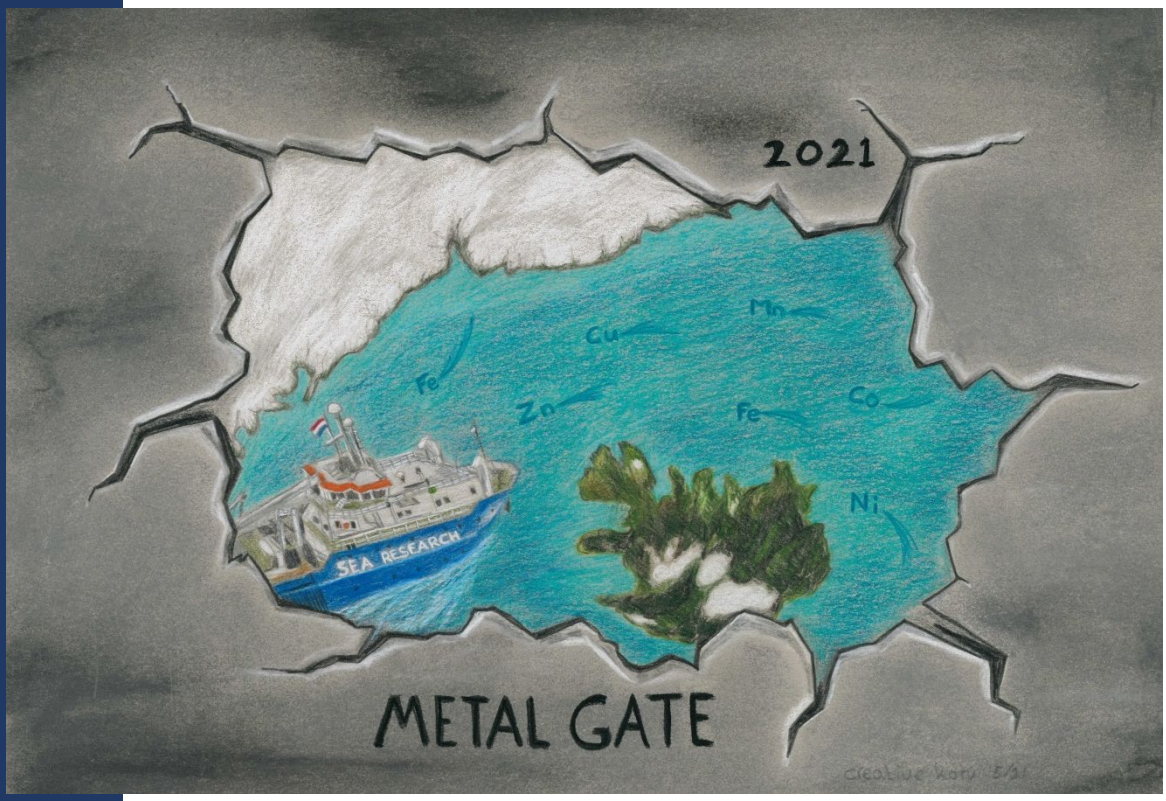
Cruise report PE474 on RV Pelagia

MetalGate



Reykjavik (Iceland) 17-07-2021
to
Reykjavik (Iceland) 16-08-2021

By Rob Middag and Rebecca Zitoun with contributions of all participants

Acknowledgements

On behalf of all participants I want to thank captains Bert Puijman and Pieter Kremer for their help, advice, and hospitality on RV Pelagia. The crew of Pelagia consisting of Peter Lucassen, Jolanda Francke, Martin Glazema, Sergiy Andreyko, Mike Hendry, Chiel Suers, Cor Stevens, Peter Klinker, Peter van Maurik, Vitali Maksimovs, Norberto dos Santos and Alex Ruhland, helped whenever and wherever necessary. All of them made our stay on Pelagia very pleasant. We acknowledge NWO for funding of this work (grant: 016.Vidi.189.138 to R. Middag). A. Annett, R. Jones and X. Shi were supported by NERC Independent Research Fellowship project RaCE:TraX (NE/P017630/1), with additional funding for R. Jones through the NERC INSPIRE Doctoral Training Programme and X. Shi through the US National Science Foundation (grant: NSF#2123575). N. Casacuberta research is funded by European Research Council (ERC GAP-101001451).L. Jabre received a Hugh C. Morris Fellowship.

Figure 1. Picture of the MetalGate Team, including scientists and crew members. Backrow, left to right: Sergiy Andreyko, Peter van Maurik, Martin Glazema, Patrick Laan, Chiel Suers, Cor Stevens, Peter Lucassen, Vitali Maksimovs and Mike Hendry. Middle row, left to right: Peter Klinker, Alex Ruhland, Pieter Kremer, Jolanda Francke, Rob Middag, Lena Beckley, Cuun Koek, Rebecca Zitoun and Norberto dos Santos. Front row, left to right: Sharyn Ossebaar, Willem van de Poll, Dave Huijsman, Xingming Shi, Rhiannon Jones, Loay Jabre and Amber Annett.

Table of Contents

Summary

The expedition 64PE474 aboard RV Pelagia started on the 18th of July 2021, leaving from Reykjavik (Iceland), half a day later than initially planned owing to delayed luggage that also contained essential equipment for the expedition. The expedition ended on August 16th 2021, also in Reykjavik (Iceland). At the beginning of the expedition, starting in the Irminger Sea, we had some issues with the ultra-clean CTD system (UCC, see section 3.1). Parts had to be replaced and the conductive cable underwater termination had to be remade several times during the first week of the expedition. These problems led to delays and subsequently we were behind schedule. Thus, eventually 3 stations (station 4, 5 and 11) had to be cancelled in order to make the scheduled port call in Isafjordur (Iceland) on the 28th of August. This port call was not originally planned, but was necessary in order to exchange personnel that was not relieved in Reykjavik due to Covid related issues.

During the expedition, samples were taken using several systems. The 'Titan' ultraclean CTD sampling system (UCC) for trace metal collection (De Baar et al., 2008), mounted with pristine large volume samplers (Rijkenberg et al., 2015), was used the most as part of the trace metal focal point of the expedition. The large volume Pristine samplers were made from polypropylene to allow sampling for light sensitive phytoplankton. After deployment, the complete CTD sampling system was placed in a cleanroom environment inside a modified high cube shipping container where subsamples were collected for trace metals, isotopes, ligands, and various auxiliary parameters (see section 2.4). The other deployed instruments included a conventional CTD rosette system (CTD) to sample for Ra isotopes (see section 3.7.2.1), a multi-corer (MUC) to collect sediment cores from which samples were taken for both sediments and porewaters, and a novel bottom gradient sampler (BGS) to sample dissolved and particulate trace metals close to the seafloor. The BGS was custom built for this project and consists of a 1-meter-high all-titanium lander that houses 5 samplers (bottles) as well as another 5 samplers spread out over 5 meters of dynema rope above the lander, held up by 3 glass floats (see Figure 2). The samplers collect both filtered water and material on the filter to sample the interface between the MUC and the UCC as the UCC cannot sample the last 5 to 10 meters till the bottom (depending on the weather). This system is deployed under the UCC and connected via 35 m of floating and sinking rope. Usually the UCC is hanging ~15 m above the lander while the BGS is deployed at the bottom. 64PE474 was the first expedition during which the BGS system was used. Unfortunately, the malfunctioning of the ship's USBL system meant that there was no confirmation of the position of the lander relative to the UCC or the ship, leading to a substantial number of failed deployments, notably in regions with strong bottom currents. These strong currents led to failed deployments as the lander was dragged over the bottom by the UCC, deeming collected samples unreliable and not representative of natural conditions. Thus, we reverted to deploying the BGS separate from the UCC on the steel wire (with ~70 m rope between the BGS and the steel wire), also used for the MUC deployments, in regions with strong bottom currents. These individual deployments were successful after some failed attempts earlier in the expedition.

Overall, 38 full depth stations were sampled with in total 38 UCC casts, 14 CTD casts, 19 BGS casts, and 13 MUC casts (Figure 2). Additionally, 2 shallow stations (station 4 and 26) were occupied to collect surface water to start the planned bioassays. During the expedition, 2 large, 5 and 6 day bio-assays were conducted (see section 2.5) to investigate the influence of Fe concentrations and temperature on phytoplankton biomass and composition. Another 2-day bioassay was also carried out to further investigate the influence of Fe and ammonium on phytoplankton productivity and composition. For these bioassays, 2 large custom-built temperature-controlled incubators where used that were place on the deck in front of the bridge of RV Pelagia where irradiance was mostly unobstructed. Additionally, 32 smaller bioassays were conducted (see section 3.6.4.) by Willem Poll's group at

controlled temperature and irradiance levels inside a climate-controlled container laboratory on Pelagia.

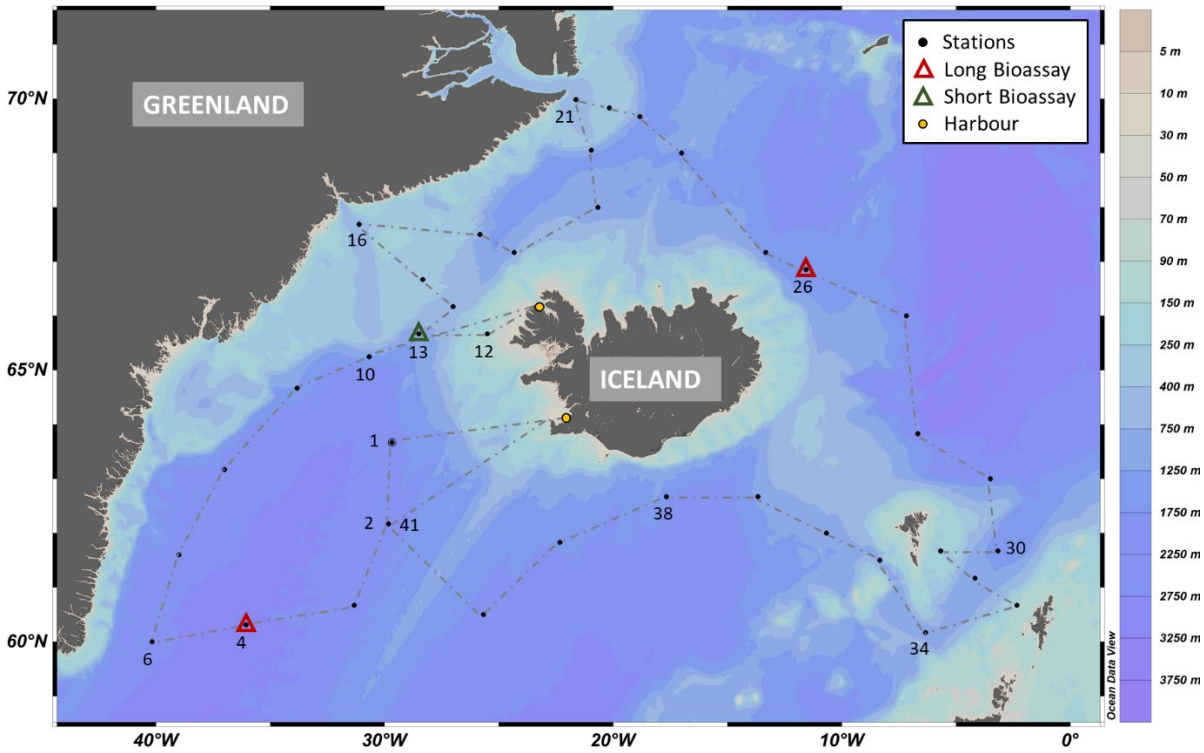


Figure 2. Locations of stations samples during the MetalGate expedition. Note there is no station 5 or 11 and station 4 and 26 were not full stations (only surface water sampled to start a bioassay). Station 41 was a re-occupation of station 2. See section 2.4 for more detail on stations.

1. General intro

Iron, together with other trace metals, is an essential micronutrient, required for the growth of all organisms, including phytoplankton that form the base of the marine food web. Given that phytoplankton convert CO_2 into biomass that partly settles into the deep ocean, trace metals are key players in global climate. However, some key ocean regions remain understudied and various crucial processes remain poorly understood, making informed-policy decisions on climate strategies and management rather challenging. One of these understudied regions is the High Latitude North Atlantic (HLNA), where phytoplankton, and thus primary productivity, is limited by the availability of iron. Since the high latitudes are changing rapidly, scientist are urged to understand how both current and future ocean changes effect global biogeochemical cycles, notably the marine iron cycle.

Consequently, the MetalGate team collected samples for trace metals, various isotopes, nutrients, phytoplankton, and sedimentological parameters during Pelagia expedition 64PE 474, to unravel the role metals play in this climate relevant region. Additionally, controlled bioassays at ecologically relevant conditions were conducted to improve current understanding of the linkages between phytoplankton physiology and biogeochemistry in the region. Samples were also collected for colleagues from the USA, UK, Spain, Switzerland, and Brazil that could not join the cruise, making this expedition a truly interdisciplinary and international endeavour. Insights from this work will enhance the understanding of local biogeochemical cycles and their connections to global cycles and thus climate. Such data will also result in better predictions of the likely impact, both now and in the future, of imminent Arctic and sub-Artic climate change on ocean health.

1.1. Overall aim and hypothesis

The production of oceanic phytoplankton that form the base of the marine food web depends on the availability of sunlight and nutrients, typically nitrogen and phosphorus (and silicate for diatoms). Micronutrients are also needed for phytoplankton growth (Bruland et al., 2014; Moore et al., 2013), where specifically iron (Fe) is known to affect the amount of atmospheric CO_2 sequestered in deep ocean waters and ocean sediments via the biological pump (De La Rocha and Passow, 2014), with far reaching implications for global climate and the local ecosystem (Arrigo et al., 2008; Boyd and Ellwood, 2010; Moore et al., 2013). However, the global Fe cycle is undergoing major changes due to the effects of acidification, stratification, warming, and deoxygenation (Hutchins and Boyd, 2016) with currently unknown consequences. Additionally, it is becoming increasingly clear that the situation is more complex, and controlled by factors beyond just the scarcity of Fe. New insights highlight the importance of other trace-metals (Morel et al., 2014), co-limitation by two or more nutrients (Arrigo, 2005; Bertrand et al., 2007; Middag et al., 2013; Saito et al., 2008) and variability in nutrient requirements between species and environmental conditions (Arrigo and van Dijken, 2003; Klunder et al., 2014; Moore et al., 2013). The importance of other bio-essential trace metals (Mn-Co-Ni-Cu-Zn) has not been assessed as thoroughly as for Fe, but neither Fe, nor most of the other bio-essential trace metals, can be effectively included in marine biogeochemical models.

Global biogeochemical models are important tools that aid in our understanding of the impacts of climate change and to test hypotheses regarding biogeochemical processes (Tagliabue et al., 2016). The current generation models do a reasonable job when it comes to the macro-nutrients such as phosphate, but cannot reproduce oceanic Fe distributions and vary widely in their predictions (Tagliabue et al., 2016). Fe has a complex biogeochemistry in the oceans interior that thus far has been poorly constrained and we need a better understanding of the underlying mechanisms controlling the complex behavior of Fe and to determine what the impact of the involved processes is.

The high latitude northern oceans are especially important as these are regions where deep-water formation takes place, and thus have global connections. As deep water makes its way around the globe, changes in the formation region will have consequences later on when the water eventually returns to the surface. Additionally, any process that occurs during advection of the deep water, will affect the eventual concentration and availability of metals. The gateway between the Arctic and the Atlantic Ocean, the *Greenland-Iceland-Norwegian Seas* (GINS), has been left largely unexplored for marine trace metals. Both the Arctic and GINS are undergoing massive changes (Arrigo et al., 2017; IPCC_2013, 2013; Orsi et al., 2017; Stroeve et al., 2012), but the effects on trace elements and the subsequent effects of those metals on the local ecosystem and 'downstream' the global thermohaline circulation, still need to be unraveled. To understand consequences of climate change on metal cycling and subsequent downstream effects, a better understanding is required of internal transformation processes. These processes occur within the ocean (hence internal) and control the ultimate fate and availability of metals in seawater. Internal transformation processes include metal uptake, recycling, and remineralization (Boyd et al., 2017), and the interaction between the ocean sediments and the water column (Homoky et al., 2016). The Benthic Boundary Layer (BBL) is the interface between the sediments and the water column and the biogeochemical exchange processes that occur in this layer in the deep ocean are insufficiently understood. However, due to the remineralisation processes, pore water chemistry, and particle re-suspension, there is significant potential for release or precipitation of metals, release or breakdown of organic metal binding ligands, and shifts in isotopic compositions.

