7. BIO-GEOCHEMISTRY (BGC)

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Grant-No. AWI_PS122_00

A comprehensive summary of the bio-geochemical measurements during all 5 cruise legs will be published in the *Special Feature: The Multidisciplinary Drifting Observatory for the Study of Arctic Climate (MOSAiC)* of the scientific journal *Elementa: Science of the Anthropocene* (https://online.ucpress.edu/elementa/collection/269/Special-Feature-The-Multidisciplinary-Drifting)

Objectives

In a changing Arctic scenario, the study of climate relevant trace gas (CRTG) fluxes is essential for the improvement of future climate models. Coupling of ice and snow dynamics and the biogeochemical processes that occur during sea-ice freezing and melt cycles trigger transformations of organic matter and elements that control the cycling of CRTG (such as, carbon dioxide (CO_2), methane (CH_4), Nitrous oxide (N_2O), and dimethyl sulfide (DMS)) across the ocean-ice-atmosphere interface. This results in CRTG exchange with both the overlying atmospheric boundary layer and the underlying ocean down to the deep layers. Therefore, the aim for the Leg 4 BGC team was to study the spatial and temporal variability of CRTG fluxes in the Central Arctic Ocean (CAO), associated with their main sources.

Work at sea

We collected seawater and freshwater samples for investigating the following parameters (Table 7.1):

- CH_4 and CO_2 concentrations + isotopic ratios
- Methane oxidation experiments
- totDNA/RNA (16s/18s rRNA gene amplicon sequencing)
- Community Respiration
- Discrete ΔO_2/Ar (Net community production - NCP)
- N_2O
- DMS(P)
- Pigments – HPLC

- PAM measurements
- Neodymium
- $\delta^{18}O$ and Deuterium

***Tab. 7.1**: Seawater sampling events from the Polarstern CTD Rosette, with sampled parameters*

DSHIP n.	Date	^{18}O	N_2O	DMSP	HPLC	CH_4	CH_4 exp	$\Delta O_2/Ar$	Resp	DNA	RNA	Nd
PS122/4_44-67 CTD_SBE9plus_321	6.16.20				X	X	X	x		X	X	
PS122/4_44-184 CTD_SBE9plus_321	6.27.20		X	X	X	X	X	X	x	X	X	
PS122/4_44-187 CTD_SBE9plus_321	6.27.20	X										x
PS122/4_45-9 CTD_SBE9plus_321	6.30.20	X										
PS122/4_45-31 CTD_SBE9plus_321	7.1.20		X	X	X	X	X	x	x	X	X	
PS122/4_45-75 CTD_SBE9plus_321	7.3.20	X										
PS122/4_46-2 CTD_SBE9plus_321	7.6.20		X		X	X	X	X		X	X	
PS122/4_46-60 CTD_SBE9plus_321	7.9.20			X	X			x				
PS122/4_47-60 CTD_SBE9plus_321	7.16.20			X		X	X	X	x	X	X	
PS122/4_47-75 CTD_SBE9plus_321	7.17.20	X										
PS122/4_48-15 CTD_SBE9plus_321	7.21.20		X									
PS122/4_48-62 CTD_SBE9plus_321	7.23.20			X	X	X	X	X	x	X	X	
PS122/4_48-96 CTD_SBE9plus_321	7.24.20	X										
PS122/4_49-10 CTD_SBE9plus_321	7.27.20			X	X							
PS122/4_49-14 CTD_SBE9plus_321	7.28.20											X
PS122/4_49-25 CTD_SBE9plus_321	7.29.20	X	X	X	X	X	X	X	x	X	X	
PS122/4_50-21 CTD_SBE9plus_321	8.5.20		X	X	X	X	X	x		X	X	

Refer to the Expedition Program for principal investigators and their scientific objectives.

- **Work on ice**

We have collected sea ice and snow for the following parameters (Table 7.2):

- Methane concentration profile
- Methane incubation
- DIC
- N_2O
- totDNA/RNA (16s/18s rRNA gene amplicon sequencing)

- DMS(P)
- Pigments – HPLC
- PAM measurements
- Nitrous oxide
- $\delta^{18}O$ & Deuterium
- 2 Cores to store

***Tab. 7.2**: Ice cores sampling events from FYI and SYI, with sampled parameters*

Core	Date	Location	DSHIP n.	^{18}O	N_2O	DMSP	HPLC	CH_4 (Meth Ox)	CH_4 exp	DNA	RNA
20200613_FYI_bgc1	6.13.20	Transit Ice Station 1	PS122/4_44-42					x			
20200613_FYI_bgc2dms	6.13.20	Transit Ice Station 1	PS122/4_44-42				x				x
20200613_FYI_salo18	6.13.20	Transit Ice Station 2	PS122/4_44-42	x							
20200622_FYI_salo18	6.22.20	FYI, "Dark Site"	PS122/4_44-134 SI_corer_9cm	x							
20200622_FYI_MethOx	6.22.20	FYI, "Dark Site"	PS122/4_44-134 SI_corer_9cm						x	x	x
20200622_FYI_DIC	6.22.20	FYI, "Dark Site"	PS122/4_44-134 SI_corer_9cm		x						
20200622_FYI_ECO POOLED CORES	6.22.20	FYI, "Dark Site"	PS122/4_44-134 SI_corer_9cm			x	x				
20200630_SYI_DMS(P)	6.30.20	new SYI, near Alli's Ridge	PS122/4_45-29 SI_corer_9cm			x	x				
20200630_SYI_MethOx	6.30.20	new SYI, near Alli's Ridge	PS122/4_45-29 SI_corer_9cm					x			x
20200630_SYI_DIC	6.30.20	new SYI, near Alli's Ridge	PS122/4_45-29 SI_corer_9cm		x						
20200630_SYI_salo18	6.30.20	new SYI, near Alli's Ridge	PS122/4_45-29 SI_corer_9cm	x							
20200706_FYI_salo18	7.06.20	FYI, "Dark Site"	PS122/4_46-18 SI_corer_9cm	x							

20200706_FYI_ECO POOLED CORES	7.06.20	FYI, "Dark Site"	PS122/4_46-18 SI_corer_9cm			x	x				
20200706_FYI_DIC	7.06.20	FYI, "Dark Site"	PS122/4_46-18 SI_corer_9cm		x						
20200706_FYI_MethOx	7.06.20	FYI, "Dark Site"	PS122/4_46-18 SI_corer_9cm						x	x	x
20200706_SYI_salo18	7.06.20	new SYI, near Alli's Ridge	PS122/4_46-20 SI_corer_9cm	x							
20200706_SYI_DIC	7.06.20	new SYI, near Alli's Ridge	PS122/4_46-20 SI_corer_9cm		x						
20200706_SYI_ECO POOLED CORES	7.06.20	new SYI, near Alli's Ridge	PS122/4_46-20 SI_corer_9cm			x	x				
20200711_RS_24Hr_MethOx	7.11.20	Remote Sensing	PS122/4_46-100 SI_corer_9cm					x	x		
20200711_RS_24Hr_SalO18	7.11.20	Remote Sensing	PS122/4_46-100 SI_corer_9cm	x							
20200713_FYI_ECO POOLED CORES	7.13.20	FYI, "Dark Site"	PS122/4_47-16 SI_corer_9cm			x	x				
20200713_FYI_SalO18	7.13.20	FYI, "Dark Site"	PS122/4_47-16 SI_corer_9cm	x							
20200713_FYI_DIC	7.13.20	FYI, "Dark Site"	PS122/4_47-16 SI_corer_9cm		x						
20200713_SYI_ECO POOLED CORES	7.13.20	new SYI, near Alli's Ridge	PS122/4_47-18 SI_corer_9cm				x				
20200713_SYI_SalO18	7.13.20	new SYI, near Alli's Ridge	PS122/4_47-18 SI_corer_9cm	x							
20200713_SYI_DIC	7.13.20	new SYI, near Alli's Ridge	PS122/4_47-18 SI_corer_9cm		x						
20200713_SYI_MethOx	7.13.20	new SYI, near Alli's Ridge	PS122/4_47-18 SI_corer_9cm						x	x	x
20200718_MeltpondB_DO18	7.18.20	meltpond b, near aft of ship	PS122/4_47-137	x							

			SI_corer_9cm								
20200718_MeltpondB_MethOx	7.18.20	meltpond b, near aft of ship	PS122/4_47-137 SI_corer_9cm						x	x	x
2020020_FYI_SalO18	7.20.20	FYI, "Dark Site"	PS122/4_48-23 SI_corer_9cm	x							
20200720_FYI_ECO POOLED CORES	7.20.20	FYI, "Dark Site"	PS122/4_48-23 SI_corer_9cm				x				
20200720_FYI_DIC	7.20.20	FYI, "Dark Site"	PS122/4_48-23 SI_corer_9cm		x						
20200720_SYI_ECO POOLED CORES	7.20.20	new SYI, near Alli's Ridge	PS122/4_48-25 SI_corer_9cm				x				
20200720_SYI_SalO18	7.20.20	new SYI, near Alli's Ridge	PS122/4_48-25 SI_corer_9cm	x							
20200720_SYI_DIC	7.20.20	new SYI, near Alli's Ridge	PS122/4_48-25 SI_corer_9cm		x						
20200720_FYI_MethOx	7.20.20	FYI, "Dark Site"	PS122/4_48-23 SI_corer_9cm						x	x	x
20200729_FYI_ECO POOLED CORES	7.29.20	FYI, "Dark Site"	PS122/4_49-34 SI_corer_9cm			x	x				
20200729_FYI_SalO18	7.29.20	FYI, "Dark Site"	PS122/4_49-34 SI_corer_9cm	x							
20200729_FYI_DIC	7.29.20	FYI, "Dark Site"	PS122/4_49-34 SI_corer_9cm		x						

As part of the trace gas ice coring program, the BGC team deployed CO_2 and CH_4 gas flux chambers at multiple sites. Due to the onset of ice melt, the path to the coring site became wet and treacherous and we couldn't deploy the chamber very often. The scientific background and the objectives of the project are stated in the Leg 1 Cruise Report. The chamber was deployed at the locations reported in Table 7.3.

