

# **Baltic Sea Research Institute Warnemünde**

## **C r u i s e R e p o r t**

r/v " Heincke "

Cruise - No. 330 / 2010

This report is based on preliminary data

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1. **Cruise No.:** HE330
2. **Dates of the cruise:** from June 26 – July 8 2010
3. **Particulars of the research vessel:**
  - Name: R/V Heincke
  - Nationality: Germany
  - Operating Authority: Alfred Wegener Institute, Bremerhaven
4. **Geographical area in which ship has operated:**  
Baltic Sea, Gotland Basin, Arkona Basin, Gdansk Basin
5. **Dates and names of ports of call**
  - 26.6.2010 Warnemünde
  - 6.8.2010 Gdansk, Poland
  - 8.8.2010 Warnemünde
6. **Purpose of the cruise**  
HYPER investigates the current past situation of oxygen supply
7. **Crew:**
  - Name of master: Robert Voss
  - Number of crew: 11
8. **Research staff:**
  - Chief scientist: Dr. Maren Voß
  - Scientists: 10
  - Engineers: 0
  - Technicians: 2
9. **Co-operating institutions:**  
Universities in Lund (Sweden), Gdansk (Poland), Utrecht (Netherlands), and Helsinki (Finland)
10. **Scientific equipment**  
CTD with water bottles, Gravity corer, Multicorer, Van Veen grab, Dredge

## 11. General remarks and preliminary result (7 pages)

### General scientific program execution

The cruise started at June 26 in Warnemünde and ended at July 8 in the same place. The past and present hypoxic and anoxic situation of the central Baltic Sea was our main focus. Processes of nitrogen removal, animal metabolism and pore water chemistry were investigated. We fulfilled an intense bottom and water column sampling program in redoxcline depths. Altogether 15 stations were visited mostly located around the island of Gotland and three in the Arkona Basin (German waters) and four in Gdansk Basin (Polish waters). Since we had very good weather conditions we could accomplish all planned sampling successfully (Table 1, Figure 1).

Table 1 overview over the stations sampled and the gear used at the stations

#	station name	date	latitude (Deg. N)	longitude (Deg. E)	depth (m)	CTD	Multi- corer	gravity core	Van Veen grab	dredg e
1	Arkona 1	27. Jun 10	54 42.5936	013 56.9	26	x	x	-	x	x
2	Arkona 2	27. Jun 10	54 48.215	013 57.442	36.6	x	x	-	x	x
3	Arkona 3	27. Jun 10	54 53.44	013 58.323	40.7	x	x	-	x	x
4	LZ_GB_1	28. Jun 10	57 55.2572	017 41.3281	145	x	x	x	-	-
5	LZ_GB_2	29. Jun 10	58 21.5474	017 49.8507	106.4	x	x	x	-	-
6	LZ_LD	29. Jun 10	58 37.4764	018 15.2277	439	x	x	x	-	-
7	CS_BY31	30. Jun 10	58 35.0765	018 35.1739	186	x	x	x	-	-
8	CS_LL19	01. Jul 10	58 52.5730	020 18.6723	168	x	x	x	-	-
9	MM_NCB 3	01. Jul 10	58 48.5118	020 24.0292	189	x	x	-	-	-
10	CS_F80	02. Jul 10	57 59.5664	019 53.3960	191	x	x	x	-	-
11	CS_LF3	02. Jul 10	57 55.0986	020 46.0455	100	x	x	-	-	-
12	MM_GB1	03. Jul 10	57 20.275	020 13.265	232	x	x	-	-	-
13	MM_GB2	03. Jul 10	57 22.884	020 15.259	232	x	x	-	-	-
14	CS_BY15	04. Jul 10	57 19.3774	020 03.1856	233	x	x	x	-	-
15	X_0019	05. Jul 10	54 49.5221	019 14.8964	105	x	-	x	-	-
16	UJ_GD_1	05. Jul 10	54 49.519	019 01.792	95	x	x	-	x	x
17	X_018_new	05. Jul 10	54 55.484	019 05.1775	96.2	x	-	-	-	-
18	X_019_new	05. Jul 10	54 49.522	019 14.896	103	x	-	-	-	-
19	UJ_GD_3	05. Jul 10	54 42.5156	018 51.2571	80	x	x	-	-	-

