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Phycotoxins in the Arctic and Southern Ocean - Generation of baseline data in an unknown field

Master Thesis

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„Das habe ich vorher noch nie versucht!

Also bin ich mir völlig sicher, dass ich es schaffe!“

- Pippi Langstrumpf (Astrid Lindgren)

Cover photo: Sea ice in the Central Arctic Ocean (Franziska Linke)

Danksagung

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Zudem konnte dank eines Stipendiums für die Arktis Expedition von der KSB-Stiftung, diese Arbeit umgesetzt werden und über 500 Proben in der Arktis gesammelt werden.

Danke!

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III Abbreviation

ACC	Antarctic circumpolar current
ASP	Amnesic shellfish poisoning
AWI	Alfred-Wegener-Institute
AZA	Azaspiracid
AZP	Azaspiracid poisoning
C	N-sulfocarbamoyl toxin
CFP	Ciguatera fish poisoning
CI	Cyclic imine
CP-4	Compound 4
CTD	Conductivity, temperature, and depth
DA	Domoic acid
dcSTX	Decarbamoylsaxitoxin
DNA	Deoxyribonucleic acid
DSP	Diarrhetic shellfish poisoning
DTX	Dinophysistoxin
epi DA	Epidomoic acid
FLD	Fluorescence detection
FSW	Filtered seawater
GARS	German Antarctic Receiving Station
GDA	Goniodomin A
GF/F	Glass-fiber filters
GTX	Gonyautoxin
GYM	Gymnodimine
HAB	Harmful algal bloom
HPLC	High-performance liquid chromatography
HSS	High-strength silica
iso DA	Isodomoic acid
KGI	King George Island
LC-MS/MS	Liquid Chromatography-Tandem Mass Spectrometry
LCC_NW	Northwest-Passage-Expedition
LCC_SO	Southern-Ocean Expedition
LCC_TA	Transarctic-Expedition

LoD	Limit of detection
Me	Methyl
MeOH	Methanol
MRM	Multiple reaction monitoring
N_2	Nitrogen
neoSTX	Neosaxitoxin
NSP	Neurotoxic shellfish poisoning
NT	Net tow
OA	Okadaic acid
PFA	Paraformaldehyde
PSP	Paralytic shellfish poisoning
PTX	Pectenotoxin
PTX-2sa	Pectenotoxin-2 seco acid
rpm	Rounds per minute
RT	Retention time
SPATT	Solid-phase adsorption toxin tracking
SPX	Spirolide
SRM	Selected reaction monitoring
STX	Saxitoxin
UHPLC	Ultra-high-performance liquid chromatography
YTX	Yessotoxins

1 Zusammenfassung

Die Ozeane sind aufgrund anthropogener Einflüsse wie Verschmutzung, Überfischung, Schifffahrt und Klimawandel zunehmenden Bedrohungen ausgesetzt. Durch diese verändern sich die Arktis und der Südliche Ozean schneller als andere Meeresregionen. Das Schmelzen des Meereises, steigende Temperaturen und Veränderungen in der Zusammensetzung der polaren Lebensgemeinschaften sind bereits zu verzeichnen. Diese Veränderungen können zu einer Zunahme und Intensivierung schädlicher Algenblüten (HABs) führen, die erheblichen Risiken für marine Lebewesen und Menschen darstellen. Diese Studie zielt darauf ab, eine Basis an Daten für das Vorkommen von Phycotoxinen in den ersten Stufen des polaren Nahrungsnetzes zu schaffen. Zu diesem Zweck wurden Proben des Phytoplanktons, Zooplanktons und gelösten Toxinen während vier Expeditionen in den Jahren 2023 und 2024 sowie an der German Antarctic Receiving Station/O'Higgins (2022 bis 2023) genommen. Lipophile, hydrophile Phycotoxine und Domoinsäure wurden sowohl im Phytoplankton als auch im Zooplankton innerhalb der arktischen Nahrungskette in hohen Konzentrationen nachgewiesen. An der Südspitze Grönlands wurden 2023 Konzetrationen von bis zu 617 $ng \cdot m^{-1}$ NT Domoinsäure im Phytoplankton gemessen. In Zooplanktonproben aus dem Jahr 2024 wurden Phycotoxine bis 84 °N nachgewiesen, dem nördlichsten Punkt, an dem Phycotoxine gefunden wurden. Außerdem wurde der Transfer von lipophilen und hydrophilen Toxinen von der Pteropodenart *Limacina helicina* auf *Clione limacina* nachgewiesen. Im Südlichen Ozean wurde PTX-2 erstmals in Phytoplanktonproben nachgewiesen. Insgesamt zeigen die Ergebnisse anhaltende Veränderungen in den polaren Planktongemeinschaften und unterstreichen die Notwendigkeit einer kontinuierlichen Toxinüberwachung, um die Gesundheit der Ozeane unter dem zunehmendem anthropogenem Druck bewerten zu können.

