ALKOR
Scientific Cruise Report

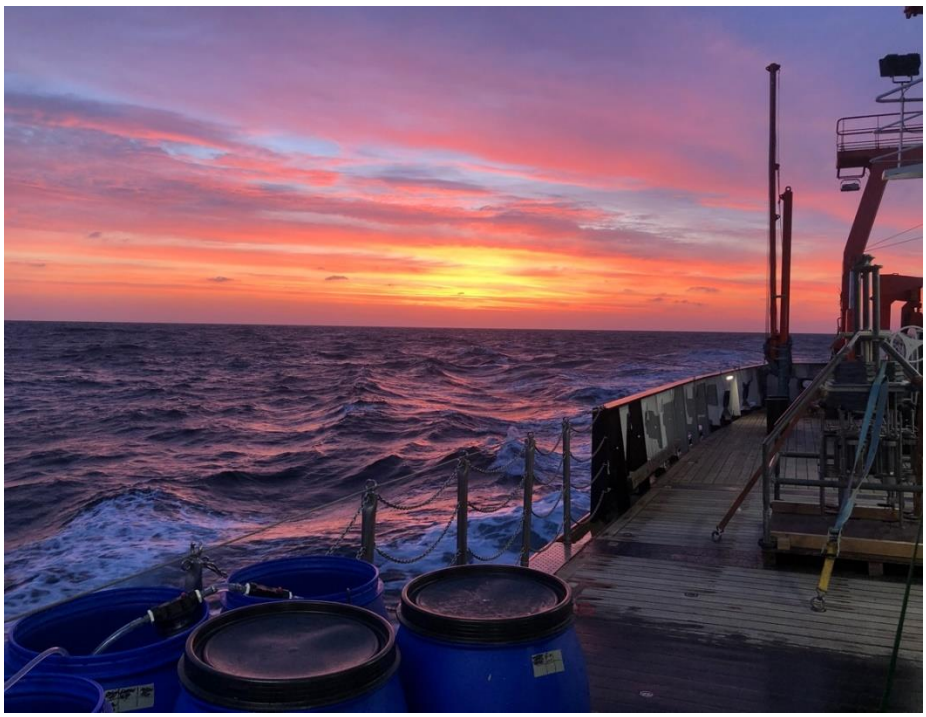
# The Ocean's Alkalinity - Connecting geological and metabolic processes and time-scales: mechanisms and magnitude of metabolic alkalinity generation in the North Sea

Cruise No. AL557

June 04 – June 23, 2021

Cuxhaven (Germany) – Cuxhaven (Germany)

North Sea Alkalinity



**Wiebke Freund, Chantal Mears, Eva-Maria Meckel, Fabrizio Minutolo, Carla Nantke, Andreas Neumann, Michael Seidel, Helmuth Thomas, Bryce van Dam**

Chief scientist: Prof. Dr. Helmuth Thomas

Helmholtz-Zentrum hereon GmbH

2022

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# 1 Cruise Summary

## 1.1 Summary in English

We investigated the alkalinity formation in the Wadden Sea and the southern North Sea, as well as respective exchange processes with and impacts on the open North Sea. The new observations of this expedition constitute the pivotal point of the DAAD project "The ocean's alkalinity: Connecting geological and metabolic processes and time-scales", which has been funded by the BMBF as part of the German-French initiative "Make Our Planet Great Again" (MOPGA) in support of the Paris Agreement (COP21). The project addresses the role of oceans as regulators of atmospheric carbon dioxide ($CO_2$), thus making a crucial contribution to maintaining climate on Earth in a habitable range. This regulatory function is biogeochemically performed by the ocean's $CO_2$ and pH buffer capacity: alkalinity. Alkalinity is generated by rock weathering, and by natural and human-induced anaerobic processes in sediments of coastal seas. The processes in coastal seas are related to eutrophication such that enhanced nutrient runoff increases alkalinity generation and the risk of deoxygenation and acidification. Climate change and its mitigation both have the potential to perturb the long-term stability of the ocean's alkalinity: ice retraction will expose rock surface, hitherto covered, to weathering and erosion. Attempts to mitigate and lower atmospheric $CO_2$ levels will necessarily involve the use of bioenergy to a large extent, which in turn comes with the need to massively employ fertilizers and consequently, eutrophication of coastal seas. Our research will investigate in which measure and to which extent human activities and climate change affect the ocean's alkalinity, particularly the impact of nitrogen fertilizers on coastal seas including the subsequent risk of acidification and deoxygenation. The project will be carried out collaboratively with the Universities of Oldenburg, Hamburg and Exeter (UK), and the Alfred Wegener Institute for Polar and Sea Research.

## 1.2 Zusammenfassung

Wir haben die Alkalinitätsbildung im Wattenmeer und in der südlichen Nordsee sowie die entsprechenden Austauschprozesse mit der offenen Nordsee und deren Auswirkungen auf die Nordsee untersucht. Die neuen Beobachtungen dieser Expedition bilden den Dreh- und Angelpunkt des DAAD-Projekts "The ocean's alkalinity: Connecting geological and metabolic processes and time-scales", das vom BMBF im Rahmen der deutsch-französischen Initiative "Make Our Planet Great Again" (MOPGA) zur Unterstützung des Pariser Abkommens (COP21) gefördert wurde. Das Projekt befasst sich mit der Rolle der Ozeane als Regulatoren des atmosphärischen Kohlendioxids ($CO_2$), die einen entscheidenden Beitrag dazu leisten, das Klima auf der Erde in einem bewohnbaren Bereich zu halten. Diese Regulierungsfunktion wird biogeochemisch durch die $CO_2$- und pH-Pufferkapazität des Ozeans erfüllt: die Alkalinität. Die Alkalinität wird durch Gesteinsverwitterung und durch natürliche und vom Menschen verursachte anaerobe Prozesse in den Sedimenten der Küstenmeere erzeugt. Die Prozesse in den Küstenmeeren hängen mit der Eutrophierung zusammen, so dass der verstärkte Nährstoffabfluss die Alkalinitätsbildung und das Risiko der Desoxygenierung und Versauerung erhöht. Sowohl der Klimawandel als auch seine Abschwächung haben das Potenzial, die langfristige Stabilität der Alkalinität des Ozeans zu beeinträchtigen: Der Rückzug des Eises wird die bisher bedeckte Felsoberfläche der Verwitterung und Erosion aussetzen. Versuche, den $CO_2$-Gehalt in der Atmosphäre zu verringern und zu senken, werden zwangsläufig zu einem großen Teil die Nutzung

von Bioenergie mit sich bringen, was wiederum den massiven Einsatz von Düngemitteln und die damit verbundene Eutrophierung der Küstenmeere zur Folge hat. Im Rahmen der Forschungsarbeiten soll untersucht werden, in welchem Maße und in welchem Ausmaß menschliche Aktivitäten und der Klimawandel die Alkalinität des Ozeans beeinflussen, insbesondere die Auswirkungen von Stickstoffdüngern auf die Küstenmeere, einschließlich der daraus resultierenden Gefahr der Versauerung und Desoxygenierung. Das Projekt wird in Zusammenarbeit mit den Universitäten Oldenburg, Hamburg und Exeter (UK) sowie dem Alfred-Wegener-Institut für Polar- und Meeresforschung durchgeführt.