The water column work was supposed contribute to the understanding of nitrogen losses via denitrification (Anammox) processes by means of rate measurements (see details below) and by natural abundance of  $^{15}\text{N}$  and  $^{18}\text{O}$  in nitrate. Both approaches from the Leibniz Institute in Warnemünde and the University Helsinki will complement each other. Oxygen, Hydrogen sulfide, and nutrients were measured from discrete depth in a relatively fine resolution through the redoxcline.

Short (Multicore of 30cm length) and long cores (up to 500cm depth) were collected to better understand the anoxic and hypoxic past of the deep Baltic Sea basins (Table 1). Basic sediment parameters like grain size and porosity will be analysed in the University of Lund. Phosphorous compounds will be studied by the group from Utrecht.

The performance of animals like mussels (*Macoma baltica*) under oxygen stress is being studied by the group from the University of Gdansk. Multicore, Van Veen grab and dredge were used to extract life animals. Samples were supposed to be collected from the two shallower basins, the Arkona Basin and the Basin of Gdansk. Unfortunately, the planned stations in the Gdansk deep could not properly be visited because of an unannounced military exercise by the Polish navy in the exact area and at the exact time where sampling was planned. We tried to select another site without much success.

In the morning of July 6 Gdansk was visited and a group of journalists from 2 TV and 2 radio stations came to the ship to learn about the cruise and the ecological status of the Baltic Sea. In the next morning RV Heincke sailed back to Rostock Warnemünde, where the cruise ended at July 8.

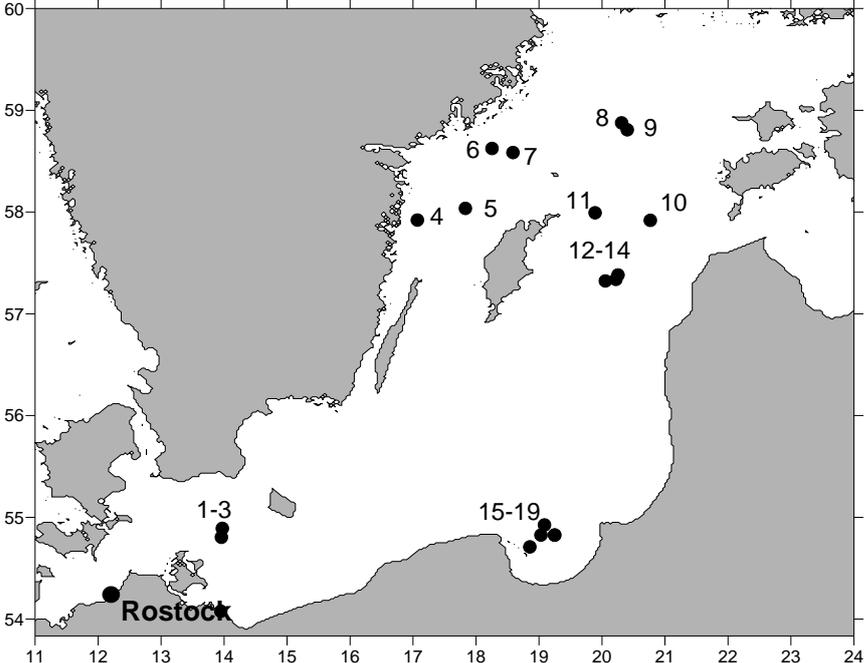


Fig. 1 stations which were sampled during the HE 330 cruise according to table 1 (above)

**Preliminary results**

Preliminary data from the cruise are shown and briefly described below. Water column profiles from the redoxcline show clearly that oxygen decreases towards zero around 50-80m depth at all stations around the island of Gotland. Temperature drops below the surface mixed layer to approximately 2°C and slightly increases again together with the salinity. This salinity increase of 2-3 is the important barrier for the exchange of substances and in these horizons oxygen rapidly falls to zero values. The figures 2-4 show only a small part of the profile.

