 mbss)
The core has a length of about 45 cm. The first 0.5 cm consists of dark brown sediment, followed by 1.5 cm of little less dark brown sediment. In the next 2 cm the dark brown color gradually shifts to a grey to brownish color. From 4 cm the color becomes dark grey and sticky. The dark grey clay is intercalated with very thin (sub mm scale) black laminations that continues till 12 cm. Worms are found till a depth of 8 cm. Around 12 cm the sediments become lighter grey, but around 14 cm a 2 cm thick black layer follows. After this black layer sediments become lighter again (dark grey) which remains consistent until the base of the core.

Sunday 12th of June: Station BY2 – (47 mbss)
The core has a length of about 40 cm. The first 3 cm consists of brown sediments, with some shells (shell remains) and some worms, which are found till a depth of 7 cm. From 3 cm the brown color starts to fade out and the sediments become more greyish. Around 7 cm the sediments become consistently dark greyish to black, until ~15 cm. From here on the sediments become light grey and much stickier. Around 30 cm the sediments become greenish grey and the sediment becomes even more sticky and dry.

13. Lander deployments and macrofauna
Rob Witbaard, Ruud Groenewegen (NIOZ), Wytze Lenstra (UU)

The NIOZ ALBEX landers were deployed at all relevant stations in the Baltic where time permitted a sufficiently long deployment. Deployment length needed was approximately 10 hours. Each lander was equipped with 3 measurement chambers enclosing a bottom surface of 144 cm2. The depth that the chambers penetrated the sediment was determined by a resistivity probe mounted on the side of the measurement chamber and electronically connected to the chamber control unit. Once the resistivity changes by 12% the penetration of the measurement chamber into the sediment is interrupted.

During measurements in the Stockholm archipelago we noticed that the resistivity probe did not work properly because of the low salinity in combination with the low water temperature. The measurement chamber control units have been electronically changed to solve this problem. In addition to this the program used to set action times has been altered.
In scheme 1 an overview of the sampling schedule used for all deployments is given. Every 1.5 hours a water sample of 30 ml from inside the box (overlying water) and the outside (bottom water) was taken for flux measurements. The 30 ml of water extracted from the headspace was replaced by water entering from outside the chamber.

During the measurements the oxygen concentration in the overlying water was measured every minute with a JFE-Advantech self logging optode. The observed decrease in oxygen concentration was used to calculate the benthic oxygen demand per square meter per hour. At most stations the bottom water concentration of oxygen was extremely low which inhibited the determination of unequivocal time trends. Oxygen level and measurement error were in the same range.

Each Albex unit takes the incubated bottom sample to the surface. The closing mechanism is such that disturbance of the bottom material is minimal. In almost all cases the overlying water is perfectly clear with an undisturbed fluffy top surface. The bottom surface area of each box was photographed and the sediment was washed over a 0.5 mm screen. The residue was fixated in 4% formaldehyde.

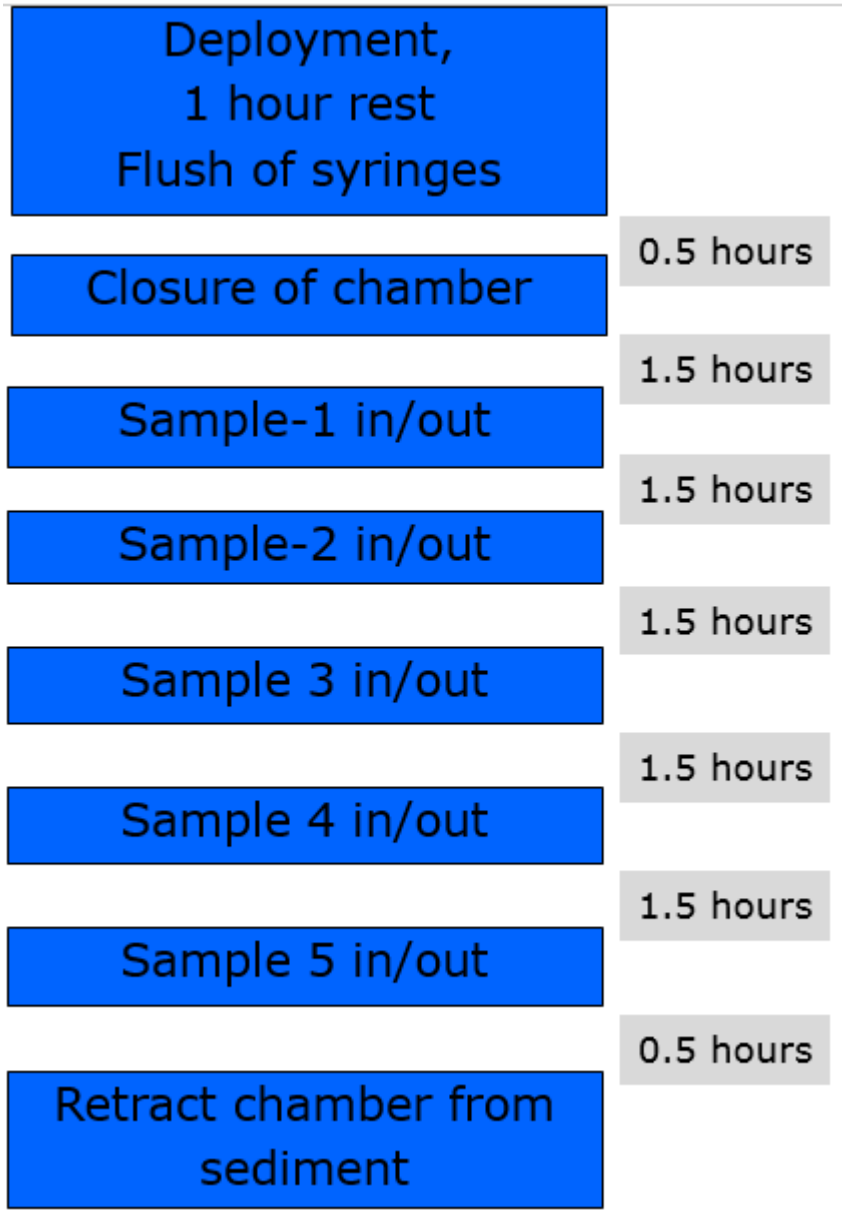


Figure 19. General Sampling scheme used to sample the headspace of the incubation chambers in all deployments during the cruise.