# 2 Participants

## 2.1 Principal Investigators

| Name | Institution |
|---|---|
| Thomas, Helmuth, Prof. Dr. | HEREON |

## 2.2 Scientific Party

| Name | Discipline | Institution |
|---|---|---|
| Van Dam, Bryce, Dr. | Radium | HEREON |
| Mears, Chantal | Radium / $CO_2$ | HEREON |
| Minutolo, Fabrizio | MUC / Sediment incubations | HEREON |
| Neumann, Andreas, Dr. | MUC / Nutrient samples | HEREON |
| Meckel, Eva-Maria | Marine Geochemistry | ICBM |
| Nantke, Carla, Dr. | Geochemistry / CTD sampling | IOW |

## 2.3 Participating Institutions

| | |
|---|---|
| HEREON | Helmholtz-Zentrum hereon GmbH |
| ICBM | Institute for Chemistry and Biology of the Marine Environment, University of Oldenburg |
| IOW | Leibniz Institute for Baltic Sea Research Warnemünde |

# 3 Research Program

## 3.1 Description of the Work Area

The working area included stations within the German Bight as well as the entire North Sea. The stations were located within and outside the German EEZ, outside of national parks or other restricted areas. Figure 3.1 shows the cruise track, where stars representing CTD stations and white circles MUC stations. A detailed station list with coordinates and supplement information can be found in a separate excel spreadsheet.

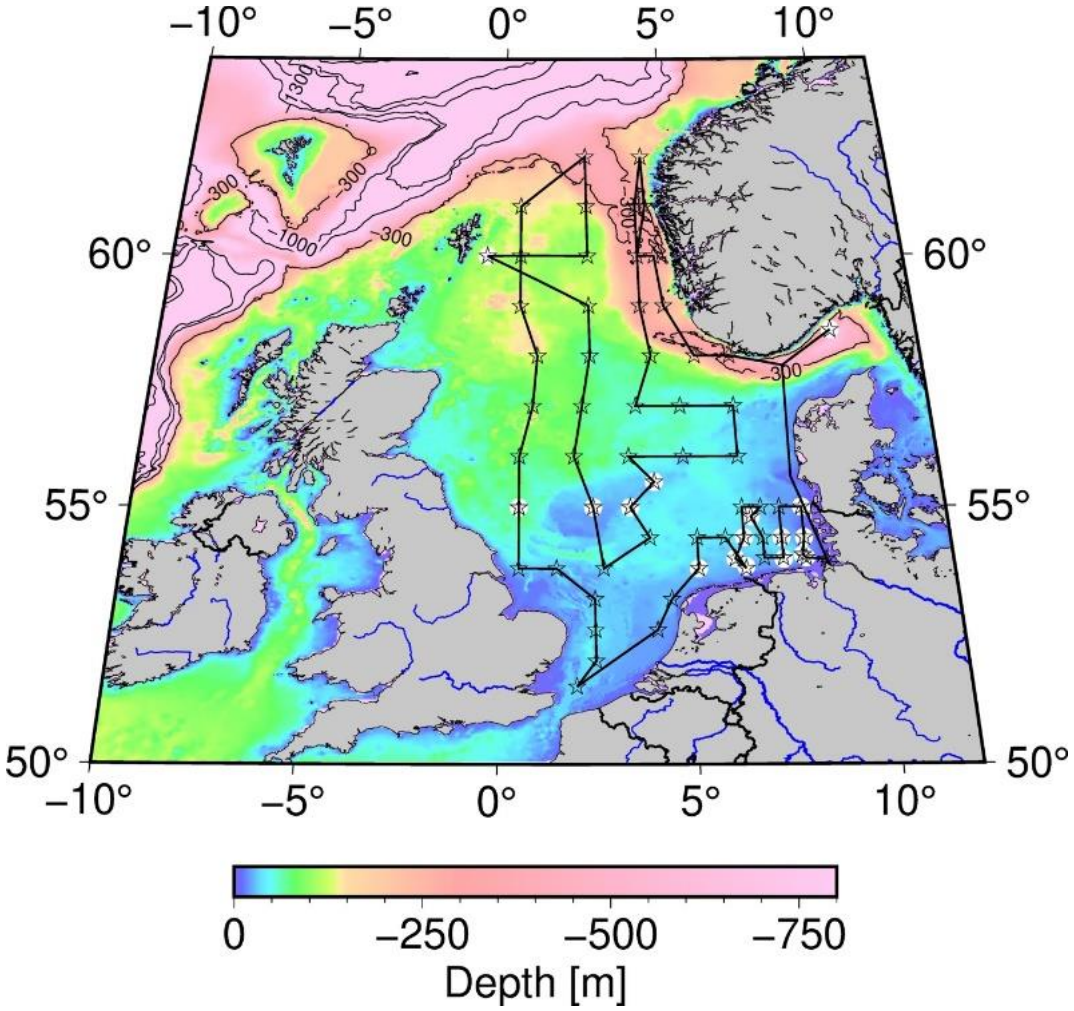


**Fig. 3.1** Track chart of R/V ALKOR Cruise AL557, stars represent CTD stations, white circles MUC stations.

## 3.2 Aims of the Cruise

The voyage on RV ALKOR (AL557) supports three projects dedicated to the study of material cycles and how they are influenced by climate and anthropogenic change. The focus of the data collected is on the German Academic Exchange Service (DAAD). German Academic Exchange Service (DAAD) The ocean's alkalinity - connecting geological and metabolic timescales, which is funded by the BMBF within the framework of "Make Our Planet Great Again". is financed. Furthermore, the BMBF supports the cruise within the FONA / MARE:N project CARBOSTORE, as well as within the framework of the DAM pilot mission Mobile Ground-touching Fisheries (MGF).

In a large station grid (about 1 degree x 1 degree), the water column is sampled with a CTD rosette and the sediment was sampled with a multicorer. These samples help to measure the distributions of $CO_2$, nutrients, trace metals and organic compounds in the North Sea to qualitatively and quantitatively determine their sources, sinks and transport pathways. In addition, to better understand the contribution of sediments and benthos to marine cycles in the water column, we measured the intensity of the exchange of nutrients and $CO_2$ between sediment and the water column.

## 3.3 Agenda of the Cruise

(H. Thomas)

The cruise was doiminate by water column sampling using the CTD, which was paralleled at selcetion stations by coring work using a multicorer (Fig. 3.1).

# 4 Narrative of the Cruise

(H. Thomas)

After a very calm, summery start in Cuxhaven, the exceptional weather conditions initially stayed with us, so within the first three days of the cruise the stations in the German Bight were sampled successfully and according to the program. This is an early success of the cruise, as this region is a central focus of the trip. In the further course the sampling of the channel region occurred followed by a long transect to the north along approximately along 0°30' E. North of the Shetland Islands we reached the Atlantic Ocean at 62°N' in comparatively rough weather, which finally forced us to take a break in the shelter of Shetland about halfway out.