In the western Gotland Basin / Landsort Deep this is the case around 70 meter depth (Fig. 2). Immediately H<sub>2</sub>S develops and ammonium accumulates.

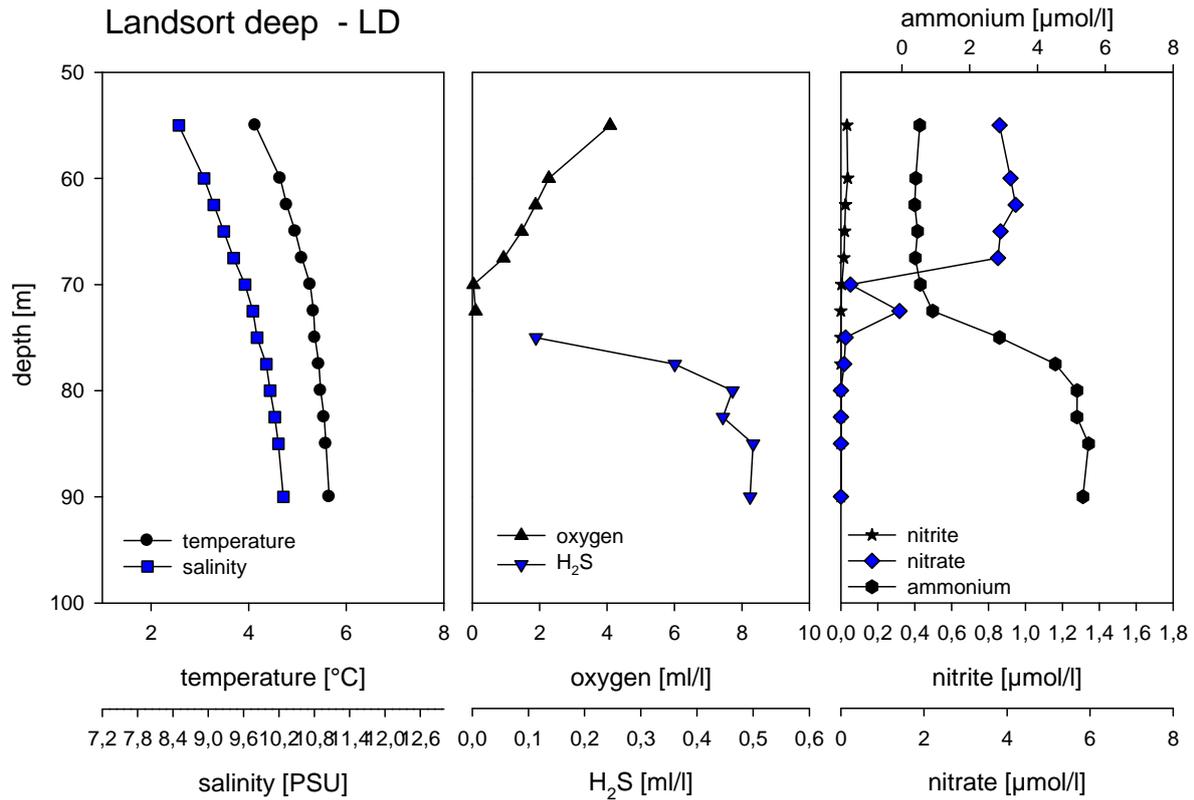


Fig. 2 profiles of temperature and salinity (left panel), oxygen and hydrogen sulfide (middle panel), and nutrients (right panel) from redoxcline depth between 55 and 90m in the Landsort Deep.