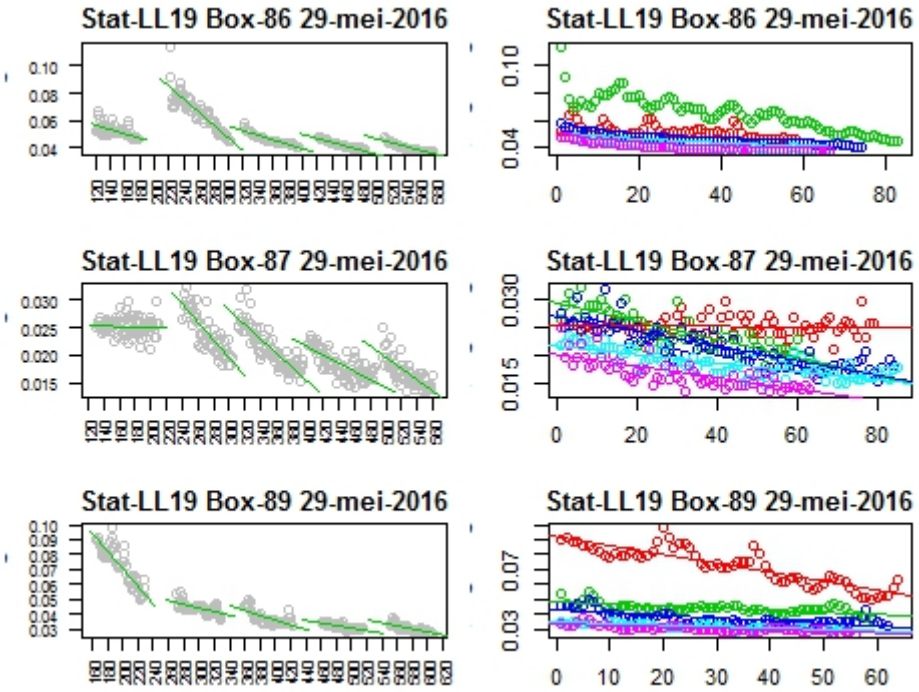


Figure 20 Result of the box incubations at Station 17 (LL19). The left panel shows the decrease in oxygen with the concentration (mg/l) along the vertical axis against time (minutes) along the horizontal axis. Green lines are fitted linear regressions. The right hand panels also give the oxygen concentration but the time axis has been adjusted to time (minutes) after sampling from the headspace. Total data points is not always 90 (1:30 hr) as fractions influenced by the influx from outside water have been clipped away.

Table 13. Subsample scheme for samples from lander incubations

Parameter	Vol (ml)	Vial	Treatment	Code	Analysis	Storage
$PO_{4,}$, Si	1	Pony vial	5 ul suprapur 35% HCl/ml	Land PO_4	NIOZ Texel	4
NH^{4+}, NO_3^-	3	Pony vial	None	Lan Bulk	On board	4
DIC	5	Glass vial	None	Lan DIC	On board	4
Fe, Mn	20	Nalgene vial	10 ul suprapur 35% HCl per ml	Lan ME	ICP-OES Utrecht	4
HS	0.5 [a]	Glass vial	1.5 ml 8mmol/L NaOH	Lan HS	On board	4
Total	28,5					

[a] HS: only for anoxic stations

14. Benthic Flux Measurements. Wytze Lenstra (UU)

The benthic flux of iron and other chemical components was determined in 3 different types of incubations using whole cores:

• Oxic incubations
To measure the benthic flux of Fe, Mn, DIC, PO4 , Si, NH_4^+ and NO_3^- under oxygen-saturated conditions in the overlying water.
• Closed incubations
To measure the benthic flux of Fe, Mn, DIC, PO4 , Si, NH_4^+, NO_3^-, HS and oxygen respiration of sediment that is incubated with oxygen-depleted overlying water.
• Bromide incubations
Where dissolved bromide is added to the overlying water and its penetration into the sediment is measured to determine the rate of bio-irrigation.

Table 14. Subsample scheme for samples from core incubations

Parameter	Vol (ml)	Vial	Treatment	Code	Analysis	Storage temperature
PO_4,, Si	1	Pony vial	5 ul suprapur 35% HCl per ml	Inc PO_4, Si	NIOZ Texel	4 C
NH^{4+}, NO_3^-	3	Pony vial	None	Inc Bulk	On board	4 C
DIC	5	Glass vial	None	Inc DIC	On board	4 C
Fe, Mn and other elements	1[a]	Pony vial	10 ul suprapur 35% HCl per ml	Inc ME	ICP-OES Utrecht	4 C
HS	0.5[b]	Glass vial	1.5 ml 8mmol/L NaOH	Inc HS	On board	4 C
Total	10.5					

[a] Before and after the experiment 10 ml of the overlying water was subsampled in a greiner tube of 15 ml to be analyzed for dissolved Fe through flow injection.
[b] HS samples were only taken for anoxic conditions

Methodology
Oxic incubations

Incubations of three cores per station were done for 9 stations. Cores were taken from the multicorer and immediately brought to a temperature regulated laboratory (temperature at bottom water temperature). Here the rubber stoppers at the top of the core were removed and the overlying water was brought back to 550 ml (7 cm of overlying water). A tube connected to an aquarium pump was placed in the overlying water to saturate the water with oxygen (Figure 113). This oxygen flow also keeps the water well mixed. Incubations had a duration of 8 hours, samples were taken at 7 moments in time. The volume lost when taking a sample was replaced with bottom water from the CTD.

Anoxic incubations

Anoxic incubations of three cores per station were done at 12 stations. Cores were taken from the multicorer and immediately brought to a temperature regulated laboratory (temperature at bottom water temperature). Here the stoppers were removed and the cores were pushed up the tube until there was a volume of 550 ml of overlying water (7 cm of overlying water). The oxygen level was brought back to approximately 1.5 mg/L by bubbling the overlying water with nitrogen. After this a cap was placed on top of the tubes, this way the overlying water was not in contact with the air (see Figure 114). An oxygen meter was placed in 1 or 2 of the caps to monitor the oxygen level, the decrease over time was used to calculate the rate of oxygen respiration. A stirrer in the cap mixed the overlying water. The incubation had a duration of at least 24 hours, samples were taken at 10 moments in time. The volume lost when a sample was taken was replaced with bottom water from the CTD. After the incubation experiment was done the cores were sieved through a sieve of 0.5 mm and the macrofauna in the cores was collected (see section on landers).

Bromide incubations

Bromide incubations were performed to determine the degree of bio-irrigation in the sediment. Cores were taken from the multicorer and immediately brought to a temperature regulated laboratory (temperature at bottom water temperature). The volume of the overlying water was brought back to 550 ml. A tube connected to an aquarium pump was placed in the overlying water to establish well mixed conditions. NaBr was added to the overlying water to increase the bromide concentrations approximately by 10 times. Incubations with bromide were done with 2 cores at 3 different days. After incubation the cores were sliced at high resolution (0.5 cm (0-5 cm), 1 cm (5-10 cm), 2 cm (10-20 cm) and 4 cm resolution after 20 cm). The three cores were incubated for two days. The samples were centrifuged for 20 minutes at 4500 rpm and filtered through a 0.45 um filter. The pore water was stored at 4 degrees. The solid phase of one core was stored at -20 degrees.

Table 15. Cores used for benthic flux incubations, per station.