The bad weather break at the end of the first week allowed us to conduct additional sediment sampling in the shelter of Shetland Islands. Thus, in addition to the shallower stations in the southern North Sea, one in the somewhat deeper northwestern North Sea can also be investigated, which lies in the inflow area of the water from the North Atlantic. Towards the evening of June 13, the weather and sea had calmed down enough for us to resume the planned program and continued our transect along 2°30' E in southern direction. In the further course we took two further sediment samples in addition to the CTD stations – on the right and left side of the Dogger Bank, respectively, before our way led us to the Norwegian Trench along 4° E. Here we were able to sample on both the western and eastern slopes of the Norwegian Channel, which are responsible for the transport of continental water masses from the North Sea into the deeper layers of the Atlantic.

This water exchange could be traced between our two northernmost stations at about 62° N up to the Skagerrak. At the Skagerrak we had the last station, where detailed sampling of the water column as well as sediment work was carried out. The latter are of particular importance, since the water column is about 500m deep and the sediments are beyond the seasonal influence range. This allows the longer-term fixation of sedimentary organic material, which otherwise is rather not or hardly observed in the North Sea.

In total, 65 stations were sampled during the cruise AL557, seven of them including sediment work. Not least due to the great support of Captain Petrikowski and his whole crew we could finish the cruise very successfully on June 22$^{nd}$ a little earlier than planned, but with a little more work than planned. We are now very excited about the analysis and evaluation of the collected samples.

# 5 Preliminary Results

## 5.1 Water Sampling with CTD/Rosette

### 5.1.1 CTD Measurements and Sampling for Stable Isotopes, Metals and Nutrients

(Carla Nantke[1], Andreas Neumann[2], Eva-Maria Meckel[3], Anna Przibilla[2], Tina Sanders[2], Daniel Pröfrock[2], Michael E. Böttcher[1])

[1]IOW, [2]HEREON, [3]ICBM

All 65 CTD Stations were sampled for the following stable isotopes: $\delta^{13}C_{DIC}$, $\delta^{13}C_{DOC}$, water isotopes ($\delta^{18}O$, $\delta^{2}H$) nutrients and metals. Sample depths were chosen based on CTD salinity and temperature profiles. For the stable isotopes approximately 50 ml of CTD water was sampled for each depth using 60 ml syringes and then transferred in different vials. Samples for inorganic carbon ($\delta^{13}C_{DIC}$), was transferred firth to minimize outgassing. Here 12 ml sample water was filtered with 0.45µm celloluse acetate (CA) filters and transferred into a glas Exetainer with 100 µl $HgCl_2$. For the water isotopes ($\delta^{18}O$, $\delta^{2}H$) 1.5 ml was filtered and transferred into a glas vial and for $\delta^{13}C_{DOC}$ about 15 ml of sample water was filtered with a Nylon filter into a brown glas vial and acidified under the fume hood with 150µl 37% HCl. All samples were stored in a fridge (4°C) for the whole cruise.
For metals approximately 2 x 500 ml were sampled for each depth using an adapter to avoid contamination. The samples were stored in a freezer during the whole cruise for further preparations in clean conditions at HEREON institute. The same depths were sampled for nutrients. 2 x 15 ml water were sampled and filtered with 0.45µm CA filters, collected in plastic tubes and frozen directly. 50 ml of filtered (0.45µm CA) sample water was collected in a separate plastic tube for $^{15}N$ analyses and stored in a freezer during the whole cruise.

### 5.1.2 Water Sampling for Dissolved Organic Matter Analyses

(Eva-Maria Meckel[1], Wiebke Freund[1], Carla Nantke[2], Thorsten Dittmar[1], Michael Seidel[1])

[1] ICBM, [2] IOW

Surface and bottom water was collected using the CTD rosette at 64 stations for the analysis of dissolved organic matter (DOM) (Table 5.1). Approximately 5 L of CTD water sample was collected at each site and depth into pre-rinsed HDPE canisters. Water samples for the analysis of fluorescent dissolved organic matter (FDOM), total dissolved nitrogen (TDN), dissolved organic carbon (DOC) were filtered with a Masterflex peristaltic pump using thoroughly pre-rinsed 1.0 µm Causapure PP and Causa PES 0.1 µm filter cartridges (Infiltec). Filtered samples for the quantification of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were acidified to pH 2 (25% HCl, p.a.). As a fraction of FDOM, total humic-like fluorescence was measured in filtered water samples (without acidification) as relative fluorescence units (rfu) using a AquaFluor Handheld Fluorometer/Turbidimeter 8000-010 device (Turner Designs; wavelength 350 nm excitation, 420 nm detection) directly after sampling. Additionally, porewater and bottom water samples were taken at selected stations (Table WATER1) in collaboration with Carla Nantke

(IOW) using the multicorer. Porewater was retrieved from the sediment cores using pre-rinsed rhizones. All DOC and DOM samples were stored frozen on board and transported cooled to the University of Oldenburg. Bulk seawater DOC and TDN concentrations were measured in triplicates at the ICBM via high-temperature catalytic oxidation. The molecular composition of solid-phase extracted DOM (SPE-DOM) will be analyzed via Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and dissolved organic sulfur (DOS) concentrations of SPE-DOM will be measured on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at the ICBM (University of Oldenburg). Additional water samples for dissolved thallium analysis were taken from CTD stations and were filtered through 0.45 µm SFCA (surfactant-free cellulose acetate) syringe filters into LDPE bottles (acid-washed and rinsed with ultrapure water prior to usage). Ultrapure $HNO_3$ (2 v/v %) was added to thallium samples for preservation.

**Table 5.1.2.1:** DOM sampling sites at CTD and MUC stations. CTD sampling was conducted at surface (S), bottom (B) and mid-depths (M). Multicorer (MUC) samples were used to acquire bottom water (BW) and porewater (PW).

| Station | Date | Latitude [°N] | Longitude [°W] | CTD sampling | MUC sampling |
|---|---|---|---|---|---|
| 1 | 04.06.21 | 53.9618 | 8.6222 | S; B | |
| 2 | 04.06.21 | 54.0001 | 8.0989 | S; B | |
| 3 | 04.06.21 | 54.0611 | 8.0159 | S; B | BW |
| 4 | 04.06.21 | 54.4002 | 8.0986 | S; B | |
| 5 | 04.06.21 | 54.9992 | 8.0988 | S; B | |
| 6 | 04.06.21 | 54.9987 | 7.4985 | S; B | |
| 7 | 04.06.21 | 54.3997 | 7.4993 | S; B | |
| 8 | 04.06.21 | 53.9998 | 7.5001 | S; B | |
| 9 | 05.06.21 | 53.9818 | 7.0025 | S; B | |
| 10 | 05.06.21 | 54.3988 | 6.9981 | S; B | |
| 11 | 05.06.21 | 54.8094 | 6.7429 | S; B | BW |
| 12 | 05.06.21 | 55.0008 | 6.9999 | S; B | |
| 13 | 06.06.21 | 54.9997 | 6.4999 | S; B | |
| 14 | 06.06.21 | 54.4001 | 6.5007 | S; B | |
| 15 | 06.06.21 | 53.9892 | 6.2285 | S; B | BW |
| 16 | 06.06.21 | 53.8005 | 6.5016 | S; B | |
| 17 | 06.06.21 | 54.4004 | 6.0564 | S; B | |
| 18 | 07.06.21 | 54.4009 | 5.2499 | S; B | |
| 19 | 07.06.21 | 53.7997 | 5.2508 | S; B | |
| 20 | 08.06.21 | 53.2004 | 4.4981 | S; B | |
| 21 | 07.06.21 | 52.5996 | 4.1119 | S; B | |
| 22 | 08.06.21 | 51.5018 | 1.9994 | S; B | |
| 23 | 08.06.21 | 51.9998 | 2.4993 | S; B | |
| 24 | 08.06.21 | 52.6000 | 2.4998 | S; B | |
| 25 | 08.06.21 | 53.2012 | 2.5006 | S; B | BW |
| 26 | 08.06.21 | 53.8002 | 1.4988 | S; B | |
| 27 | 08.06.21 | 53.8010 | 0.4995 | S; B | |
| 28 | 09.06.21 | 54.9999 | 0.5002 | S; B | |
| 29 | 09.06.21 | 56.0013 | 0.4979 | S; B | |