Internal transformation processes not only affect the trace metal distributions, but also ratios of metals and macro-nutrients. The GINS and sub-arctic North Atlantic are crucial oceanic regions as they form the conduit for the majority of North Atlantic Deep Water (NADW) that forms in the high northern latitudes (Dickson et al., 2008; Dickson and Brown, 1994; Østerhus et al., 2008; Yashayaev et al., 2008). NADW is a crucial component of the global thermohaline circulation that eventually upwells and supplies nutrients, including trace metals and metal binding ligands, to the HNLC Southern Ocean. Especially for Fe, its solubility and probably also its availability depend strongly on the Fe-binding dissolved organic ligands that keep Fe in solution. In the Artic, rivers are important sources of nutrients, Fe, and Fe binding ligands (Klunder et al., 2012; Slagter et al., under minor revision; Thuróczy et al., 2011). Both the river discharge (Peterson et al., 2002) as well as the amount and nature of organic molecules that have the potential to complex Fe (Fe binding ligands), are changing (Slagter et al., 2017; Vonk et al., 2013; Vonk et al., 2012). In addition to increased river discharge, glacial melt inputs and associated Fe (Bhatia et al., 2013) are increasing as well. These increases in Fe inputs have been suggested to stimulate local primary production (Arrigo et al., 2017) but the effects on the local ecosystem have not been studied in detail, nor the potential downstream effects. Specifically for the Fe-binding ligands, the residence time has been estimated to surpass the transit time of NADW from the high north to the Southern Ocean (Gerringa et al., 2015), implying these ligands have the potential to transport Fe with NADW to the Southern Ocean. Thus, changes in inputs and internal transformations in the far north, will eventually affect the Antarctic and potentially its carbon sequestration due to changes in both macro-nutrient and metal concentrations as well as the ratios in which these are supplied.

Not only is the supply of Fe, ligands and other metals changing, also the ratios relative to one and other and the macro nutrients. The changing of Fe to nutrient supply ratios may affect co-limitation relationships. For example, Fe requirements of a phytoplankton community depend on the nitrogen source as NO_3 uptake or N_2 fixation require more Fe than NH_4 uptake (Morel et al., 2014) and the interaction between PO_4 and Fe plays a crucial role in primary production and community composition (Schoffman et al., 2016; Snow et al., 2015). Small fluctuations in Fe supply on the order of 0.1 nM can cause shifts in cell physiology and stoichiometry, while larger changes can cause a shift in the

phytoplankton community composition and subsequently changes the Fe demand as different phytoplankton groups have different Fe requirements and Fe-cycling (Hutchins and Boyd, 2016). The size and nutrient stoichiometry of phytoplankton affect the entire ecosystem and are a function of environmental conditions and interactions. For example, a change in temperature can cause a change in phytoplankton Fe requirements (Sunda and Huntsman, 2011) and changes in stoichiometry can result in limited regeneration of the limiting nutrient in zooplankton, creating a negative feedback on primary production (Finkel et al., 2010). Model studies predict that changes in nutrient supply ratios can have large consequences for primary and export production as well as the community composition (Ward et al., 2013). Currently we have limited knowledge about the complex interactions that lead to co-limitation, changes in stoichiometry, community composition or the evolution thereof. Thus, carefully designed experiments under ecologically relevant conditions are needed with a focus on both the dissolved concentrations as well as the concentrations in the biogenic particles, complemented by observations of particulate and dissolved concentrations in the field.

1.2. Objectives

In awareness of the importance of trace metals for the local ecosystem and the connections between local processes and global biogeochemical cycles MetalGate is an interdisciplinary study to unravel the cycling of trace metals in the crucial GINS region and the connection to the Atlantic Ocean**.** This study addresses both a key region as well as crucial, insufficiently constrained processes in global marine biogeochemistry. While this study focusses on Fe, other (bio-essential) metals are targeted as well to identify their potential roles as co-limiting factors, actors in governing uptake and remineralisation ratios, and/or tracers of biogeochemical processes.

The research is subdivided in three main objectives

1. To constrain the sources and sinks of trace metals and ligands to the GINS and North Atlantic
2. Determine the effects of changing Fe concentrations and increasing temperatures on natural phytoplankton and their nutrient stoichiometry in bioassays
3. Identify and quantify the effects of internal transformations on the trace metal, Fe-binding ligand, and nutrient distributions in both the water column and the Benthic Boundary Layer (BBL)

2. Participants and sampling info

2.1. List of participants

1.	Rob Middag	NIOZ; PI	TM Team
2.	Patrick Laan	NIOZ	TM Team
3.	Rebecca Zitoun	NIOZ	TM Team
4.	Sharyn Ossebaar	NIOZ	Nutrient analysis
5.	Dave Huijsman	NIOZ	Technical support
6.	Willem van de Poll	Groningen;	Bio Team (team leader)
7.	Anna Cunera Koek	Groningen	Bio Team
8.	Lena Beckley	Dalhousie University	Bio Team
9.	Loay Jabre	Dalhousie University	Bio Team
10.	Amber Annett	University of Southampton	Mud Team (team leader)
11.	Rhiannon Jones	University of Southampton	Mud Team
12.	Xiangming Shi	University of Connecticut	Mud Team

2.2. List of collaborators (not on board)

1.	Patrick Blaser	University of Lausanne
2.	Luis Laglera	University of the Balearic Islands
3.	Nuria Casacuberta Arola	ETH Zurich
4.	Vanessa Hatje	Universidade Federal da Bahia
5.	Tim Conway	University of South Florida
6.	Will Homoky	University of Leeds
7.	Erin Bertrand	Dalhousie University
8.	Rachel Sipler	Memorial University of Newfoundland
9.	Jonathan Hawkings	Florida State University
10.	Korinna Kunde	University of Washington
11.	Peter Kraal	NIOZ
12.	Laura Hepburn	University of Southampton
13.	Pinghe Cai	Xiamen University
14.	Robert Mason	University of Connecticut

2.3. List of parameters

Parameter	**Collected by**	**responsible for analysis and data**
Dissolved metals	TM Team	P. Laan, R. Middag
Particulate metals	TM Team	P. Laan, R. Middag
Fe Isotopes	TM Team	R. Middag, T. Conway
Ni Isotopes	TM Team	T. Conway
Fe Ligands	TM Team	R. Zitoun
Siderophores	TM Team	R. Zitoun
Nd Isotopes	TM Team	P. Blaser
U and I Isotopes	TM Team	N. Casacuberta Arola
REE	TM Team	V. Hatje
Humics	TM Team	L. Laglera
Mercury	TM Team	X. Shi
Salinity	TM Team	NIOZ
Oxygen	TM Team	NIOZ

$\Delta^{18}O$	TM Team	NIOZ
Nutrients	TM Team	S. Ossebaar
C/N	Bio Team	S. Ossebaar
Proteins	Bio Team	E. Bertrand
Fv/Fm	Bio Team	W. van de Poll
HPLC	Bio Team	W. van de Poll
N-uptake	Bio Team	R. Sipler
RNA	Bio Team	E. Bertrand
Radium isotopes (Water column)	Mud Team	A. Annett
Ra/Th isotopes (sediment & porewater)	Mud team	A. Annett
226-Radium (sediment & porewater)	Mud Team	P. Cai
Trace metals (sediment & porewater)	Mud Team	W. Homoky
Nutrients (sediment & porewater)	Mud Team	S. Ossebaar/W. Homoky
Sediment porosity	Mud Team	A. Annett/W. Homoky
DOC (sediment porewater)	Mud Team	J. Hawkings
Hg (sediment & porewater)	Mud Team	X. Shi
234-Th (sediment)	Mud Team	X. Shi
Reactive iron	Mud Team	L. Hepburn
$P/CaCO_3$	Mud Team	P. Kraal
SWINC Dissolved metals	Mud Team	R. Jones
SWINC Nutrients	Mud Team	S. Ossebaar
SWINC Fe Ligands	Mud Team	R. Jones
SWINC DOM	Mud Team	R. Jones
SWINC DOC-spec flr	Mud Team	J. Hawkings
SWINC Siderophores	Mud Team	K. Kunde

2.4. List of stations

Date	Station	Latitude	Longitude	Water Depth	Deployed Instruments	Parameters Sampled	Remarks
19/7/2021	1	N 63° 40' 12.151''	W 29° 40' 11.215''	1982	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library	
20/7/2021	2	N 62° 10' 12.22''	W 29° 49' 46.524''	2009	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, N-uptake	
21/7/2021	3	N 60° 40' 12.547''	W 31° 19' 46.348''	2153	UCC, CTD, Bottom UCC	Salinity, Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, I and U iso, Ra (water column)	
22/7/2021	4	N 60° 18' 38.185''	W 36° 3' 12.672''	2399	UCC	Proteins, RNA, N-uptake	Start of long bioassay 1
23/7/2021	6	N 60° 0' 0.14''	W 40° 10' 12.479''	2589	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, PM, C/N, I and U iso, Nd iso, REE, Humics, Siderophores, Ligands, Oxygen, Ra (water column), Sediment [nutrients, trace metals, porosity, reactive iron, $P/CaCO_3$]	
24/7/2021	7	N 61° 36' 0.295''	W 38° 59' 58.351''	2330	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library,Hg, $\delta^{18}O$, N-uptake	

24/7/2021	8	N 63° 10' 11.899''	W 37° 0' 2.178''	2254	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, U and I iso, PM, C/N, REE, Hg, Ligands, Siderophores, Humics, SWINC all, $\delta^{18}O$, Ra (water column), Sediment [nutrients, trace metals, porosity, Ra/Th, 234-Th, SWINC, Hg]	
25/7/2021	9	N 64° 40' 11.114''	W 33° 49' 47.762''	1357	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, $\delta^{18}O$, N-uptake	
26/7/2017	10	N 65° 14' 59.856''	W 30° 40' 12.677''	1241	UCC, CTD, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, I and U iso, Nd iso, REE, Hg, SWINC all, $\delta^{18}O$, Ra (water column), Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 234-Th, $P/CaCO_3$]	
28/7/2021	12	N 65° 40' 12.637''	W 25° 30' 3.438''	997	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, Hg, Ligands, Siderophores, Humics, $\delta^{18}O$	
29/7/2021	13	N 65° 40' 10.69''	W 28° 30' 0.155''	117	UCC, CTD, Bottom UCC, MUC	Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, Nd iso, REE, Hg, Oxygen, Ra (water column), N-uptake, RNA	Start of short bioassay 1
30/7/2021	14	N 66° 10' 11.212''	N 66° 10' 11.212''	624	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, U and I iso, Nd iso, Hg, Ligands, Siderophores, Humics, $\delta^{18}O$, Ra (water column)	
30/7/2021	15	N 66° 40' 13.476''	W 28° 19' 44.893''	313	UCC, Bottom UCC, MUC	Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, Hg, Ligands, Humics, SWINC all, $\delta^{18}O$, Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 234-Th]	
31/7/2021	16	N 67° 41' 19.223''	W 31° 6' 50.897''	460	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, U and I iso, Nd iso, Hg, Ligands, Siderophores, Humics, SWINC all, $\delta^{18}O$, Ra (water column), Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 226-Ra, 234-Th, $P/CaCO_3$, reactive iron]	
1/8/2021	17	N 67° 30' 1.89''	W 25° 49' 46.668''	739	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, U and I iso, Nd iso, Hg, Ligands, Siderophores, Humics, $\delta^{18}O$, Ra (water column), Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 226-Ra, 234-Th, reactive iron, $P/CaCO_3$]	
1/8/2021	18	N 67° 10' 12.133''	W 24° 19' 52.576''	741	Bottom UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, Nd iso, Hg, $\delta^{18}O$	
2/8/2021	19	N 68° 0' 0.284''	W 20° 40' 5.329''	948	UCC, CTD, Bottom UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, Nd iso, Hg, Ligands, Siderophores, Oxygen, $\delta^{18}O$, Ra (water column)	
2/8/2021	20	N 69° 3' 0.695''	W 20° 56' 59.856''	953	Bottom UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, Hg, Humics, $\delta^{18}O$, RNA	
3/8/2021	21	N 69° 59' 2.119''	W 21° 37' 51.481''	498	Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, Nd iso, REE, Hg, Humics, Ligands, Siderophores, SWINC all, $\delta^{18}O$, Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 234-Th, reactive iron], N-uptake, RNA	

3/8/2021	22	N 69° 49' 48.349''	W 20° 10' 13.436''	295	UCC	Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, Humics, $\delta^{18}O$	
4/8/2021	23	N 69° 40' 11.147''	W 18° 49' 49.184''	1205	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, REE, Hg, Humics, $\delta^{18}O$, RNA	
4/8/2021	24	N 69° 0' 0.162''	W 17° 0' 1.555''	1807	UCC	Salinity, Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Nd iso, REE, Hg, Ligands, Siderophores, Humics	
5/8/2021	25	N 67° 10' 11.474''	W 13° 19' 35.8''	1614	UCC, Fish	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Nd iso, REE, Hg, Ligands, Humics	
5/8/2021	26	N 66° 51' 7.254''	W 11° 33' 54.511''	2211	UCC, Fish	Proteins, RNA, N-uptake	Start of long bioassay 2
6/8/2021	27	N 66° 0' 0.702''	W 7° 10' 4.966''	2107	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Nd iso, REE, Hg	
6/8/2021	28	N 63° 49' 47.777''	W 6° 40' 13.606''	2264	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, Oxygen	
7/8/2021	29	N 63° 0' 0.472''	W 3° 30' 2.225''	1730	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, REE, Hg, Ligands, Siderophores, Humics, N-uptake	
7/8/2021	30	N 61° 40' 10.596''	W 3° 10' 17.58''	1452	UCC, CTD, Bottom UCC, MUC	Nutrients, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, PM, C/N, REE, U and I iso, Nd iso, Hg, Ligands, Siderophores, Humics, Ra (water column), Sediment [nutrients, trace metals, porosity, Hg, Ra/Th, 226-Ra, 234-Th, reactive iron, $P/CaCO_3$]	
8/8/2021	31	N 60° 40' 13.134''	W 2° 19' 53.706''	201	UCC	Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, REE, Hg	
8/8/2021	32	N 61° 10' 11.28''	W 4° 10' 10.546''	1105	UCC, Bottom UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, PM, C/N, DFe, DM, Iso Fe, Iso Ni, Library, REE, Hg, Ligands, Siderophores	
9/8/2021	33	N 61° 40' 12.256''	W 5° 40' 12.94''	134	UCC	Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg	
9/8/2021	34	N 60° 10' 12''	W 6° 19' 46.931''	1204	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, PM, C/N, DFe, DM, Iso Fe, Iso Ni, Library, REE, Hg, Ligands, Siderophores, Humics, Ra (water column)	
10/8/2021	35	N 61° 29' 57.566''	W 8° 19' 48.616''	796	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, REE	
11/8/2021	36	N 61° 59' 58.963''	W 10° 40' 10.718''	996	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Fv/FM, HPLC, PM, C/N, DFe, DM, Iso Fe, Iso Ni, Library, Hg, REE, Ligands, Siderophores, Humics, Ra (water column), Sediment [nutrients, trace metals, porosity, Ra/Th]	
11/8/2021	37	N 62° 40' 12.925''	W 13° 40' 20.143''	1137	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, REE	
12/08/2021	38	N 62° 40' 12.432''	W 17° 40' 13.825''	1623	UCC, CTD, Bottom UCC, MUC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, PM, C/N, DFe, DM, Iso Fe, Iso Ni, Library, I and U iso, Nd iso, Hg, REE, Ra (water column)	
13/8/2021	39	N 61° 49' 47.795''	W 22° 19' 42.1''	1702	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library, Hg, REE	
14/8/2021	40	N 60° 29' 59.77''	W 25° 40' 11.348''	2093	Bottom UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, PM, C/N, DFe, DM, Iso Fe, Iso Ni, Library, Hg, REE, Ligands, U and I iso, Nd iso, Hg, Ligands, Siderophores, Humics, Oxygen	