Date	Station	Bromide incubations	Anoxic incubations	Oxic Incubations
29 May	17		3	
30 May	13	3	3	3
31 May				
1-Jun	19		3	
2-Jun	18		3	
3-Jun	1		3	3
4-Jun	3		3	3
5-Jun				
6-Jun	9		3	3
7-Jun	10		3	3
8-Jun	7		3	3
9-Jun	16		3	3
10-Jun				
11-Jun	22		3	3
12-Jun	21	3	3	3

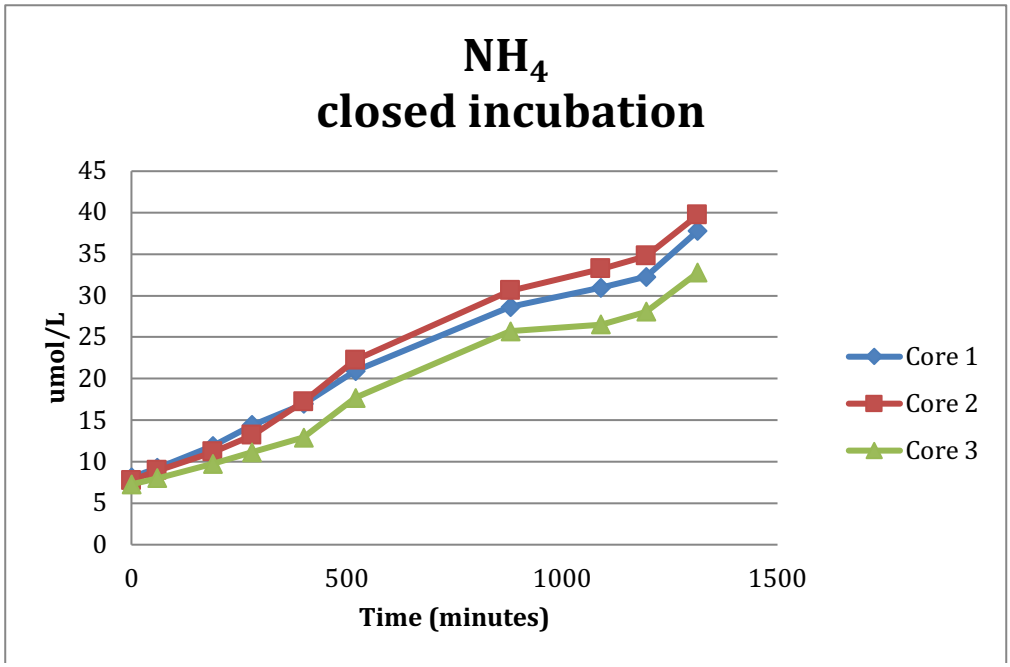


Figure 21.: NH_4 concentration in three incubated cores for station 1.

We find an increase in NH_4 indicating that the sediments act as a source of NH4.

15. Sediment Nitrogen cycling

Elizabeth K. Robertson (Lund University, Sweden)

Experiments to determine processes and rates of sediment nitrogen cycling were performed at 11 stations during the cruise:

- Station 1 – Baggensfjärden (3.6.16)
- Station 3 – PLU_002 (4.6.16)
- Station 4 – F64 (5.6.16)
- Station 7 – JML (8.6.16)
- Station 9 - GOF5 (6.6.16)
- Station 10 – LL3a (7.6.16)
- Station 13 - LF1 (30.05.16)
- Station 16 – Scholz 311 (9.6.16)
- Station 17 - LL19 (29.05.16)
- Station 21 – Arkona (12.6.16)
- Station 22 – Bornholm (11.6.16)

Three experiments were conducted at each station:

- 1: Whole core sediment incubations with ^{15}N-nitrate
    - Aim: determining denitrification, anammox, DNRA, nitrification-denitrification, nitrate source for nitrate reduction (i.e. water column vs nitrification)
- 2: Surface sediment slurries
    - Aim: determining contributions of N_2 producing processes (denitrification vs anammox)
- 3: Whole core sediment incubations with acetylene addition
    - Aim: determine rates of nitrification via differences in ammonium fluxes before and after inhibition by acetylene. Also compare results with mass balance and coupled nitrification-denitrification in ^{15}N whole core experiment.
    - *NOTE: Not carried out at Stations 17 (LL19) and 7 (JML)*

Experiment 1: ***Whole core experiments with ^{15}N-nitrate***

Sediment nitrogen cycling processes were determined using isotope pairing techniques (IPT). Sediment cores (8-12 cores per station, 6cm ø) were placed into a holding rack in a temperature controlled room and each fitted with an internal magnet 5-10cm above the sediment surface. These magnets were turned by an external magnet in the centre of the core rack to ensure mixing of the water column and maintenance of the benthic boundary layer. Background nutrient samples were taken from cores (see **Table 16**) before 100µL 200mM isotopically labelled (98%) sodium ^{15}N-nitrate ($Na^{15}NO_3$) was added to the overlying water and a second water sample taken for each core. The overlying water of the cores was bubbled with gas mixtures of Helium and air to within 30uM of *in situ* oxygen concentrations for 45min – 2h (depending on oxygen penetration) to allow labelled nitrate to diffuse into the zone of nitrate reduction. Following this pre-incubation period, cores were sealed with rubber stoppers, ensuring no air space. Triplicate cores were sacrificed at approximately 0, 1.5, 3 and 4 h after the pre-incubation period. At each of these time points a sample of overlying water was taken before the internal magnet was removed and the core was gently slurried with a metal pole. Sediment was allowed to settle for 1-2 minutes before 60 mL of the slurry was taken. Samples for excess $^{29}N_2$ and $^{30}N_2$ were taken by overflowing the samples into a 12.3 mL exetainer (Labco, UK). Microbial activity was inhibited by addition of 250µL zinc chloride (50% w/v)

before samples were sealed without gas space. A further sample (10mL) of slurried sediment core was taken for analysis of 15N in the ammonium pool and 250 µL zinc chloride added to inhibit microbial activity and frozen. The remaining sample was filtered (0.2um cellulose acetate filter) and frozen for analysis of other nutrients.