| | | | | | |
|---|---|---|---|---|---|
| 30 | 09.06.21 | 57.0003 | 0.8705 | S; B | |
| 31 | 09.06.21 | 58.0007 | 1.0044 | S; B | |
| 32 | 10.06.21 | 59.0001 | 0.5010 | S; B | |
| 33 | 10.06.21 | 60.0003 | 0.4996 | S; B | BW |
| 34 | 10.06.21 | 61.0001 | 0.5000 | S; B | |
| 35 | 11.06.21 | 61.9985 | 2.5053 | S; B | |
| 36 | 11.06.21 | 61.0007 | 2.5007 | S; B | |
| 37 | 11.06.21 | 60.0000 | 2.4995 | S; B | |
| 38 | 12.06.21 | 60.0002 | -0.5007 | S; B | |
| 39 | 13.06.21 | 59.0008 | 2.5004 | S; B | |
| 40 | 13.06.21 | 57.9999 | 2.5014 | S; B | |
| 41 | 13.06.21 | 56.9997 | 2.2488 | S; B | |
| 42 | 14.06.21 | 56.0009 | 2.0017 | S; B | |
| 43 | 14.06.21 | 55.0001 | 2.5009 | S; B | BW |
| 44 | 14.06.21 | 53.7994 | 2.7503 | S; B | |
| 45 | 14.06.21 | 54.4002 | 3.9990 | S; B | |
| 46 | 14.06.21 | 54.9997 | 3.5013 | S; B | |
| 47 | 15.06.21 | 55.4996 | 4.1719 | S; B | BW |
| 48 | 15.06.21 | 56.0003 | 3.5014 | S; B | |
| 49 | 15.06.21 | 55.9998 | 5.0004 | S; B | |
| 50 | 15.06.21 | 56.0004 | 6.5002 | S; B | |
| 51 | 16.06.21 | 57.0001 | 6.5013 | S; B | |
| 52 | 16.06.21 | 56.9995 | 5.0018 | S; B | |
| 53 | 16.06.21 | 57.0010 | 3.7508 | S; B | |
| 54 | 16.06.21 | 58.0007 | 4.2504 | S; B | |
| 55 | 17.06.21 | 59.0014 | 3.9715 | S; M; B | |
| 56 | 17.06.21 | 60.0004 | 4.0003 | S; M; B | |
| 57 | 17.06.21 | 61.0013 | 4.0010 | S; M; B | |
| 58 | 18.06.21 | 62.0000 | 4.2509 | S; M; B | |
| 59 | 18.06.21 | 61.0008 | 4.2987 | S; M; B | |
| 61 | 18.06.21 | 59.9996 | 4.4992 | S; M; B | |
| 62 | 19.06.21 | 58.9995 | 4.6992 | S; M; B | |
| 63 | 19.06.21 | 57.9997 | 5.5005 | S; M; B | |
| 64 | 19.06.21 | 58.0005 | 6.4998 | S; M; B | |
| 65 | 20.06.21 | 58.5003 | 9.4995 | S; M; B | BW & PW |

### 5.1.3 Radium

(B. van Dam)

Samples for $^{224}$Ra and $^{226/228}$Ra were collected by pumping approximately 100 L of water from the ship's seawater line (or collected at depth with the CTD) through a cascade of 10 and 1 µm filters. This water was then pumped slowly (1 L min$^{-1}$) through a cartridge containing manganese-oxide-coated fibers which quantitatively adsorb Ra (confirmed with efficiency samples). After rinsing and drying, samples were counted for $^{224}$Ra first within 24 h of collection on board the ship with a radium delayed coincidence counting (RaDeCC) system (Moore and Arnold, 1996), and again

after 7-14 days. In addition to the bulk seawater samples, porewaters were also collected from selected sites using Rhizons, with water from the top 20 cm combined into a single sample (~ 100–200 mL) that was treated and counted on a RaDeCC as described above.

## 5.2 Sediment Sampling and Experimental Work

(Carla Nantke[2], Andreas Neumann[1], Bryce van Dam[1], Anna Przibilla[1], Tina Sanders[1], Daniel Pröfrock[1], Michael E. Böttcher[2], Fabrizio Minutolo[1])

[1]: Helmholtz-Zentrum hereon Geesthacht, [2]: Leibnitz-Institut für Ostseeforschung Warnemünde

### 5.2.1 Overview

(A. Neumann)

During the ALKOR cruise 557, we obtained sediment samples of the surface sediment by means of a HELCOM-type grab and a Multicorer (Oktopus Kiel, Germany). The grab samples were used to collect the oxidized surface layer of sandy sediment that was subsequently incubated in flow-through reactors (FTR) as presented below in section 5.3.4. Several undisturbed sediment cores with intact pore water were retrieved at sediment sites (Tab. 5.3.1) by means of a Multicorer. Specifically prepared core liners were sampled for pore water for later measurement of nutrients, DIC, and dissolved metals (see 5.3.2). A second set of cores was sliced for the posterior analysis of the solids for particle-bound metals, C/N analysis, and chlorophyll content (see 5.3.3). A third set of cores was subject to a whole-core incubation experiment for the direct measurement of benthic fluxes of oxygen, nutrients, metals, DIC / TA (see 5.3.5).