1 Abstract

The world's oceans face increasing threats due to anthropogenic influences, including pollution, overfishing, shipping activities, and climate change. Among them, the Arctic and Southern Ocean are changing at a much faster rate than other marine regions. Melting sea ice, rising temperatures, and shifts in polar community composition have already been observed. These changes may lead to an increase in the frequency and intensity of harmful algal blooms (HABs), posing significant risks to marine life, human health and well-being. This study aims to provide a baseline about the occurrence of phycotoxins in the base of the polar food webs. For that, phytoplankton, zooplankton and dissolved toxin samples were analysed from four expeditions in 2023 and 2024 and the German Antarctic Receiving Station/O'Higgins. Lipophilic, hydrophilic phycotoxins and domoic acid (DA) were detected in high values both in phytoplankton and zooplankton within the Arctic food web. At the south tip of Greenland in 2023, amounts up to 617 $ng \cdot m^{-1}$ of NT of DA in phytoplankton were measured. In zooplankton samples from 2024, phycotoxins were detected at 84 °N, which is the most northern point where phycotoxins were found. Also, the transfer of lipophilic and hydrophilic toxins from the pteropod species *Limacina helicina* to *Clione limacina* was proven. In the Southern Ocean, PTX-2 was first detected in phytoplankton samples. Overall, the results reveal ongoing changes in polar plankton communities, highlighting the need for continued toxin monitoring to assess ocean health under increased anthropogenic pressures.

2 Microalgae and Harmful Algal Blooms

The aquatic primary production is dominated by phytoplankton (microalgae) worldwide. These are essential microscopic organisms, including dinoflagellates, diatoms, and cyanobacteria, that form the base of the marine food chain and play a crucial role in the global carbon cycle (Geider et al., 2014). They comprise more than 25,000 different species, whose size varies from small cyanobacteria (0.1 μm^3) to diatoms with a size of 10^8 μm^3 (Marañón, 2009; Prants, 2022).

Approximately 300 phytoplankton species have the potential to grow exponentially under favourable environmental conditions, forming dense aggregations called blooms. The growth is mediated by physical (e.g., currents) and chemical factors, such as salinity, temperature, and nutrient availability (Sellner et al., 2003). Blooms of algal species are natural seasonal events that play a crucial role in supporting the food web and providing energy for higher trophic levels (Sommer et al., 2012). When hurtful to the environment, aquatic life, or human health, these are called harmful algal blooms (HABs) (Fig. 1). The harmful effects of HABs are due to oxygen depletion (hypoxia) and reduced light incidence (Hallegraeff & Enevoldsen, 2004; Blay et al., 2011; Watson et al., 2015; Bresnan et al., 2021). Moreover, several microalgae species produce toxic metabolites known as phycotoxins (Farabegoli et al., 2018).