Table 16: Overview of samples taken during Experiment 1

Parameter	Vol (mL)	Vial	Treatment	Analysis	Storage
Nutrients in overlying water before tracer addition	**5-10mL**	**15mL Flacon/5mL pony vial**	**Filtered 0.2µm**	**Nitrate, nitrite, ammonium. Photometer, Lund Uni**	**-20°C**
Nutrients in overlying water following tracer addition	**5-10mL**	**15mL Flacon/5mL pony vial**	**Filtered 0.2µm**	**Nitrate, nitrite, ammonium. Photometer, Lund Uni**	**-20°C**
Nutrients in overlying water at time of core termination	**5-10mL**	**15mL Flacon/5mL pony vial**	**Filtered 0.2µm**	**Nitrate, nitrite, ammonium. Photometer, Lund Uni**	**-20°C**
^{15}N in N_2	**12.3mL**	**Exetainer**	**Vial filled (overflowed), 250µL ZnCl2 (50% w/v) added**	**GC-IRMS, University of Southern Denmark**	**Room temperature**
^{15}N in NH_4^+	**10mL**	**15mL Flacon/12.3mL Exetainer**	**250µL ZnCl2 (50% w/v) added**	**Hypobromite conversion, GC-IRMS, University of Southern Denmark**	**-20°C**
Nutrients in sediment	**5-10mL**	**15mL Flacon/5mL pony vial**	**Filtered 0.2µm**	**Nitrate, nitrite, ammonium. Photometer, Lund Uni**	**-20°C**

Experiment 2: *Sediment slurries*

To determine the contribution of denitrification and/or anammox to dinitrogen production, a sediment slurry experiment was conducted. Briefly, glass beads (5 x 2mm) were added to 12.3mL exetainers before filtered bottom water was purged with Helium and used to fill the exetainers. Homogenised surface (upper 0-1.5cm) sediment (2 mL) was quickly added to the exetainers and sealed without air bubbles. The filled exetainers were pre-incubated for 12-15 h in the dark at *in situ* temperature on a shaker table to allow residual oxygen and nitrate to be consumed. Following pre incubation, exetainers were divided into three treatments (approx. 9 vials each) and labelled substrates were injected through the septum:

- 100 µL 20mM sodium ^{15}N-nitrate
- 100 µL 20mM mixed solution ^{15}N-ammonium chloride and sodium ^{14}N-nitrite
- No addition

Triplicate vials of each treatment were treated with zinc chloride as in Experiment 1 to inhibit microbial activity at approximately 0, 4 and 8 h after substrate addition.
Samples will be measured for $^{29}N_2$ and $^{30}N_2$ isotopes on GC-IRMS at the University of Southern Denmark.

Experiment 3: ***Whole core nitrification with acetylene***
Whole core experiments were also conducted to determine rates of nitrification via inhibition with acetylene. Cores (3-4 x 6cm ø) were brought from the deck to a temperature controlled room. Experiments always begun within 30 minutes of cores being brought to the surface to ensure oxygen concentrations were representative to that of the bottom water. Cores were placed in a rack and fitted with internal magnets as described in Experiment 1. Initial water samples were withdrawn from the overlying water and cores immediately sealed with rubber stoppers. Overlying water of the cores were sampled every hour for four hours to determine an initial ammonium flux. A small volume (10-20mL) of site bottom water was used to replace the volume removed. Following this, approximately 10 mL of acetylene-saturated bottom water was added to the overlying water to achieve a minimum of 1% acetylene saturation in the bottom water. Samples were taken immediately after acetylene addition and once every out for the next four hours and replaced as before. The difference in ammonium fluxes can be used to infer the ammonium otherwise used by nitrification.
Ammonium will be measured spectrophotometrically at Lund University.

Further comments
The gas mixer brought along to accurately mix Helium and air to the correct oxygen concentrations was unable to put out enough pressure to simultaneously bubble 12 cores and so gases were mixed manually. This lead to some difficulties in mixing the final oxygen concentrations achieved in whole core experiments (typically 20-30uM higher than *in situ* concentrations). For further studies, gas mixer should be used and adapted to provide more back pressure to ensure more accurate oxygen concentrations are achieved during whole core pre-incubation.
All nutrient samples were transported back to Lund Unviersity at -20oC, exetainers filled for gas samples (whole core and slurry experiments) were transported in Zarges boxes at ambient temperature. Before gas measurement a 2mL Helium headspace will be introduced.

16. DNA/FISH sampling, Fe reduction. Silvia Hidalgo-Martinez (NIOZ-Texel)

Samples for DNA/FISH sampling were collected from cores where pore water microprofiling was previously done (note: only at st. 1 and 9, the cores were not the same as the microprofiled core. At st.1 this was because methane bubbles disturbed the sediment). The samples were taken at either 0.5 or 1 cm resolution.

For handling of the samples and slicing, all the material was cleaned with Ethanol 70%. Slices were collected in petri dishes and sediment was homogenized with a cut 3ml plastic syringe. Three subsamples were taken from the different depth intervals, and were stored a follows:

1) 0.5 ml sediment frozen at -80ºC for DNA analysis
2) 1 ml sediment frozen at -80ºC for DNA analysis
3) 0.5 ml sediment fixed with 0.5 ml Ethanol 99.8% molecular grade, frozen at -20ºC, for Fluorescence *in situ* Hybridization

Iron reduction experiments were performed with sediment from stations 13 and 21. Three sediment cores, collected with the multicorer, were sliced anaerobically using a glovebox and pulled into a plastic beaker at four depth resolutions (0-1cm; 1-2cm; 2-4cm; 4-6cm) to obtain 200 ml sediment. The sediment was homogenized and 100 ml sediment was poured to a new plastic beaker where 12.5 ml of sodium molybdate (0.2M) was added for a final concentration of 20mM. Beakers with and without sodium molybdate (SM) were incubated for 24 hours and 10ml subsamples (duplo) were collected at time 0, 8, 16 and 24 hours. Pore water was extracted and filtered through a 0.45 µm pore size filter. 1 ml of porewater with 10 µl of suprapur 35% HCl was stored at 4 degrees for iron measurements with the ICP-OES in Utrecht. The left over porewater was measured on board for NH4.
*Notes: St. 21, due to a lack of sodium molybdate, the layers 0-1 cm, 1-2 cm have 12.5 ml of sodium molybdate added; and the layers 2-4 cm and 4-6 cm had only 10 ml sodium molybdate.

17. Sulfate reduction rates. Niels van Helmond, Wytze Lenstra (UU)

Samples were taken for measurements of sulfate reduction rates for sediments from multicores at selected sites. One core tube from each cast was pre-drilled with 2 cm diameter holes (two rows of holes at a distance of 10 cm resolution holes on opposing sides of the tube, offset by 5 cm). The holes were taped with electrical tape prior to coring. Sediment samples were taken with 5 ml cutoff syringes. Immediately after the sample was taken the cutoff syringes were closed with parafilm and rubber bands so the sediment was not in contact with the air. Samples were brought to the radio-isotope lab and were injected with 35S with the use of a pipet with a needle on top. After injection a new layer of parafilm was added with rubber bands to close the hole which was made by the syringe. Samples were stored under nitrogen at 4 degrees Celsius in aluminum bags. After incubation of 20-24 hours the samples were preserved in 20 ml 20 % Zinc Acetate. Samples were stored anoxically in aluminum bags at -20 degrees Celsius. Processing of the samples will continue at NIOZ-Texel upon return.

Appendix I CTD sampling overview and depths (parts A, B and C)

Part A.