***Tab. 7.3**: Nomura/Delille flux chamber deployment activities*

Date Collected	Snow vs. Ice	DSHIP n.	Related to coring event/snow pit:
06.22.2020	Ice	PS122/4_44-133 gasflux-ice-chamber	PS122/4_44-134 SI_corer_9cm
07.08.2020	Snow	PS122/4_46-55 gasflux-ice-chamber	PS122/4_46-48 Snowpit D $RS5$, PS122/4_46-31 Snowpit B $RS5$

07.10.2020-07.11.2020	Snow	PS122/4_46-155 gasflux-ice-chamber	PS122/4_46-100 SI_corer_9cm, PS122/4_46-135 Snowpit B $RS5$, PS122/4_46-110 Snowpit B $RS5$, PS122/4_46-107 Snowpit B $RS5$, PS122/4_46-105 Snowpit B $RS5$
07.18.2020	ice	PS122/4_47-120 gasflux-ice-chamber	yes, PS122/4_47-137 SI_corer_9cm

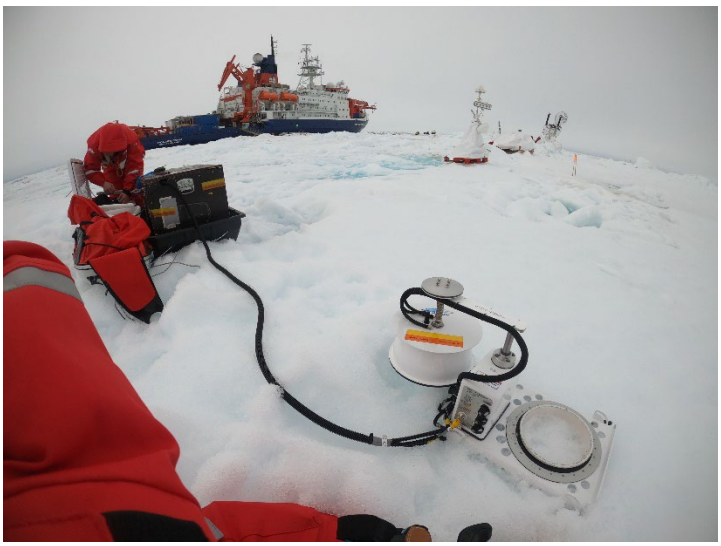

***Fig. 7.1**: Nomura/Delille flux chamber deployment (photo: Emelia Chamberlain)*

- **Work in the atmosphere**

We measured continuous and discrete outside air measurements and ran airborne activities, weather permitting. The scientific background and the objectives of the project are stated in the Chapter 7.7.

- **Crosscutting activities**

During Leg 4, we developed several crosscutting activities with the teams OCEAN, ECO, ICE, ATMOS (see Table 7.4). The scientific background and the objectives of such activities are stated in the Chapter 7.1.

***Tab. 7.4**: Crosscutting activities*

DSHIP n.	Date	^{18}O	N_2O	DMSP	PAM	HPLC	CH_4	CH_4 exp	NCP	Resp	DNA	RNA	DNA (S)	FRRf	Nd	B12
PS122/4_44-118 BUCKET_PS	6.14				x	x					x					
PS122/4_44-234 hand pump	6.27			PvsI experiment, B12 experiment									x			x
PS122/4_45-120 water_probe	7.01				x									x		

PS122/4_46-160 hand pump	7.10			PvsI experiment												
PS122/4_46-161 water_probe	7.11			x	x		x				x	x				
PS122/4_46-163 hand pump	7.11				x	x								x		
PS122/4_46-164 hand pump	7.11				x	x								x		
PS122/4_46-165 hand pump	7.11				x	x								x		
PS122/4_46-166 hand pump	7.11				x	x								x		
PS122/4_46-167 hand pump	7.11				x	x								x		
PS122/4_46-168 water_sampler	7.10						x	x			x	x				
PS122/4_46-220 hand_pump	7.10										x					
PS122/4_46-169 water_sampler	7.11						x	x	x		x	x				
PS122/4_46-170 water_sampler	7.11								x		x	x				
PS122/4_46-171 water_sampler	7.11						x	x	x	x	x	x				
PS122/4_47-20 falcon_tube	7.14			x	x									x		
PS122/4_47-145 peristaltic_pump	7.17			x	x		x				x			x		
PS122/4_47-146 peristaltic_pump	7.17			x	x		x				x			x		
PS122/4_47-144 peristaltic_pump	7.18	x		x	x	x	x				x				x	
PS122/4_48-9 BUCKET_PS	7.20	x														
PS122/4_48-28 BUCKET_PS	7.21	x														

PS122/4_48-123 hand pump	7.21			PvsI experiment, B12 experiment									x			x
PS122/4_48-111 peristaltic_pump	7.22	x		x	x		x				x					
PS122/4_48-112 peristaltic_pump	7.22	x		x	x		x				x					
PS122/4_48-113 peristaltic_pump	7.22	x		x	x		x				x					
PS122/4_49-77 water_probe	7.28	x		x	x						x					

7.1 CROSSCUTTING ACTIVITIES

7.1.1 Diurnal cycle

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Background and objectives
A large fraction of marine methane migrating into the atmosphere is produced in high-sulfate, fully oxygenated surface waters characterized by methane concentrations above atmospheric equilibrium values, a phenomenon is called "marine methane paradox" (Kiene et al., 1991, Reeburgh et al., 2007, Repeta et al., 2016). To discriminate the forcing triggering this phenomenon in melt-water environments, we designed an 8h coupled investigation of: methane concentration ([CH_4]), CH_4 potential microbial oxidation, microbial community structure, dimetylsulfoniopropionate ($DMSP_t$) and particle fluxes.

Field work
Collaboration with the team ECO (Jessie Gardner, UiT). The sampling site was characterized by first-year ice (FYI). The sediment trap was deployed at 12 pm on 10 July and was exchanged every 8 hours (see HAVOC, ECO). It was retrieved on 11 July at 12pm. For each exchange of the trap cylinders, we collected water samples from two depths, surface (underneath the ice) and 5m (sediment trap depth).

Device operation number	Date	CH4	CH4 exp	NCP	Respiration	DNA	RNA	DMSP
PS122/4_46-168 water_sampler	7.10	x	x	x		x	x	x
PS122/4_46-220 hand_pump	7.10					x		
PS122/4_46-169 water_sampler	7.11	x	x	x		x	x	

PS122/4_46-170 water_sampler	7.11			x		x	x	
PS122/4_46-171 water_sampler	7.11	x	x	x	x	x	x	

Preliminary results
Further analysis needed.

References

Kiene, R. P. Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes (ASM, 1991).

Reeburgh,W. S. Oceanic methane biogeochemistry. Chem. Rev. 107, 486-513 (2007).

Repeta, D.J, Ferrón, S, Sosa, O.A., Johnson, C.G., Repeta, L.D., Acker, M., DeLong E.F. and Karl, D.M. (2016). Marine methane paradox explained by bacterial degradation of dissolved organic matter. Nature Geosciences. Vol. 9, 884-887.

7.1.2 Leads

See Chapter 8.4 - Leads

Fig. 7.1.1: The BGC team, together with teams ICE, OCEAN, ATMOS, DATA and ECO, sampling at the leads (photos: Aikaterini Tavri, Alessandra D'Angelo, Maddie Smith)

7.1.3 Melt ponds

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Background and objectives
The transition from permanent to seasonal sea ice in the Arctic Ocean triggers a cascading effect on air sea gas exchange (Loose et al., 2011; Parmentier et al, 2014). Vast surface areas of the Arctic Ocean are exposed to solar radiation and wind stress during the summer which were previously below permanent ice cover (Meier, 2014), and the remaining perennial sea ice decreases in age (Maslanik et al., 2011) and thickness (Kwok and Rothrock, 2009). Therefore, it is essential to capture meltwater features for a better understanding of their effect on CRTG fluxes. The aim of this activity was to assess the importance of meltwater formation on the CO_2, CH_4, and DMS cycles (climate-gases), in addition to the characterization of the methane-associated microbial community.

Samples were collected:

- to investigate pigment occurrence associated to DMSP production
- to produce DMS quantitative info
- to estimate CO_2 and CH_4 concentrations and isotopic signatures
- to analyze microbial taxonomic composition
- to produce information about sources of freshwater, through the $\delta^{18}O$ analysis
- to investigate Nd occurrence
- to measure CO_2 and CH_4 fluxes in proximity of the melt water source

Fieldwork

Collaboration with the ICE and ECO Teams (Maddie Smith, Giulia Castellani, Felix Linhardt, Melinda Webster, Allison Fong, Amy McFarlane).