### Gotland deep - BY15

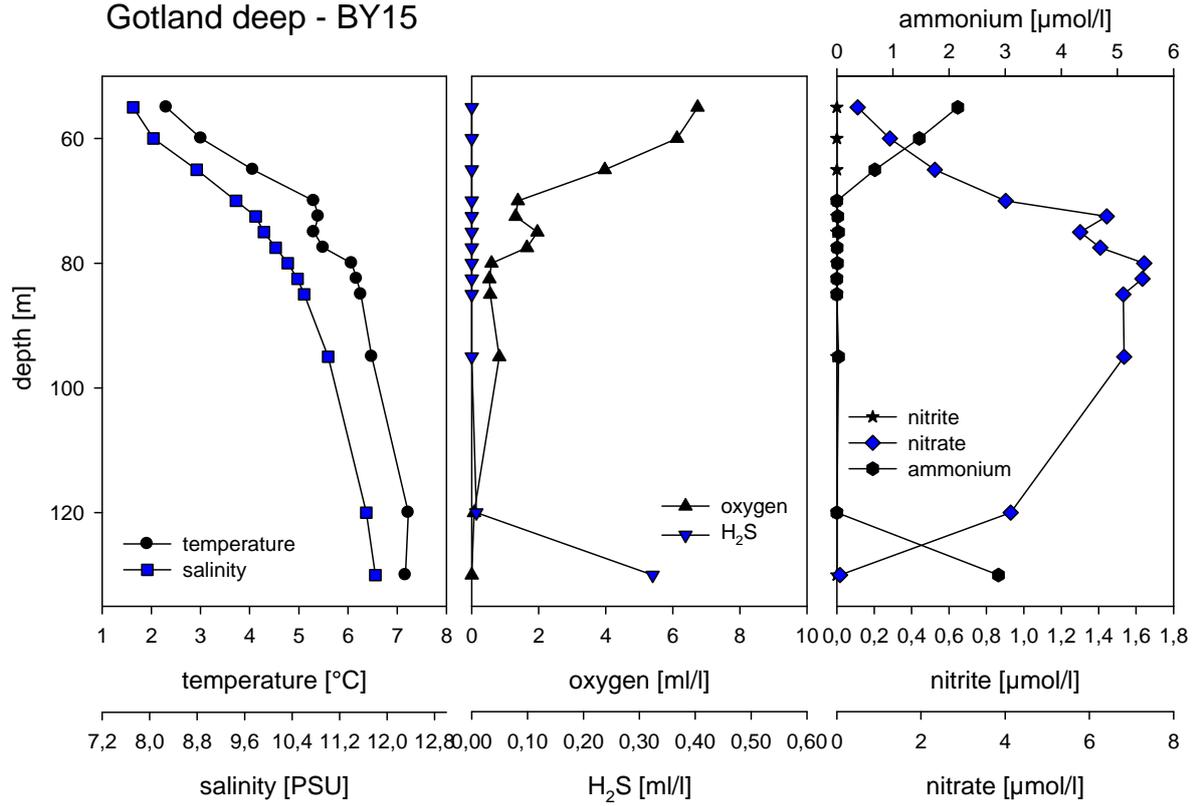


Fig. 3 profiles of temperature and salinity (left panel), oxygen and hydrogen sulfide (middle panel), and nutrients (right panel) from redoxcline depth between 55 and 150m in the Gotland Deep.