15/8/2021	41	N 62° 10' 15.719''	W 29° 49' 45.03''	2009	UCC	Salinity, Nutrients, Proteins, Fv/FM, HPLC, DFe, DM, Iso Fe, Iso Ni, Library	Re-occupation of station 2

2.5. Bioassays

Date	Bioassay	Duration	Treatments	Parameters Samples T_0	Parameters Samples T_{half}	Parameters Samples T_{final}	Remarks
22/7/2021	Long 1	5 days	Control – low temp; Fe – low temp; Control – high temp; Fe – high temp	DFe, DM, Ligands, Siderophores, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake	DM, DFe, flow cytometry abundance, pigments, Fv/Fm, nutrients, Proteins	DFe, DM, Ligands, Siderophores, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake	Eluent (filtered seawater) was added at day 2 to replenish nutrients
29/7/2021	Short	2 days	Control – low temp, Fe – low temp; ammonium - low temp; Fe + ammonium – low temp.	DFe, DM, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake		DFe, DM, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake	
5/8/2021	Long 2	6 days	Control – low temp; Fe – low temp	DFe, DM, Ligands, Siderophores, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake		DFe, DM, Ligands, Siderophores, PM, Nucleic acids, flow cytometry abundance, pigments, Fv/Fm, nutrients, C/N, Proteins, RNA, N-uptake	All cubitainers were spiked with nitrate (10 µM) and phosphate (1:16) prior to incubation

3. Sampling and analysis

3.1 CTD systems

Mike D Hendry

During the expedition two CTD systems were used. The main workhorse being the UCC CTD, designed and built by the NIOZ in the Netherlands, comprising of a rectangular Titanium metal frame, holding 24 vertically mounted PolyProp sampling bottles, each holding 23 L of water and activated via a water based hydraulic system, closing butterfly valves at both the upper and lower ends of the sampling bottles. Instrumentation attached to the frame consisted of Sea Bird SBE 9 plus underwater control unit, with Sea bird SBE 3 temperature sensor, SBE 4 conductivity sensor, SBE 43 dissolved oxygen sensor, using a SBE 5 underwater pump to continually circulate new water along the sensors. Further instrumentation comprised of Chelsea Aquatracka MK III, chlorophyll sensor, Wet Labs C-Star transmissometer, Satlantic PAR-sensor, Valeport VA-500 altimeter and an in house designed and built multivalve triggering system for the closing the sampling bottles and accumulator for storage of the hydraulic pressure required. The second system, no less important, consisted of a Rosette system, comprising 24 sampling bottles of 11.3 L, of the same design and manufacture as the above mentioned UCC system. Instrumentation comprised of the same setup as the UCC CTD. Both CTD-systems were lowered into the water and controlled down to the sampling depths through two different winch systems. The UCC CTD, due to non-ferric interference, was lowered using the Kley France winch, comprising of a super aramide cable. The second CTD lowered on a steel twisted single core cable, though not used for ferric sampling.

3.1.1. Performance

The beginning of the project did not start on a high note, as bottles did not close and anomalies were noted in the shipboard nutrients indicating bottles closed at the wrong depth. This anomaly took some time to diagnose given the time lag between stations and sample analysis. At the time of the third station, the accumulator was unable to hold any pressure, a leaking multivalve was suspected. The accumulator and the multivalve were replaced with spare items from the vessel. This fix resolved both problems in a single stroke. On subsequent investigation, it was also found that the accumulator plunger shaft badly scored, pitted and burrs on the titanium shaft. With this part replaced using a spare part from out the spares box and new seals placed, the instrument was able to hold the pressure required. As for the multi valve, once opened, revealed a serious issue which was obvious to see. Namely the gearing was never aligned to the correct positions, thus bottle closing started at bottle 23 and ended at bottle 22. Additionally, the transmissometer was not functioning properly and had to be replaced with a spare sensor.

Unfortunately, this was not the end of the problems, as there were further issues with the Super Aramide tether. The error message “FFFFFFFF Unsupported modem message FF FE FF” kept on popping up during deployments in the Seabird software. After consultation with experts at NIOZ this appeared as water ingress in the tether. With having terminated the tether a number of times, only after a few dives, this message popped up again, it was diagnosed that there was more on hand, as the splice appeared dry every time it was re-terminated. Two central cores had been connected to a third subcon pigtail, which was not being used, and could be removed and split between the positive and negative power lines. Additionally, removing the “Y” splice in the slipring junction box on deck proved most effective, as the project since has been without further CTD issues. The regular CTD has performed without fault, though the turbidity sensor, has been giving data, which appears questionable and thus the sensor will need to be checked.

On every deep station 3 salinity samples were taken in duplicate to be analysed at NIOZ to calibrate the salinity sensors. Moreover, once a week, samples were taken for oxygen in parallel with salinity. These samples will also be analysed at NIOZ.

3.1.2. Conclusion

It is a pity that the first three stations are with dubious results, but by having time to do station 2 again at the end of the cruise, the impact was minimized.

Further the normal CTD has performed without fault, though the beam transmissometer, has been giving data, which appears questionable, thus would like to have that serviced once again in the Netherlands.

3.1.3. Further Issues

The HiPAP (USBL system) was not working whereas it was essential for the BGS deployments. In contact with Kongsberg support (the manufacturer), it was recommended to test the communication with the HiPAP transceiver. This revealed no ethernet connection with the remote MOXA unit. A bypass system was rigged up, using the Deck unit MOXA and a separately run UTP cable to the transceiver cabinet. All setup measures taken and checked, revealed no communication with the transceiver. Thus, not having spares or time, was decided to abandon further investigation.

3.2 Nutrient sampling

Sharyn Ossebaar

The availability of sunlight and nutrients play a crucial role for the production of oceanic phytoplankton which form the base of the marine food web. Knowing the variability in macronutrients (Phosphate, Ammonium, Nitrite, Nitrate, and Silicate) can help understand requirements between species, environmental conditions, and the role of nutrient cycling. At all stations and from various experiments, samples were collected for shipboard macronutrient determination. The macronutrient measurements were made simultaneously on four channels for Phosphate Ammonium, Nitrite and Nitrate, using a continuous gas-segmented flow QuAAtro Auto-Analyser produced by SEAL Analytical. In total 1435 samples were measured on board during the research cruise. Samples for Silicate were also taken and will be stored in a refrigerator until further analysis back at the NIOZ, The Netherlands. All results were reported as concentrations in micro mole per litre (µmol/L).

3.2.1. Sample Handling

Sample water was obtained from the Ultra-Clean 'Titan' CTD (UCC) from all depths. All samples were collected in high-density polyethylene syringes (Terumo®) with a three-way valve directly after the oxygen and salinity sampling when sampled. The UCC nutrient samples were transferred into 5 mL polyethylene vials (known as ponyvials) after rinsing three times with the sample before being capped. Samples from the bioassays were collected in 125 mL polypropylene bottles, drawn into a 20 mL syringe and filtered over a 0.8/0.2 µm Acrodisc® filter into a ponyvial. Experiment samples were also filtered over a 0.2 µm Acrodisc® filter with a syringe into a ponyvial. Samples from the multicore porewaters were obtained through rizon filters and sub-sampled into ponyvials. Samples from the Bottom Gradient Sampler (BGS) equipped with 10 sample bags were filtered in-line underwater into the sampling bags that contained a known amount of hydrochloric acid and were sub-sampled into pre-cleaned ponyvials in an ultraclean container. Samples that weren't analysed within two to four hours of sampling were stored in the refrigerator at 4 ^{o}C and analysed in the following analytical run. All analyses (PO_4, NH_4 and NO_3 plus NO_2) were generally made within 2-14 hours of sampling and very occasionally up to a maximum of 20 hours later. Samples for Silicate, were also taken and will be stored in a refrigerator until further analysis back at the NIOZ, The Netherlands.

3.2.2. Analytical Methods

All measurements were calibrated with standards diluted in low nutrient seawater (LNSW) in the salinity range of the stations at approximately 35°/$_{oo}$ to ensure that analysis remained within the same ionic strength. Calibration standards were diluted from stock solutions of the different nutrients in 0.2 µm filtered LNSW and were freshly prepared every day. The LNSW is surface seawater depleted of most nutrients; it is also used as baseline water for the analysis between the samples. Each run of the system had a correlation coefficient of at least 0.9999 for 10 calibration points, but typically 1.0000 for linear chemistry was achieved. 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. Prior to analysis, all samples and standards were brought to laboratory temperature of 22.0°C (container temperature range 21.5-22.5°C) in about one to two hours in a dark draw. On 01 August 2021 the lab container had an air-conditioning failure and only on this day, all samples were measured at 23.5°C instead of the previously reported container temperature.

Before analysis the caps were removed and the ponyvials covered with parafilm under tension against exchange of ammonium from the air and evaporation, and placed in the sampler. The QuAAtro manufactured by SEAL Analytical, 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. A sampler rate of 60 samples per hour was used. Concentrations were recorded in µmol per liter (µmol/L) at the average container temperature of 22.0°C. During every run a daily freshly diluted mixed nutrient standard, containing silicate, phosphate and nitrate (a so-called nutrient cocktail), was measured in triplicate. Additionally, a natural sterilized Reference Material Nutrient Sample (CRM) from Kanso, Japan, containing known concentrations of silicate, phosphate, nitrate and nitrite in Pacific Ocean water, was analysed in triplicate for 5 days during the cruise. The cocktail and the CRM were both used to monitor the performance of the analyser. From every station the deepest sample bottle was sub-sampled for nutrients in duplicate, the duplicate sample-vials were all stored dark at 4 °C, and measured again in the following run with the upcoming stations for statistical purposes. In total 1435 samples were analysed for phosphate, ammonium, nitrate, and nitrite during the cruise. The breakdown of samples was 915 samples at UCC and BGS stations, 57 samples for the bioassays, 113 samples in support of the biological work of Jabre et al, 165 samples for the SWINC experiments of Jones et. al and 187 analyses were performed on the 89 porewater samples for the work of Annett et al. The porewater samples were diluted 11 times for NO_3 and NO_2 analysis and diluted 101 times for NH_4 analysis. The porewater PO_4^- and Si sample will be analysed back at the NIOZ in a combined 1.5 - 2.0 mL sample that contains 10 µmL of suprapur HCl to ensure that iron hydroxides don't sorb PO_4^-.

The following is a brief overview of the colorimetric methods used on the QuAAtro auto-analyser:

- 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 880 nm (Murphy and Riley, 1962).
- 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 colour is measured at 630 nm (Helder and 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 coloured complex and measured at 550 nm. Nitrate is calculated by subtracting the Nitrite value measured on the Nitrite channel from the 'NO_3+NO_2' value (Grasshoff et al., 2009).
- Nitrite (NO_2) is diazotated with sulphanylamide and naphtylethylene-diamine to form a pink

colored complex and measured at 550 nm (Grasshoff et al., 2009).

- 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 820 nm. Oxalic acid is added to prevent formation of the blue phosphate-molybdenum complex (Strickland and Parsons, 1972).

3.2.3. Calibration and Standards

Nutrient primary stock standards were prepared at the NIOZ as follows:

- Ortho-Phosphate (PO_4): by weighing Potassium dihydrogen phosphate in a calibrated volumetric polypropylene (PP) flask to make 1 mM PO_4 stock solution.
- Nitrate (NO_3): by weighing Potassium nitrate in a calibrated volumetric PP flask set to make a 10 mM NO_3 stock solution.
- Nitrite (NO_2): by weighing Sodium nitrite in a calibrated volumetric PP flask set to make a 0.5 mM NO_2 stock solution.
- Silicate: by weighing Na_2SiF_6 in a calibrated volumetric PP flask to 19.84 mM Si 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 100 mL PP volumetric flasks (calibrated at the NIOZ) filled with diluted LNSW. The blank values of the diluted LNSW were measured and added to the calibration values to get the absolute nutrient values.

3.2.4.Data Management & Statistics & Data Quality

The standards are continuously being monitored by participating in inter-calibration exercises organised by external organisations such as ICES, Quasimeme and the inter-comparison exercise organised by MRI, Japan.

To gain some accuracy, the NIOZ made an in-house 'Cocktail' standard which contains PO_4, NO_3 and Si to monitor the performance of the analyser throughout the cruise. This cocktail standard has been used for analytical performance monitoring since 2008. The following values (Table 1) were obtained from the cocktail which was diluted 250 times in a calibrated PP volumetric flask, being measured in triplicate and sometimes twice in triplicate in every analytical run.

Table 1. Nutrient values of the 1008 cocktail standard.

Nutrient	Average value	±STDEV	N	Dilution Factor
PO_4	0.927 µM	0.008	214	250
NO_3+NO_2	14.179 µM	0.061	214	250

The cocktail measurements showed that there were no trends observed, thus concluding that the calibration standards were stable during the cruise.

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 (Mean detection limit (M.D.L) = Standard Deviation of 10 samples x 2.82) (Table 2).

Table 2. Detection limits of the nutrient analysis.

	2% Standard	M.D.L	Used measuring ranges
	STDEV	µM/L	µM/L
PO_4	0.001	0.004	0.005 - 1.505
NH_4	0.004	0.011	0.050 - 3.050
NO_3+NO_2	0.003	0.007	0.010 - 25.51
NO_2	0.001	0.001	0.000 - 0.500

The third standard was measured ten times to calculate the precision of a specific concentration level in µM/l with the respective standard deviation of that concentration (Table 3):

Table 3. Precision of the nutrient analysis.

	Conc.	±STDEV
	µM/L	µM/L
PO_4	1.05	0.002
NH_4	2.05	0.014
NO_3	17.5	0.044
NO_2	0.35	0.001

For further management of analysis precision and verifying analytical performance, Kanso Technos from Japan have made a macro-nutrient certified reference material (CRM). The CRM is produced using treated natural seawater. Batch BU with salinity 34.538 psu was analysed in triplicate for 5 consecutive days during the cruise. The average value of measurements (n=38) of CRM "BU" with sub-batch number 2080 at 22.0°C are as follows (Table 4):

Table 4. Nutrient values of the CRM (BU-2080).

	Average ± STDEV	Converted to µM/kg	Assigned by *KANSO*
	µM/L	22°C	µM/kg ± Expanded Uncertainty
PO_4	0.362 ± 0.005	0.354	0.345 ± 0.010
NH_4	3.200 ± 0.142	3.125	not reported
NO_3+NO_2	4.093 ± 0.03	3.997	*3.937* ± 0.019
NO_2	0.092 ± 0.001	0.090	*0.072* ± 0.0085

The CRM values obtained are in equitable agreement with the assigned values and in good agreement with previously analysed data produced by the NIOZ, therefore no post cruise adjustments are needed.

After finalisation of the data processing, the data will be submitted to data centres decided by R. Middag. All raw data will be stored on the NIOZ-server for secured back-up and is available to collaborators via R. Middag.

3.3 Trace metal sampling

Rob Middag, Patrick Laan, Rebecca Zitoun

At all 38 stations and during three bio-assays, samples were collected for shipboard dissolved iron (DFe) determination, dissolved metals (0.2 µm filtered), and metal isotopes. At 19 stations, samples for particulate metals and particulate carbon and nitrogen were collected at a maximum of 12 depths. Additionally, samples were collected for Fe binding ligands, humic substances, mercury, neodymium isotopes, Iodine and uranium isotopes, and rare earth elements at selected stations and depths (see section 2.4).

Moreover, the BGS was deployed at 19 stations, of which 13 were deemed likely to be successful. The relatively low success rate was mostly due to the malfunctioning of the ship's USBL system. The water samples collected with the BGS were subsampled for nutrients, which were analyzed shipboard (see section 3.2), dissolved metals (see section 3.3.1), and metal isotopes (see section 3.3.3). The BGS filters, containing the filtered material on 25 mm poly-ether-sulfone (PES) disc filters (0.45 µm PAll Supor) deployed in polypropylene filter holders (Advantec) were prepared and stored frozen for the quantification of particulate metals in the land-based laboratory (see section 3.3.4).