Plan of sampling:

a. Before draining:

- Nomura/Delille flux chamber deployment
- ~ 500 ml per depth, for Nd isotopes
- ~ 300 ml per depth, for $\delta^{18}O$
- ~ 800 ml per depth, for CO_2 and CH_4 concentrations and isotopic ratios
- ~ 1L per depth, for DNA - accordingly with CO_2 and CH_4 sampling
- ~ 300 ml per depth, for DMSP - accordingly with CO_2 and CH_4 sampling

b. Coring:

- 1 core for CH_4 and CO_2 profile + incubation of the bottom core (10 cm)
- 1 core for Sal/$\delta^{18}O$
- 1 core for DIC/TA

***Fig. 7.1.2**: „Distructive meltpond“ BGC, ICE, ECO joint activity (photo: Alessandra D'Angelo)*

Preliminary results

Further analysis needed.

References

Kwok, R., and Rothrock, D.A. (2009). Decline in Arctic sea ice thickness from submarine and ICESat records: 1958-2008. Geophys. Res. Lett. 36, 1–5.

Loose, B., Schlosser, P., Perovich, D., Ringelberg, D., Ho, D.T., Takahashi, T., Richter-Menge, J., Reynolds, C.M., Mcgillis, W.R., and Tison, J.-L. (2011). Gas diffusion through columnar laboratory sea ice: implications for mixed-layer ventilation of CO2 in the seasonal ice zone. Tellus B 63, 23–39.

Maslanik, J., Stroeve, J., Fowler, C., and Emery, W. (2011). Distribution and trends in Arctic sea ice age through spring 2011. Geophys. Res. Lett. 38, 2–7.

Meier, W. (2014). Arctic sea ice in transformation: A review of recent observed changes and impacts on biology and human activity.

Parmentier, F.-J.W., Christensen, T.R., Sørensen, L.L., Rysgaard, S., McGuire, a. D., Miller, P. a., and Walker, D. a. (2013). The impact of lower sea-ice extent on Arctic greenhouse-gas exchange. Nat. Clim. Change 3, 195–202.

7.2 QUANTIFYING MICROBIAL CONTROLS ON THE ANNUAL CYCLE OF METHANE AND OXYGEN WITHIN THE ULTRA-OLIGOTROPHIC CENTRAL ARCTIC (JOINT WITH ECO)

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Background and objectives

The ocean is a source (Damm et al., 2010; Karl et al., 2008) and biological sink (Reeburgh, 2007) of methane (CH_4); together with carbon dioxide (CO_2) these greenhouse gases (GHG) are keystone compounds in the Arctic climate system. CH_4 and oxygen (O_2) fluxes are closely tied to biological and physical drivers, such as phytoplankton blooms (Meskhidze & Nenes, 2006; Repeta et al., 2016) and, in the Arctic, sea ice cover (Yokouchi et al., 2013). Therefore, this project aims to identify the primary features triggering the production and consumption of CH_4 and CO_2 in an effort to establish the metabolic balance of O_2 and CH_4 in the oligotrophic Central Arctic. The microbial oxidation rate of CH_4 will be investigated to assess the potential for microbial oxidation/production in this region. Such microbial activities control the migration of these GHG into the atmosphere, highlighting the importance of such investigations at the ice-water interface and in association with data from the water column underneath. During Leg 4, we measured the rates of net community production (NCP), methane oxidation and production, and bacterial respiration (BR) in seawater, from the air-ice interface to deep bottom water. These measurements, together with the ones from the previous legs, will be used to functionally constrain metabolic processes in two regional models of the Arctic and to produce model-based budgets of methane and net community production for the central Arctic.

The objectives for Leg 4 were:

- Make weekly discrete profiles of seawater CH_4, CO_2 concentration, and stable isotope ratios using Cavity Ring Down Spectrometry (CRDS) coupled with the Small Sampler Inlet Measurement (SSIM)
- Conduct continuous and weekly sampling for microbial community structure (16S/18S rRNA gene analysis)
- Make discrete bi-weekly profiles of these same variables within sea ice cores
- Conduct bi-weekly measurements of BR (bacterial and phytoplankton abundance, BP, and PP will be provided for these same samples by ECO core measurements)
- Experimentally determine methane oxidation and methane production and evaluate the microbial community structure, gene expression, and oxidation potential using elevated methane in select incubations

- These data will then be used to identify patterns of expression for genes involved in methanotrophy by using metatranscriptomics to identify genes differentially expressed under high methane conditions.
- Through modeling, we will identify the microbial taxa and physicochemical conditions that best predict the key ecosystem functions of methane production, methane oxidation, BR, CR, BP, NCP, nitrification, and DMS production

Field work

The following tables (7.2.1 and 7.2.2) summarize the samples collected during Leg 4 09/06/2020-05/08/2020.

***Tab. 7.2.1**. Core project sample collection*

Sample type	Frequency	Purpose	Total # of samples
Underway seawater	daily	DNA filtration	62
CTD seawater at 6-13 horizons (At least: PSW, chlmax, 100 m, T_{max}, 500 m, 1500 m, O_2 min, 10 m above bottom)	weekly	DNA filtration	88
CTD seawater at 3-4 horizons (PSW, Chl_{max}, T_{max}, 10 m above bottom)	weekly	RNA filtration	15
CTD seawater at ~8 horizons (PSW, chlmax, 100 m, T_{max}, 500 m, 1500 m, O_2 min, 10 m above bottom)	weekly	ambient CH_4	56
CTD seawater at 3-4 horizons (Duplicates: PSW, Chl_{max}, T_{max}, 10 m above bottom)	weekly	CH_4 incubations	56
CTD seawater at 2-3 horizons (Triplicates: PSW, Chl_{max}, and T_{max})	weekly	respiration (DO)	36
Ice core (bottom 15 cm at FYI site)	Bi-weekly	ambient CH_4 / Incubation	3
Ice core (bottom 15 cm at FYI site)	Bi-weekly	DNA filtration	3
Ice core (bottom 15 cm at FYI site)	Bi-weekly	RNA filtration	3
Ice core (top and bottom 15 cm at SYI site)	Bi-weekly	ambient CH_4 / Incubation	4
Ice core (top and bottom 15 cm at SYI site)	Bi-weekly	DNA filtration	3
Ice core (top and bottom 15 cm at SYI site)	Bi-weekly	RNA filtration	4
TOTAL:			278

**PSW = Polar surface water*

***Tab. 7.2.2**: Opportunistic sample collection to capture unique melt features during the summer season and cross-cutting multi-team activities*

Sample type	Frequency	Purpose	Total # of samples
Meltpond Water (surface)	Opportunistic	ambient CH_4	2
Meltpond Water (surface)	Opportunistic	DNA filtration	3
Meltpond Ice (10 cm sections)	Opportunistic	ambient CH_4	1 core
Meltpond Ice (Bottom 10 cm)	Opportunistic	CH_4 incubations	2
Meltpond Ice (Bottom 10 cm)	Opportunistic	DNA filtration	1
Meltpond Ice (Bottom 10 cm)	Opportunistic	RNA filtration	1
SYI Ice, Remote Sensing Site (5 cm sections)	Opportunistic	Ambient CH_4	1 core
SYI Ice, Remote Sensing Site (Bottom 10 cm)	Opportunistic	CH_4 incubations	2
Seawater from the surface/ice interface collected from FYI sediment trap site collected at multiple time points during opportunistic 24 hr diurnal cycle study	Opportunistic	ambient CH_4	4
Seawater from the surface/ice interface collected from FYI sediment trap site collected at multiple time points during opportunistic 24 hr diurnal cycle study	Opportunistic	CH_4 incubations	4
Seawater from the surface/ice interface collected from FYI sediment trap site collected at multiple time points during opportunistic 24 hr diurnal cycle study	Opportunistic	DNA filtration	6
Seawater from the surface/ice interface collected from FYI sediment trap site collected at multiple time points during opportunistic 24 hr diurnal cycle study	Opportunistic	RNA filtration	6
Seawater from the surface/ice interface collected from FYI sediment trap site collected at multiple time points during opportunistic 24 hr diurnal cycle study	Opportunistic	Respiration (DO)	4
Lead water at 3 horizons (underlying seawater, brackish biomass laden layer, fresh-water lens)	Opportunistic	CH_4 incubations	3
Lead water at 3 horizons (underlying seawater, brackish biomass laden layer, fresh-water lens)	Opportunistic	ambient CH_4	17
Lead water at 3 horizons (underlying seawater, brackish biomass laden layer, fresh-water lens)	Opportunistic	DNA filtration	18
Lead water at 3 horizons (underlying seawater, brackish biomass laden layer, fresh-water lens)	Opportunistic	RNA filtration	3
Biomass bloom beneath freshwater lens (from lead or pumped directly from under ice)	Opportunistic	DNA filtration	2

Biomass bloom beneath freshwater lens (from lead or pumped directly from under ice)	Opportunistic	Potential culture stock, preserved in glycerol/enriched sample stored at 0ºC	2
TOTAL:			82

Lab work

DNA and RNA filtration required filtering 500 mL – 1000 mL of seawater from either the underway system or CTD rosette and approximately 250 – 500 mL of direct sea ice melt from a ~15-cm ice core segment. Filter volumes dependent on biomass present and melted ice volume available. 1 mL of DNA/RNA shield buffer solution added to samples tagged for potential metatranscriptomic analysis. Filters stored at –80°C for future extraction and 16s/18s rRNA gene amplicon sequencing (analysis not conducted on board).