### northern Gotland Basin - LL19

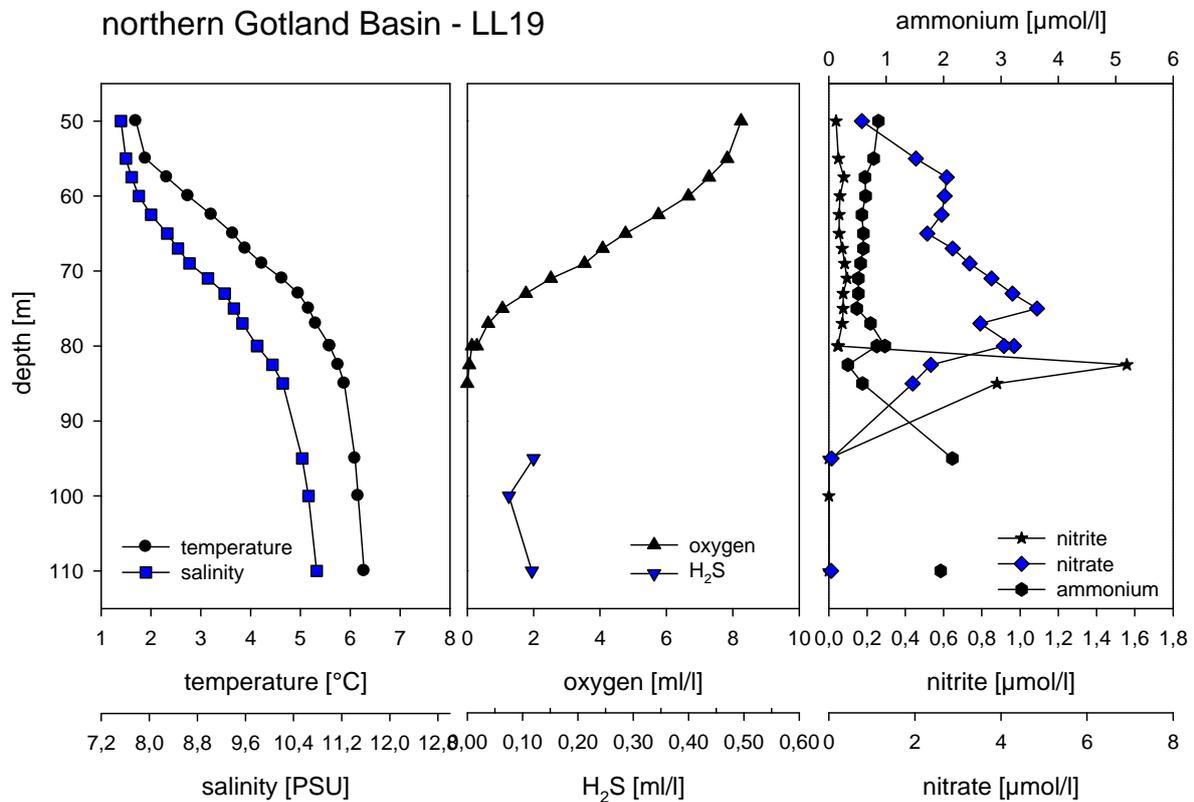


Fig. 4 profiles of temperature and salinity (left panel), oxygen and hydrogen sulfide (middle panel), and nutrients (right panel) from redoxcline depth between 50 and 110m in the Northern Gotland Basin.

During the cruise we measured the nitrogen removing processes, denitrification and anammox, both in the sediments (Arkona Bay), in the oxic-anoxic interface, and in anoxic depths (Western and Eastern Gotland Basin, Landsort Deep). The processes were measured using Isotope Pairing Technique according to Nielsen 1992 and Dalsgaard et al. 2003. In short, samples are incubated with added  $^{15}\text{NO}_3^-$  and with added  $^{15}\text{NH}_4^+$  and  $^{14}\text{NO}_3^-$ . Production of labelled nitrogen gas ( $^{29}\text{N}_2$  and  $^{30}\text{N}_2$ ) is followed over time, and the ratios of different labels in different treatments reveal the relative importance of the two processes. In case naturally occurring nitrate is present, nitrogen removal taking place *in situ* can be calculated from the incubation results and nitrate concentrations. Additionally the process feeding these removal processes, nitrification, was measured on the water column on the three stations (Western and Eastern Gotland Basin, Landsort Deep). Measurements were made on altogether 6 Stations (table 2). The isotope samples collected will be sent to isotope ratio mass spectrometer analyse later this year.

These measurements contribute to the BONUS+ program under projects HYPER and AMBER.

Table . 2 Samples for nitrogen removing processes (denitrification) were taken on the following stations:

Station	Date	Depth	Type	Sampling depth
Arkona 1	27 June	37 m	sediment	37 m
Arkona 3	27 June	40 m	sediment	40 m
LZ_GB1	28 June	146 m	water	132, 115, 100, 85 m
LZ_LD	30 June	438 m	water	180, 160, 140, 120. 100, 80, 75, 68 m
CS_BY15	4 July	233 m	water	200, 180, 160, 140, 130, 125, 120, 110 m
UJ_GD1	5 July	96 m	sediment	96 m

### Samples for porewater analysis

To investigate the porewater distributions of methane, sulfate, sulfide and other dissolved species in the upper ~5m of sediment in the deep basins of the Baltic Proper, in order to parameterize Reactive Transport Modeling simulations of diagenetic processes and their impacts on the burial phases of P and Fe.