3.3.1. DISSOLVED METALS

Rob Middag, Patrick Laan, Rebecca Zitoun

For dissolved metals, samples were filtered over a 0.2 µm PES Acropak filter under 0.5 bar inline filtered nitrogen pressure directly from the Pristine polypropylene samples. Samples were acidified to ~1.7 pH immediately after filtration using ultra clean HCL (Normatom Ultrapure, VWR). Samples will be transported back to the shore-based laboratory for Multi-Element (ME) determination that will give the concentrations of Cd, Co, Cu, Fe, Mn, Ni, Zn, Ti, Y, La, Pb, and Ga. This analysis will be done using a SeaFAST system and a High-Resolution Sector Field Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) (Gerringa et al., 2020). The seaFAST pico system is an ultra-clean, in-line, automated, low-pressure ion chromatography system that utilises a three-step process in order to pre-concentrate an acidified seawater sample. The seaFAST system takes up a 20 mL volume of acidified seawater (0.024 M HCl) into a sample loop using a vacuum and subsequently transports the sample over a chelating resin (Nobias PA1) using a syringe pump. Directly before the sample is passed over the resin, it is mixed with an ammonium acetate buffer (~pH 6.2), to raise the pH of the acidified seawater sample to 5.8. At this pH, the trace metals of interest in the sample complex with the resin and are quantitatively removed from the seawater and its matrix. The second step in the pre-concentration process is the resin wash with 'ultra pure' milliQ water. This second rinse aims to remove any loosely bound major constituent ions from the resin, such as Na^+, Cl^-, and Ca^{2+}, and to flush the small amount of seawater present after pre-concentration out of the column. The third and final step in the pre-concentration process of a sample is the elution of the trace metals from the resin. This step is achieved by passing 0.5 mL of eluent acid (~1.7 M HNO_3), using a syringe pump, over the resin to elute the trace metals from the resin, resulting in a pre-concentration factor of 40. The eluate is transferred into a destination vial using N_2 gas as a carrier gas. Subsequently samples will be analysed on the Element 2 HR-ICP-MS at NIOZ.

3.3.2. DISSOLVED FE

Patrick Laan, Rebecca Zitoun

Dissolved iron (DFe) concentrations of 38 stations with a maximum of 20 depths were measured directly on board by an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998.

Filtered (0.2µm) and acidified (pH 1.8, 2 mL/L 12M Baseline grade Seastar HCl) seawater was concentrated on a column containing aminodiacetid acid (IDA). This material binds only transition metals and not the interfering salts. After washing the column with ultrapure water, the column is eluted with diluted hydrochloric acid (HCl). After mixing with luminol, peroxide, and ammonium, the oxidation of luminol with peroxide is catalyzed by Fe and a blue light is produced and detected with a photon counter. The amount of iron is calculated using a standard calibration line, where a known amount of iron is added to low iron containing seawater. During the expedition, a multi-element standard was used for the standard addition. Using this calibration line, a number of counts per nM Fe is obtained. Samples were analyzed in triplicate but the method produced some questionable results and profiles and thus the FIA results were deemed unreliable. The issue with the FIA method could not be solved during the expedition and a systematic error analysis has to be conducted back in the land-based laboratory.

3.3.3. METAL ISOTOPES

Rob Middag, Patrick Laan, Rebecca Zitoun, Tim Conway

Due to the isotopic signatures caused by fractionation in different Fe sources, DFe isotopes have been used as a promising tool for identifying DFe sources and quantifying these sources during recent years, as well as investigating *in situ* cycling processes (Conway and John, 2014). The isotopic signatures of other metals (Ni, Cu, Zn, Cd) can also be useful as source and process tracers in the ocean. For this expedition, filtered (0.2 µm) seawater samples were taken for trace metal isotopes at 38 stations. Zn and Cd isotopes can be measured on the same seawater sample as Fe, and Ni requires a separate aliquot. For Fe, Zn and Cd: due to anticipated low DFe concentrations in surface water, 4L filtered seawater was sampled for surface waters (mostly shallower than 100m) and 1L filtered seawater was sampled for the remaining, deeper depths. For Ni: 1L filtered sample was collected for surface water and 0.5L filtered seawater at depth. All samples were acidified to pH ~1.8 using ultrapure HCl (Normatom Ultrapure, VWR) on the ship after sampling and will be taken back to our shore-based laboratory for further metal isotope analysis. Samples will be processed for isotope ratios using previously published techniques, i.e. chemical processing with Nobias PA-1 chelating resin and analysis by double spike mass spectrometry using a Thermo Neptune MC-ICPMS (Conway et al., 2013). In total, there were 595 isotope samples (595 for Fe, Zn and Cd and 595 for Ni) collected from 38 stations (7-20 for each station) during this expedition.

3.3.4. PARTICULATE METALS

Rob Middag, Patrick Laan, Rebecca Zitoun

For particulate metals sampling, a maximum of six liter (i.e. up to 6 L for deep waters and less for surface waters) of unfiltered seawater was collected from up to 12 depths of 19 stations (Table 5). For particulate trace metals, unfiltered samples were collected in 10L, acid cleaned, carboys (VWR Collection) and stored in dark plastic bags close to the ambient seawater temperature until the moment of filtration. Before the expedition, 25 mm poly-ether-sulfone (PES) disc filters (0.45 µm PAll Supor) and polypropylene filter holders (Advantec) were cleaned by heating them at 60°C for 24h in 3x sub-boiled distilled 1.2M HCl (VWR Chemicals – AnalaR NORMAPUR) and rinsing them 5 times with MQ water (18.2 MΩ) (Ohnemus et al., 2014). Filters were stored in MQ water (18.2 MΩ) until use. Filtrations were started within a maximum of two hours after sampling (Cutter et al., 2017). Before the start of the filtrations, samples were gently homogenized (i.e. by shaking the carboys) and the PES filters were placed on the filter holders. Filter holders were placed on the caps (Nalgene) of the carboys using polypropylene luer-locks (Cole-Palmer). Carboys were then hung upside down onto the CTD frame using a custom-made polypropylene carboy frame. Filtration was done under nitrogen gas

pressure (0.3 bar overpressure). Samples were filtered for a maximum of 2.5 hours and checked regularly for leaks. For each filter, filtered water was collected into a waste container for subsequent quantification of the amount of seawater that passed the filter. After filtration excess seawater on top of the filters was removed by gentle air pressure. In the clean laboratory, under the fume hood, the filters were removed from the filter holders and were folded in half, placed in a clean Eppendorf tube and stored frozen (-20°C) until analysis. Beside the trace metal stations, particulate metals samples were also collected at the end of the bioassays (see section 2.5). Particulate metals analysis will be subjected to acid digestion at NIOZ and elemental composition will be quantified using the Element 2 HR-ICP-MS.

Table 5. Particulate metal sampling information

Station	Depth sampled (initial)												# Samples
3	10	25	50	75	100	200	600	1000	1700	2369	2394		11
6	10	25	50	75	100	200	600	1000	1700	2400	2559	2584	12
8	10	25	50	75	100	200	600	1000	1700	2224	2249		11
12	10	25	50	100	200	600	992						6
13	10	25	50	62	102	112							6
14	10	25	50	100	200	300	500	582	607				9
15	10	25	50	75	100	200	283	308					8
16	10	25	50	75	100	200	430	455					8
17	10	25	50	75	100	200	575	709	734				9
18	10	25	50	75	100	200	300	400	550	700	774	799	12
19	10	25	50	75	100	200	500	800	918	943			10
20	10	25	50	75	100	200	500	800	927	952			10
21	10	25	50	75	100	200	300	400	468	493			10
30	10	25	50	75	100	200	600	1000	1422	1447			10
32	10	25	50	75	100	200	600	900	1075	1100			10
34	10	25	50	75	100	200	600	1000	1100	1182	1207		11
36	10	25	50	75	100	200	600	860	966	991			10
38	10	25	50	75	100	200	600	820	1000	1475	1593	1618	12
40	10	25	50	75	100	100	600	1000	1700	2063	2088		11
												Total	**186**

3.3.5. MERCURY

Xiangming Shi

3.3.5.1. Objectives:

Along with the radioisotope approach, we would like to study the benthic contributions to mercury (Hg) inventory, as the organic form methyl mercury (MeHg) is toxic to mammals and humans. Given the proposed net flux of Hg from the Arctic into the North Atlantic, it's also important to examine the Hg distributions in the cruise region where the transport of Hg and MeHg supply during deep water formation is rarely characterized. In addition to water circulation, the potential for exchange across the sediment-water interface cannot be overlooked for understanding Hg and TMeHg cycling when dense water flows along the seafloor.

3.3.5.2. Water column sampling for total Hg and MeHg

Hg sampling at the 20 selected stations followed the protocol of the GEOTRACES cookbook (Table 6). In total, 271 PE bottles (~120 mL) were filled with unfiltered seawater for MeHg. Total Hg samples (n= 271) were stored in glass or Teflon bottle (125 mL). After sampling, the MeHg was acidified with 0.5% H_2SO_4 (1 mL 50% H_2SO_4) or 1% HCl (1 mL concentrated HCl). All seawater samples are preserved in cold conditions (4 ℃). At some selected stations (Stn. 6, 23, 28, and 38), 2 L seawater was collected for particulate Hg (n= 23). These samples will be filtered through quartz filters (QMA, 47 mm i.d.) at the home laboratory. The filters will be stored frozen.

3.3.5.3. Multicorer sampling:

Two cores were processed for Hg in porewater. The procedure is similar to the porewater extraction described in section 3.7 using Rhizons. The extraction intervals were 0-1 cm, 1-2 cm, 2-4 cm, 4-6 cm, 6-8 cm, and 8-10 cm. 6 mL of porewater were also subsampled for pH measurements. The obtained porewater (n= 41) was collected in acid cleaned Teflon bottles and preserved frozen. ~5 g of sediment was subsampled (n= 47) from the Ra/Th core for the solid phase Hg using the same sampling intervals as those used for porewaters. At the same time, ~8 g of sediment was subsampled from the Ra/Th core for the ^{234}Th in sediment (n= 49), aiming to trace bioturbation and the redeposition of suspended particles near the seafloor. The excess ^{234}Th will be analyzed at University of Southampton, UK (see section 3.7), all Hg samples will be analyzed at University of Connecticut, US.

Table 6. Number of depths sampled for Hg at each sampling station, including both water column and sediment cores

Stn.	Time	Seawater			Sediment					
		MeHg	Total Hg	Part. Hg	Core top water*	Core top particle#	Pore-water Hg	Solid Hg	Bulk Th	Porewater pH
6	7/23/2021	19	19	6						
8	7/24/2021	17	17		2	2	6	6	7	
10	7/26/2021	13	13		2	2	5	5	7	
12	7/28/2021	7	7							
13	7/29/2021	12	12							
14	7/30/2021	14	14							
15	7/30/2021	9	9		2	2	6	6	7	6
16	7/31/2021	11	11		2	2	6	6	7	6
17	8/1/2021	12	12		2	2	6	6	7	6
19	8/2/2021	13	13							
20	8/2/2021	13	13							
21	8/3/2021	11	11		2	2	6	6	7	6
23	8/3/2021	13	13	5						
28	8/6/2021	17	17	6						
30	8/8/2021	14	14		2	2	6	6	7	6
34	8/9/2021	15	15							
36	8/11/2021	14	14					6		
37	8/11/2021	13	13							
38	8/12/2021	17	17	6						
40	8/14/2021	17	17							
Sum		**271**	**271**	**23**	**14**	**14**	**41**	**47**	**49**	**30**

**Core top water: one for MeHg, one for total Hg; # Core top particle: one for Hg, one for Th.*

3.3.5.4. Future lab work:

MeHg in seawater will be determined by purge and trap (Tenax solid absorbent) gas chromatographic cold vapor atomic fluorescence spectrometry (CVAFS; Tekran 2700) following the addition of ascorbic acid to reduce interferences, buffering to a suitable pH for derivitization, and ethylation with sodium tetraethylborate to convert CH_3Hg into volatile methylethylmercury. Total Hg in seawater will be first acidified to ensure desorption of Hg from the container walls, digested in vials with bromine monochloride (BrCl), and subsequently neutralized with hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$). This process converts all forms of Hg into ionic Hg. It is then reduced to Hg^0 with the addition of stannous chloride ($SnCl_2$) and analyzed by dual gold-amalgamation CVAFS using an automated Tekran 2600.

Particulate Hg samples will be extracted overnight in 4M HNO_3 at 60°C and an aliquot of the digest analyzed as above. The MeHg in porewater and sediment samples will be extracted by distillation from the matrix with 50% H_2SO_4 and 20% KCl, and the distillate analyzed as above. Total Hg in sediments will be determined by a direct mercury analyzer (Nippon MA-3000), which combusts the sample at high temperature in the presence of oxygen, and measures the volatile Hg^0 produced by cold vapor atomic absorption.

3.3.6. NEODYMIUM ISOTOPES

Patrick Blaser

70 water column seawater samples were collected from 15 stations at selected depths (Table 7). These samples will be analysed at the University of Lausanne, Switzerland, for their dissolved neodymium (Nd) isotope and thorium (Th) isotope compositions. The radiogenic Nd isotope composition (εNd) differs in rocks depending on their composition and age, and is imprinted on local seawater. Thus, it can be used to distinguish water masses by their geographical origin, or if the origin is known, to estimate weathering rates and thus Nd contributions of different rocks. The region around Iceland is particularly interesting in this respect, because the surrounding continents and islands are composed of very different rocks from Archaean to recent ages with vastly differing weathering properties. Samples from close to the sediment boundary may be used to infer fluxes of Nd from the sediments themselves. We will therefore combine our data with those from prior studies (e.g. (Lacan and Jeandel, 2004; Lambelet et al., 2016; Morrison et al., 2019)) and try to get deeper insights in the weathering rates and pathways of the regional continents and islands. The naturally occurring isotopes ^{230}Th and ^{232}Th analysed from the same samples can furthermore be used to infer the intensity of trace metal scavenging from seawater by marine particles. This process is very important for the vertical transport of trace metals such as Nd through the water column and into sediments.

The analytical methods follow those from Pérez-Tribouillier et al. (2019) and Pinedo-González et al. (2021) and will be carried out at the University of Lausanne, Switzerland. These methods rely on the extraction of both Nd and Th with a batch reaction with the Nobias chelating resin in order to separate them from remaining seawater and their subsequent elution in two different fractions. These two fractions containing Nd and Th, respectively, will then be further purified separately via ion exchange chromatography and their isotopic compositions measured on multi collector inductively coupled plasma mass spectrometers (MC-ICP-MS).

Table 7. Nd sampling information

Station	Depth sampled (initial)							# Samples
6	50	400	800	1350	2050	2534	2574	7
10	50	400	600	800	1186	1226		6
13	10	112						2
14	100	557	607					3
16	10	250	445					3
17	50	450	724					3
18	10	550	798					3
19	10	50	500	933				4
21	10	150	483					3
24	10	150	400	800	1250	1735		6
25	10	200	600	1000	1350	1609		6
27	10	200	600	1000	1350	1900	2102	7
30	10	150	400	800	1437			5

38	50	150	700	900	1400	1608		6
40	200	600	800	1350	1900	2078		6
							Total	**70**

3.3.7. ^{129}I AND ^{236}U ISOTOPES

Nuria Casacuberta Arola

Transient tracers generally stand for artificial substances that human activities have generated and ultimately released to the marine environment. Depending on their biological, chemical and physical characteristics, they are capable of labeling different ocean processes (Jenkins and Smethie, 1996). In particular, those behaving conservatively in seawater, either because they are soluble or gases, have been used as powerful tools that provide scientists with a unique opportunity to study the effects of the changing climate on the ocean. Good examples of transient tracers are the CFCs and SF_6 gas tracers, and radionuclides of either natural or artificial origin (^{14}C, ^{137}Cs, ^{3}H, etc.).

The long-lived (i.e. $T_{1/2}$ of millions of years) artificial radionuclides ^{129}I and ^{236}U are two novel oceanographic transient tracers that have emerged in the last 20 years thanks to advancements in Accelerator Mass Spectrometry (AMS) techniques (Casacuberta et al., 2014; Smith et al., 2011). Both radionuclides have been introduced to the marine environment either from controlled releases from the Nuclear Reprocessing Plants (NRPs) of Sellafield (UK) and La Hague (France) and/or atmospheric weapon tests (global fallout) (Christl et al., 2015). Given their recent input to the oceans (from 1950s) and due to the different release history (input functions), they are used today as excellent markers to understand the origin of water masses, their circulation timescales and the mixing regimes of waters (advection and diffusion processes) (Casacuberta et al., 2018; Wefing et al., 2021).