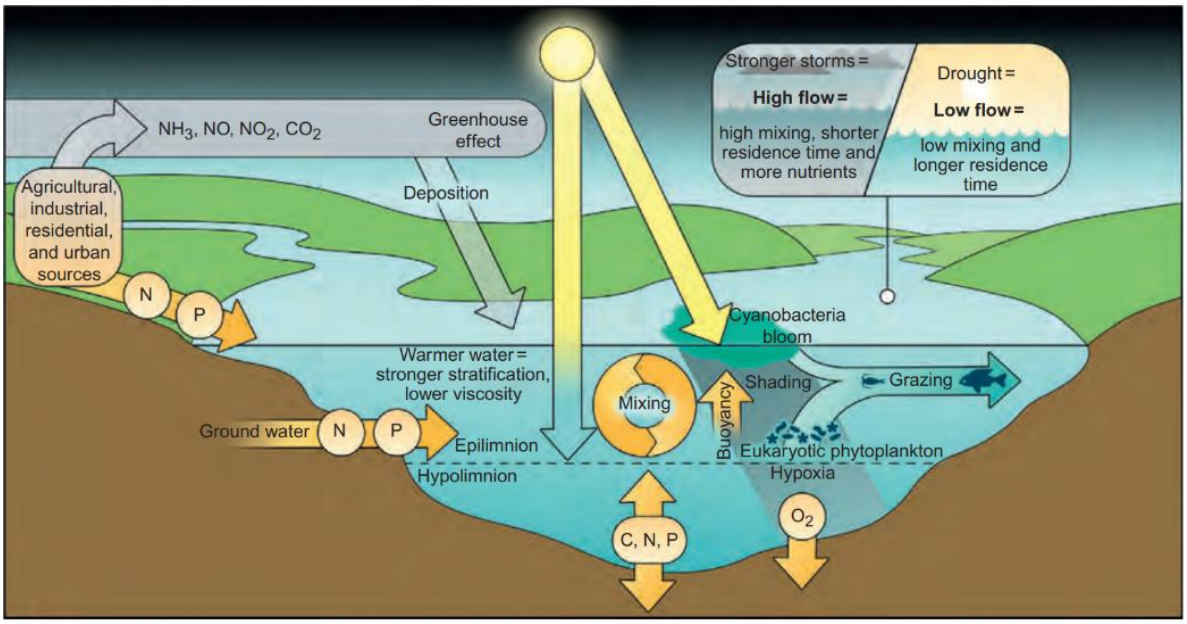

Figure 1: External and internal factors controlling growth, accumulation (as blooms), and fate of harmful algae blooms in freshwater; N: Nitrogen, P: Phosphate; C: Carbonate, O_2: Oxygen (Watson et al., 2015).

HABs have been reported worldwide, but during the last decades, anthropogenic activities leading to eutrophication and global warming have increased the frequency, intensity and distribution of these events (Gobler, 2020). Anthropogenic influence is one of the biggest dangers to the ocean ecosystem. It leads to pollution, overfishing, intensive shipping, and climate change, all of which negatively impact ocean habitats (Steidinger, 1993; Landrigan et al., 2020; Anderson et al., 2021; Karlson et al., 2021).

Even anthropogenic activities, such as aquaculture and mariculture, can create favourable conditions for HAB development (Sellner et al., 2003).

2.1 Phycotoxins

Algal toxins, also known as phycotoxins, are natural second metabolites produced by several microalgae species, primarily dinoflagellates and diatoms, ranging in size from small to medium (300 to over 3000 Da). These are amino acids, alkaloids or polyketides (Rossini & Hess, 2010). Many phycotoxins have isomers that are structurally similar but differ in at least one compound, e.g., a different atom or group, and may differ in toxicity compared to the original toxin. This metabolites can be produced by the phytoplankton species themselves or generated due to the predators' metabolism. Although several isomers have already been described, many are still unknown (Daranas et al., 2001; Villarino et al., 2018).

Toxin-producing algae are consumed by filter-feeding and herbivorous organisms, allowing phycotoxins and their isomers to enter and accumulate along the marine food web (Daranas et al., 2001), potentially leading to toxic effects in vertebrates (Fire & Dolah, 2012; Lefebvre et al., 2016; Hendrix et al., 2021). In recent decades, HABs and phycotoxins have been associated with several events of morbidity and mortality of marine mammals worldwide (Broadwater et al., 2018; Fire et al., 2021), including lower reproductive rates, foetal losses, disorientation and abnormal behaviour observed in species like the California sea lion (Fire & Dolah, 2012; Lefebvre et al., 2016; Hendrix et al., 2021).

Beyond their effects on wildlife, phycotoxins also pose a significant threat to human health. Through the consumption of contaminated seafood, skin contact, or the inhalation of aerosols, these compounds can accumulate in the human body and cause different clinical pictures depending on the toxin class, concentration and exposure level (Hallegraeff, 1993; Berdalet et al.; 2016). Based on the symptoms they cause in humans when consuming poisoned seafood, these toxins are classified into six different syndromes: paralytic shellfish poisoning (PSP), neurotoxic shellfish poisoning (NSP), ciguatera fish poisoning (CFP), diarrhetic shellfish poisoning (DSP), amnesic shellfish poisoning (ASP), and azaspiracid shellfish poisoning (AZP).