1. Porewater extraction with Rhizones to measure  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in nitrate
2. Sampling of porewaters by core slicing and/or syringe extraction, followed by specific treatments dependent on parameter to be measured; see details below
3. Onboard analysis of porewater subsamples for alkalinity. Storage of samples for analysis at IOW:  $\text{NH}_4$ ,  $\text{H}_4\text{SiO}_4$ . Storage of samples for analysis in the Netherlands:  $\text{CH}_4$ ; P, S, Fe, Mn; HS; DIC
4. Storage of long cores and selected multicores for stratigraphic descriptions, plus potential water content,  $^{210}\text{Pb}$  dating, total elemental and P speciation, organic carbon and organic geochemical analyses.

### Multicore sampling:

Tube 1: predrilled with holes for  $\text{CH}_4$  sampling (5cm vertical separation, holes of diameter ~1.5cm to fit 10ml syringe), and taped prior to coring. 10ml sediment extracted by syringe and injected directly into 65ml glass bottle filled with saturated salt solution. Rubber stopper and cap applied, taking care that no air enters. Bottle shaken to make suspension. 10ml headspace injected using glass syringe filled direct from septum connection to gas supply. Bottle stored upside down at room temperature.

Tube 2: predrilled with holes for regular porewater sampling (5cm vertical separation, holes of diameter ~2cm to fit 20ml syringe), and taped prior to coring. Bottom water sample taken directly after recovery. Through holes, 20ml sediment extracted by syringe, sealed with parafilm and an elastic band, and transferred to glovebox. Inside glovebox, sediment transferred to 50ml greiner tube. Greiner removed from glove box, centrifuged and returned to glove box. Supernatant water filtered via 20ml syringe and 0.4 $\mu\text{m}$  filter into 15ml greiner. Subsampling performed from this 15ml greiner in glove bag (Table 3).

Table 3 List of planned analysis from long and short cores

Rank	Analysis	Vol. (ml)	Vial	Treatment	Code	Method	Storage
1	Alkalinity	2	Greiner 15ml	-	<b>Alk</b>	Onboard titration	4°C
2	NH <sub>4</sub> , Silica	2	Greiner 15ml	-	<b>NH<sub>4</sub>, Si</b>	AA (IOW)	-20°C
3	P, S, Fe, Mn	2	Greiner 15ml	10 µl suprapur conc. HCl per ml	<b>P, S, Fe, Mn</b>	ICP-OES (Utrecht)	4°C
4	HS	2	PE vial	1 ml 2% degassed Zn-acetate soln. per ml	<b>HS</b>	AA (Utrecht)	-20°C
5	DIC	0.5	DIC vial	4 ml degassed 41g/L NaCl soln. spiked with saturated HgCl (10µL per sample)	<b>DIC</b>	(NIOZ)	4°C

### Gravity core sampling:

5m coreliner predrilled with holes for all sampling and taped prior to coring: Upper 2m drilled at 10cm resolution, lower 3m drilled at 20cm resolution. Two series of holes on opposite sides of the core liner: one for CH<sub>4</sub> and one for all other porewater parameters. Vertical offset between series = 5cm. Hole dimensions as per multicores. Cores cut into 1m sections after recovery, and sampled by syringe in the wet lab. Samples treated identically to multicores (see above). Remaining core material was frozen for later stratigraphic descriptions.

### Samples for sedimentological variables from gravity cores:

Hypoxia, defined as < 2mg/l dissolved oxygen, is not unique to the modern era. Investigations have shown that intermittent hypoxia has occurred since the beginning of the Littorina Sea (i.e. the last c. 8000 years). With the aim to spatially and temporally reconstruct hypoxia in the past, long (gravity cores) and short (multi cores or MUC) sediment cores, were retrieved during this research cruise. Two major goals have been fulfilled on this cruise. First, sediment cores were retrieved from the western Gotland Basin (LZ GB1, LZ GB2 and CS BY31) and the Landsort Deep (LZ LD) extending our spatial coverage and second, we revisited stations in the Baltic Proper (CS LL19, CS F80 and CS BY15) to have additional material for analyses. An additional previously unplanned core was taken in the Gdansk Deep (GD).

