



TNA User Report

*The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr*

Project title	EFFECTS OF ICE STESSORS AND POLLUTANTS ON THE ARCTIC MARINE CRYOSPHERE (EISPAC)
Name of the accessed chamber	RvG-ASIC (formerly ASIBIA)
Number of users in the project	1
Project objectives (max 100 words)	<p>In this work, we place our emphasis on the behavior of poly- and perfluoroalkyl substances (PFASs) in sea ice and how the sea ice dynamics as well as the brine dynamics impact on their distribution.</p> <p>Using the RvG-ASIC facility, we investigated the exchange of PFASs between the sea ice and the underlying seawater during sea ice growth, stabilization and melting.</p>
Description of work (max 100 words):	<p>The experiment was carried out to investigate the exchange of PFASs between the sea ice and the underlying seawater during sea ice growth, stabilization and melting under defined conditions.</p> <p>The tank was filled with artificial seawater and subsequently spiked with PFASs. The experiment started with the growth of frost flowers. After 7 days of congelation growth, sea ice was stabilized for 3 day and followed by the seasonal melt process. During the experiment samples from all compartments were taken.</p>

Principal Investigator's and group's information	
First name	Zhiyong
Family name	Xie
Nationality	Chinese
Activity domain ¹	Chemistry
Home institution	Helmholtz-Zentrum Geesthacht (HZG)
Institution legal status ²	RES
Email	zhiyong.xie@hzg.de
Gender	M
User status ³	RES
New user	Yes

User 1 Information ⁴	
First name	Rui
Family name	Shen
Nationality	Chinese
Activity domain	Chemistry
Home institution	Helmholtz-Zentrum Geesthacht (HZG)
Institution legal status	RES
Email	ruishen@hzg.de
Gender	F
User status	PGR
New user	Yes

¹ Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

*The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr*

Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version.

The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Zhiyong Xie

Chamber name and location: RvG-ASIC (formerly ASIBIA), University of East Anglia, Norwich, UK

Campaign name and period: EFFECTS OF ICE STESSORS AND POLLUTANTS ON THE ARCTIC MARINE CRYOSPHERE (EISPAC), April 23rd – May 22nd 2019

Text:

1 Introduction and Motivation

It has been widely recognized that global climate change is leading to substantial changes in Arctic ecosystems. Sea ice is often quoted as a key indicator of these changes. Continuing losses of multi-year sea ice (MYI) across the Arctic are causing first-year sea ice (FYI) to dominate the Arctic ice pack. Seasonal freezing and thawing of FYI affect contaminant cycling and behavior.

However, the mechanistic input of organic contaminants into the Arctic marine environment is not well understood. To date, the behavior of organic contaminants during ice formation and growth has not been well studied. There have been only few works taking insight into contaminant pathways in sea ice environment. Therefore, our project aims to investigate the dynamics, such as uptake, accumulation and release mechanism, of organic pollutant in the Arctic sea ice during seasonal growth and melt using the Roland von Glasow Air-Sea-Ice Chamber (RVG-ASIC), at University of East Anglia, UK.

In this work, we place our emphasis on the behavior of poly- and perfluoroalkyl substances (PFASs) in sea ice and how the sea ice dynamics as well as the brine dynamics impact on their distribution. Poly- and perfluoroalkyl substances (PFASs), including neutral PFASs and perfluoroalkyl acids (PFAAs) have numerous industrial and consumer sources and therefore. PFASs are present in air, water soil and biota worldwide.¹⁻³ Recently, they have been detected in the Arctic.⁴⁻⁶ PFASs are persistent in the environment and bioaccumulative in animals and humans, raising serious health and environmental concerns.^{7, 8}

2 Scientific Objectives

As per- and polyfluoroalkyl substances (PFASs) have very low acid dissociation constants (pK_a). They are almost fully ionized under most environmental conditions. Therefore, they may behave like salt in seawater.