The new methods established on Leg 3 for respiration experiments using the handheld PyroScience FireSting GO2 and dissolved oxygen sensor spots is still under development. Discrepancies between the *in situ* (-1.7ºC) and F-deck incubator (1ºC) temperatures lead to supersaturation in all shallow surface samples. Following the iterative bubble removal protocol tested on Leg 3 (see chapter 6 of the PS122.3 cruise report), several respiration experiments were conducted with seawater from the CTD rosette on Leg 4 along with one light/dark incubation with direct under-ice seawater to calculate potential NCP. Preliminary results were promising, but other methods for mitigating solubility changes during incubation will continue to be explored by the Leg 5 personnel.

In-situ seawater, sea ice and freshwater [CH_4] and [CO_2] with stable isotope ratios were analyzed by the Picarro CRDS, coupled with the SSIM. To assess the microbial potential for methane oxidation, duplicate samples were incubated for N measurement times. The samples were collected in muti-layer foil bags (capacity 1000 mL and 3000mL, Restek, Bellfonte, Pennsylvania, U.S.A.) and processed with hydrocarbon-free air (100 mL for experimental bags and 50 mL for the discrete samples). The experimental samples were spiked with 12 mL of methane standard „1005“, 500ppmv and -70 permil. The samples were stored in a water bath at 1°C until analysis. The volume analyzed for the discrete samples was 10mL, while the volume injected into the analyzer for the incubation bags was 2 mL. The measurements were run for each sample until $^{12}CH_4$ concentration reached a standard deviation < 5%.

The following Table 7.2.3 lists all methane incubation samples and associated device operations collected on Leg 4.

***Tab. 7.2.3**: Methane incubation samples*

Bag Num	Sample ID	Date collection	Device operation
109	20200616_PS_23_A	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324
110	20200616_PS_23_B	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324
111	20200616_PS_8_A	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324
112	20200616_PS_8_B	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324
113	20200616_PS_16_A	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324

114	20200616_PS_16_B	2020-06-16	PS122/4_44_67 CTD_SBE9plus-324
IC001	20200622_FYI_A	2020-06-23	PS122/4_44_134 SI ice corer 9cm
IC002	20200622_FYI_B	2020-06-23	PS122/4_44_134 SI ice corer 9cm
115	20200627_PS_N2_A	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
116	20200627_PS_N2_B	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
117	20200627_PS_N8_A	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
118	20200627_PS_N8_B	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
119	20200627_PS_N17_A	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
120	20200627_PS_N17_B	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
121	20200627_PS_N24_A	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
122	20200627_PS_N24_B	2020-06-27	PS122/4_44_184 CTD_SBE9plus-324
123	20200701_PS_N8_A	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
124	20200701_PS_N8_B	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
125	20200701_PS_N2_A	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
126	20200701_PS_N2_B	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
127	20200701_PS_N17_A	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
128	20200701_PS_N17_B	2020-07-01	PS122/4_45_31 CTD_SBE9plus-324
IC004	20200630_SYI_bottom	2020-07-01	PS122/4_45_29 SI ice corer 9cm
IC005	20200630_SYI_top	2020-07-01	PS122/4_45_29 SI ice corer 9cm
129	20200706_PS_N8_A	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
130	20200706_PS_N8_B	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
131	20200706_PS_N14_A	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
132	20200706_PS_N14_B	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
133	20200706_PS_N24_A	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
134	20200706_PS_N24_B	2020-07-06	PS122/4_46_60 CTD_SBE9plus-324
135	20200710_Oreoh24_below	2020-07-11	PS122/4_46-161 water_probe
136	20200710_Oreoh24_surface	2020-07-11	PS122/4_46-161 water_probe
137	20200710_Oreoh24_creamy	2020-07-11	PS122/4_46-161 water_probe
138	20200711_traps24_surface	2020-07-11	PS122/4_46-161 water_probe
139	20200711_traps24_hole1m	2020-07-11	PS122/4_46-161 water_probe
145	20200711_traps24_5m	2020-07-12	PS122/4_46-168 water_sampler
146	20200711_traps24_surface	2020-07-12	PS122/4_46-168 water_sampler
140	20200711_traps24_5m	2020-07-13	PS122/4_46-169 water_sampler

141	20200711_traps24_5m	2020-07-13	PS122/4_46-169 water_sampler
142	20200711_Oreoh24_surface	2020-07-12	PS122/4_46-161 water_probe
143	20200711_Oreoh24_creamy	2020-07-12	PS122/4_46-161 water_probe
144	20200711_Oreoh24_below	2020-07-12	PS122/4_46-161 water_probe
IC006	20200713_SYI_top15cm	2020-07-15	PS122/4_47-18 SI_corer_9cm
IC007	20200713_SYI_bottom15cm	2020-07-15	PS122/4_47-18 SI_corer_9cm
IC009	20200711_SYI_RS_bottom0-5cm	2020-07-15	PS122/4_46-100 SI_corer_9cm
IC010	20200711_SYI_RS_bottom5-10cm	2020-07-15	PS122/4_46-100 SI_corer_9cm
IC003	20200706_FYI_bottom15cm	2020-07-07	PS122/4_48-23 SI_corer_9cm
147	20200716_PS_N11_A	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
148	20200716_PS_N11_B	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
149	20200716_PS_N2_A	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
150	20200716_PS_N2_B	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
151	20200716_PS_N18_A	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
152	20200716_PS_N18_B	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
153	20200716_PS_N23_A	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
154	20200716_PS_N23_B	2020-07-16	PS122/4_47_60 CTD_SBE9plus-324
155	20200723_PS_N2_A	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
156	20200723_PS_N2_B	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
157	20200723_PS_N10_A	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
158	20200723_PS_N10_B	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
159	20200723_PS_N23_A	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
160	20200723_PS_N23_B	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
161	20200723_PS_N18_A	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
162	20200723_PS_N18_B	2020-07-23	PS122/4_48_62 CTD_SBE9plus-324
163	20200805_PS_N2_A	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
164	20200805_PS_N2_B	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
165	20200729_PS_N10_A	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321
166	20200729_PS_N10_B	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321
167	20200729_PS_N17_A	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321
168	20200729_PS_N17_B	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321
169	20200729_PS_N23_A	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321
170	20200729_PS_N23_B	2020-07-29	PS122/4_49-25 CTD_SBE9plus_321

171	20200805_PS_N16_A	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
172	20200805_PS_N16_B	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
173	20200805_PS_N23_A	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
174	20200805_PS_N23_B	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
175	20200805_PS_N13_A	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325
176	20200805_PS_N13_B	2020-08-05	PS122/4_50_21 CTD_SBE9plus-325

Additionally, biological oxygen supersaturation ($\Delta(O_2/Ar)$) was measured continuously by a Membrane Inlet Mass Spectrometeter (MIMS) provided by Sebastian Rokitta (AWI) as part of the ECO core sampling program (see section X for details). In addition to continuous operation, discrete bottle samples from CTD casts (see Table 7.2.4) were analyzed. From these measurements, we expect to develop a stronger understanding of how net community production (based on high-resolution O_2/Ar measurements) relate to community structure, sea ice and light conditions, and nutrient supply, as well as the variability in physical and biological controls of CO_2 and O_2. To capture how NCP is related to microbial community structure in time and space, discrete bottle measurements were always paired with samples collected for DNA filtration. During Leg 4, the MIMS was operated onboard by Emelia Chamberlain.

***Tab. 7.2.4**: Device operations from which discrete seawater samples for O_2/Ar were taken and analyzed by MIMS*

Date	Device operation	Device	Total # of bottles
2020-06-16	PS122/4_44-67	CTD_SBE9plus_321	5
2020-06-27	PS122/4_44-184	CTD_SBE9plus_321	6
2020-07-01	PS122/4_45-31	CTD_SBE9plus_321	6
2020-07-06	PS122/4_46-2	CTD_SBE9plus_321	6
2020-07-09	PS122/4_46-60	CTD_SBE9plus_321	6
2020-07-11	PS122/4_46-169	water_sampler	2
2020-07-11	PS122/4_46-170	water_sampler	2
2020-07-11	PS122/4_46-171	water_sampler	2
2020-07-16	PS122/4_47-60	CTD_SBE9plus_321	10
2020-07-23	PS122/4_48-62	CTD_SBE9plus_321	10
2020-07-29	PS122/4_49-25	CTD_SBE9plus_321	10
2020-08-05	PS122/4_50-21	CTD_SBE9plus_321	11
TOTAL:			76

***Fig. 7.2.1**: Measurement of discrete seawater samples for O_2/Ar, through the MIMS (photo: Emelia Chamberlain)*

Preliminary results

Preliminary results were simultaneously plotted to observe the trend of the incubation samples overtime (Fig. 7.2.2). Once reached a clear trend of oxidation, production or non-activity, the samples were filtered for future DNA and RNA analysis.

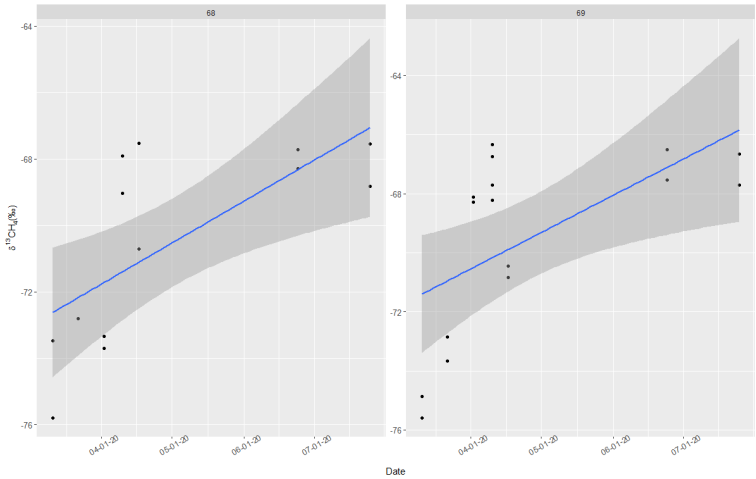

***Fig. 7.2.2**: Isotopic ratio of samples 68 and 69 (duplicate) over time. The black points show the measurements, while the blue line is the linear regression between the values. The trend of the isotopic signature is increasing over time, indicating a potential oxidation of $^{12}CH_4$ over the incubation period.*

Results and metadata from such measurements are provided on the MCS. All methane incubation bags were preserved for further incubation experimentation during subsequent legs.