Station	Depths sampled	Number and type of samples
20	24	72 total and dissolved
17	23	69 total and dissolved; 29 particulate
13	16	48 total and dissolved; 23 particulate
19	24	72 total and dissolved; 24 particulate
18	24	72 total and dissolved; 31 particulate
2	7	21 total and dissolved
1	7	21 total and dissolved; 7 particulate
5	14	42 total and dissolved; 14 particulate
4	24	72 total and dissolved; 24 particulate
9	12	36 total and dissolved; 12 particulate
10	12	36 total and dissolved; 15 particulate
7	15	45 total and dissolved; 15 particulate
12	24	72 total and dissolved
16	12	36 total and dissolved; 12 particulate
22	16	48 total and dissolved; 16 particulate
21	10	30 total and dissolved; 18 particulate
Total		**792 total and dissolved** **240 particulate**

Part B.

Water Column – bottle depths

Station 20

Bottle number	Depth (m)
24	10.0
23	20.1
22	30.0
21	39.6
20	50.1
19	60.3
18	64.3
17	68.5
16	70.3
15	72.3
14	74.5
13	76.5
12	78.4
11	80.3
10	82.5
9	84.3
8	86.5
7	88.3
6	91.3
5	100.4
4	201.0
3	301.9
2	403.1
1	428.0

Station 17

Bottle number	Depth (m)
23	5.2
22	10.0
21	15.4
20	20.1
19	25.0
18	30.4
17	40.7
16	50.7
15	60.6
14	70.7
13	74.7
12	78.9
11	80.8
10	86.0
9	90.8
8	96.0
7	101.3
6	111.2
5	121.4
4	131.5
3	141.6
2	151.8
1	161.1

Station 13

Bottle number	Depth (m)
24	5.0
23	10.1
22	16.2
21	17.2
20	20.1
19	25.0
18	30.2
17	35.3
16	40.3
15	45.6
13	50.5
11	53.6
9	55.6
7	57.4
5	59.5
1	61.8

Station 19	
Bottle number	Depth (m)
24	10.0
23	20.1
22	30.0
21	40.2
20	45.3
19	50.4
18	55.5
17	60.4
16	65.6
15	70.5
14	75.6
13	80.4
12	85.5
11	90.6
10	95.8
9	101.0
8	106.0
7	110.9
6	126.0
5	151.2
4	176.4
3	201.7
2	222.0
1	229.8

Station 18	
Bottle number	Depth (m)
24	10.2
23	20.1
22	30.2
21	30.3
20	40.3
19	50.4
18	55.4
17	60.5
16	65.7
15	70.8
14	75.8
13	80.7
12	85.7
11	90.7
10	95.8
9	100.9
8	110.9
7	121.0
6	131.3
5	141.2
4	151.4
3	166.5
2	176.7
1	186.2

Station 2	
Bottle number	Depth (m)
21	5.0
18	10.1
14	15.0
11	19.9
7	25.3
4	30.0
1	35.2

Station 1	
Bottle number	Depth (m)
21	5.2
18	10.1
15	15.1
13	20.0
8	25.1
5	30.1
1	35.4

Station 5	
Bottle number	Depth (m)
23	5.1
22	9.9
21	14.9
19	20.2
17	25.2
15	30.2
13	35.3
11	40.4
10	43.6
9	47.3
7	50.9
5	55.8
3	60.5
1	63.5

Station 4	
Bottle number	Depth (m)
24	5.0
23	10.1
22	15.0
21	20.0
20	25.3
19	30.3
18	35.4
17	40.3
16	45.3
15	50.5
14	55.5
13	60.6
12	70.7
11	80.9
10	90.8
9	101.0
8	126.2
7	151.4
6	176.7
5	201.9
4	227.2
3	252.5
2	262.4
1	278.6

Station 9	
Bottle number	Depth (m)
23	4.7
21	9.9
19	15.0
17	20.1
15	25.1
13	30.2
11	35.1
9	40.4
7	45.2
5	50.5
3	55.7
1	60.5

Station 10	
Bottle number	Depth (m)
23	5.3
21	10.5
19	15.5
17	20.5
15	25.4
13	30.4
11	35.7
9	40.7
7	45.5
5	50.6
3	55.8
1	57.9

Station 7	
Bottle number	Depth (m)
23	5.2
21	10.2
19	15.1
17	20.3
16	25.1
15	30.2
14	35.5
13	40.5
12	45.4
11	50.4
9	55.6
7	60.7
5	65.6
3	70.6
1	73.6

Station 12	
Bottle number	Depth (m)
24	5.0
23	10.1
22	14.9
21	20.1
20	24.6
19	30.2
18	35.3
17	40.6
16	45.6
15	50.5
14	55.6
13	60.1
12	65.4
11	70.6
10	75.8
9	80.8
8	86.1
7	90.9
6	95.8
5	101.1
4	105.9
3	110.7
2	121.2
1	130.5

Station 16	
Bottle number	Depth (m)
23	5.2
21	10.1
19	15.2
17	20.2
15	25.4
13	30.7
11	35.7
9	40.3
7	45.8
5	51.1
3	55.2
1	60.1

Station 22	
Bottle number	Depth (m)
23	5.4
21	10.1
19	15.5
17	20.4
16	25.4
15	30.3
14	35.6
13	40.5
12	45.3
11	50.6
10	55.7
9	60.6
7	65.7
5	70.3
3	75.8
1	78.4

Station 21	
Bottle number	Depth (m)
22	4.9
19	10.0
17	15.2
15	20.3
13	25.3
11	30.0
9	34.9
7	38.4
4	40.4
1	43.5