3.3.7.1. ^{129}I and ^{236}U in the MetalGate cruise

The use of ^{129}I and ^{236}U as transient tracers in the subpolar North Atlantic (SPNA) is timely because the plume of the NRPs releases is now penetrating to the North Atlantic Deep Waters (Castrillejo et al., 2018). Therefore, these are now valuable tracers that will help understanding the pathways of overflow waters, their circulation timescales and mixing processes.

During the MetalGate cruise, 91 samples were collected at 10 stations at selected depths (Table 8) for the analysis of these two isotopes. In particular, station 3, 6, 8, 10, 14, 16, 17, 30, 38 and 40 were chosen as they were close to the source region of Denmark Strait Overflow Waters (DSOW) and Iceland Scotland Overflow Waters (ISOW). Results will be put in the context of other cruises that took place during 2020 and 2021 both in the SPNA (OVIDE and AR7W sections) and Arctic Ocean (Arctic Century Expedition, Arctic Ventilation and JOIS).

Table 8. ^{129}I and ^{236}U sampling information

Station	Depth sampled (initial)															# Samples
3	150	400	800	1350	1900	2098	2138									7
6	159	400	800	1350	2050	2534	2574									7
8	10	150	400	600	800	1000	1350	1700	1900	2199	2224	2239	2249			13
10	10	100	200	400	600	800	1000	1186	1236							9
14	10	100	200	300	400	500	607									7
16	10	100	200	350	445											5
17	10	100	200	325	575	724										6
30	10	100	200	400	600	800	1000	1300	1397	1437						10
38	10	100	200	400	600	810	1000	1200	1400	1475	1568	1608				12
40	50	75	100	200	400	600	800	1000	1350	1700	1900	2038	1063	1078	2088	15
															Total	**91**

3.3.7.2. Analysis of samples

Seawater samples will be analyzed at Department of Environmental System Sciences and measurements will be performed with the AMS Tandy at Laboratory of Ion Beam Physics (ETH Zurich). A PhD student will be involved with the processing, measurement of the samples and interpretation of the final results.

3.3.8. RARE EARTH ELEMENTS

Vanessa Hatje

The rare earth elements (REEs) are a coherent group of elements that share chemical properties due to their uniform trivalent charge (except for Ce^{4+} and Eu^{2+}), and the gradual decrease in their ionic radii with increasing atomic number across the REE series. These element abundances are fractionated during environmental processes in a subtle and predictable manner (e.g., (Elderfield, 1988)). This fractionation across the REE series can be used to trace and provide insight into biogeochemical processes, atmospheric-driven particles, water mass pathway, and mixing of the modern ocean that single element tracers cannot discriminate (e.g., (Elderfield et al., 1990; Haley et al., 2014; Sholkovitz et al., 1994; Zhang and Nozaki, 1996)). Understanding the REE chemical behavior is thus essential for their successful application as tracers of natural processes.

Although several studies have been performed in the Iceland region, none of them attempted to comprehensively evaluate the dissolved REE elements. Here we will examine the distribution, transport, and sources of the dissolved REEs to contribute to the growing resolution of REE distributions in water masses in the Iceland region.

Twenty-one full profile stations (8 to 19 depths) were chosen (Table 9) to (i) provide a spatial REE signature as chemical traces of water masses, (ii) investigate the input of continental waters where terrestrial runoff is expected, and (ii) investigate if benthic processes impact REE concentrations in bottom waters.

Table 9. REE sampling information

Station	Depth sampled (initial)																				# Samples
6	10	25	50	75	100	150	200	400	600	800	1000	1350	1700	2050	2400	2534	2559	2574	2584		19
8	10	25	50	75	100	150	200	400	600	800	1000	1350	1700	1900	2199	2224	2239	2249			18
10	10	25	50	75	100	150	200	400	600	800	1000	1186	1211	1226	1236						15
13	10	25	50	62	87	102	112														7
14	10	25	50	75	100	150	200	300	400	500	607										11
16	10	25	50	75	100	150	200	350	405	430	445	455									12
17	10	25	50	75	100	150	200	325	450	575	684	709	724	734							14
20	10	25	50	75	100	200	350	500	650	800	902	952									12
21	10	25	50	75	100	200	300	400	443	493											10
22	10	25	50	75	100	150	200	290													8
23	10	25	50	75	100	200	400	600	800	1000	1200										11
24	10	25	50	75	100	200	400	600	800	1000	1250	1500	1745								13
25	10	25	50	75	100	200	400	600	800	1000	1350	1609									12
26	10	25	50	75	100	200	400	600	800	1000	1350	1700	2050	2206							14
27	10	25	50	75	100	200	400	600	800	1000	1350	1700	1900	2102							14
28	10	25	50	75	100	200	400	600	800	1000	1350	1700	2000	2300	2444						15
30	10	25	50	75	100	200	400	600	800	1000	1300	1447									12
32	10	25	50	75	100	200	400	600	800	900	1100										11
34	10	25	50	75	100	200	400	500	600	800	1000	1100	1207								13
36	10	25	50	75	100	200	400	600	700	800	860	991									12
38	10	25	50	75	100	200	400	600	700	810	900	1000	1200	1400	1475	1618					16

40	10	25	50	75	100	200	400	600	800	1000	1350	1700	1900	2088		14
															Total	**283**

The REE analyses will be carried out by isotope dilution (ID) ICP-MS following adapted procedures previously described in Behrens et al. (2016). Aliquots of samples will be weighted and spiked with a multi-element REE isotope spike, then they will be left to homogenize for at least 48 h. The samples will be pre-concentrated using the automated seaFAST system (Elemental Scientific Inc. Omaha, Nebraska, USA). The REE measurements will be performed by ICP-MS (iCAP RQ, Thermo Scientific, Germany) coupled to a desolvation introduction system (Aridus 3, Teledyne CETAC, Omaha, USA) to obtain higher sensitivity and lower oxide formation (< 0.03% for Ce oxide). Blanks and replicates will be included in each batch. Accuracy will be checked using GEOTRACES reference samples (North Pacific SAFe 3000 m and GEOTRACES Santa Barbara Coastal water, GSC). All samples will be analyzed at CIEnAm, Universidade Federal da Bahia, Brazil.

3.4 Ligand and Humic sampling

3.4.1. IRON BINDING LIGANDS QUANTIFICATION AND CHARACTERIZATION

Rebeca Zitoun

The presence of DFe in seawater at concentrations beyond the inorganic solubility of Fe is facilitated by complexation processes of Fe with prevalent organic ligands. Commonly more than 99 % of the DFe in seawater is bound to organic ligands, inhibiting the hydrolysis and precipitation of DFe, and thereby its loss in the water column (Boye et al., 2001; Gledhill and Buck, 2012; Hunter and Boyd, 2007; Liu and Millero, 2002). Organic complexation also influences the bioavailability of Fe for prevalent phytoplankton and other organisms. However, despite the importance of organic ligands for the DFe cycle, only limited knowledge exists about the sources and fate of these ligands and knowledge about their molecular structures is only just emerging (Boiteau et al., 2013; Boiteau and Repeta, 2015). Further, the residence time of Fe-binding ligands has been estimated to surpass the transit time of NADW from the high north to the Southern Ocean (Gerringa et al., 2015), implying these ligands have the potential to transport Fe with NADW to the Fe limited Southern Ocean.

In order to expand our current understanding of the importance and characterisation of Fe binding ligands in the understudied High Latitude North Atlantic, which is a climate relevant region (i.e. deep water formation) defined by iron limitation, a total of 17 (n = 181) and 15 (n = 113) stations were sampled with the UCC (Table 10) for the quantification of Fe-binding organic ligand concentrations including associated binding constants (known as conditional stability constant, $K^{cond}_{FeL,\,Fe(III)}$) and the characterisation of prevalant Fe-binding ligands, respectively. Special attention was given to sampling distinct water masses and features (glacial freswater input) along the cruise track. Samples for both parameters were also taken at the beginning (T_0) and the end of 3 bioassays (see section 2.5). Samples for ligand analysis were taken at a maximum of 14 depths per station and filtered in the clean container (0.2 µm filtered). Samples reserved for bulk ligand analysis were double bagged and stored frozen at -20 degrees. These samples will be processes at NIOZ using competitive ligand exchange -cathodic stripping voltammetry (CLE-CSV) with Salicylaldoxime (SA) as competing ligands (Abualhaija and van den Berg, 2014; Buck et al., 2015; Gledhill and van den Berg, 1994). Samples (2 L) reserved for ligand characterizaton were extracted after filtration using a SPE-resin-cartridges following the method of Boiteau et al. (2013). The latter was processed as soon as possible, i.e. usually within 24 hours of sample collection using a flow rate of 6 mL/min. Samples were stored in the dark at 4°C before and during extraction to avoid photodegradation of prevalent organic ligands. The resin binds organic ligands, namely siderophores, and seperates these from the interferring saltwarer matrix. After extraction, the loaded resin columns were double bagged and stored frozen at -20°C for later analysis

at NIOZ using High-Performance Liquid Chromatography–Inductively Coupled Plasma-Mass Spectrometry (Boiteau et al., 2013).

Table 10. Ligand and siderophore sampling information

Station	Ligands	# Samples	Siderophores	# Samples
6	X	12	X	12
8	X	12	X	12
12	X	10	X	10
14	X	10	X	10
15	X	8		
6	X	9	X	6
17	X	10	X	6
19	X	10	X	6
21	X	11	X	6
24	X	11	X	8
25	X	11		
29	X	11	X	6
30	X	11	X	6
32	X	10	X	6
34	X	11	X	6
36	X	10	X	6
40	X	14	X	7

3.4.2. HUMIC SUBSTANCES

Luis Laglera

There is no consensus about the relevance of humic substances (HS) as Fe-binding ligands in the ocean. So far, the traditional understanding is that HS and DFe coprecipitate in estuaries and thereby minimize the contribution of riverine Fe to marine DFe inventories. Recent findings, however, proved that HS stabilizes riverine DFe, specifically DFe that originates in Siberian rivers which is then transported under the Arctic ice sheet. Recent studies also showed that a fraction of Fe-HS complexes could potentially be strong enough to compete for DFe with other marine biological ligands, raising further questions about the importance of HS in the marine DFe cycle. In response to the need to resolve the natural DFe speciation in marine waters including HS, a new voltammetric method was established that targets specifically Fe-HS complexes and provides a Fe-HS/DFe ratio. With this method Luis Laglera's team found that an astonishing 80% of DFe in Polar Surface Waters (PSW) exists in the form of Fe-HS complexes in the upper 200 m.

Laglera's team is planning on analyzing samples for Fe-HS complexes collected in 2016 in the Fram Strait by NIOZ personnel and collected in 2021 during the current expedition using the above mentioned new analytical protocol. Both expeditions will help to define if Fe-Hs complexes are able to make the transit from the Arctic ocean to the North Atlantic following the Southbound surface currents that run along the Western coast of Greenland. Another objective of the team is to find out if shelves and sills are source areas of HS in the High Latitude North Atlantic. Thus, along with the quantification of HS, a size fractionation of HS including photo stability laboratory experiments will be carried out at the Universidad de las Islas Baleares.

In order to achieve the above-mentioned objectives, a total of 18 and 3 stations were sampled with a maximum of 10 depths per station for HS and HS size fractionation, respectively (Table 11). Samples for humic substances were commonly collected together with the bulk ligand samples. Samples were

filteres in the clean container, double bagged, and kept frozen at -20°C for later analysis at the Universidad de las Islas Baleares using voltammetric analysis.

Table 11. Humic and size fractination sampling information

Humics												
Station	**Depth sampled (initial)**											**# Samples**
6	10	25	50	75	100	200	600	1000	1700	2584		10
8	10	25	50	75	100	200	600	1000	1700	2249		10
12	10	25	50	75	100	200	600	800	967	992		10
14	10	25	50	75	100	200	300	500	607			9
15	10	25	50	75	100	200	308					7
16	10	25	50	75	100	200	350	455				8
17	10	25	50	75	100	200	575	709	734			8
20	10	25	50	75	100	200	500	800	952			9
21	10	25	50	75	100	150	200	300	400	493		10
22	10	25	50	75	100	200	265	290				8
23	10	25	50	75	100	200	600	1000	1200			9
24	10	25	50	75	100	200	600	1000	1500	1720	1745	11
25	10	25	50	75	100	200	600	1000	1350	1609		10
29	10	25	50	75	100	200	600	1000	1500	1725		10
30	10	25	50	75	100	200	600	1300	1447			9
34	10	25	50	75	100	200	600	1000	1207			9
36	10	25	50	75	100	200	600	800	991			9
40	10	25	50	75	100	200	600	1000	1700	2088		10
											Total	**166**
Size fractionation												
21	10	25	50	75	100	150	200	300	400	493		10
22	10	25	50	75	100	200	240	265	280	290		10
23	10	25	50	75	100	200	600	1000	1175	1200		10
											Total	**30**

3.5 Additional parameter sampling

3.5.1. PARTICULATE ORGANIC CARBON (POC) AND NITROGEN (PON)

Willem van de Poll, Anna Cunera Koek

The quantification of particulate carbon (POC) and nitrogen (PON) provides a useful estimate for organic biomass, mostly algae. Changes in the ratio between carbon and nitrogen can reveal degradation (recycling) of particulate matter in the water column. Furthermore, ratios between carbon and chlorophyll may be indicative for nutrient limitation and changes in taxonomic composition.

For POC and PON sampling, 1-4 L unfiltered sea water was collected from the UCC at up to 12 depths of 19 stations (Table 12). These samples were stored in dark bottles and filtered through pre-combusted 25 mm glass microfiber filters (GF/F; 0.7 µm) using a mild vacuum pump system (< 0.2 mbar). After filtration, the filters were wrapped in aluminum foil and snap frozen in liquid nitrogen and at -80 ˚C. In addition to normal cast samplings, POC and PON samples were also collected from bio-assay experiments (see section 2.5). For this, 1L unfiltered water were sampled. The procedure was the same as above. The C/N analysis will be conducted in the shore-based laboratory at NIOZ using a Thermo-Interscience Flash EA1112 Series Elemental Analyzer (Thermo Scientific) according to Verardo et al. (1990), with a detection limit of 100ppm and a precision of 0.3%. In short, the sample is

introduced in the oxidation column and incinerated by flash combustion with excess oxygen at 900˚C. The solid sample disintegrates into the gas phase and the components combine with oxygen to oxides. The organic carbon is converted into CO2 and the organic nitrogen into N2 gas and the carrier gas (helium) carries the gas via the reduction column (Verardo et al., 1990). Before analysis, GF/F filters are folded into an eighth and placed into a tin cup. The tin cup is folded into a tight ball using two forceps ensuring that all atmospheric N is removed. The machine blank is included by the analyzer calibration. Blanks for filters, filtration and sample handling will be analyzed. Carbon and nitrogen content of samples and blanks will be computed according to the results of the standard measurements. Thereafter the blank is subtracted from the sample. The results are given in mg Carbon or Nitrogen on the filter. This number is then divided by the volume filtered to calculate mg/L.

Table 12. C/N sampling information

Station	Depth sampled (initial)												# Samples
3	10	25	50	75	100	200	600	1000	1700	2369	2394		11
6	10	25	50	75	100	200	600	1000	1700	2400	2559	2584	12
8	10	25	50	75	100	200	600	1000	1700	2224	2249		11
12	10	25	50	100	200	600	992						6
13	10	25	50	62	102	112							6
14	10	25	50	100	200	300	500	582	607				9
15	10	25	50	75	100	200	283	308					8
16	10	25	50	75	100	200	430	455					8
17	10	25	50	75	100	200	575	709	734				9
18	10	25	50	75	100	200	300	400	550	700	774	799	12
19	10	25	50	75	100	200	500	800	918	943			10
20	10	25	50	75	100	200	500	800	927	952			10
21	10	25	50	75	100	200	300	400	468	493			10
30	10	25	50	75	100	200	600	1000	1422	1447			10
32	10	25	50	75	100	200	600	900	1075	1100			10
34	10	25	50	75	100	200	600	1000	1100	1182	1207		11
36	10	25	50	75	100	200	600	860	966	991			10
38	10	25	50	75	100	200	600	820	1000	1475	1593	1618	12
40	10	25	50	75	100	100	600	1000	1700	2063	2088		11
												Total	**186**

3.5.2. OXYGEN

Sharyn Ossebaar

Oxygen samples were taken from the UCC at 5 deep stations to determine the concentration of dissolved oxygen, in order to calibrate the CTD sensors (Table 13). Samples were taken from a minimum of three depths, usually in duplicate. Samples were drawn into volume-calibrated ~120 mL Pyrex glass bottles using Tygon tubing, flushing the bottle with at least 3 times its volume. Addition of chemicals was performed immediately afterwards, after which glass stoppers were secured in place with an elastic band. The samples were stored underwater and in the dark at 20 ˚C and analysis will be performed at NIOZ.