The in-situ profiles of the $\delta^{13}CH_4$ (Fig. 7.2.3), [CH_4] and [CO_2] will provide quantitative information of the occurrence of these gases along the water column.

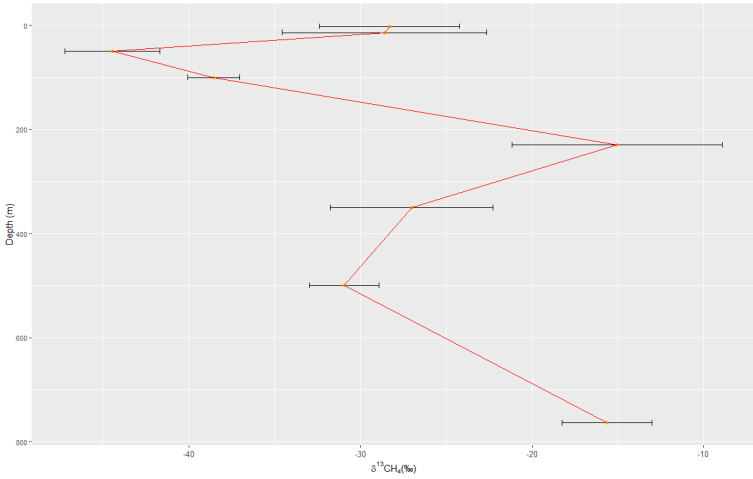

***Fig. 7.2.3**: Example of $\delta^{13}CH_4$ profile along the water column, from 2 to 780m.*

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). Data are stored on the MCS and will be stored at the Arctic Data Centre, following the agreement between NSF and the MOSAiC Project lead. DOIs will be communicated to PANGAEA for later access via the future MOSAiC Data Portal. Exceptions will to be documented in written agreements between the data provider and the MOSAiC Project Board and data manager.

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7.3 ORGANIC SULFUR CYCLING IN ARTIC SEA ICE AND SEAWATER

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Objectives

The aim of the project is to carry out a detailed analysis of the organosulfur cycle and its microbial players in the Arctic Ocean. The work combines measurements of concentrations of dimethylsulfoniopropionate (DMSP), dimethylsulfide (DMS), dimethylsulfoxide (DMSO), transformation rates of these compounds and identification of the microorganisms (microalgae, bacteria, archaea) driving these processes using molecular biological approaches. This suite of organic sulfur compounds plays a significant role in marine and sea ice environments, due to DMSP having varied physiological roles in phytoplankton, ice algae and bacteria (Stefels et al 2007), including osmoregulation, cryoprotection and antioxidant function, as well as being a key carbon and sulfur source for heterotrophs. Impressively, algae invest between 1 and 10% of total primary production in DMSP, thereby making it a key compound in the lower trophic levels.

DMSP is also the precursor of the climate active gas dimethyl sulphide (DMS). Upon sea-ice melt, DMS is released from the huge pool of DMSP, present in sea-ice organisms. After emission to the atmosphere, the oxidation of DMS affects atmospheric chemistry, potentially promoting the formation of new aerosol particles and cloud condensation nuclei (CCN) in remote marine regions. The impact and relevance of this pathway for the polar climate is not yet clear (e.g. Quinn & Bates 2012, Cameron-Smith et al. 2011) and is a subject of investigation within ATMOS Working group (see chapter 3.6, DMS flux chamber). Sea-ice melt zones are without a doubt the areas with highest DMS concentrations (Lana et al. 2011, Levasseur 2013) and sea ice itself is hypothesized to play a key role in this. Concentrations of both DMS and DMSP are three orders of magnitude higher in sea ice than in surface waters (Tison et al. 2010, Stefels et al. 2012). Data on the direct coupling between sea ice, surface ocean and atmosphere is, however, still limited. Consequently, the impact of a changing sea-ice extent is uncertain. Although the first data on high DMSP concentrations in sea ice were published in the 1990's (Kirst 1991, Levasseur 1994), the number of studies on sea-ice DMSP have remained limited (e.g. Trevena and Jones 2006 and references therein). The development of new techniques to measure both DMS and DMSP in high-resolution sea-ice samples and to do in-depth process studies using stable isotopes gave this research a new impulse and forms the basis of this project proposal (Tison et al. 2010, Stefels et al. 2012).

Recent work by Uhlig et al. (2019) has also shown that the concentrations and ratios of DMS, DMSP and chlorophyll *a* in the Arctic Ocean are not uniform. Higher DMS and DMSP and a correlation with chlorophyll *a* were found in areas influenced by nutrient rich Atlantic water, whereas more stratified conditions under influence of mixed Atlantic/Pacific water mass in the central Arctic Ocean had lower DMS and DMSP concentration suggesting changes in the relative importance of pathways contributing to DMSP cycling (Uhlig et al, 2019). It is therefore of particular interest to better estimate the magnitude and rates of the microbial processes that drive the biosynthesis, and degradation of DMS and related compounds in Arctic samples and to relate the data obtained on the flux of the compounds in the organic sulfur cycle to the relevant microbial pathways and populations. The dynamics of the microalgal community throughout the seasonal changes will be explored through the use of HPLC, chlorophyll fluorescence and microscopic analysis.

Work at sea

Work onboard during leg 4 included sampling of:

1) sea ice, from the FYI and SYI coring sites (in coordination with Team ICE and ECO);

2) seawater collected from CTD-Rosette deployments from *Polarstern* (in coordination with Team Ocean and Team ECO);

3) under-ice water for incubations experiments with stable D3-DMSP;

4) opportunistically, water from meltponds and leads.

Samples were taken for the concentration and rates of processes transforming organosulfur compounds using Proton Transfer Reaction Mass Spectrometry (PTRMS, IONICON) with addition of stable isotope labelled tracers of DMSP during dedicated incubation experiments (Stefels et al 2009). In the case of sea ice, this will be achieved following the procedure described in Section 8.5 (pooled ice-core sections). Melted samples had been filtered to preserve the microalgal biomass and stored at -80° for subsequent work back at home. Chl fluorescence measurements had been measured with a Pulse Amplitude Multiplier (PAM, Walz) to give information about fitness and light adaptation of the phytoplankton.

Preliminary (expected) results

1) Sea-ice samples

108 samples for DMSPt and 187 GF/F filters for photosynthetic pigments were collected. The former have been stored at -20°C., the latter at -80°C and will be analyzed back home using the PTRMS and HPLC, respectively. These samples were collected at both the first-year (FYI) and second-year ice (SYI) sites. The FYI site was the original one, established by both the sea ICE and ECO teams in late September 2019 during Leg 1. A new SYI site next to Alli's Ridge was chosen since the old SYI site detached from our floe during leg 3/4 exchange.

The FYI location was visited 6 times and SYI location was visited 4 times during Leg 4. DMSPt samples were collected weekly alternating between FYI and SYI (except one visit). HPLC samples were collected at both sites, if they were happening in parallel. Ice core samples were sectioned in 10-cm intervals (except the bottom 2x5cm intervals) from the ECO pooled-core sections (see Section 8.5 – pooled ice-core sections).

2) Water samples

Water samples were taken in conjunction with the CTD team for biogeochemical and physical parameters of the ocean. During Leg 4 only the *Polarstern* CTD rosette was deployed for water sampling. Specifically, the following parameters were collected from 9 CTD casts, covering the euphotic zone and/or surface mixed layer, depending on fluorescence parameters and sampling strategy:

- 96 samples of total DMSP concentration
- 48 GF/F filters for phytoplankton pigments

PAM measurements were performed for each sample (i.e. 96).

Since microalgal biomass increased rapidly from week 47 on, the CTD sampling rate increased from weekly to biweekly for all the parameters mentioned above.

From week 48 on samples for DMS were taken and given to Steve Archer for analysis on board (see chapter 3.6 – GC, DMS).

3) Incubation experiments

Three incubation experiments were performed by pumping under-ice water (see Table 7.3.1).

***Tab. 7.3.1**: Device operations and associated samples for incubation experiments (Pvs.I, nutrients and vitamin B12 addition) during Leg 4.*

Date	ActionLog_ID	Site	Sample type
27.06.20	PS122/4_44-234 hand pump	Sediment trap site	Pvs.I and vit.B12 experiments (40L)
10.07.20	PS122/4_46-160 hand pump	Water from the bottom of Jaridge	PvsI experiments (20L)
21.07.20	PS122/4_48-123 hand pump	Eco lodge	Pvs.I and vit.B12 experiments (40L)

Two carboys (10L each) were spiked with D3-DMSP and ^{13}C-$NaHCO_3$ and incubated at different light intensities for Pvs.I experiments. Samples for DIC, nutrients, cells, HPLC, PAM and DMSPt, were collected at the beginning of the experiment. After 24 hours (end of the experiment) samples for sulfur compounds (total, dissociate and particulate DMSP, total DMS), POC and PAM were taken.