Table 4 List of gravity cores taken by the University of Lund for analysis in the lab.

Station	Latitude	Longitude	Depth	Area
LZ GB1	57 55.357 N	017 41.413 E	149 m	Western GB
LZ GB2	58 21.517 N	017 49.905 E	109 m	Western GB
LZ LD	58 37.378 N	017 15.175 E	457 m	Landsort Deep
CS BY31	58 34.971 N	018 35.294 E	187 m	Western GB
CS LL19	58 52.547 N	020 18.608 E	173 m	Baltic Proper
CS F80/CS F80B	57 59.639 N	019 53.574 E	181 m	Baltic Proper
CS BY15	57 19.138 N	020 03.085 E	238 m	Gotland Deep
GD	54 55.45 N	019 05.28 E	100 m	Gdansk Deep

These sediment cores will be described with emphasis on identifying periods with laminations, dated using <sup>14</sup>C, lead isotopes and palaeomagnetism and analyzed for geochemical characteristics including biogenic silica, organic carbon, nitrogen, phosphorous and total element distribution as palaeoenvironmental markers and indicators of hypoxia.

### First/preliminary results from the alkalinity titrations:

Roughly 2ml of porewater titrated with 0.01M HCl using Dosimat system to estimate alkalinity. Results below; alkalinity in milliequivalents, depth in cm

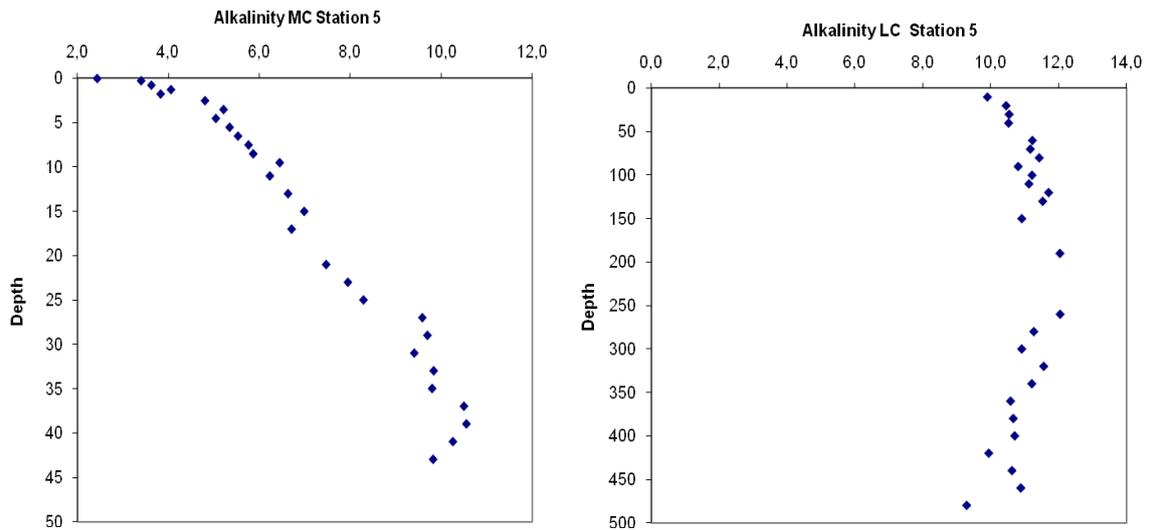


Figure 5 Results of Alkalinity from the Lansort Deep station, left from the short Multicores and right from the gravity core.

Alkalinity and other porewater parameters will be used to splice multicore and gravity core profiles (LC). The above data of one station already suggest that a depth overlap is present at all stations where both MC and LC were taken. Furthermore, the LC profiles at several sites show similar depth trends in alkalinity; namely an increase with depth from ~0-2m and a decrease with depth from ~2-5m. The possibility that these profiles are associated with precipitation of authigenic carbonate-phosphate minerals will be investigated when further data is ready.