**Table 5.2.1.1:** Sediment samples retrieved during ALKOR cruise 557. FTR: Flow-through reactor incubation; PW: pore water sampling; Slice: Sliced core; WCI: Whole-core incubation.

| Site | Latitude (deg) | Longitude (deg) | samples |
|---|---|---|---|
| 3 | 54.061 | 8.015 | PW, Slice, WCI |
| 11 | 54.809 | 6.742 | FTR, PW, Slice, WCI |
| 15 | 53.989 | 6.229 | FTR, PW, Slice, WCI |
| 25 | 53.202 | 2.500 | PW, Slice, WCI |
| 38 | 59.999 | -0.498 | Slice, PW |
| 43 | 55.000 | 2.500 | PW, Slice |
| 47 | 55.502 | 4.168 | FTR, PW, Slice, WCI |
| 65 | 58.499 | 9.500 | Slice, PW, WCI |
| 66 | 54.061 | 8.017 | Slice |

### 5.2.2 Porewater

(Carla Nantke[1], Andreas Neumann[2], Bryce van Dam[2], Anna Przibilla[2], Tina Sanders[2], Daniel Pröfrock[2], Michael E. Böttcher[1])

[1]IOW, [2]HEREON

For pore water sampling 60 cm long core liners with pre-drilled holes (1 cm resolution) were used to retrieve sediment cores using the Multicorer (see 5.3.1). Before sampling, the holes were covered with scotch tape to prevent pore water loss during the coring procedure. After retrieval, the cores were placed and secured in holders. Approximately 3 pore water cores were sampled at each sediment station directly after coring. The outer layer of the scotch tape was removed to place plastic adapters in the respective sample depths. According to the sediment porosity the core length and resolution of the sampling was differing. Rhizons (CSS 5 cm, female luer), that were pre-soaked in MilliQ water, were used to sample the pore water by creating a vacuum with 15 ml syringes (see figure 5.2.2.1). At all 8 sediment stations pore water cores were sampled for: $\delta^{13}C_{DIC}$, $\delta^{13}C_{DOC}$, $\delta^{18}O$, total Alkalinity ($A_T$), $H_2S$, $\delta^{30}Si$, metals and nutrients. At some sediment stations a reduced set of parameters were sampled due to pore water volume limitations (see pore water table).

**Figure 5.2.2.1:** Porewater sampling with Rhizons

Pore water samples for $\delta^{13}C_{DIC}$ were filled without headspace in 3 ml glas Exetainer previously cleaned with 2% HNO3, washed, died and prefilled with 25µl saturated $HgCl_2$ solution. For $\delta^{13}C_{DOC}$ measurements about 3 ml of pore water sample was transferred to pre cleaned brown glas vials and acidified with 30µl 37% HCl under the fume hood. Samples for stable water isotope ($\delta^{18}O$ and $\delta^{2}H$) analysis were collected in 1.5 ml glass vials, sealed with a PTFE-coated septum cap. 0.7 ml of pore water was sampled for total alkalinity and transferred to Eppendorf vials with 25µl 0.1M HCl. For $H_2S$ about 2 ml of sample was transferred to Eppendorf vials prefilled with 100µl 5% ZnAc. Samples for $\delta^{30}Si$ about 3 ml are transferred to pre cleaned plastic vials and acidified with 30µl 37% HCl. All samples were kept in a fridge at 4°C for the whole cruise. For metal analysis at the hereon institute 2 x 2 ml of pore water sample were transferred to pre cleaned plastic vials and frozen directly after sampling. Nutrient samples were collected in plastic tubes and frozen immediately.

**Table 5.2.2.1:** Amount of pore water samples at all 8 Sediment (MUC) Stations for the different parameters.

**Table 5.2.2.1:** Amount of pore water samples at all 8 Sediment (MUC) Stations for the different parameters.

| Station | N | E | $\delta^{13}C_{DIC}$ | $\delta^{13}C_{DOC}$ | $\delta^{18}O$ | $A_T$ | $H_2S$ | $\delta^{30}Si$ | Metals (IOW) | Metals / Nutrients (Hereon) | Radium (volume) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | 54°03,674' | 8°00,917' | 12 | 17 | 9 | 17 | 17 | 17 | 9 | 18 | - |
| **11** | 54°48,565' | 6°44,561' | 18 | 16 | 16 | 18 | 18 | 18 | 15 | 17 | 263 mL |
| **15** | 53°59,346' | 6°13,713' | 11 | 14 | 14 | 11 | 11 | 11 | 8 | 9 | 208 |
| **25** | 53°12,100' | 2°30,019' | 10 | - | 10 | 10 | 10 | 10 | | 8 | 282 |
| **38** | 60°00,013' | 0°30,052' | 3 | - | - | 3 | - | 4 | | 4 | 179 |
| **43** | 54°59,993' | 2°30,066' | 8 | 6 | 10 | 8 | - | 9 | | 10 | 209 |
| **47** | 55°29,987' | 4°10,341' | 9 | 9 | - | 9 | 9 | - | | 7 | - |
| **65** | 58° 29,914' | 9°30,021 | 28 | 26 | 25 | 23 | 22 | 24 | 32 | 25 | - |

## 5.3.3 Sediment Solids Analyses

Sediment cores retrieved by the Multicorer and intended for the characterisation of the solids were sliced in 1 cm intervals. Sediment samples for TC, TIC, TN, TS, $\delta^{13}C_{carbonates}$ and Hg were stored

in plastic vials; sediment samples for TRIS and AVS were transferred into 50 ml plastic tubes with 10 ml 20% ZnAc; samples or metals analysis were transferred to pre-cleaned plastic containers. Directly during slicing, the pore water pH was measured with a WTW pH/ION 340i sensor at stations 3, 11, 25, and 65 (see figure 5.3.3.1). All sediment samples were frozen directly after sampling and stored at -20 °C until analysis in land-based laboratories at IOW and hereon.

At hereon, the sediments were freeze-dried, sieved (2mm) to remove mussel shells, and half of the sample was ground with a planetary mill. The fraction >2mm was investigated visually, while the grains size distribution of the < 2 mm fraction of selected samples from each core was measured by laser-diffractometry. The ground samples were digested to analyze the total metal content of the sediments by ICP-MS/MS. Further, the total carbon and nitrogen content of the samples and on selected samples also the $^{15}N$ isotopic signature and organic carbon content will be measured. IOW will perform sequential extraction on some of the samples. Aliquots of the unground sediment samples were analysed for the chlorophyll content by spectrophotometry to estimate particle diffusivities ($D_B$) and chlorophyll-associated carbon fluxes to the sediment.

The initial analysis of the measured chlorophyll profiles in the sediment delivered clear evidence for local and non-local transport of particle-associated chlorophyll into the sediment, which can be attributed to sediment deposition- resuspension and bioturbation (Fig. 5.3.3.2). The corresponding apparent particle diffusivities ($D_B$) were in the range of 0.004 to 0.99 $cm^2$ / d, and the chlorophyll-associated total POC fluxes were in the range of 1.7 to 9.5 mmol C / $m^2$ d. These results are preliminary and are still to be validated at the time this report was prepared.