From a chemical perspective, they can be divided into hydrophilic and lipophilic toxins. Hydrophilic toxins are soluble in water, and lipophilic toxins are soluble in organic solvents. NSPs, CFPs, DSPs, and AZAs are lipophilic and extracted using organic solvents, such as methanol (MeOH). Domoic acid (DA) and its isomers are neither hydrophilic nor lipophilic and are usually extracted using a mixture of MeOH and water (50:50), or with MeOH and analysed together with lipophilic toxins (Daranas et al., 2001). Additionally, the class of cyclic imine (CI) toxins was added in recent years and belongs to the lipophilic toxins (Guéret & Brimble, 2010). In contrast, PSPs are hydrophilic and extracted using acidic aqueous solutions.

2.1.1 Lipophilic Toxins

DSP toxins inhibit the serine/threonine phosphatases 1 and 2A, causing diarrhea, nausea, vomits and abdominal pain. Monitoring programs have documented outbreaks frequently and worldwide (Tachibana et al., 1981; Daranas et al., 2001; Nielsen et al., 2012; Valdiglesias et al., 2013; Farabegoli et al., 2018). Dinophysistoxins (DTX), okadaic acid (OA) (Fig. 2), pectenotoxin (PTX) and isomers belong to this class. These toxins are chemically related and often produced by the same phytoplankton species, e.g., the dinoflagellates *Dinophysis acuminata* or *Dinophysis acuta and Prorocentrum lima* (Krock et al., 2020; Möller et al., 2022). As precursor units of phycotoxins produced by dinoflagellates, acetate, glycolate, and the amino acid glycine have been identified (Van Wagoner et al., 2014).

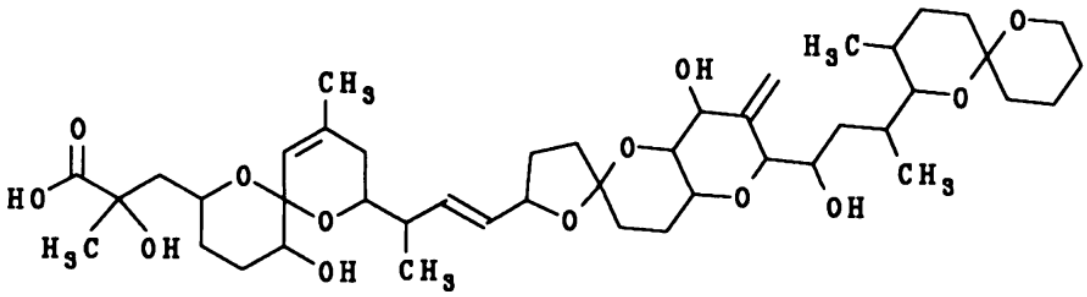

Figure 2: Chemical structure of okadaic acid (Tachibana et al., 1981).

Azaspiracids (AZA) and isomers are oxygenated polyethers produced by the family *Amphidomataceae*. They cause AZP, which leads to a reduction of T- and B-lymphocytes and fatty acid changes in the liver (Farabegoli et al., 2018; Wietkamp et al., 2020). The main symptom in humans is diarrhea that occurs after consuming shellfish contaminated with AZAs (Satake et al., 1998).

Brevetoxins, which cause NSP, are polyethers that bind to voltage-gated sodium channels in the human body, leading to inappropriate channel opening (Huang et al., 1984). Approximately 24 to 48 hours after exposure, the following symptoms may occur: nausea, tingling and numbness of the perioral area, muscle aches, loss of motor control, and seizures. Massive coastal fish kills have been associated with brevetoxins (Steidinger, 1993). The algae species that produce brevetoxins is *Karenia brevis* (Steidinger, 1993; Monroe & van Dolah, 2008).