Part C. Detailed overview of water column samples collected from CTD

Station	Name	Past cruise	Date	Number of depths	Water depth (m)	Type of samples collected
20	Landsort Deep	IODP-LD	28-May	24	10.0, 20.1, 30.0, 39.6, 50.1, 60.3, 64.3, 68.5, 70.2, 72.3, 74.5, 76.5, 78.4, 80.3, 82.5, 84.3, 86.5, 88.3, 91.3, 100.4, 20.0, 301.9, 403.1, 428.0	Unfiltered, 0.2 µm and 0.02 µm dissolved
17	North Gotland	LL19	29-May	23	5.2, 10.0, 1.54, 20.1, 25.0, 30.4, 40.7, 50.7, 60.6, 70.7, 74.7, 78.9, 80.8, 86.0, 90.8, 96.0, 101.3, 111.2, 121.4, 131.5, 141.6, 151.8, 161.1	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm and 0.02 µm particulate, GEOTRACES samples, Cr and U samples
13	East Gotland	LF1	30-May	16	5.0, 10.1, 16.2, 17.2, 20.1, 25.0, 30.2, 35.3, 40.3, 45.6, 50.5, 53.6, 55.6, 57.4, 59.5, 61.8	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm and 0.02 µm particulate, GEOTRACES samples
19	Gotland Basin	BY15	1-Jun	24	10.0, 20.1, 30.0, 40.2, 45.3, 50.4, 55.5, 60.4, 65.6, 70.5, 75.6, 80.4, 85.5, 90.6, 95.8, 101.0, 106.0, 110.9, 126.0, 151.2, 176.4, 201.7, 222.0, 229.8	Unfiltered, 0.2 µm and 0.02 µm dissolved, Cr and U samples
18	Faro Deep	F80	2-Jun	24	10.2, 20.1, 30.2, 30.3, 40.3, 50.4, 55.4, 60.5, 65.7, 70.8, 75.8, 80.7, 85.7, 90.7, 95.8, 100.9, 110.9, 121.0, 131.3, 141.2, 151.4, 166.5, 176.7, 186.2	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm and 0.02 µm particulate, GEOTRACES samples, Cr and U samples
2	Stockholm Archipelago		3-Jun	7	5.0, 10.1, 15.0, 19.9, 25.3, 30.0, 35.2	Unfiltered, 0.2 µm and 0.02 µm dissolved
1	Baggensfjarden	PLU005	3-Jun	7	5.2, 10.1, 15.1, 20.0, 25.1, 30.1, 35.4	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
5	Baltic-Aland	TAH	4-Jun	14	5.1, 9.9, 14.9, 20.2, 25.2, 30.2, 35.3, 40.4, 43.6, 47.3, 50.9, 55.8, 60.5, 63.5	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulatesamples
4	Aland-Bothnian	F64	5-Jun	24	5.0, 10.1, 15.0, 20.0, 25.3, 30.3, 35.4, 40.3, 45.3, 50.5, 60.6, 70.7, 80.9, 90.8, 101.0, 126.2, 151.4, 176.7, 201.9, 227.2, 252.5, 262.4, 278.6	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
9	Gulf of Finland	GOF5	6-Jun	12	4.7, 9.9, 15.0, 20.1, 25.1, 30.2, 35.1, 40.4, 45.2, 50.5, 55.7, 60.5	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
10	Gulf of Finland	LL3A	7-Jun	12	5.3, 10.5, 15.5, 20.5, 25.4, 30.4, 35.7, 40.7, 45.5, 50.6, 55.8, 57.9	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm and 0.02 µm particulate, Cr and U samples
7	Gulf of Finland	JML	8-Jun	15	5.2, 10.2, 15.1, 20.3, 25.1, 30.2, 35.5, 40.5, 45.4, 50.4, 55.6, 60.7, 65.6, 70.6, 73.6	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
12	East Gotland	LL15	8-Jun	24	5.0, 10.1, 14.9, 20.1, 24.6, 30.2, 35.3, 40.6, 45.6, 50.5, 55.6, 60.1, 65.4, 70.6, 75.8, 80.8, 86.1, 90.9, 95.8, 101.1, 105.9, 110.7, 121.2, 130.5	Unfiltered, 0.2 µm and 0.02 µm dissolved, Cr and U samples
16	East Gotland	Scholz 311	9-Jun	12	5.2, 10.1, 15.2, 20.2, 25.4, 30.7, 35.7, 40.3, 45.8, 51.1, 55.2, 60.1	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
22	Bornholm	BY5	11-Jun	16	5.4, 10.1, 15.5, 20.4, 25.4, 30.3, 35.6, 40.5, 45.3, 50.6, 55.7, 60.6, 65.7, 70.3, 75.8, 78.4	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm particulate, Cr and U samples
21	Arkona	BY2	12-Jun	10	4.9, 10.0, 15.2, 20.3, 25.3, 30.0, 34.9, 38.3, 40.4, 43.5	Unfiltered, 0.2 µm and 0.02 µm dissolved, 0.2 µm and 0.02 µm particulate, GEOTRACES samples

Appendix II In-situ pump sampling overview

Station #	ISP #	Date GMT	Start GMT	Duration (min)	Latitude N	Longitude E	Water depth (m)	Pump #	Target depth (m)	Prefilter	Total flow meter	Treated anoxically	Comment
17 (LL19)	1	29/05/2016	9:00	120	58° 52.82	20° 18.59	170	C	10	✔	48		minimum flow reached
								B	70	✔	163		minimum flow reached
								A	90	✔	72		minimum flow reached
								Dual FH1			97	✔	
								Dual FH2	140		87	✔	for Silke
								Dual comb			184		minimum flow reached
13 (LF1)	2	30/05/2016	8:00	120	57° 58.95	21° 16.85	68	A	10	✔	33		initial flow rate changed to
								C	17	✔	170		6L/min for all pumps, min flow
								B	30	✔	195		rate changed to 3L/min for A
								Dual FH1			183		and anoxic pump
								Dual FH2	55		173		for Silke
								Dual comb			357		minimum flow reached
18 (F80)	3	01/06/2016	19:00	360	57° 59.5	19° 53.85	199	A	50		715		Quartz filter for Silke
								B	100		958		Quartz filter for Silke
								C	150		739		Quartz filter for Silke
								Dual FH1			381	✔	Quartz filter for Silke
								Dual FH2	175		357	✔	Quartz filter for Silke
								Dual comb			740		
18 (F80)	4	02/06/2016	8:20	120	57° 59.5	19° 53.85	199	A	10	✔	29		minimum flow reached
								B	70	✔	94		low battery
								C	100	✔	192		low battery
								Dual FH1			80	✔	
								Dual FH2	175		82	✔	
								Dual comb			164		minimum flow reached
4 (F64)	5	05/06/2016	7:45	60	60° 10.9	19° 8.8	291	A	10	✔	47		minimum flow reached
								B	30	✔	265		time up
								C	40	✔	248		time up
								Dual FH1			144		
								Dual FH2	50		133		for Silke
								Dual comb			276		minimum flow reached
10 (LL3A)	6	07/06/2016	11:30	60	60° 2.71	26° 19.06	64	A		✔	27		minimum flow reached
								B		✔	112		minimum flow reached
								C		✔	279		time up
								Dual FH1			120	✔	for Silke
								Dual FH2			111	✔	
								Dual comb			237		time up
Station #	**ISP #**	**Date GMT**	**Start GMT**	**Duration (min)**	**Latitude N**	**Longitude E**	**Water depth (m)**	**Pump #**	**Target depth (m)**	**Prefilter**	**Total flow meter**	**Treated anoxically**	**Comment**
7 (JML)	7	08/06/2016	7:15	75	59° 34.91	23° 37.5	81	B	10	✔	79		sudden flow obstruction
								A	40	✔	119		minimum flow reached
								C	55	✔	177		minimum flow reached
								Dual FH1			65	✔	
								Dual FH2	70		59	✔	for Silke
								Dual comb			124		minimum flow reached
19 (BY15)	8	10/06/2016	6:30	120	57° 19.19	20° 2.99	237	B	85	✔	280		minimum flow reached
								A	175	✔	215		minimum flow reached
								C	200	✔	285		minimum flow reached
								Dual FH1			165	✔	
								Dual FH2	220		162	✔	for Silke
								Dual comb			327		minimum flow reached
22 (Bornholm	9	11/06/2016	10:15	120	55° 28.62	15° 28.99	87	A		✔	30		minimum flow reached
								B		✔	330		time up
								C		✔	151		minimum flow reached
								Dual FH1			76		
								Dual FH2			68		
								Dual comb			143		minimum flow reached
22 (Bornholm	10	11/06/2016	13:30	210	55° 28.62	15° 28.99	87	A	45		612		Quartz filter for Silke
								B	55		732		Quartz filter for Silke
								C	65		386		Quartz filter for Silke
								Dual FH1			104	✔	Quartz filter for Silke
								Dual FH2	75		99	✔	Quartz filter for Silke
								Dual comb			204		
21 (Arkona)	11	12/06/2016	9:45	120	54° 58.5	14° 5.05	47	A	10	✔	33		minimum flow reached
								B	20	✔	87		minimum flow reached
								C	30	✔	94		minimum flow reached
								Dual FH1			104		
								Dual FH2	40		102		for Silke
								Dual comb			206		minimum flow reached