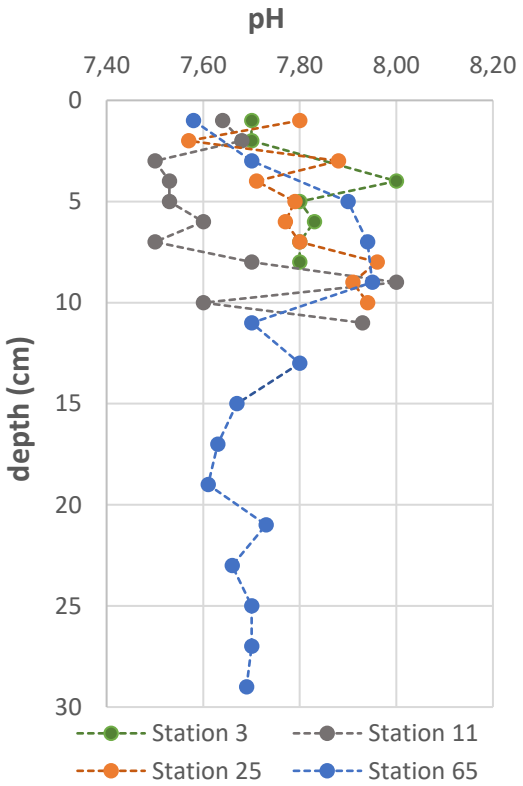


**Fig. 5.3.3.1:** In-situ measured pH values in the sediment pore water at stations: 3, 11, 25 and 65.

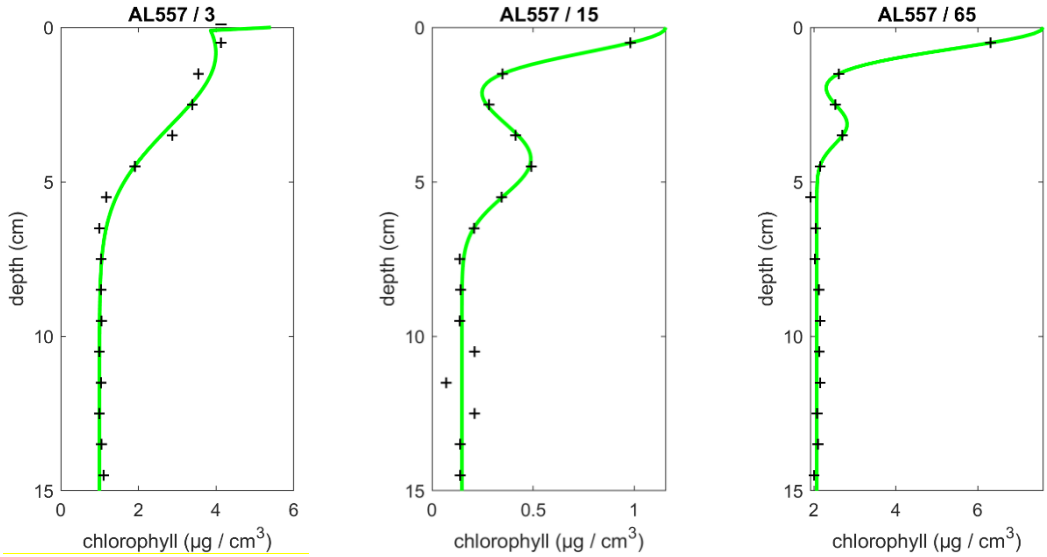


**Figure 5.3.3.2:** Exemplary chlorophyll profiles in the surface sediment at three sites as sampled during AL-557.

## 5.3.4 Flow-Through Reactors

(F. Minutolo)

In order to identify proxies for the sedimentary turnover of nitrogen in permeable sands, three sandy stations (11, 15 and 47) were sampled for aerobic flow through reactor (FTR) incubation experiments (Fig. 5.3.4.1 and Fig. 5.3.4.2). FTRs simulate natural advective transport and promote uniform flow (Rao et al., 2007). Surface sediment (<3-4cm) was taken from grab samples and sieved through a 1mm mesh, in order to exclude macrofauna from the sediment. Two FTR´s were then carefully filled with filtered (0.2µm) bottom water previously collected via the CTD-Rosette. Upon closure of the FTRs, continuously oxygenated water, amended with $^{15}NH_4$, was pumped through them. Two more FTRs were filled and treated in the same way, but the water reservoir was amended with $^{15}NO_3$. Flowrates were chosen to mimic natural porewater flow. Optodes at the inlet and outlet of the FTRs continuously measured oxygen concentrations. Samples for nutrients ($NO_3^-$, $NO_2^-$, $NH_4^+$, $PO_4^{3-}$ and silicate), DIC, TA, metals and stable isotopes of $NH_4$ (FTRs 1-2) and $NO_3$ (FTRs 3-4) were taken from the inlet before and after the incubations, as well as for the outlet three times during steady state. Afterwards, resazurin was added to the water reservoirs and once all porewater in the FTR´s had been exchanged, samples of the inlet (water reservoir) and outlet were taken. Resazurin is irreversibly reduced to fluorescent resorufin during bacterial aerobic respiration. This may be used to quantify microbial oxygen turnover. By applying the stable isotope dilution method, $15NH_4$ and $15NO_3$ amended samples may be used to determine gross ammonification and gross nitrification, respectively.

Once all water samples had been taken, a sediment sample of each FTR was taken and stored frozen at -20°C for further analyses on sediment characteristics (TC, TOC, TN, chlorophyll-a, phaeophytin-a, grain size, mud content and carbohydrates) onshore.

**Table 5.3.4.1:** Volumetric rates, and sediment characteristics at the sampled stations in the south eastern North Sea. Note: TOC = total organic carbon of the homogenized sediment. Mud = mud content and Phaeo-a = phaeophytin-a content. Ammonification and nitrification are net rates. Negative values for respiration and ammonification indicate consumption of oxygen and ammonium within the sediment, respectively.

| Station | Respiration | Ammonification | Nitrification | Si release | TC | TOC | TN | Chl-a | Phaeo-a | Chlorin |
|---|---|---|---|---|---|---|---|---|---|---|
| | | µmol $L^{-1}$ $h^{-1}$ | | | | (%) | | µg g $dw^{-1}$ | | |
| 15 | -8,98 | -0,06 | 0,25 | 0,54 | 0,14 | 0,04 | 0,02 | 0,17 | 0,29 | 0,46 |
| 47 | -14,77 | 0,01 | 0,16 | 0,21 | 0,06 | 0,05 | 0,02 | 0,73 | 0,35 | 1,08 |

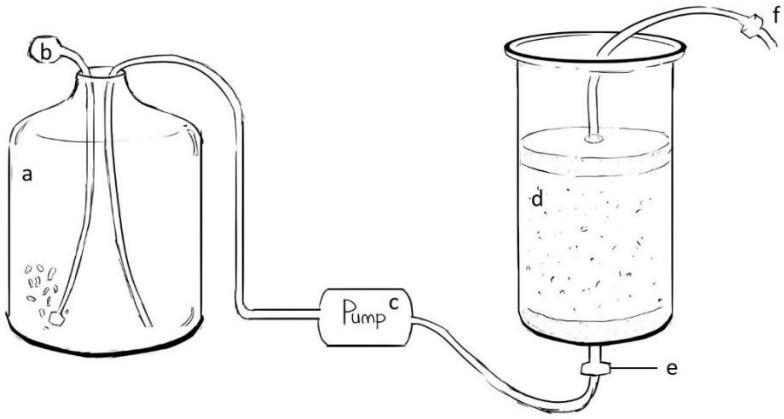


**Figure 5.3.4.1:** FTR incubation setup. a: water reservoir. b: aquarium pump aerating the FTR feedwater. c: peristaltic pump, pumping water from the reservoir through the FTRs. d: FTR containing homogenized sand. e: inlet sampling and flow through optode, measuring oxygen concentrations. f: : outlet sampling and flow through optode, measuring oxygen concentrations.