Ciguatoxin, maitotoxin, scaritoxin, or gambiertoxin cause CFP and are produced by dinoflagellates, such as *Gambierdiscus* species. The chemical structure, pharmacological target, and symptoms are similar to brevetoxins. The toxin accumulates in piscivorous reef fishes like groups, snappers and barracuda, and every year, more than 50,000 people get intoxicated. Normally, the symptoms last for some weeks, but some people have them also for years after exposure (Steidinger, 1993; Daranas et al., 2001; Fire & Dolah, 2012).

Cyclic imines (CI) are among the most recently discovered group. They have 14 to 27 carbonate atoms arranged in a macrocyclic ring system (Guéret & Brimble, 2010). CIs are a class of lipophilic shellfish

toxins comprising gymnodimines (GYM), spirolides (SPX), pinnatoxins, portimines, pteriatoxins, prorocentrolides, spiro-prorocentrimine, symbiomines and kabirimine (Stivala et al., 2015; Finch et al., 2024). Several dinoflagellates produce these toxins worldwide. The *Prorocentrum* species *P. lima* and *P. maculosum* produce procentrolides (Hu et al., 1996; Lu et al., 2001; Torigoe et al., 1988). GYMs are known to be produced by *Karenia selliformis* (Haywood et al., 2004). The mixotrophic dinoflagellate *Alexandrium ostenfeldii* produces several SPXs (Cembella et al., 2000), GYMs (Van Wagoner et al., 2011) and, in addition, PSP toxins (Hansen et al., 1995). So far, it is the only known species that produces three different toxin classes (Martens et al., 2017).

2.1.2 Domoic Acid and Isomers

DA is a water-soluble tricarboxylic acid and one of the most recognized algae toxins in seafood worldwide (Fig. 3). The production of DA and its isomers is reported in the red macroalgal species *Chondria armata* and *Digenea simplex*. However, DA is primarily produced by the diatom genus *Pseudo-nitzschia*. This toxin causes the ASP syndrome by binding to specific neuron receptors, damaging neuronal pathways, leading to clinical symptoms like nausea, vomiting, abdominal cramps, diarrhea, headache, neuronal dysfunction, and memory loss (Tachibana et al., 1981; Daranas et al., 2001; Nielsen et al., 2012; Valdiglesias et al., 2013; Bates et al., 2018; Farabegoli et al., 2018).

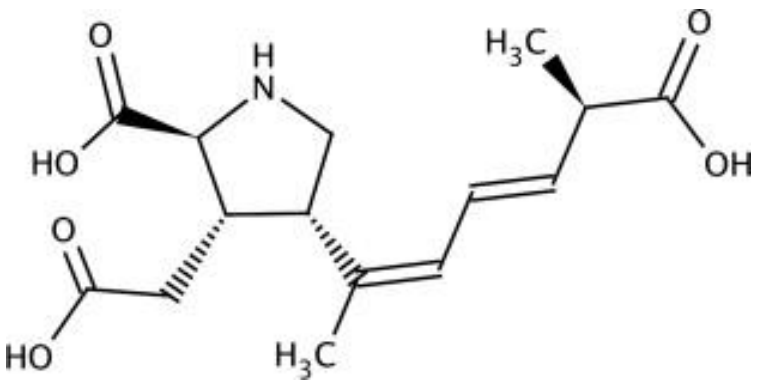

Figure 3: Chemical structure of domoic acid (Hambright et al., 2014).

2.1.3 Hydrophilic Toxins

The dinoflagellate species from the genera *Alexandrium, Gymnodinium* and *Pyrodinium* produce saxitoxin (STX) and isomers that cause PSP (Daranas et al., 2001). These toxins block the voltage-gated sodium channels, causing neurological problems, like paralysis and tingling (Egmond, 2004), immediately after consumption and leading to death in the most severe cases (Daranas et al., 2001; Lefebvre et al., 2016).

2.2 Polar Waters

The polar waters at the northern and southernmost points of our planet are two unique distinct regions (Lannuzel et al., 2020). These are one of the most productive ecosystems worldwide. In both regions, harsh climate conditions prevail, characterized by winters without sunlight and summers with prolonged daylight, as well as cold temperatures year-round. Other factors, such as the influence of surrounding oceans, differ between them. The Arctic waters are surrounded by land and influenced by the adjacent oceans, specifically the Pacific and Atlantic Oceans (Krucke et al., 2021). In contrast, the Southern Ocean is characterized by the strong Antarctic Circumpolar Current (ACC) that surrounds the Antarctic continent and exchanges water with the surrounding oceans in the North. The ACC between latitudes 45 and 55 °S is a wind-driven system and the most powerful current worldwide. It has a high influence on the regional climate and biodiversity, while connecting the Atlantic, Indian and Pacific Oceans (Lamy et al., 2024). The Antarctic and the surrounding Southern Ocean are also one of the driest regions in the world and are often referred to as the coldest desert (Benninghoff, 1987).