3 Reason for Choosing the Simulation Chamber

Considering the need to better understand organic contaminant cycling in sea ice, and the difficulties of performing these measurements on natural sea ice, a controlled sea ice growth and melt experiment using the chamber method is highly relevant.

4 Method and Experimental Set-up

4.1 Experiment Set-Up

4.1.1 General

The 15-day experiment took place at the the RvG-ASIC facility.

The cuboid glass tank (2.4 m * 1.4 m footprint, 1.2 m deep, 25 mm wall thickness) referring the 'ocean' was filled with 3300 L (98 cm in depth) MilliQ water. The salinity of the artificial seawater was adjusted to the Arctic seawater value by adding aquarium standard salt (Tropic Marin®). Two submerged pumps were used to mix the seawater (flow rate 1000 L/h). The tank was equipped with an *in-situ* conductivity-temperature sensor along with a series of automated *in-situ* thermistors to measure the ice temperature throughout the experimental period (Figure. 1). PFASs were spiked into the tank using a stock solution to give concentration in 0.01 μM range resulting in a concentration of about 5 μg PFASs per Liter seawater.

Chamber Sep-Up

Coordination in cm

Pump:

Pump-1: (0, 0, 0)
Pump-2: (2.5, 1.5, 0)
Mini pump: side tank

Temperature :

Tice-1: (72, 80, 98(t)) (80(b))
Tice-2: (168, 69, 97(t)) (77(b))
WH-N1: (122, 73, 97 (t)) (82(b))
WH-W2: (122, 73, 81(t)) (66(b))

Water sampling line:

SW-C1: out of the tank
SW-C2: out of the tank
SW-C3: out of the tank
SW-Y1: (145, 24, 23)
SW-Y2: side tank
SW-Y3: (115, 70, 78)

Sonar:

S_a-0.5: (44.5, 26, 49.3)-green
S_b-5: (47, 100, 49.5)-red
S_c-5: (180, 104, 50.4)-white
S_d-1: (216, 36, 49.3)-blue

CTD: (117, 82, 57(t))

Temperature probe:

- 1 Outside cold room
- 2 In the cold room water line top
- 3 In the cold room
- 4 In the cold room
- 5 N/A
- 6 In the cold room water line bottom

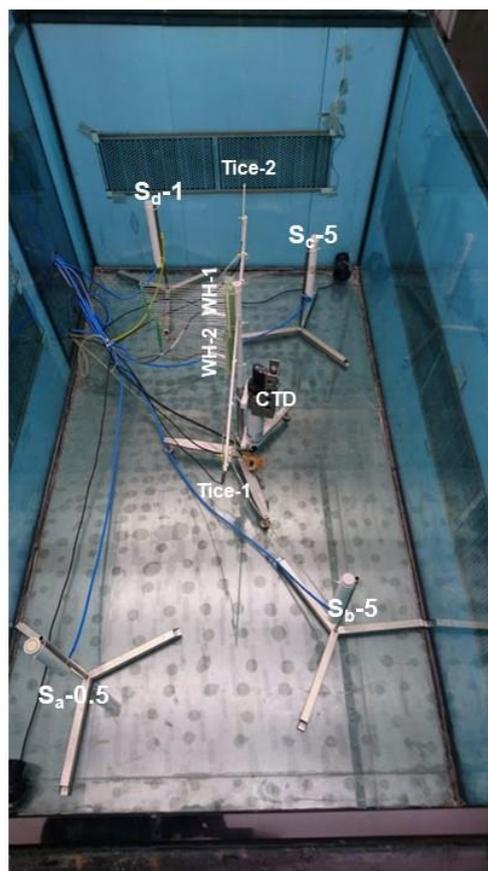
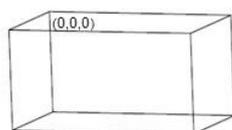


Figure 1. Tank Setup

In this experiment, the inclusion and release of PFASs were characterized during the growth and evolution of young ice. The experiment began with the growth of frost flowers. Young ice grew under quiescent and turbulent conditions up to 25 cm for 7 days. This young ice was stabilized for 3 days. After the stabilization period, the grown sea ice was warmed up in the sea-ice tank to induce internal sea ice melt. This simulated the decay phase (full-depth convection) of first year sea ice. Besides baseline data on physical properties regarding the evolution of sea ice (e.g. temperature, salinity, density and brine volume *etc.*), the development of PFASs concentration in the sea ice and the underlying seawater during sea ice growth and melting were determined from analyzing extracted ice slabs and seawater sampling. The general approach is tabulated below (Table 1).