Table 13. Oxygen sampling information

Station	Bottles Sampled			Remarks
6	2	7	9	Single Samples
13	3	5	8	Single Samples6
19	3	5	6	Duplicate Samples
28	4	6	9	Duplicate Samples
40	4	6	11	Duplicate Samples

The determination of the volumetric dissolved oxygen concentration of water samples will performed colourimetrically by measuring the absorbance of iodine at 456nm on a Brann + Luebbe (now known as SEAL Analytical) TrAAcs autoanalyzer spectrophotometer (see (Pai et al., 1993)). The spectrophotometer will be calibrated using standards of seawater spiked with known amounts of KIO_3.

Subsequent utilization of the bottle oxygen measurements for the calibration of the CTD frames' oxygen sensors will be performed back at NIOZ.

3.5.3. $\delta^{18}0$

Piet van Gaever, NIOZ

Oxygen isotopes ($\delta^{18}O$) were sampled (unfiltered) in 2 mL glass vials at 15 stations along the Denmark Straight (Table 14) to quantify the oceanic freshwater input in the study region from rivers and glacial melt. Both, full depth profiles and surface waters (up to 150 m) were sampled. $\delta^{18}O$ will be analyzed using a stable isotope ratio mass spectrometer at NIOZ.

Table 14. $\delta^{18}O$ sampling information

Station	Bottles sampled							# Samples
7	14	15	16	18	19	24		6
8	14	15	17	19	21	24		6
9	6	9	10	11	12	14	16	10
	18	20	24					
10	1	3	7					3
12	1	2	3	4	5	7	10	7
14	11	13	15	17	19	22		6
15	7	8	9	11	13	16		6
16	1	2	3	4	5	6	7	14
	8	9	10	12	13	14	16	
17	11	12	14	17	19	22		6
18	11	12	13	15	17	20		6
19	10	11	13	15	17	20		6
20	10	11	13	15	17	22		6
21	14	15	17	19	21	24		6
22	6	7	8	10	12	14		6
23	10	11	12	14	16	18		6

3.6 Biological sampling

Willem van de Poll, Anna Cunera Koek

Unfiltered water samples were collected from the UCC at 32 stations for phytoplankton biology and physiology, namely, the quantification of phytoplankton pigments, the evaluation of photosynthetic characteristics, and the determination of phytoplankton, bacteria and virus abundances (Table 15). The goal was to link biology and physiology to the geochemical conditions of the water column (see section 3.3.) and to the detailed protein mapping efforts (see section 3.6.5 and following).

3.6.1. PHYTOPLANKTON PIGMENTS

Pigments can resolve phytoplankton composition roughly to the taxonomic level. Furthermore, their abundance is a useful estimate for algal biomass (e.g. chlorophyll a). Pigment samples were collected at 3 depths between 10 and 50 m at all stations. After filtration of 3-4 L of the water collected from the UCC, using a 47 mm GF/F filter under mild vacuum (<0.2 mBar), samples were snap frozen in liquid

nitrogen and stored at -80°C. Analysis will be completed at the University of Groningen, the Netherlands, by high performance liquid chromatography (HPLC).

3.6.2. PHOTOSYNTHETIC CHARACTERISTICS

Fast repetition rate fluorometry (FRRf) measurements were done for 3 depths between 10 and 50 m at all stations and for all the small and large bioassays (incubations). FRRf measures photosynthetic characteristics related to the efficiency of electron transport by photosystem 2. The characteristics were measured after 30 min dark incubation and during a series of irradiance exposures (photosynthesis vs irradiance curves; 8 levels of 40 sec, each up to 1000 µmol photons m^{-2} s^{-1}). Changes in PSII characteristics are indicative for nutrient limitation (particularly iron limitation) and taxonomic composition.

3.6.3. PHYTOPLANKTON ABUNDANCE

Flow cytometry samples for phytoplankton. 2 mL samples were collected at 3 depths between 10 and 50 m between stations 27 and 41. Samples were fixed with hexamide buffered formalin for 30 min, snap frozen in liquid nitrogen and stored at -80°C. Flow cytometry can quantify abundances of small phytoplankton (<20 µm), bacteria and viruses.

3.6.4. BIOASSAYS

Water collected from the UCC (3 L) at 37 stations was spiked under trace metal clean conditions with Fe (0.5 nM final concentration), ammonium (2 µM final concentration), and/or nitrate (10 µM final concentration), and incubated under constant irradiance (20 µmol photons m^{-2} s^{-1}) for 48-72 h in a temperature-controlled room adjusted to water temperature. Triplicates of 200 mL were used for all conditions. The goal was to identify responses in photosynthetic characteristics and changes in biomass to the nutrient additions. After incubation the experiment was sampled for FRRf (photosynthetic characteristics) and for pigments (filtration on 25 mm GF/F). Implemented incubation bottles were acid cleaned before use using mild HCl.

Large Bio assay (XL)s were a collaborative effort together with Loay Jabre and Lena Beckley (Dalhousy University; see section below), the trace metal team (NIOZ; see section 3.3), and numerous water carriers between the trace metal free container and the incubators. The cubitainers used for the bioassay were acid cleaned and filled in the trace metal clean container using trace metal clean protocols.

For the large bioassays both short (48 h, 10 L cubis) and long (up to 6 days, 20 L cubis) large volume incubations were performed in temperature-controlled incubators under natural irradiance (filtered by 2 layers of neutral density screens). Water samples were incubated in transparent, acid cleaned (using a mild HCL wash) cubitainers in triplicates:

- ***Bio XL 1 (5 days) –*** Implemented treatments included iron addition (2 nM; ^{57}Fe) and control, both at ambient and at ambient plus 4 degrees temperature. Goal was to assess interactions between iron addition and temperature on phytoplankton biomass, activity, and composition. Measurements were made at T_0 (triplicates), $T_{48\,h}$, and T_{final} (5 days). All conditions were diluted with fresh sea water at $T_{48\,h}$ under trace metal clean conditions to replenish the nutrients and this give the biology enough time to show some effects to the treatments. Sampling was done for pigments, PON, POC, flow cytometry, and FRRf. Loay and Lena sampled for proteins, RNA, and N uptake experiments. Furthermore, nutrients and trace metals (including samples for particulate metals, Fe-ligands, and siderophores) were sampled by the trace metal team.
- ***Bio XL 2 (48 h) -*** Implemented treatments included controls, plus iron (2 nM; ^{57}Fe), and plus ammonium (2 µM), in triplicates. Sampling was done for pigments, CN, flow cytometry, and

FRRf at T_0 and $T_{48\ h}$. Loay and Lena sampled for protein, RNA, and N uptake experiments. Furthermore, nutrients and trace metals were sampled by the trace metal team.

- ***Bio XL 3 (6 days) -*** Implemented treatments included iron addition (2 nM; ^{57}Fe) and control, both at ambient and at ambient plus 4 degrees temperature. All cubitainers were spiked with nitrate (10 µM) and phosphate (1:16) prior to incubation. Sampling was done at T_0 (triplicates) and on day 6 for pigments, C/N, flow cytometry, and FRRf. Loay and Lena sampled for protein, RNA, and N uptake experiments. Furthermore, nutrients and trace metals were sampled by the trace metal team, including samples for particulate metals, Fe-binding ligands, and siderophores.

Table 15. Biology sampling information

Date	Station	# HPLC, FRRf depths	# C/N depths	Remarks
19-7-2021	**1**	3	3	
20-7-2021	**2**	3	3	
21-7-2021	**3**	3	3	
22-7-2021	**4**	1	1	Start bioassay 1
23-7-2021	**6**	3	12	
24-7-2021	**7**	3	3	
25-7-2021	**8**	3	12	
25-7-2021	**9**	3	3	
26-7-2021	**10**	3	12	
28-7-2021	**12**	3	3	
29-7-2021	**13**	3	9	Start bioassay 2
30-7-2021	**14**	3	9	
30-7-2021	**15**	3	8	
31-7-2021	**16**	3	8	
8/01/2021	**17**	3	9	
8/02/2021	**18**	3	10	
8/02/2021	**19**	3	9	
8/02/2021	**20**	3	10	
8/02/2021	**21**	3	10	
8/03/2021	**22**	3	3	
8/04/2021	**24**	3	3	
8/05/2021	**25**	3	3	Start bioassay 3
8/06/2021	**27**	3	3	flow cytometry at 3 depths
8/06/2021	**28**	3	3	fc3
8/07/2021	**29**	3	3	fc3
8/08/2021	**30**	3	9	fc3
8/08/2021	**31**	3	3	fc3
8/08/2021	**32**	3	3	fc3
8/09/2021	**33**	3	3	fc3
8/09/2021	**34**	3	11	fc3
8/10/2021	**35**	3	3	fc3
8/11/2021	**36**	3	10	fc3
8/11/2021	**37**	3	3	fc3
8/12/2021	**38**	3	11	fc3
8/13/2021	**39**	3	3	fc3
8/14/2021	**40**	3	11	fc3
8/15/2021	**41**	3	3	fc3

3.6.5. IN SITU PROTEIN AND RNA SAMPLES

Loay Jabre, Lena Beckley

With collaboration and help from all other scientists and the crew onboard, samples for protein, RNA and nutrient-uptake measurements were collected from the UCC. These samples were collected from in situ stations and from three different large bioassays conducted on board.

We collected phytoplankton biomass for protein and RNA analyses from 32 different stations at various depths (see Table 16). For protein samples, ~10L of seawater from each depth was filtered sequentially through 3 µm and 0.2 µm polycarbonate filters. For RNA samples, ~4L of seawater was filtered through 0.2 µm polycarbonate filters from each depth (see Table 16). All filters were stored at -80 °C for subsequent analysis.

Proteomics samples will be analyzed at Dalhousie University in the Bertrand lab using mass spectrometry. These measurements will provide information about the microbial community composition at different depths and locations at the time of sampling, as well as the physiological state of the phytoplankton at the time of sampling (e.g. were the phytoplankton experiencing iron stress). RNA samples will be sequenced to create a database that will be used in conjunction with mass spectrometry measurements to enable us to identify, quantify, and assign taxonomic groupings to the various proteins present in the samples. Protein and RNA samples were also collected from the large bioassay experiments (see below).

Table 16. In situ protein and RNA samples collected on 3.0 µm and 0.2 µm polycarbonate filters.

Station	Protein	RNA
1	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 30, 50, 75	-
2	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
4*	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 25	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 25
6	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 30, 50, 75	-
7	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
9	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 20, 30, 50	-
10	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
13**	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 25	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 25
14	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
15	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 22, 50, 75	-
16	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 22, 50, 75	-
18	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 30, 50, 75	-
19	- Sequential filtration: 3.0 µm and 0.2 µm	-

	- Depths (m): 10, 27, 50, 75	
20	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 37, 50, 75	-Non-sequential filtration: 0.2 µm - Depths (m): 10, 37
21	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 22, 50, 75	-Non-sequential filtration: 0.2 µm - Depths (m): 10, 22
22	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 44	-
23	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75, 108	-Non-sequential filtration: 0.2 µm - Depths (m): 25, 108
25	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75, 108	-
26* **	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 18	- Non-sequential filtration: 0.2 µm; triplicates - Depths (m): 18
27	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75	-
28	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
29	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75	-
31	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75	-
32	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 20, 50, 75	-
33	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 20, 50, 75	-
34	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75	-
35	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 12, 25, 50, 75	-
37	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 25	-Non-sequential filtration: 0.2 µm - Depths (m): 25
38	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 15, 25	-
39	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 10, 25, 50, 75	-
40	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 15, 25, 50, 75	-
41	- Sequential filtration: 3.0 µm and 0.2 µm - Depths (m): 15, 25, 50, 75	-

***** Start of long-term bioassay #1; ** Start of short-term bioassay #1; *** Start of long-term bioassay #2***

3.6.6. IN SITU NUTRIENT UPTAKE EXPERIMENTS

This work was conducted in collaboration with Dr. Rachel Sipler's group (Bigelow Laboratory), who was not present on board. For these experiments, we added isotopically labelled nutrients (bicarbonate, nitrate, ammonium, amino acids) to microbial community samples that we collected at various stations (see Table 17). We then incubated these samples under different temperatures for 6-24 hours and harvested the microbial community by vacuum filtering on 0.3 µm GF filters. The filtrate and filters from these samples were collected and stored at -20 °C for subsequent analysis. Samples from these experiments will be analyzed by Dr. Rachel Sipler's group to provide an understanding of primary productivity rates, nutrient uptake rates, and the different nitrogen sources used by microbial communities around

Iceland. Nutrient uptake experiments were also conducted from the large bioassay experiments (see below).

Table 17. Station nutrient uptake experiments conducted in triplicates for each temperature and nutrient treatment.

Station	Isotopically Labelled Nutrients Used	Notes
2	Nitrate, Ammonium, Bicarbonate	Incubated at 9.7 °C for ~6 hours
4*	Nitrate, Ammonium, Bicarbonate, Amino Acids	Incubated at 9.1 °C for ~11 hours
7	Ammonium, Bicarbonate	Incubated at 9.1 °C for ~17 hours
9	Ammonium, Bicarbonate	Incubated at 9.1 °C and 13.1 °C for ~13 hours
13**	Nitrate, Ammonium, Bicarbonate, Amino Acids	Incubated at 10 °C for ~13 hours
21	Nitrate, Ammonium, Bicarbonate	Incubated at 1.5 °C for ~24 hours
26***	Nitrate, Ammonium, Bicarbonate, Amino Acids	Incubated at 9 °C for ~18 hours
29	Nitrate, Ammonium, Bicarbonate	Incubated at 9 °C and 13 °C for ~19 hours

** Start of long-term bioassay #1; ** Start of short-term bioassay #1; *** Start of long-term bioassay #2*

3.6.6.1 LARGE BIOASSAY EXPERIMENTS

We conducted three large bioassay experiments (two long term, one short term) to examine how microbial communities around Iceland respond to changes in nutrients and temperature (see Table 18 to 21). For these experiments, we collected microbial communities from three different locations and incubated them under different nutrient and temperature conditions in 20L cubitainers for the long-term bioassays or 10L cubitainers for the short-term bioassay. Samples (cubitainers) were incubated for several days inside temperature and light controlled incubators mounted on the top deck of the vessel. Our group then harvested a portion of the biomass from these incubations for protein and RNA samples, and conducted nutrient uptake experiments using another portion. The large bioassay treatments were as follows:

Table 18. Long term bioassay #1 experimental design – total samples: 12

	Ambient temperature (9 °C)	High temperature (13 °C)
No iron added	Replicate I, II, II	Replicate I, II, II
2 nM iron added	Replicate I, II, II	Replicate I, II, II

Table 19. Long term bioassay #2 experimental design – total samples: 14

	Ambient temperature (9 °C)	High temperature (13 °C)
No iron, nitrate or phosphate added	Replicate I	Replicate I
10 µM nitrate, 0.63 µM phosphate added	Replicate I, II, II	Replicate I, II, II
2 nM iron, 10 µM nitrate, 0.63 µM phosphate added	Replicate I, II, II	Replicate I, II, II

Table 20. Short term bioassay #1 experimental design – total samples: 12

	Ambient temperature (10 °C)
No iron, or ammonium added	Replicate I, II, II
2 nM iron added	Replicate I, II, II
2 µM ammonium added	Replicate I, II, II
2 nM iron, 2 µM ammonium added	Replicate I, II, II

Table 21 – Parameters samples during the bioassays.