**Figure 5.3.4.2:** Photo of the FTR incubation setup in the temperature-controlled lab of RV ALKOR. (Photo: C. Nantke)

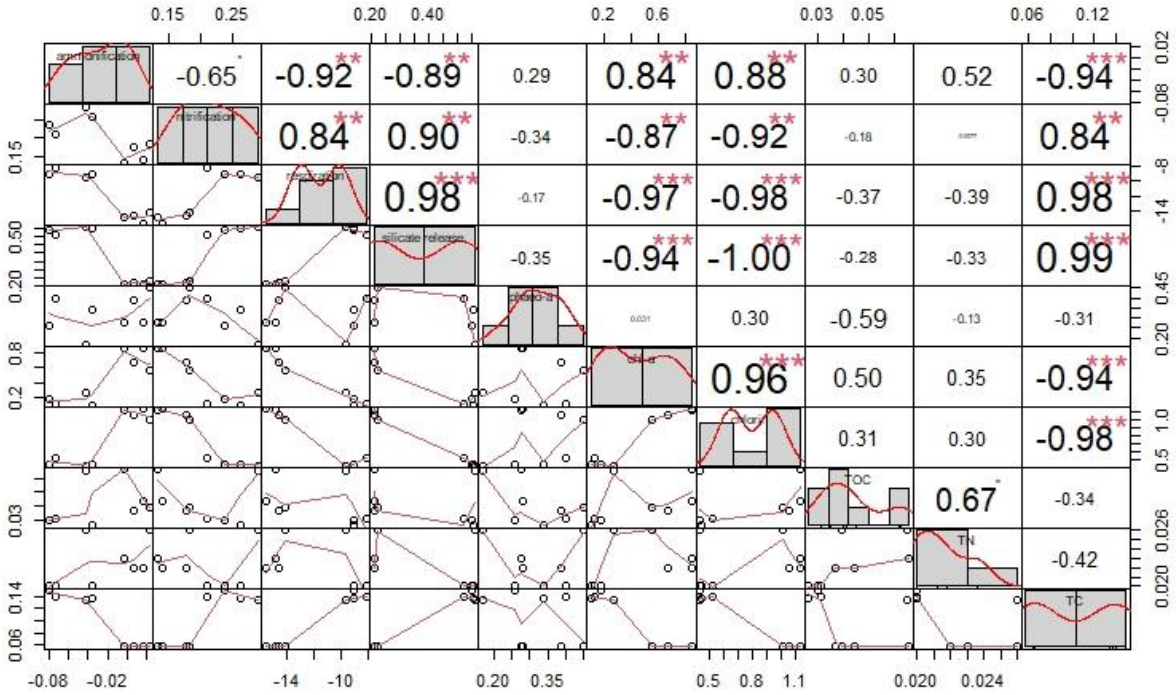


**Figure 5.3.4.3:** Pearson correlation matrix of selected parameters. Note: Correlation values and corresponding significance levels (stars) are represented above the diagonal. Three, two and one star correspond to p-values of 0.001, 0.01 and 0.1, respectively.

The preliminary results show significant correlations of chlorophyll-a, chlorin (sum of chloropyll-a and phaeophytin-a) and TC (total carbon) with ammonification and nitrification.

### 5.3.5 Whole-Core Incubations

(A. Neumann, F. Minutolo)

Whole-core incubations were employed to measure the fauna-mediated fluxes of oxygen, nutrients, metals, DIC / TA. The method is described in detail in Neumann et al. (2021). Typically, four suitable cores were selected and the incubation was set up within 1 hour after retrieval (Fig. 5.3.5.1). Oxygen was measured online with fibre-optical optodes and was used to assess the course of the incubation. After initial samples for dissolved metals and nutrients, tracers for nitrogen turnover ($^{15}NO_3^-$ and $^{15}NH_4^+$) and bioirrigation (NaBr) were injected into the supernatant. During the incubation, subsamples from the supernatant were collected at multiple times throughout the incubation, filtered through 0.45 µm CA filters. Samples for nutrient analysis were stored frozen, and stored refrigerated for Bromide measurement, respectively. Additional aliquots were stored refrigerated in gas-tight Exetainers for $^{15}N_2$ measurement via Membrane-Inlet-Mass-Spectrometry (MIMS). After the termination of the incubation after 24 – 36 h and at typically > 80 % oxygen saturation, additional endpoint samples for metal analysis and DIC / TA were taken.

The first preliminary results (Fig. 5.3.5.2) show a good agreement of observed fluxes of oxygen, DIC, and total alkalinity (TA). However, the results were not yet validated at the time this report was prepared.

**Figure 5.3.5.1:** Photo of the whole-core incubation setup in the temperature-controlled lab of RV ALKOR. (Photo: C. Nantke)

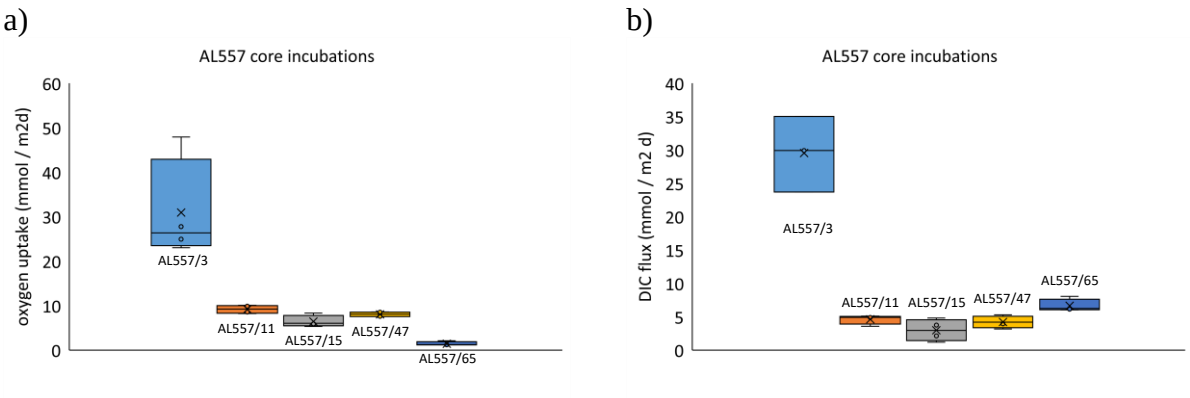


**Figure 5.3.5.2:** Box plots of preliminary benthic fluxes of a) oxygen, b) DIC.

# 6 Station List AL557

See 5.1.2

# 7 Data and Sample Storage and Availability

(H. Thomas)

Data will be stored to hereon's data center HCDC and will be made accessible after finalization of involved PhD theses work.

# 8 Acknowledgements

The cruise contributed to and was supported by the German Academic Exchange Service (DAAD) project The Ocean's Alkalinity - Connecting geological and metabolic processes and time-scales as part of the MOPGA program, wih funds from the BMBF (#57429828), and the FONA/MARE:N project CAROBSTORE.

# 9 Appendices

## 9.1 Selected Pictures of Shipboard Operations

All pictures shown here are taken by Chantal Mears.