Table 1. Timeline.

Experiment Phase	Start	End	Time Length [d]	Temp. [°C]	Depth [cm]
frost flowers	08.05.2019	10.05.2019	3	-30	12
congelation growth	10.05.2019	17.05.2019	7	-15	25
stabilization	17.05.2019	20.05.2019	3	-5	25
melting	20.05.2019	21.05.2019	1	-3	25
melting	21.05.2019	22.05.2019	1	-2	25
Experiment end	22.05.2019				

4.1.2 Frost Flowers

Prior to the experiment, the artificial seawater was cooled to -2 °C.

We then started the fans and the vaporizer and lowered the room temperature to -22 °C. The overall behavior and growth of the frost flowers was recorded by a combination of the photos, the salinity samples, and our direct observations of the ice surface.

A number of control samples were taken during this period. This array of experiments started with frost flower growth. The air temperature of the chamber was cooled to about -30 °C for 3 days resulting in a final ice layer up to 12 cm (young ice) in thickness.

4.1.3 Congelation Ice Growth

Multiple sea ice samples were collected at different time points to help define the progression of PFASs dynamics. The first charge of samples were collected after 3 days of growth (the 3rd experiment day) for the baseline data of the early stage of growth. The experimental sea-ice chamber was slowly warmed up from -25 °C to -15 °C for 4 days resulting in the maximal ice thickness of 25 cm (young ice). Samples were collected at the maximum of ice thickness (the 7th experiment day) to observe its progression.

A vertical understanding of PFASs distribution in sea ice was investigated. Extracted sea ice slabs on selected sampling points were cut as 5 cm subsections for subsequent laboratory analysis. Measurements throughout a full length of ice slabs were establish the vertical profile of PFASs in sea ice.

4.1.4 Stabilization

The experimental sea-ice chamber was slowly warmed up from -15 °C to -5 °C. The sea ice was stabilized at -5 °C for 4 days (the 11th experiment day). The series showed the inclusion progression of PFASs from recognizable congelation ice in its advanced stage of growth to the development of winter sea ice.

4.1.5 Melting

The experimental sea-ice chamber was warmed up from -5 °C to -2 °C for 1 day. Subsequently, the ice temperature was close to 0 °C in its advanced melting stage. Ice slabs were sampled (the 13th and the 15th experiment day) to capture the evolution of PFASs and baseline data on the physical properties of sea ice as it warms.

A number of sea ice samples were used to conduct a slow-melt experiment with a designed experimental setup to assess the release pattern of PFASs from sea ice pack during seasonal melting. The sea ice slabs were weathered at air temperature of 0 °C and undergo seasonal melting. Fractions of meltwater were collected for subsequent laboratory analysis.

4.2 Sampling Method

4.2.1 Frost Flowers

During the experiments, the grown frost flowers were collected from the ice surface with a cold, thin-blade knife and placed into a PE sampling bag. The flowers were weathered to melt and measured for baseline data.

4.2.2 Seawater

Samples for analyses were stored unfrozen in 100 mL PP bottles.

4.2.3 Sea Ice Slab

All ice slabs were taken using the Cottier-Method to preserve brine in porous ice and subsequently cut in a cold room (-25 °C).⁹ Seawater were sampled regularly at set intervals.