Bioassay	Protein	RNA	Nutrient Uptakes
Long Term #1 – T0hrs	0.2 µm polycarbonate filters in triplicates.	0.2 µm polycarbonate filters in triplicates.	Nitrate, Ammonium, Bicarbonate and Amino Acid uptake rate experiments
Long Term #1 – T48hrs	0.2 µm polycarbonate filters from each treatment		
Long Term #1 – T120hrs	0.2 µm polycarbonate filters from each treatment	0.2 µm polycarbonate filters from each treatment	Nitrate, Ammonium and Bicarbonate uptake rate experiments
Long Term #2 – T0hrs	0.2 µm polycarbonate filters in triplicates.	0.2 µm polycarbonate filters in triplicates.	Nitrate, Ammonium, Bicarbonate and Amino Acid uptake rate experiments
Long Term #2 – T144hrs	0.2 µm polycarbonate filters from each treatment	0.2 µm polycarbonate filters from each treatment	Nitrate, Ammonium, and Bicarbonate, uptake rate experiments
Short Term #1 – T0hrs	0.2 µm polycarbonate filters in triplicates.	0.2 µm polycarbonate filters in triplicates.	Nitrate, Ammonium, Bicarbonate and Amino Acid uptake rate experiments
Short Term #1 – T48hrs	0.2 µm polycarbonate filters from each treatment	0.2 µm polycarbonate filters from each treatment	Nitrate, Ammonium, and Bicarbonate, uptake rate experiments

3.7 Radium and Sediment sampling

Amber Annett, Rhiannon Jones, Xiangming Shi

Objectives:

Sediments release macro- and micro-nutrients into the overlying water column. Organic material in sediment is remineralised into macronutrients, and the consumption of oxygen during this process can fuel reductive dissolution of iron. Following efflux from sediment, these dissolved nutrients have the potential to be dispersed over long distances. The RaCE:TraX project (Radium in Changing Environments: Tracing Fluxes) complements the MetalGate project by quantifying macro- and micronutrient release from marine sediment and tracing downstream advection as waters flow from the Arctic basin into the deep North Atlantic.

Naturally occurring radioisotopes of radium (Ra) are especially useful tracers of lithogenic inputs, produced from particle reactive thorium (Th). Th decays, producing highly soluble Ra, thus distributions of Ra show a strong source at the sediment-water interface. The so-called "Ra quartet" of four isotopes decay at different rates, and can be used to investigate a range of time scales from days/weeks (e.g. transport within/across benthic nepheloid layers) to months/years (e.g. advection). Pairs of Ra isotopes can be used to account for mixing during transport.

A complementary component of this work in collaboration with Dr Will Homoky (University of Leeds, UK) investigates chemical distributions of trace metals and macronutrients in pore waters from sediments at several MetalGate stations. In addition, the RaCe:Trax work uses a Ra/Th disequilibrium approach to quantify benthic fluxes of these race metals and nutrients. This novel technique leverages the solubility of the daughter isotope Ra and the high particle affinity of Th, where the deficit of Ra in sediments relative to the expected activity determined from Th content reflects solute loss from diffusion, bioirrigation and porewater exchange over a time period of 1-2 weeks. Ratios of nutrients or metals to Ra in porewaters can be used to determine efflux from sediments using Ra/Th method.

3.7.1. Water column sampling:

3.7.1.1. RADIUM ISOTOPES IN SEAWATER

Ra sampling requires very large volumes of water, as Ra activities are typically very low away from sediment sources. Samples of 100-140 L were collected at 13 station from the UCC and CTD, with 6 depths for each profile (Table 22), for water column Ra profiles. Samples were transferred using 20 L carboys into 160 L bins for processing. Using a submersible pump, the samples were then passed through a column holding 20 g of MnO_2-coated acrylic fiber, which strongly binds Ra at the flow rates <2L/min used here. The fibers were then rinsed with Milli-Q, partially dried, and loaded into a Ra Delayed Coincidence Counter (RaDeCC; Scientific Computer Instruments, USA) system purged with He gas. Decay of Ra was counted for 6-10 h to quantify supported plus excess ^{223}Ra and ^{224}Ra content. Following decay of these short-lived isotopes, the fibers will be re-analysed using the RaDeCC to determine the activity of the parent isotopes (^{227}Ac and ^{228}Th), to account for the supported fractions and calculate excess ^{223}Ra and ^{224}Ra. After a suitable period for in-growth from ^{228}Ra (~18 months), fibers will be re-analysed to quantify ^{228}Ra activities as a longer-lived tracer of sedimentary interaction. The primary focus was on Denmark Strait Overflow Water (DSOW), hence the collected samples mainly targeted the bottom waters and sill depth north and south of the Denmark Strait, with additional profiles targeting equivalent waters on the western leg of the expedition. Discrete 1L samples were collected for ^{226}Ra calibration, to verify extraction efficiency on the fibers. These subsamples are indicated in Table 22.

Table 22. List of large-volume water column samples collected for analysis of radium isotopes. Time of sampling is taken as CTD bottom time. Samples designated yes ("y") for ^{226}Ra had 1 L subsamples collected and preserved for ^{226}Ra analysis.

Station	Cast	Depth	Sampler	Volume (L)	Date_time	226Ra
3	C03	2170	UCC	125	21/07/2021 10:24:00	y
3	C03	2160	UCC	126	21/07/2021 10:24:00	
3	C03	1900	UCC	126	21/07/2021 10:24:00	
3	C03	1600	UCC	126	21/07/2021 10:24:00	
3	C02	2115	CTD	139.4	21/07/2021 08:25:00	y
3	C02	2000	CTD	140.4	21/07/2021 08:25:00	
6	C01	2455	CTD	139.4	23/07/2021 01:22:00	y
6	C01	2430	CTD	128.7	23/07/2021 01:22:00	
6	C02	2406	CTD	139.4	23/07/2021 03:35:00	y
6	C02	2300	CTD	128.7	23/07/2021 03:35:00	
6	C04	2200	CTD	128.7	23/07/2021 10:41:00	
6	C04	1900	CTD	127.7	23/07/2021 10:41:00	y
8	C01	2116	UCC	104	24/07/2021 17:34:00	y
8	C01	2089	UCC	105	24/07/2021 17:34:00	
8	C01	1998	UCC	104	24/07/2021 17:34:00	y
8	C01	1900	UCC	105	24/07/2021 17:34:00	
8	C02	1696	CTD	139.4	24/07/2021 19:47:00	y
8	C02	1502	CTD	140.4	24/07/2021 19:47:00	
10	C01	1222	UCC	83	26/07/2021 11:47:00	y
10	C01	1195	UCC	105	26/07/2021 11:47:00	
10	C01	1122	UCC	105	26/07/2021 11:47:00	
10	C01	975	UCC	104	26/07/2021 11:47:00	y
10	C02	715	CTD	140.4	26/07/2021 12:58:00	
10	C02	600	CTD	140.4	26/07/2021 12:58:00	
13	C01	1008	UCC	126	29/07/2021 13:20:00	
13	C01	976	UCC	126	29/07/2021 13:20:00	
13	C01	956	UCC	125	29/07/2021 13:20:00	y

13	C01	912	UCC	125	29/07/2021 13:20:00	y
13	C02	700	CTD	139.4	29/07/2021 14:43:00	y
13	C02	500	CTD	140.4	29/07/2021 14:43:00	
14	C01	603	UCC	140	30/07/2021 04:39:00	y
14	C01	580	UCC	105	30/07/2021 04:39:00	
14	C01	554	UCC	105	30/07/2021 04:39:00	
14	C01	508	UCC	104	30/07/2021 04:39:00	y
14	C02	400	CTD	139.4	30/07/2021 05:38:00	y
14	C02	300	CTD	139.4	30/07/2021 05:38:00	y
16	C01	470	UCC	104	31/07/2021 06:00:00	y
16	C01	444	UCC	105	31/07/2021 06:00:00	
16	C01	420	UCC	105	31/07/2021 06:00:00	
16	C01	370	UCC	104	31/07/2021 06:00:00	y
16	C02	300	CTD	140.4	31/07/2021 06:55:00	
16	C02	200	CTD	139.4	31/07/2021 06:55:00	y
17	C01	805	UCC	125	01/08/2021 02:55:00	y
17	C01	755	UCC	126	01/08/2021 02:55:00	
17	C01	705	UCC	147	01/08/2021 02:55:00	
17	C01	650	UCC	104	01/08/2021 02:55:00	y
17	C02	525	CTD	140.4	01/08/2021 03:46:00	
17	C02	350	CTD	140.4	01/08/2021 03:46:00	
19	C02	952	UCC	125	02/08/2021 08:53:00	y
19	C02	902	UCC	126	02/08/2021 08:53:00	
19	C02	800	UCC	125	02/08/2021 08:53:00	y
19	C02	700	UCC	125	02/08/2021 08:53:00	y
19	C03	600	CTD	0	02/08/2021 09:58:00	y
19	C03	500	CTD	139.4	02/08/2021 09:58:00	y
30	C01	1467	UCC	126	07/08/2021 23:26:00	y
30	C01	1417	UCC	126	07/08/2021 23:26:00	
30	C01	1350	UCC	126	07/08/2021 23:26:00	
30	C01	1225	UCC	126	07/08/2021 23:26:00	y
30	C02	1100	CTD	140.4	08/08/2021 00:46:00	y
30	C02	1000	CTD	140.4	08/08/2021 00:46:00	y
34	C01	1194	UCC	126	09/08/2021 21:00:00	y
34	C01	1144	UCC	126	09/08/2021 21:00:00	
34	C01	1094	UCC	126	09/08/2021 21:00:00	
34	C01	1000	UCC	126	09/08/2021 21:00:00	y
34	C02	925	CTD	140.4	09/08/2021 22:15:00	y
34	C02	750	CTD	140.4	09/08/2021 22:15:00	y
36	C01	973	UCC	126	11/08/2021 01:31:00	y
36	C01	948	UCC	126	11/08/2021 01:31:00	
36	C01	920	UCC	126	11/08/2021 01:31:00	
36	C01	860	UCC	126	11/08/2021 01:31:00	
36	C02	800	CTD	140.4	11/08/2021 02:23:00	y
36	C02	700	CTD	140.4	11/08/2021 02:23:00	y
38	C01	1577	UCC	126	12/08/2021 09:41:00	y
38	C01	1475	UCC	126	12/08/2021 09:41:00	y
38	C01	1400	UCC	126	12/08/2021 09:41:00	
38	C01	1300	UCC	126	12/08/2021 09:41:00	
38	C02	1200	CTD	140.4	12/08/2021 10:57:00	y
38	C02	1000	CTD	140.4	12/08/2021 10:57:00	y

3.7.1.2. SALINITY SAMPLING

When using the CTD, samples were also collected for salinity to calibrate the sensor package starting with station 6. As only two depths were sampled per CTD cast, only two samples were collected per cast, in duplicate starting at station 16. Some stations were missed because it was late and we forgot. Table 23 gives a list of all salinity samples collected and corresponding bottle numbers.

Table23. Salinity samples collected from the CTD, listing Station, Cast, Bottle number and depth.

Salinity bottle	Station	Cast	Bottle (& depth)
289	6	C04	B11 (2200m)
290	6	C04	B12 (2000m)
291	6	C04	B13 (1900m)
292	13	C02	B12 (700m)
293	13	C02	B13 (500m)
294	14	C02	B01 (400m)
295	14	C02	B24 (300m)
296	16	C02	B01 (300m)
297	16	C02	B01 (300m)
289	16	C02	B24 (200m)
299	16	C02	B24 (200m)
300	17	C02	B21 (525m)
301	17	C02	B21 (525m)
302	17	C02	B05 (350m)
303	17	C02	B05 (350m)
304	34	C02	B12 (925m)
305	34	C02	B13 (750m)
306	36	C02	B24 (700m)
307	36	C02	B24 (700m)
308	36	C02	B01 (800m)
309	36	C02	B01 (800m)
310	38	C02	B06 (1200m)
311	38	C02	B06 (1200m)
312	38	C02	B21 (1000m)
168	38	C02	B21 (1000m)

3.7.2. MULTICORER SAMPLING

3.7.2.1. Multicorer deployment

Coring was attempted at 13 stations, with successful core recovery at 10 of these (see Table 24). The multicorer (MUC) was deployed with full weights (~300kg), 10-20m of cable was spooled out after the MUC touched the seafloor (to prevent drag on the cable pulling the MUC along the seafloor), and the MUC was left for 2-3 minutes on the bottom to allow time for the core tubes to penetrate the sediment. At station 14 we reduced the number of core tubes to redistribute the weight and increase pressure, but even with these efforts we were unable to recover any cores at three of the stations, due to strong bottom currents associated with DSOW resulting in rocky or sandy, hard-packed sediments and/or drag. In successful deployments, there were usually 11-12 full core tubes, with incomplete recovery generally due to non-cohesive sediments being lost during unloading from the MUC. The MUC performed very well in this regard relative to other corers on different ships!

Table 24. List of multicorer stations

Stn	Cast	DateTime	Recovery	Notes
6	C05	23/07/2021 12:48	8 good cores, ~10cm long	Muddy
8	C04	25/07/2021 02:19	10 good cores on 2nd attempt, ~15cm	Muddy, gave extra slack to counter the wire angle and prevent drag
10	C04	26/07/2021 16:10	10 good cores on 2nd attempt, ~10cm long	Sticky mud under ~3cm black gravel
12	C03	28/07/2021 01:05	No cores	~1mm of sand recovered, significant wire angle
13	C06	29/07/2021 21:10	No cores	Dusting of coarse sand, again strong bottom currents
14	C05	30/07/2021 08:30	No cores, tried with only 8 tubes loaded	Very strong bottom currents, one bottom closure bent (now fixed)
15	C03	30/07/2021 18:38	9 Good cores, ~10cm	Muddy
15	C04	30/07/2021 19:14	4 more cores	Muddy
16	C05	31/07/2021 11:35	12 good cores, ~40cm	Muddy, colour transition visible
16	C06	31/07/2021 12:32	6 more cores	Muddy
17	C04	01/08/2021 08:20	10 good cores, 20cm	Muddy
21	C02	03/08/2021 11:08	11 short cores on 2nd attempt	Muddy
21	C03	03/08/2021 11:34	4 more good cores, ~10cm	Muddy with sand
30	C04	08/08/2021 05:44	12 good ~20cm cores	Sandy mud, 3 colour layers
36	C05	11/08/2021 07:33	10 good cores, ~15cm	Very sandy, high fraction shell fragments
38	C05	12/08/2021 17:14	No cores	One lump of mud - very dense

3.7.2.1.1 Core-top water

After unloading core tubes, core-top water was siphoned off of cores on deck into acid-cleaned bottles and a 20 L cubitainer. Smaller volumes were preserved for ^{226}Ra analysis, Hg analysis, and subsamples filtered for nutrients (on-board by Sharyn Ossebaar) and dissolved trace metals. The larger ~20 L sample was processed for radium isotopes using Mn-coated fiber as for CTD samples (above).

3.7.2.1.2. Trace metal and nutrient sample collection

Cores at each station were processed for (1) nutrients and (2) trace metals in porewaters. Rhizon samplers (Rhizosphere) which filter the porewater at ~0.18 µm were inserted into the cores at 1cm intervals (or 2cm intervals after the first 10 cm), and samples were collected into syringes after rinsing the Rhizon and syringe with filtrate. 3-4 mL of porewater were subsampled for on-board nutrient analysis (NO_3^-, NO_2^-, NH_4^+), and a further 1.5-2 mL for PO_4^{3-} collected separately and acidifed to release any PO_4^{3-} bound to iron (oxyhydr)oxides. Subsamples of these will be returned to NIOZ for determination of silicic acid concentrations. Where sample volume remained, it was frozen for dissolved organic carbon analysis, which will be performed back in the UK (University of Southampton).

From the trace metal core, the full porewater volume extracted was collected, either in its entirety for dissolved metal analysis; or, at a subset of stations, one third of the volume was filtered through Anotop 25mm 0.02 µm filters fitted to the syringe for soluble iron analysis. In these stations the remaining two-thirds volume was kept for dissolved metal analysis. At station 30, an additional core was also processed using 0.6 µm Rhizon samplers to compare the 0.6 µm fraction to the standard 0.18 µm Rhizon fraction. All trace metal porewaters were acidified with 1 µL/mL of UpA-grade HCl in a laminar flow hood, and sealed with parafilm for transport at room temperature.

Following porewater extraction, the remaining sediment was sectioned at 1 cm (0-10 cm) or 2 cm (>10 cm) intervals, and frozen for archiving.