Appendix III Multicore Allocation

Day 1 Station 20 – Landsort deep

Casts 1, 2 and 3 (12 x 10 cm) all failed. Multicore tubes too full.

Day 2 Station 17 – Northern Gotland (LL19/BY29)

Cast 1 (12 x 10 cm)

- 1 porewater core (centrifugation)
- 1 nitrate core
- 1 methane core
- 1 sulfate reduction core
- 2 micro-electrode cores
- 3 flux cores
- 1 frozen core
- 1 resin embedding
- 1 spare

Cast 2-7 (8 x 6 cm; 4 x 10 cm)

4 failed casts, 2 successful

- 16 x 6 cm core for N-cycling
- 4 rhizon cores for isotopes

Day 3 Station 13 – LF1

Cast 1 (12 x 10 cm)

- 1 sliced pw
- 1 nitrate
- 1 methane
- 1 sulfate reduction
- 2 micro-electrodes, microbes, 210Pb
- 1 frozen
- 3 reduction experiments
- 2 incubations (Martijn)

Cast 2 (12 x 10 cm)

- 6 flux (Wytze)
- 3 Br (Wytze)
- 3 incubations (Martijn)

Cast 3 (12 x 10 cm)

- 12 incubations (Martijn)

Cast 4 (8 x 6 cm + 4 x 10 cm)

- 8 N-cycling
- 4 rhizons (Silke)

Cast 5 (8 x 6 cm + 4 x 10 cm)
- 8 N-cycling
- 3 incubations (Martijn)

Day 5 Station 19 (BY15)

Cast 1 (12 x 10 cm)
- 1 sliced pw
- 1 nitrate
- 1 methane
- 1 sulfate reduction
- 2 micro-electrodes, microbes, 210Pb
- 1 frozen
- 1 resin-embedding
- 2 incubations (Martijn)
- 1 sediment (Silke)
- 1 lost

Cast 2 (12 x 10 cm)
- 3 flux cores Wytze
- 9 incubations (Martijn)

Day 5 Station 14 (BY15a)

Cast 1 (12 x 10 cm)
- 1 sliced porewater
- 1 nitrate
- 2 micro-electrodes
- 1 resin-embedding
- 3 flux cores (Wytze)
- 1 rhizon (Silke)
- 3 incubations (Martijn)

Day 6 Station 18 (F80)
- 1 sliced pw
- 1 CH4
- 1 SO4 red
- 2 microelectrodes
- 1 frozen
- 3 flux
- 1 DOC
- 1 sediment (Silke)

Day 7 Station 2 (wrong coordinate received from SGU)
- 1 microelectrodes

Station 1 (PLU_005)
Cast 1 (12 x 10 cm)
- 1 sliced pw (Matthias)

- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 1 resin embedding (Matthias)
- 1 DOC (Mathilde)
- 1 rhizon (Silke)
- 1 grey tube, whole core storage

Cast 2
- 3 flux cores (Wytze)
- 2 grey tubes, whole core storage
- 7 cores incubations (Martijn)

Cast 3 and 4 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)
- 8 cores incubations (Martijn)

Day 8. Station 3 (PLU_002) (notes not fully clear)

Cast 1 (12 x 10 cm)
- Micro-electrode (Martijn) not used

Cast 2 (12 x 10 cm)
- 1 sliced pw
- 1 NOx
- 1 CH4
- 1 SO4
- 1 frozen
- 1 micro-electode
- 2 flux Wytze

Cast 3 (8 x 6 cm, 4 x 8 cm)
- 8 N-cycling (Liz)
- 1 rhizon (Silke) (not used)
- 1 micro-electrods (Martijn)

Cast 4 (8 x 6 cm, 4 x 8 cm)
- 4 flux (Wytze)
- 8 N-cycling (Liz)

Cast 5 (8 x 6 cm, 4 x 8 cm)
- 1 grey core Niels
- 1 rhizon Silke

Day 9. Station 4 (F64)

Cast 1 (8 x 6 cm, 4 x 10 cm)
- 8 cores N-cycling Liz

- 1 core CH4 (Wytze, Niels)
- 1 core SO4 (Niels, Wytze)
- 1 oxic slicing for 210Pb (Niels)
- 1 frozen core (Niels)

Cast 2 (8 x 6 cm, 4 x 10 cm)
- 8 cores N-cycling (Liz)
- 1 Nox and microprofiling (Martijn/Niels)
- 1 porewater slicing (Matthias)
- 1 failed core
- 1 core top sliced for porewater Fe isotopes (Silke)

Day 10. Station 9 (GOF5)

Cast 1 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 1 rhizon (Silke)
- 3 flux cores (Wytze)
- 1 spare

Cast 2 (12 x 10 cm)
- 3 flux cores (Wytze)
- 9 cores incubations (Martijn)

Cast 3 and 4 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)
- 7 cores incubations (Martijn)

Station GOF3 (60 m) (12 x 10 cm)
Cores not used (visually similar to GOF5)

Station GOF3 (55m) (12 x 10 cm)
- 1 sliced pw (to 10 cm depth)
- 1 CH4
- 1 SO4 red
- 1 micro-electrode
- 1 rhizon (Silke)
- 1 frozen

Day 11. Station 10 LL3A

Cast 1 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)

- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 1 rhizon (Silke)
- 3 flux cores (Wytze)
- 1 spare

Cast 2 (12 x 10 cm)
- 3 flux cores (Wytze)

Cast 3, 4 and 5 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)

Day 12. Station 7 – JML

Cast 1 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 1 rhizon (Silke)
- 3 flux cores (Wytze)
- 1 spare

Cast 2 (12 x 10 cm)
- 3 flux cores (Wytze)

Cast 3 and 4 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)