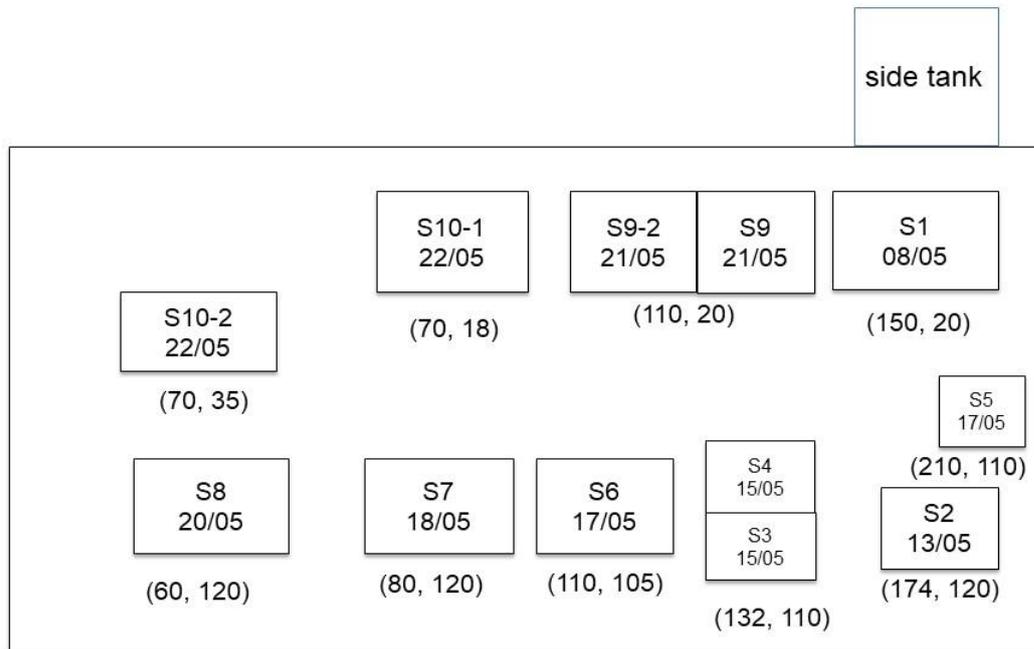


Figure 2. Sampling Map.

4.3 Physical Characters of Sea Ice

Salinity was measured with a portable conductivity meter (HACH salinometer / WTW Tetracon 325 probe) on melted ice samples at room temperature.

5 Data Description

5 frost flowers samples, 12 sea ice slab samples and 35 seawater samples were taken during the experiment.

6 Preliminary Results and Conclusions

6.1 The Growth of Frost Flowers

The evolution of the ice surface over the two days of the experiment is presented (Figure 3 & 4). The frost flowers appeared more on Day 2 than Day 1.



Figure 3. Growth of Frost Flowers - Day 1.



Figure 4. Growth of Frost Flowers - Day 2.

The grown frost flowers on Day 2 are more saline than the grown flowers on Day 1 (Table. 2.)

Table 2. Salinity of Frost Flowers.

Sample	V [ml]	Salinity [PSU]	Temperature [°C]
S _{FF-1-1}	18.0	56.3	21.8
S _{FF-1-2}	37.0	59.1	25.2
S _{FF-1-3}	37.5	63.6	22.1
S _{FF-2-1}	25.0	73.3	22.1
S _{FF-2-2}	62.0	72.5	22.4
S _{FF-2-3}	48.0	82.6	23.1
S _{FF-2-4}	58.0	85.4	23.6

6.2 Sea Ice Dynamics

The ice thickness increased until day 10, reaching a maximum of 25 cm, and then stabilized for 3 days and slightly decreased towards the end of the experiment.

There was an increasing temperature gradient between the top and the bottom of the ice from day 1 to 10 (the freezing phase). In the subsequent melting phase, the ice temperatures became more vertically homogeneous, approaching $-1.8\text{ }^{\circ}\text{C}$ on day 15.