Apart from PAM measurements, which were analysed on *Polarstern*, all the samples collected will be processed back home.

For 2 of these 3 experiments, incubations with and without nutrients, and vitamin B12 addition were performed. The experiments were started at the same time as the procedure written above, with an additional 16L of water used and, in this case, 7-9 day incubation periods were used before spiking the bags with D3-DMSP and ^{13}C-$NaHCO_3$. Samples for sulfur compound and PAM were taken as well. Instead of POC, water was filtered for totDNA analysis (by Emelia Chamberlain – see chapter 7.2), for community identification through 16S/18S DNA sequencing and RNA metatranscriptome analyses for selected incubation samples (collaboration H. Schäfer).

4) Opportunistic samples
   a) Meltponds

Occasionally, samples from meltponds were taken (see Table 7.4) and chlorophyll *a* fluorescence measured, together with microscope pictures (Fig. 7.3.1), when possible. Once the biomass started to increase, samples for DMSPt were also stored.

The sampling was organized as a cross-cutting activity between Team ICE (special thanks to Felix Linhardt for helping with melt pond-survey, see chapter 4.1.2 Melt ponds) and Team ECO (dimples and melt ponds, see chapter 6.X and 7.1.3, respectively).

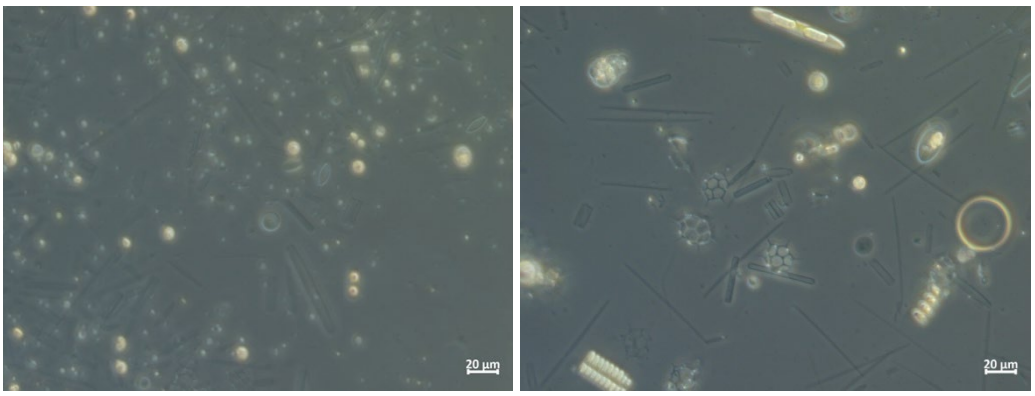

***Fig. 7.3.1**: Microscope pictures of melt pond samples on 14 July. Different phytoplankton species are recognisable, especially diatoms. Interestingly, the sampling technique might have also played a role in the quality of the sample analysed (left: "dimple" technique, using a pipette to sample the concentrated biomass, right: the water in proximity of the dimple was collected using an amber glass bottles only). Pictures: D. Bozzato.*

b) Leads

Multiple samples were taken from leads, either based on personal initiative to survey the best spot for further experiments (week 45 and 46) or as a cross-cutting activity (from week 47, see Chapter 8.4 Leads).

***Tab. 7.3.2**: Device operations and associated samples from Lead sampling during Leg 4.*

Date	ActionLog_ID	Sample type
01.07.20	PS122/4_45-120 water_probe	10 samples in different locations, during Lead transect next to ROV site. Analysed parameters: DMSPt (stored at -20°), PAM, FRRf, stereo- & light-microscopy
11.07.20	PS122/4_46-161 water_probe	3 different depths were sampled: surface, 1m and 2m. PAM analysis performed (duplicates). 2xDMSPt, 1xDIC and 1xnutrients for each depth stored at -20°
17.07.20	PS122/4_47-145 peristaltic_pump	Samples for DMSPt, PAM, FRRf. Lead A - near Lemon drop albedo line
17.07.20	PS122/4_47-145 peristaltic_pump	Samples for DMSPt, PAM, FRRf. Lead B - Between Root Beer albedo line & picnic ridge (along the transect)
22.07.20	PS122/4_48-111 peristaltic_pump	Samples for DMSPt, PAM. Lead C (between ROV & Drone-ville)
22.07.20	PS122/4_48-112 peristaltic_pump	Samples for DMSPt, PAM. Lead A
22.07.20	PS122/4_48-113 peristaltic_pump	Samples for DMSPt, PAM. Lead D, near Alli's ridge
28.07.20	PS122/4_49-77 water_probe	Samples for DMSPt, PAM. Lead D

c) 24 hours sampling

For our project, a simple plan was developed to be able to take all the samples autonomously and process them immediately after being back on *Polarstern*. The location chosen for sampling was the ROV site, where optics measurements were run in parallel from Team ICE (Ilkka Matero, see chapter 4.6 ROV). The samples collected are listed in Table 7.3.3. Our aim is to compare the data from phytoplankton photophysiology with *in situ* light measurements to detect short-term adaptation of the photosynthetic apparatus with the changing light spectra.

***Tab. 7.3.3**: Device operations and associated samples from ROV site during 24 hours sampling.*

Date	Time (UTC)	ActionLog_ID	Samples
10.07.20	12:00	PS122/4_46-163_hand pump	HPLC, PAM, FRRf
10.07.20	17:30	PS122/4_46-164_hand pump	HPLC, PAM, FRRf
11.07.20	23:00	PS122/4_46-165_hand pump	HPLC, PAM, FRRf
11.07.20	05:00	PS122/4_46-166_hand pump	HPLC, PAM, FRRf
11.07.20	11:30	PS122/4_46-167_hand pump	HPLC, PAM, FRRf

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). Processed data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

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7.4 UNDERWAY CONTINUOUS OUTSIDE AIR METHANE ANALYSIS

F. Pätzold1, E. Damm2 (not on board), A. Lampert1 (not on board)

1 TU Braunschweig

2 AWI

Objectives

A Picarro G2132-i methane concentration and $\delta^{13}CH_4$ isotopy analyzer – used for samples obtained from water and ice samples during leg 1 to 3 – was connected to an outside air intake to acquire these data along the ship track.

Work at sea

The methane concentration and δC^{13} methane isotope analyzer Picarro G2132-i (Sensorweb: Pic2132ed) was running throughout leg 4. As this device was also used to analyze air samples obtained with (airborne) air extracting systems, the time series is irregularly interrupted. A calibration using two secondary standards was done.

The air intake on P-deck at 21 m above sea surface was shared with the halocarbon analyzer (see chapter 7.8), which dominates the air flow rate through the tube. When the halocarbon analyzer was not operating anymore since 26 July 2020 a Boxer 3KQ diaphragm pump was installed instead.

Preliminary (expected) results

The data were observed but not analyzed onboard. A small increase in methane concentration and shift in δC^{13} methane isotopy was observed while moving closer to the marginal ice zone. The influence of ship exhaust must be taken into account when analyzing the data.

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). All device operations were logged in the AWI sensorweb portal and all sensor raw data files are stored in platform section of MCS. Data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

7.5 UNDERWAY CONTINUOUS SEA WATER ANALYZER

F. Pätzold1, W. Geibert2 (not on board), L. Zhan3 (not on board), L. Wang4 (not onboard)

1 TU Braunschweig

2 AWI

3 Third Institute of Oceanograhy, China

4 Beijing Normal University, China

Objectives

Three continuously seawater analyzing devices were running throughout leg4:

- RAD7 radon counter (sensorweb: AWI-Radon-counter; Dship: PS122/4_43-13; PI: W. Geibert)
- N_2O and CO analyzer (sensorweb: OA-ICOS_N2O; Dship: PS122/4_43-14; PI: L. Zhan)
- CH_4 concentration and $\delta^{13}CH_4$ isotopy, CO_2 concentration and $\delta^{13}CO_2$ isotopy (sensorweb: BNU-CRDS; Dship: PS122/4_43-15; PI: L. Wang)

For more details refer to the corresponding PI cruise report sections from other PS122 legs.

Work at sea

The three systems were maintained and the data were managed.

Preliminary (expected) results

Initial results for the Rad7 radon counter show that the system could be maintained to measure and record radon-222 in seawater continuously, apart from short interruptions for maintenance and when approaching land (EEZ regulations). The data were not analyzed onboard. Only a detailed statistical analysis of all legs will show trends and determine the significance of the dataset.

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). All device operations were logged in the AWI sensorweb portal and all sensor raw data files are stored in platform section of MCS. Data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

7.6 DISCRETE AIRSAMPLING FOR $\delta C^{14}CH_4$ ANALYSIS

F. Pätzold[2], H. Chen[1] (not on board), E. Damm[3] (not on board), A. Lampert[2] (not on board)

1 RU Groningen
2 TU Braunschweig
3 AWI

Objectives

Analyzing air samples for $\delta C^{14}CH_4$ isotope can give information about the origin of the methane. As the needed analyzer is not on board, air samples for analysis on land were taken using usual sample bags.