Day 13. Station Scholz 311

Cast 1 (12 x 10 cm)
- 1 micro-electrode (Martijn)

Cast 2 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 3 flux cores (Wytze)
- 1 rhizon (Silke)
- 1 spare

Cast 2 (12 x 10 cm)
- 3 flux cores (Wytze)

- 4 rhizon (Silke)

Cast 3 and 4 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)

Stations BY15b, c, d

BY15b, 1 multicore (12 x 10 cm); 3 used
- Porewater (top 5 cm)
- Micro-electrode profiling
- Grey core for storage

BY15c, 1 multicore (12 x 10 cm); 3 used, see above

BY15d, 1 multicore (12 x 10 cm); 3 used, see above

Day 15. Station 21 – Bornholm (BY5)

Cast 1 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 2 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)
- 3 flux cores (Wytze)
- 1 rhizon (Silke)
- 1 spare

Cast 2 (12 x 10 cm)
- 3 flux cores (Wytze)
- 1 rhizon (Silke)

Cast 3 and 4 (8 x 6 cm; 4 x 10 cm)
- 16 N-cycling (Liz)

Day 16. Station 22 – Arkona (BY2)

Cast 1 (12 x 10 cm)
- 3 oxic flux (Wytze)
- 1 micro-electrode (Martijn)

Cast 2 (12 x 10 cm)
- 1 sliced pw (Matthias)
- 1 NOx (Niels)
- 1 CH4 (Wytze, Niels)
- 1 SO4 red (Niels, Wytze)
- 1 micro-electrodes (Martijn, Silvia)
- 1 frozen (Niels)

- 4 rhizon (Silke)
- 1 rhizon (Matthias)
- 1 DOC (Mathilde)
- 1 anoxic flux Wytze

Cast 3 (12 x 10 cm)

- 3 Br cores (Wytze)
- 2 anoxic flux (Wytze)
- 3 Fe reduction (Silvia)

Cast 4 and 5 (8 x 6 cm; 4 x 10 cm)

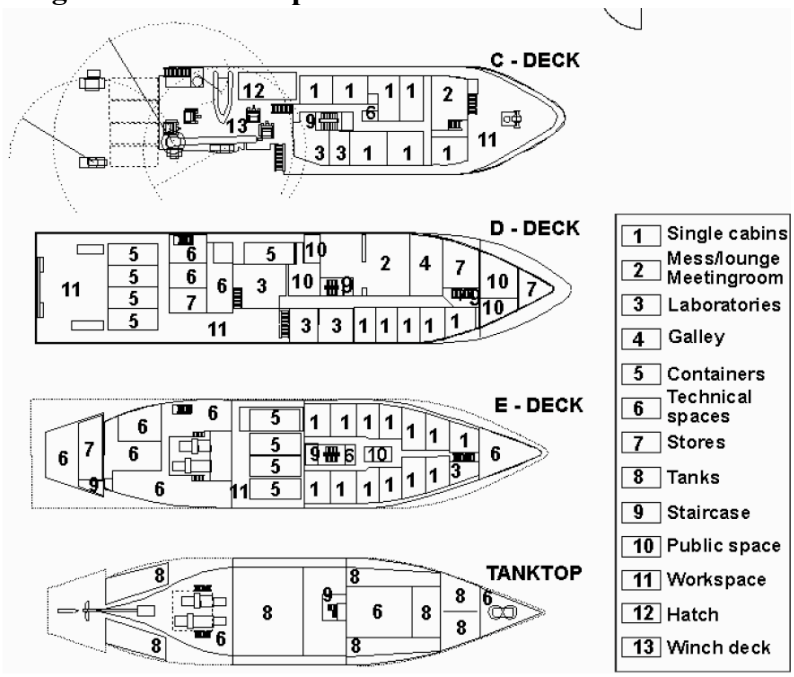
- 16 N-cycling (Liz)
- 1 micro-electrode (Martijn)

End of multicoring

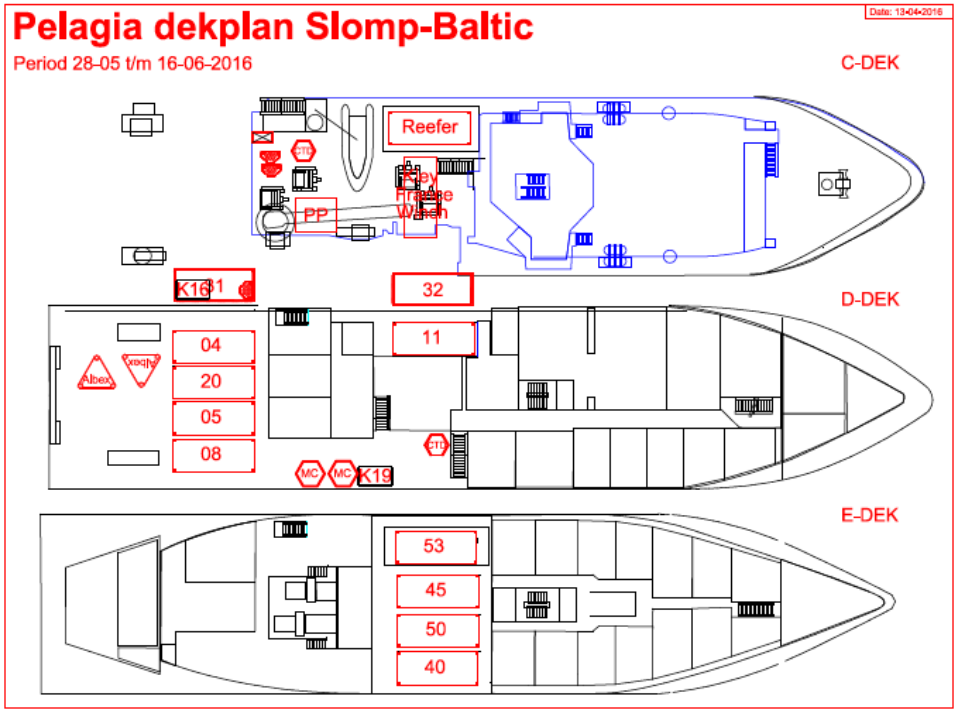
Appendix IV - Working arrangements on the ship

Cruise acronym for lables on cores: 64PE411
First number: station (up to 14); Second number: sample (up to 50)
CTD: water sample
PW: pore water
BW: bottom water
SED: sediment: numbered continuously

Working decks on the ship



Container plan



Working arrangements:

- chemical lab: alkalinity, micro-electrodes, microscope
- wet lab: sieving for macrofauna, oxic core slicing
- container 45: preparation water sampling, (in-situ) filters
- container 40 and 50: nutrient analyses
- container 53: water column alkalinity
- container 20: large glovebox, core slicing, N-cycling
- container 11: small glovebox, subsampling, glove bags, whole core flux incubations
- container 8: clean sampling
- container 5: lander material
- container 4: radio-isotope lab