The salinity of the bulk ice was homogeneous at day 1, before developing a typical C-shape profile with a higher salinity at the top and the bottom of the ice compared to the ice interior (Figure. 5). From day 3 to 10, the ice bulk salinity ranged between 8.7 and 13.0 (Figure. 5). Overtime, desalination of sea ice took place (Figure. 5, 6 & 7). From day 10 onwards, the salinity decreased in both the top and the bottom and ranged between 4.1 and 12.2 (Figure. 7).

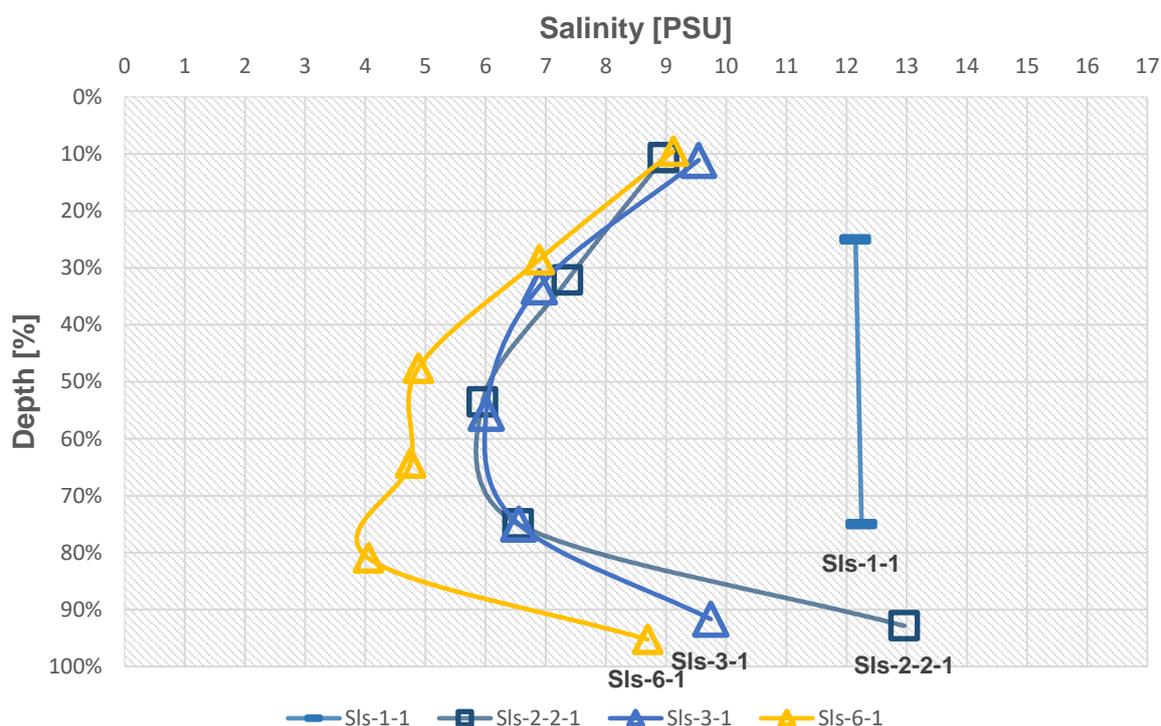


Figure 5. Congelation Growth of Sea Ice.