Work at sea

A series of air samples was taken from 10 July until 6 August 2020. While the first phase sampling was done 10 cm above the surface at locations on the MOSAiC floe upstream to the ship, to minimize direct human impact. After the breakup of the floe on 31 July the second phase samples were taken near the stern of Polarstern on the ship side exposed to the wind at about 3 m above surface. To fill the 25l SKC multifoil bags a box with a battery powered pump was used, facilitating air sampling during higher wind speed (sensorweb: Airsampler for

C14CH4air). One sampling took 3 minutes. On board the methane concentration and □C^{13} methane isotopy was analyzed using a Picarro G2132-i (sensorweb: Pic2132ed). Three samples were taken twice and two bags were filled with a secondary standard gas to observe the influence of the storage time several weeks. See table 7.3.1.

***Fig. 7.6.1**: Air sampling at balloon town, 25 July 2020, wind from right to left (photo: F. Pätzold)*

Preliminary (expected) results

The raw analyzer output plotted in figure 7.6.2 shows correlations of carbon dioxide concentration and methane $\delta^{13}CH_4$ isotope with methane concentration, which is consistent with the continuous underway methane analysis (see chapter 7.5). Combining the on land $\delta^{14}CH_4$ analysis of these air samples with all other methane related measurements during MOSAiC will draw a good picture of the methane processes in the Arctic.

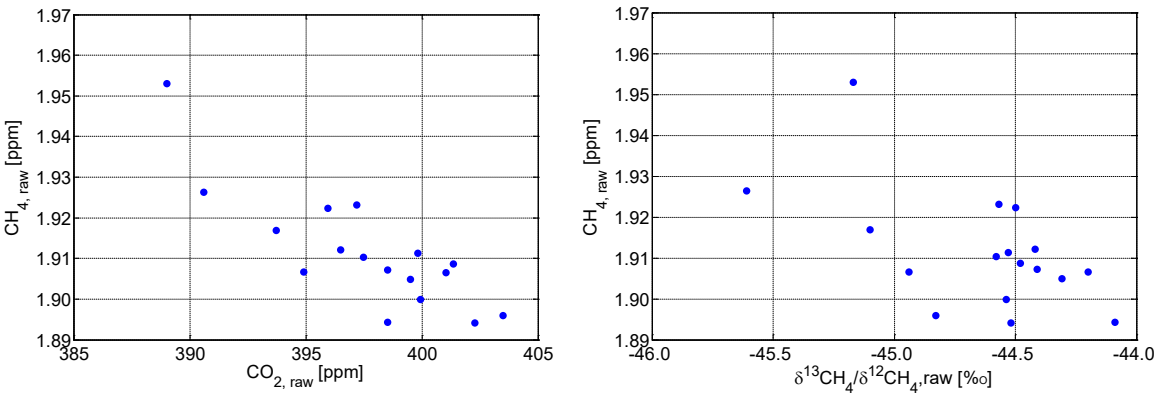

***Fig. 7.6.2**: Methane concentration in relation to carbon dioxide concentration and methane isotopic composition*

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). All device operations were logged in the AWI sensorweb portal and all sensor raw data files are stored in platform section of MCS. Data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

***Tab. 7.6.1**: List of sampling events.*

Sample	Date	Time [UTC]	Dship	Lat	Lon	Wind dir/speed [deg/kn]	Location/ comment
#1	10.07.20	11:43	PS122/4_46-85	N 80.51091	E002.3757	050/05	MET city
#2	10.07.20	11:46	PS122/4_46-86	N 80.51091	E002.3757	050/05	MET city
#3	13.07.20	12:06	PS122/4_47-3	N 80.41844	E000.2973	120/06	Ocean city
#4	15.07.20	12:00	PS122/4_47-35	N 80.30094	E000.3180	330/03	MET city
#5	17.07.20	11:38	PS122/4_47-85	N 80.15031	E000.3492	330/05	MET city
#6	19.07.20	14:19	PS122/4_47-111	N80.87791	W000.2560	360/09	MET city
#7	21.07.20	11:47	PS122/4_48-30	N80.60892	W000.5842	280/06	MET city
#8	23.07.20	11:35	PS122/4_48-70	N80.35176	W000.6394	030/10	Ocean city
#9	23.07.20	11:38	PS122/4_48-71	N80.35176	W000.6394	030/10	Ocean city
#10	23.07.20	12:30	PS122/4_48-157	./.	./.	./.	Secondary standard cylinder ID1474
#11	25.07.20	08:28	PS122/4_48-122	N79.9849	W000.6549	020/10	Balloon town
#12	27.07.20	07:21	PS122/4_49-9	N79.63917	W002.2435	100/02	Stern end of logistic area (poor visibility)
#13	29.07.20	11:21	PS122/4_49-27	N79.19106	W002.5839	130/15	Balloon town
#14	31.07.20	10:22	PS122/4_49-64	N79.06836	W002.8398	170/08	Working deck, stern, portside
#15	02.08.20	08:59	PS122/4_49-97	N79.0356	W002.7439	170/08	Working deck, stern, starboard side
#16	04.08.20	11:22	PS122/4_50-13	N79.0262	W003.1678	260/05	Working deck, stern, starboard side
#17	06.08.20	07:26	PS122/4_50-41	N78.36355	W007.2015	035/05	Working deck, stern, portside
#18	06.08.20	07:29	PS122/4_50-42	N78.36355	W007.2015	035/05	Working deck, stern, portside
#19	06.08.20	04:05	PS122/4_50-43	./.	./.	./.	Secondary standard cylinder ID1474

7.7 HELIPOD ACTIVITIES

F. Pätzold[1], A. Lampert[1] (not on board), T. Sachs[1,2] (not on board), E. Damm[3] (not on board)

[1] TU Braunschweig
[2] GFZ Potsdam
[3] AWI

Please refer to Chapter 4.3 for all other helicopter borne activities.

Objectives

The HELiPOD activities during MOSAiC are funded by the DFG-project "ALEXIA - Analysis Linking Arctic Methane, Carbon Release, Heat Fluxes and Sea Ice from Local to Sub-Regional Scales by Airborne Measurements" (LA 2907/11-1). The objectives are:

a) Acquiring and analyzing a high-latitude and high-resolution data set of atmospheric and surface properties from a local scale to 100 km range as basis for all planned studies.
b) Linking turbulent sensible and latent heat fluxes to surface temperature variability induced by different sea ice properties and synoptic conditions.
c) Studying methane and carbon dioxide fluxes in the light of atmospheric stratification, conditions of the ice surface and heat fluxes, and identifying the transport pathways vertically from the ocean through sea ice or horizontally by advection from lower latitudes.
d) Exploring the provenance of methane by analysing the isotopic composition signature of methane in air samples at different altitudes.

Work at sea

The HELiPOD stayed on board from leg 3 (see cruise report PS122/3 chapter 4.4). A large variety of software improvements and calibrations were carried out during Leg3/4 exchange (transit from floe to Longyearbyen and back).

The insufficient WiFi connection from the HELiPOD to Helicopter due to an unfavorable antenna position on the helicopter was handled by reconfiguring the both WiFi modules in the HELiPOD using different antenna types and the access point module in the operator station. A short test flight on 26 July with the HELiPOD stationary on the floe confirmed the measures taken, which results in a reliable connection with a data throughput capacity of 100 to 150 Mb/s.

During the practically available operation period from 26 June till 30 July only three days could be used to conduct 4 flight with the HELiPOD. Any kind of regular flight operation was out of reach due to mostly insufficient weather conditions to operate the helicopter. An overview of the flights and the flown trajectories are listed in table 7.4.1.

<u>Static lateral stability issue during flights on 30 June and 1 July:</u>

In both flights during transition from vertical take-off to slow forward flight the HELiPOD turned to the 10 o´clock position relative to the straight flying helicopter (angle of sideslip +60° to +70°). An increased airspeed did not lead to a proper alignment by the vertical stabilizer but to an increase in side slip angle to +90° (nose pointing to 9 o´clock position relative to the helicopter). Flying a steep left turn rotated the HELiPOD into a normal position. This behavior was not observed while the flight on Leg 3 nor in the past. Contrary to the flight on Leg 3 the wind was calm which might have caused a stable rotating downwash at this distance, bringing the HELiPOD vertical stabilizer into an initial angle of incident which causes detached flow when speeding up. A rough stability calculation showed that a destabilizing momentum was present, which can only be caused by detached flow at the front section. Compared to the flight characteristics before MOSAiC, the outside insulation also may have caused this changed aerodynamic behavior.

The following measures were realized to cope with the issue:

- Increasing the vertical stabilizer surface by 40% attached to trailing edge
- A fin on top of the tail boom, a well-known measure for fixed wing aircraft

- 5 vortex generators on each side of the front section

***Fig. 7.7.2**: Positions of the added 5 vortex generators on both side of the front section*

***Fig. 7.7.1**: Vertical stabilizer modifications (green-doted line)*

During two flights on 22 July the flight characteristics were proven as very satisfying. The modifications have no negative impact on the scientific measurements and no flight option was missed.

<u>Lateral oscillations during flights on 30 June and retrospectively 10 May:</u>

In cruise flight on 30 June the HELiPOD was oscillating laterally less damped then known in the past (limit cycle oscillation). This characteristic could be also seen in footages of the flight on 10 May. In both cases an advanced flight law of the helicopter flight director was used. For the flight on 1 July a basic flight law was chosen by the pilot, which results in an increased but doable workload for the pilot. Simplifying the HELiPOD as a one point mass pendulum, the time constants of advanced flight director modes seem to couple with the eigenfrequency of this pendulum.

<u>Methane sensor damage during second take-off on 22 July:</u>

While the second take-off the front rope tangled around the housing of the Licor Li7700 methane concentration sensor, resulting in a deformation that made the sensor output invalid for this flight.