A third core was processed for porosity and dry bulk weight measurements. At 0-0.5, 0.5-1, 1 cm (over 1-10 cm) and 2 cm (>10 cm deep) intervals, 20 mL was measured using a cut-off syringe and sealed in a container for wet and dry weight. After the first two stations, the stickiness of the sediment made this approach too time consuming, and so half a sediment slice was collected, which will still yield porosity data. The remaining half of each slice was frozen for archiving. All archive samples will be stored at University of Leeds with Dr Will Homoky.

3.7.2.1.3. Radium isotopes in sediment and porewaters

Three to five cores from the multicorer were collected at stations 8, 10, 15, 16, 17, 21, 30 and 36 for radium/thorium disequilibrium analysis. One was used for sediment processing, and the remaining cores for porewater extractions. Porewaters were collected at 1 cm intervals within the cores, using rhizon samplers (Rhizosphere) which filter the porewater at ~0.18 µm, and pooled to obtain the 30-70 mL total volume at each depth interval needed for Ra analysis. Ra was precipitated and filtered onto 74 mm QMA filters. One core was sectioned at the same depths, with six depths from the upper 10 cm used for precipitation of Ra isotopes in the bulk (sediment + porewater) fraction. Sediments were then filtered onto 142 mm GF/F filters and Ra and Th content determined using the RaDeCCs. Full methodology followed (Cai et al., 2012). Below 10cm, at some sites additional depths were sampled (~1 g of sediment, frozen; and porewater from 3 adjacent depths pooled to obtain up to 100 mL, acidified) for collaborator Pinghe Cai (Xiamen University, China) for method development work of ^{226}Ra analysis in sediments.

We have completed two of the required three measurements on the sediments for Ra/Th of some stations onboard. The figures below (Figure 3) show the counting results, although without delay and efficiency calibration. So far, we observe Ra deficit (Stn.08), Ra-Th in equilibrium (Stn.10) and Ra excess (Stn.15) in the sediment, indicating different sediment flux regimes between these three stations. Additional analyses to fully quantify the parent Th isotope will continue in the home laboratory.

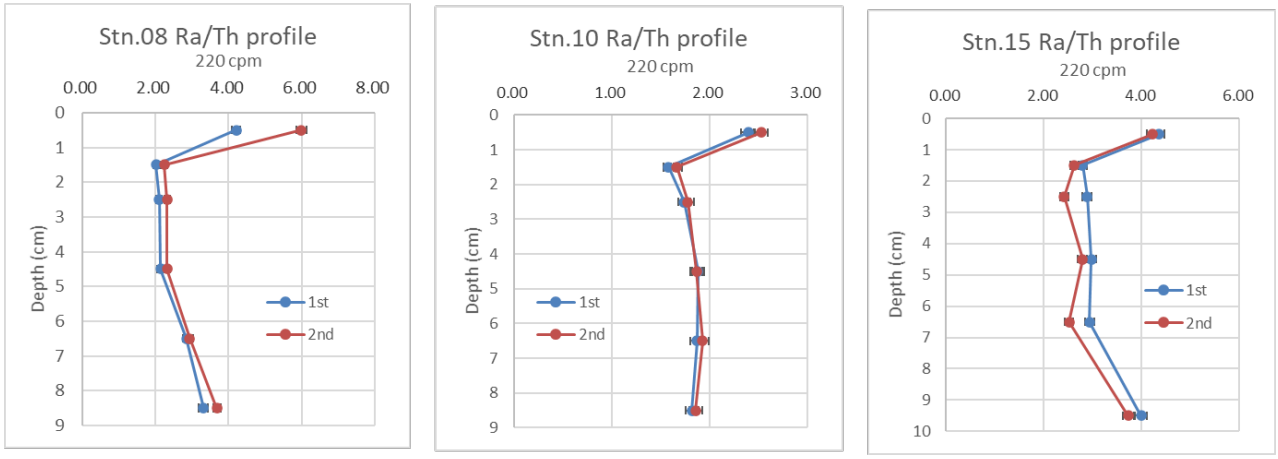


Figure 3. Shipboard results for Ra/Th measurements of the sediments at 3 stations.

The excess 234Th will be analyzed during August-September 2021 in University of Southampton in the UK. ^{234}Th in sediment will be extracted with a hot mixture of concentrated HCl and H_2O_2 solution. After being eluted through an anion exchange resin, ^{234}Th in the elution will be co-precipitated by MnO_2 and determined in low-level Risø β counters.

3.7.2.1.4. Other samples:

Cores were also sampled for additional parameters, including mercury, 234-thorium (see section 3.3.5.) and sediment-water incubations (see section 3.7.3.1). Additional cores where available were sliced at 1 cm intervals for collaborator Laura Hepburn to develop sample preparation methods suitable for Mossbauer spectroscopy (cores will be held by Amber Annett at University of Southampton until analysis). At a subset of stations, PVC core tubes were loaded on the multicorer for collaborator Peter Kraal (NIOZ), and where recovery permitted the whole cores were frozen upright (after removal of overlying water) in the PVC tubes and then sealed with caps for transport back to NIOZ.

All samples parameters collected and processed for from the multicorer are listed in Table 25.

Table 25. Sample types collected from successful MUC deployments are denoted by "§." PW = porewater, Nu = nutrients, Ra/Th = radium-thorium disequilibrium (solid and porewater), Hg = mercury samples (solid + porewater), Mos = Mossbauer spectroscopy, SWINC = sediment-water incubations.

Stn	Cast	PW Nu	Nu solids	PW trace metals	Trace Metals archive	PW soluble trace metals	Whole core	Ra/Th	Hg	Mos	SWINC
6	C05	§	§	§	§		§				
8	C04	§	§	§	§	§		§	§		
10	C04	§	§	§	§		§	§	§	§	§
15	C03	§	§	§	§	§		§	§		
15	C04										§
16	C05	§	§	§	§	§	§	§	§	§	
16	C06										§
17	C04	§	§	§	§	§	§	§	§	§	§
21	C02	§	§	§	§	§		§	§		
21	C03										§
30	C04	§	§	§	§	§	§	§	§	§	
36	C05	§	§	§	§			§	§		

3.7.3.1. SEDIMENT-WATER INCUBATION EXPERIMENT (SWINC) SAMPLING

The impact of shelf sediment mixing and resuspension as a source of dissolved and particulate iron is poorly quantified yet recognised as vital in terms of the circulation of iron and other trace metals between the sediment and the bottom water. Sediment supply from glacial erosion and subsequent resuspension into the water column along the Greenlandic shelf and Arctic basin is recognised as a source of iron to the potentially iron-limited North Atlantic. However, the bioavailability of this iron and the longevity of resuspended dissolved iron within the water column must be understood to determine the supply of bioavailable iron for primary productivity. Dissolved iron (DFe) is recognised as relatively bioavailable, with bioavailability generally increasing with decreasing size fraction. Total iron concentrations in sediments tend to be high, and fluxes between sediment and bottom water at the sediment-water interface of iron can be significant. Following efflux of iron and other trace metals from sediment, the dissolved forms have the potential to be dispersed over long distances. This project, as part of the NERC RaCE:TraX project (Radium in Changing Environments: Tracing Fluxes) forms part of the MetalGate project by elucidating the behaviour of iron and iron-related paramters at the sediment water interface.

3.7.3.1.1. Sediment-water incubation experiment aim

The sediment-water incubation experiments were planned for 5 stations along the western transect of PE474 Metalgate, in order to investigate the behaviour of iron and iron-related parameters during sediment resuspension events within varying environments over the sill, between the Irminger Sea and north along the East Greenland coast.

3.7.3.1.2. Experiment plan:

Sediment-water incubation experiments were performed with water and sediment from station 8, 10, 14/15, 16, and 2 at 21. At station 14, MUC recovery of sediment cores was not possible so bottom water from station 14 was used alongside sediment from station 15 for this incubation. Incubations at stations 14/15 and 21.2 were performed using sediment that had been frozen at -20 deg C and freeze-thawed prior to beginning the incubation. The second incubation performed at 21 (21.2) will be used as a comparison to the incubation performed on fresh coretop sediment (21.1) to determine if there is a measurable deviation in results. This process will inform if results from station 14/15 are also statistically significant.

3.7.3.1.3. Sampling

Bottom water sampling from the UCC

Bottom-depth water is collected from the 24 L UCC bottles (Table 26) following a UCC cast in the CTD clean-room under trace metal-clean room procedures, filtered through 0.2 µm Acropak Pall filters to remove > 0.2 µm biological matter into 3 x 15 L and 1 x 20 L acid-clean carboys. Carboys were rinsed 3 times. Carboys are wrapped in black bin-bags and stored in the cold-temperature lab (4°C) prior to and during the incubation time series.

Table 26. UCC deployment log for SWINC bottom water

Date	Station	Cast	Bottom Depth (m)	Bottle numbers	Depth (m)	Total volume (L)	CTD_bottom Time
24/07/2021	8	C01	2121	1 , 2 ,3, 4	2116	96	17:34
26/07/2021	10	C01	1232	1,2,3,4	1222	96	11:47
30/07/2021	14	C01	612	1,2,3,4	603	96	04:39
31/07/2021	16	C01	476	1,2,3,4	470	96	06:00
03/08/2021	21	C01	503	2,3,4,5,6,7,partial 8	493	144	07:15

Sediment sampling using the Multicorer

Sediment cores from the same site are taken for sediment addition (Table 27). Three carboys had 25 mL of coretop sediment addition, and the 4th (20 L) will be the control (CTRL) carboy with no sediment added. The larger volume was chosen for high volume initial subsampling.

Table 27. MUC deployment log for SWINC sediments

Date/time	Station	Cast	Total cores	Notes
25/07/2021 02:19	8	C04	3	Muddy, gave extra slack to counter the wire angle and prevent drag
26/07/2021 16:10	10	C04	3	Sticky mud under ~3cm black gravel
30/07/2021 18:38	15	C03	3	Muddy
31/07/2021 11:35	16	C05	3	Muddy
03/08/2021 11:08	21	C02	6	Muddy

Incubation subsampling

Prior to sediment addition, subsampling was performed from the control carboy for iron speciation: unfiltered total dissolvable iron (TDFe), dissolved iron (<0.2 µm, DFe), and soluble iron (<0.02 µm, sFe); Nutrients (N, P and Si); Fe-ligands and siderophores; DOC parameters: DOC, DOC spectro-fluorescence, and DOC FT-ICRMS. Following initial subsampling (T_0), the top 0.5 cm of 3 cores was mixed together and 25 mL added to carboys 1, 2 and 3 using an acid-clean falcon tube. This sediment addition marks the start of the 48-hour time series incubation. The carboys were shaken 1 hour prior to subsampling for each following timestep:.T_1, T_4, T_{12}, T_{24}, T_{36}, T_{48}. At all timesteps, subsampling for TDFe, DFe and sFe, and nutrients N, P and Si was performed. All bottles are double-bagged and stored for later acidification with UpA HCl to 2 mL L^{-1}.

Samples taken at each incubation:

- Total dissolvable iron (unfiltered): All timesteps
- Dissolved iron (filtered 0.2 um): All timesteps
- Soluble iron (filtered 0.2 and then 0.02 um): All timesteps
- Nutrients nitrate, nitrite, ammonia, silicic acid, phosphate (filtered 0.2 um): all timesteps
- Ligands (filtered 0.2 um, frozen -20c): T_0, T_1, T_{48}
- Fe-siderophores: T_0, T_{48}
- DOC: T_0, T_{48}
- DOM for spectro-fluorescence analysis: T_0, T_{48}
- DOM for FT-ICRMS analysis: T_0, T_{48}

3.7.3.1.4. Methodology for sample processing

Dissolved and total dissolvable iron

At all timesteps, total dissolvable iron was subsampled in-line from the incubation carboys into trace-metal clean 60 mL sample bottles, rinsed 5 times before filling to the shoulder. Samples were later acidified to 1 mL L^{-1} with UpA HCl. Dissolved iron was sampled similarly into trace-metal clean 125 mL sample bottles, filtered inline through a 0.2 um AcroPak Pall filter. Samples were later acidified to 2 mL L^{-1} with UpA HCl.

Soluble Fe filtration method

To subsample for soluble Fe sequential ultrafiltration was performed using a Gilson Minipuls peristaltic pump, with attached Teflon and Elkay accu-rated grey-grey tubing, and Anatop 25 mm 0.02 µm filters. Pump lines (without filters attached) are cleaned prior to the soluble filtration using 10% Suprapur HCl acid. Pump lines were then left to soak filled with Milli-Q in between sample timesteps. Prior to ultra-filtration, 20 mL of 0.1% Ultrapur (UpA) acid followed by >60 mL Milli-Q water is pumped through the soluble pump lines and attached filters to prime the lines for the samples. Samples are sequentially filtered from the 125 mL DFe samples in a clean bubble within a class-100 filtration hood into 60 mL LDPE Nalgene bottles. 10-20 mL was collected to rinse the bottles with before discarding. Then the pump was run at < 7 rpm (approx. 1 mL/ min) until 60 mL has been filtered through, filling the sFe sample bottles. These samples are double-bagged and acidified to 2 mL L^{-1} with UpA HCl. These samples will be analysed for total iron at the University of Southampton using Flow Injection Analysis following Lohan et al. (2006) or Mass-spectrometry for unfiltered samples.

Ligand sampling

At T_0, T_1 and T_{48}, Fe-ligand samples were taken from all carboys into 250 or 500 mL fluorinated HDPE bottles (filtered 0.2 µm). These samples were immediately frozen at – 20 deg C and will be analysed at the University of Southampton using Competitive Ligand Extraction (voltammetry).

Nutrient sampling

At every timestep, samples for N+P, and Si were taken (~ 3 mL, 0.2 µm filtered) into 5 mL ponyvials. N+P samples were analysed onboard by Sharyn Ossebaar using a macronutrient autoanalyzer. Si samples will be analysed by Sharyn Ossebaar at NIOZ after the cruise.

Siderophore subsampling

At T_0 and T_{48}, > 1 L samples were collected through 0.2 µm for siderophore sample analysis. At least 1 L of 0.2 µm filtered seawater was collected into the 4 L polycarbonate bottles, following general trace metal clean procedures. These bottles were stored in the fridge until time to process. Processing was performed in the laminar flow hood, using purple-white accu-rated tubing and a peristaltic pump. The columns were activated with methanol (approx. 12 mL), rinsed with 0.012 M UpA HCl (approx. 12 mL) and then with Milli-Q (approx. 12 mL) before placing the lines into the polycarbonate sample bottles. Total volume of sample was recorded. Once the total sample was run over the column the column was drained, rinsed with ~ 18 mL Milli-Q, and then the column was double-bagged and frozen at -20 deg C. The rest of the sampling set-up was reused for each sample. These samples will be analysed by Korinna Kunde at the University of Seattle.

DOC

Sampling for collaborator Jon Hawkings (University of Florida) for DOC spectro-fluorescence and DOC FT-ICRMS analysis at T_0 and T_{48}. Samples for DOC were collected into 3 x rinsed glass vials (20 mL), and then acidified with UpA HCl to 1 mL L^{-1}. DOC spectro-fluorescence and FT-ICRMS samples were collected as 250 mL and > 500 mL (filtered 0.2 µm) and frozen at -20 deg C.

4. Data Management

All raw data will be stored on the NIOZ-server for secured back-up and is available to collaborators upon completion of analysis. After suitable quality control, the metal data will be submitted in the final project year to the GEOTRACES International Data Management Centre (www.bodc.ac.uk/geotraces/) and the National Polar Data Centre (http://www.npdc.nl/) which is linked to other international databases. Two years after submission, data will become publicly available (www.bodc.ac.uk/geotraces/data/policy) and will also be incorporated in the next Data Product.

All raw data from the mud team will be stored on the University of Southampton server for secured back-up and is available to collaborators upon completion of analysis. After suitable quality control, the data will be supplied to the British Oceanographic Data Centre (http://www.bodc.ac.uk) which is linked to other international databases. Upon completion, sediment data will be submitted to Pangaea data repository (http://www.pangaea.de). Data will be made public two years after submission.

FRRf and HPLC data will be available to colloborators. After analysis and quality control the data will be stored at a low cost drive of the University of Groningen.

All raw and processed meta-transcriptome and meta-proteome data will be stored on the Bertrand Lab's Dropbox account and will be made available to collaborators until data is made publicly available. Publicly available data will be stored on suitable repositories such as NCBI and PRIDE.

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