**Figure 9.1.1:** CTD measurements / deployment of CTD rosette [Photo: Chantal Mears / Hereon]

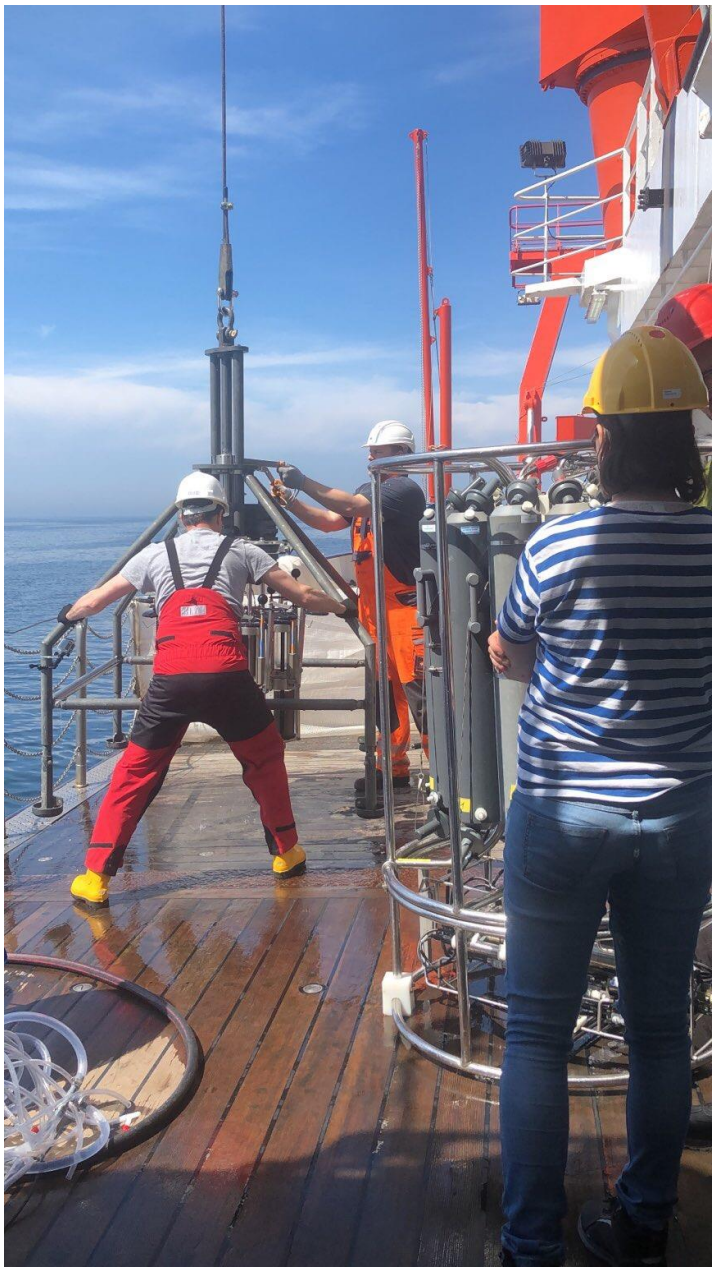

**Figure 9.1.2:** CTD measurements / deployment of CTD rosette [Photo: Chantal Mears / Hereon]

**Figure 9.1.3:** Taking the samples [Photo: Chantal Mears / Hereon]

**Figure 9.1.4:** [Photo: Chantal Mears / Hereon]

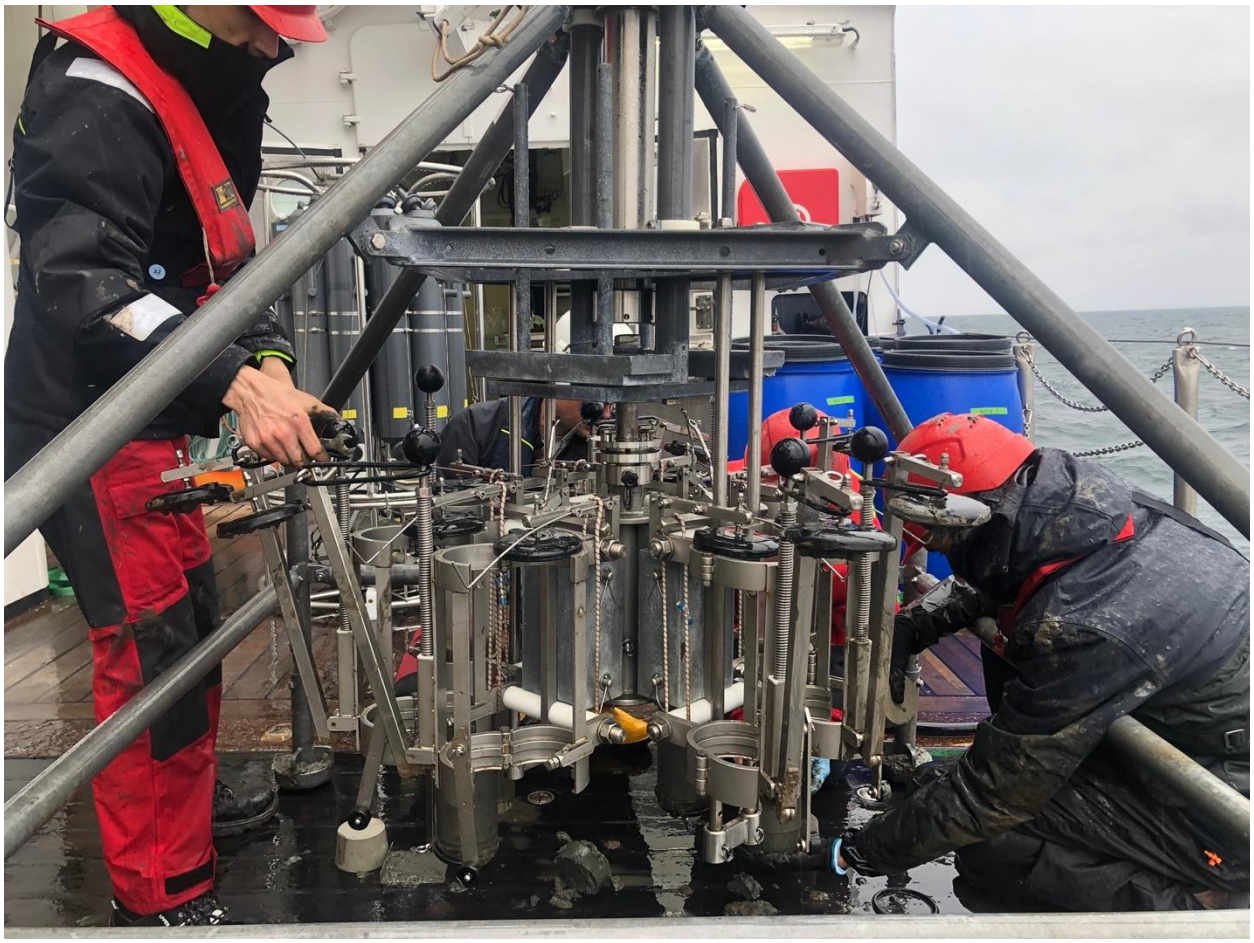

**Figure 9.1.5:** [Photo: Chantal Mears / Hereon]