Preliminary (expected) resultsAs many of the relevant data must be attitude-corrected and the attitude post-processing cannot be done onboard, no immediate results can be reported at this moment other than raw data examples: Figure 7.4.3 shows the same location captured with 4 different cameras.

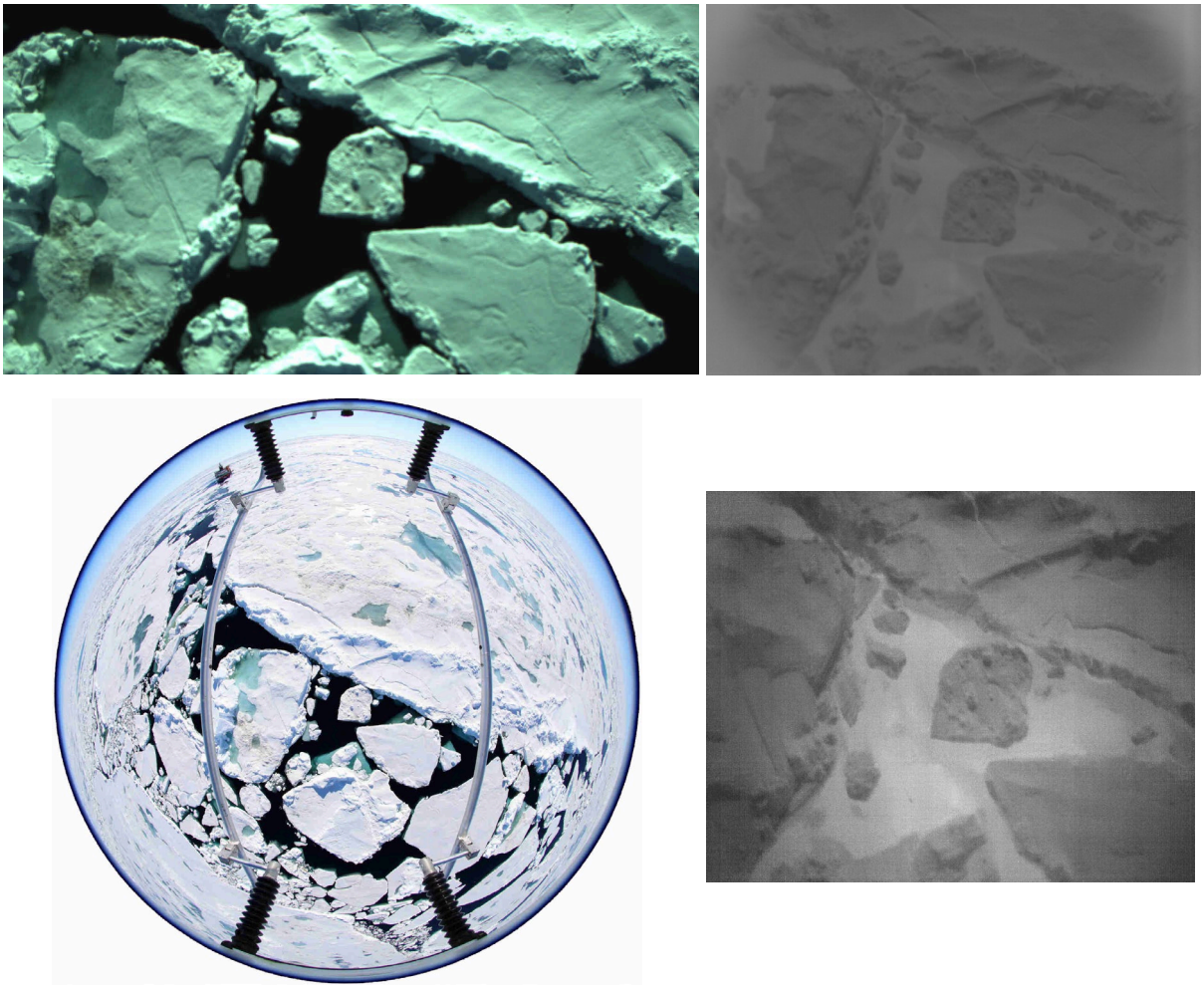

***Fig. 7.7.3**: Same location captured with different cameras. Top-left: Xenics Photonfocus MV1 (RGB , 5 Hz), Top-right: Gobi-640-GigE-5321 (IR, 10 Hz), Bottom left: EOS-RP 8mm F3.5 EX DG circular-fisheye (RGB, 1/3 Hz), bottom-right: FLIR A65 (IR, 7.5 Hz)*

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). All device operations were logged in the AWI sensorweb portal and all sensor raw data files are stored in platform section of MCS. Data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

***Tab. 7.7.1**: Overview of HELiPOD flights from Polarstern during PS122/3 (times in UTC).*

Date	Takeoff HELiPOD	Landing HELiPOD	Device Operation	Trajectory	
06/30/20	14:42	16:31	PS122/4_45-66	• wind calibration square @ 200 ft • square with 35km base @ 120 ft • vertical profile 5000 ft	Lateral stability issue
07/01/20	12:34	14:20	PS122/4_45-67	• wind calibration square • two orthogonal out and return 35 km legs @ 150 ft outbound and @ 75 ft inbound • vertical profile 5000 ft	Lateral stability issue
07/22/20	11:56	12:53	PS122/4_48-104	• wind calibration square • out and return 40 km leg to northeast • @ 120 ft outbound and 60 ft inbound	
07/22/20	13:16	14:19	PS122/4_48-105	• out and return 50 km leg to southeast @ 120 ft outbound and 60 ft inbound	Li7700 damaged while take-off, first deployment of air extracting system

7.8. SEASONAL SEA ICE – A NEW SOURCE OF BROMINE DURING POLAR NIGHT

Deborah Bozzato[1], K. Abrahamsson[2] (not onboard), A. Dumitrascu[2] (not onboard), P. Simoes Pereira[2] (not onboard) and A. Saiz Lopez[3] (not onboard)

[1] RUG
[2] UGOT, Sweden
[3] CSIC, Spain

Objectives

The aim of the project is to study emissions of biologically produced trace gases, i.e. halocarbons (VHOC). These halocarbons are ozone-depleting and are hence subject to present and future regulation under international agreements (e.g., the Montreal Protocol). Although significant effort has been made to generate global budgets of halogenated compounds, the Arctic Ocean has been neglected in these models so far, hindering accurate prediction of the ozone layer over the next decades. Additionally, there is still a wide gap in knowledge in the influence of sea ice–atmosphere interactions to these halogenated compounds, especially during polar night. Changes in sea ice distribution, concentrations, and age, in the Arctic where the extent of multi-year ice has declined substantially compared to seasonal ice, affect the atmospheric composition of halogens. Halogen species involved in the depletion of ozone are associated with new sea ice formation, particularly during polar winter. For instance, during the Antarctic winter, estimates of ozone-depleting halogen fluxes from seasonal ice are 100 to 1000 times higher than during to summer (Abrahamsson *et al.*, 2018).

During the drift, we will analyse halocarbon concentrations at the ocean-ice-atmosphere interface

during the Arctic winter to further our understanding of the biogeochemical processes that occur during sea ice growth, as well as their impact on Arctic tropospheric chemistry. We will also investigate the role of ice as a reaction surface for chemical conversion processes, and therefore as a source for halogens to the atmosphere. We will estimate the contribution of seasonal sea ice to the load of halocarbons in the troposphere during polar night, which will improve existing uncertainties in global flux models of halocarbons through air-ice-sea measurements.

Work at sea

Measurements of halocarbons including brominated, iodinated and chlorinated compounds were conducted on air and seawater in order to estimate their flux, and therefore the importance of Arctic sea ice as a source for ozone-depleting halogen compounds.

Samples were analyzed with a purge-and-trap system (Teledyne) connected to a gas chromatograph with electron capture detector (Thermo). A custom-made purge-and-trap instrument was equipped for semi-automatic air and seawater sample analysis. Air was continuously drawn through a ~100m long Teflon tube with a diameter of 4 mm with the help of an air pump located down-stream from the sampling loop. The instrument was also fed with a continuous stream of water from the ship´s surface water inlet. The determination was made with a gas chromatograph with an electron capture detector (Thermo).

Preliminary results

The IT (the purge and trap system attached to a GC-ECD, described above) was shut down at the end of Leg3, entering the 12nm zone in Svalbard, from P. Simoes Pereira. The instrument was restarted on 8 June from D. Bozzato, after the 12nm zone has been left.

***Tab. 7.8.1**: Device operation of Thermo Scientific TRACE 1310 2 device*

Date	Time (UTC)	ActionLog_ID	Description
08.06.20	21:30	PS122/4_43-10 GC-Halo2	Continuous measurements and sampling activities during leg 4

Data have been collected continuously until 19 June, when the instrument started to have problems (i.e. flat signal). P. Simoes Pereira was contacted and troubleshooting was attempted whenever possible.

During the exchange between Leg4/5 an additional attempt to restart the measurements has been attempted, in collaboration with Team BGC Leg5.

Data management

All data are handled, documented, archived and published following the MOSAiC data policy (see APPENDIX). Processed data will be stored at the PANGAEA data repository (World Data Center PANGAEA Data Publisher for Earth & Environmental Science (www.pangaea.de)).

References

Abrahamsson K, Granfors A., Ahnoff M., Cuevas C.A. and Saiz-Lopez A. (2018) Organic bromine compounds produced in sea ice in Anarctic winter. Nature comm. 95291, 1-8