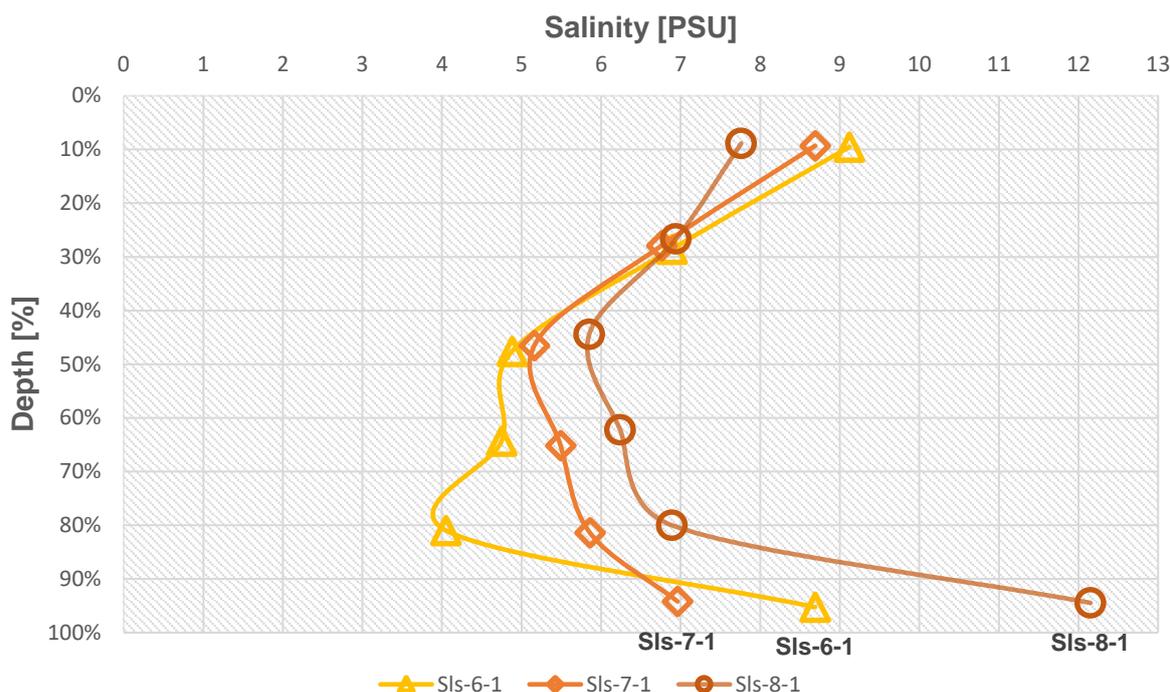


Figure 6. Stabilization of Sea Ice

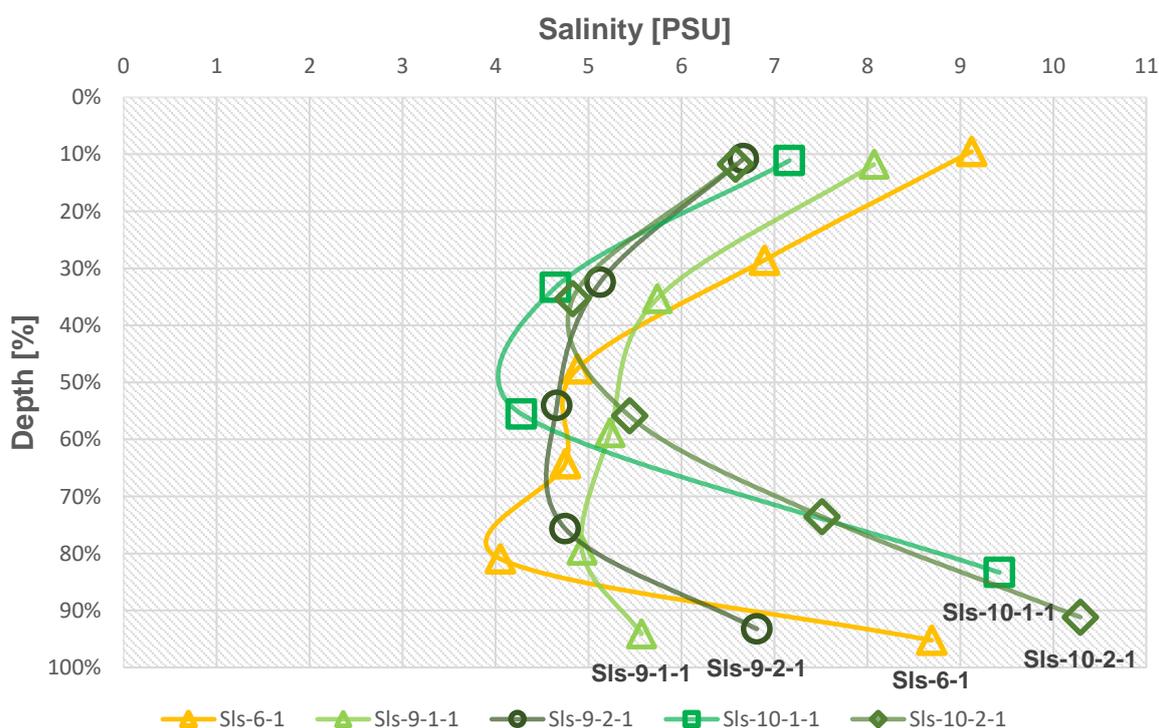


Figure 7. Seasonal Melting of Sea Ice.

The raw data demonstrated valuable information on the evolution of the grown sea ice. The influences of each parameter on the behavior of PFASs associated to the evolution of the sea ice will be discussed with the help of the laboratory analysis of PFASs. Here, we described a novel experimental design on the sea-ice chamber. A second set of experiment shall be carried out in the future work to establish the reproducibility.

6.3 PFASs Analysis

The analysis of PFASs has been carrying out in the HZG laboratory.

7 Outcome and Future Studies

The results from this experiment will be published in a scientific journal.

8 References

1. Lu, Z.; Song, L.; Zhao, Z.; Ma, Y.; Wang, J.; Yang, H.; Ma, H.; Cai, M.; Codling, G.; Ebinghaus, R.; Xie, Z.; Giesy, J. P., Occurrence and trends in concentrations of perfluoroalkyl substances (PFASs) in surface waters of eastern China. *Chemosphere* **2015**, *119*, 820-827.
2. Wang, Z.; Xie, Z.; Möller, A.; Mi, W.; Wolschke, H.; Ebinghaus, R., Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast. *Atmospheric Environment* **2014**, *95*, 207-213.
3. Wang, X.; Halsall, C.; Codling, G.; Xie, Z.; Xu, B.; Zhao, Z.; Xue, Y.; Ebinghaus, R.; Jones, K. C., Accumulation of Perfluoroalkyl Compounds in Tibetan Mountain Snow: Temporal Patterns from 1980 to 2010. *Environmental Science & Technology* **2014**, *48* (1), 173-181.
4. Xie, Z.; Wang, Z.; Mi, W.; Möller, A.; Wolschke, H.; Ebinghaus, R., Neutral Poly-/perfluoroalkyl Substances in Air and Snow from the Arctic. *Scientific Reports* **2015**, *5*, 8912.
5. Cai, M.; Zhao, Z.; Yin, Z.; Ahrens, L.; Huang, P.; Cai, M.; Yang, H.; He, J.; Sturm, R.; Ebinghaus, R.; Xie, Z., Occurrence of Perfluoroalkyl Compounds in Surface Waters from the North Pacific to the Arctic Ocean. *Environmental Science & Technology* **2012**, *46* (2), 661-668.
6. Cai, M.; Xie, Z.; Möller, A.; Yin, Z.; Huang, P.; Cai, M.; Yang, H.; Sturm, R.; He, J.; Ebinghaus, R., Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean. *Chemosphere* **2012**, *87* (9), 989-997.
7. Krafft, M. P.; Riess, J. G., Per- and polyfluorinated substances (PFASs): Environmental challenges. *Current Opinion in Colloid & Interface Science* **2015**, *20* (3), 192-212.
8. Krafft, M. P.; Riess, J. G., Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability—Part one. *Chemosphere* **2015**, *129*, 4-19.
9. Cottier, F.; Eicken, H.; Wadhams, P., Linkages between salinity and brine channel distribution in young sea ice. *Journal of Geophysical Research: Oceans* **1999**, *104* (C7), 15859-15871.