Organisms unique to both regions can be found, each adapted to the specific environmental conditions. However, these ecosystems have undergone significant changes in recent years, with rising temperatures, melting sea ice, and the replacement of polar communities by subpolar communities being reported. These shifts begin at the base of the food web, with phytoplankton, as primary production depends on the availability of nutrients, and progress to higher trophic levels. Changes in ice dynamics, such as a later freeze-up, may alter algal bloom timing, with autumn blooms becoming a more regular event. These changes are expected to have a negative downstream effect on the polar inhabitants (Lannuzel et al., 2020). Additionally, it is anticipated that in the polar regions, harmful algal species will play a more dominant role (Hoerstmann et al., 2025).

The toxin-producing dinoflagellate *Alexandrium catenella* and the diatom *Pseudo-nitzschia spp.* are well-known components of Arctic phytoplankton communities. In the western Arctic, diatoms dominate in the spring, while dinoflagellates are more prevalent in summer and autumn. *Pseudo-nitzschia spp.* are producers of DA and isomers (Bruhn et al., 2021). Already in 2005, *A. catenella* was reported at Point Barrow, the northernmost point of Alaska (Okolodkov, 2005). Some years later, this species was reported in northwest Greenland (2012) and in the subarctic region near Iceland (2009) (Baggesen et al., 2012; Burrell et al., 2013). *A. catenella* produces PSP toxins, and nowadays, Arctic waters have one of the highest incidences of PSP worldwide, with reported cases tripling from 2011 to 2020 compared to the previous 30 years (McIntyre et al., 2021). Recently, cells and cyst beds of *A. catenella* have been found from the Bering Strait to the Bering Sea, north of Alaska and Canada (Gu et al., 2013; Natsuike et al., 2013; Vandersea et al., 2017; Fachon et al., 2024) up to 76°N (Richlen et al., 2016). These cysts overwinter in the sediments and are a potential source of HABs when water temperatures rise and physical and chemical conditions change (Fachon et al., 2024).

The dinoflagellate *A. ostenfeldii,* present in temperate waters worldwide, was first described in Arctic waters in 2012 (Tillmann et al., 2017). This species is the only known producer of SPXs (Cembella et al., 2000, 2001).

In the Southern Ocean, diatoms are the dominating phytoplankton group, producing 50 to 90 % of the total biomass throughout the year (Smith et al., 2007; Armbust, 2009; David & Saucède, 2015). Within them, the genus *Pseudo-nitzschia* plays an important role (Andreoli et al., 1995; Malviya et al., 2016), with eight different species described to date (Costa et al., 2020; Saggiomo et al., 2021). The first evidence of a toxic *Pseudo-nitzschia* species in the Southern Ocean was reported in 2021 (Olesen et al., 2021). However, in the Southern Ocean, a knowledge gap in understanding phytoplankton taxonomy, diversity, distribution, and ecology still remains (Costa et al., 2020; Saggiomo et al., 2021).

2.3 Polar Food Web

Higher organisms rely on phytoplankton, directly or indirectly, in both polar regions as a primary food source (Fig. 4 and 5). Zooplankton, such as copepods, krill or pteropods, feed directly on phytoplankton and in turn, serve as prey for higher trophic levels, e.g., fish and marine mammals. Thus, zooplankton species are important vectors in the food chain, transferring phycotoxins to higher trophic levels (e.g., odontocete cetaceans and humans) (Fachon et al., 2024). Moreover, the two polar regions are among the most important feeding grounds for many marine mammals and seabirds worldwide (Riekkola et al., 2018). The replacement of native polar phytoplankton species by subpolar, toxin-producing species poses a growing threat to the whole polar food web and might contribute to mass mortality events of marine organisms in these regions (Broadwater et al., 2018; Fire et al., 2021).

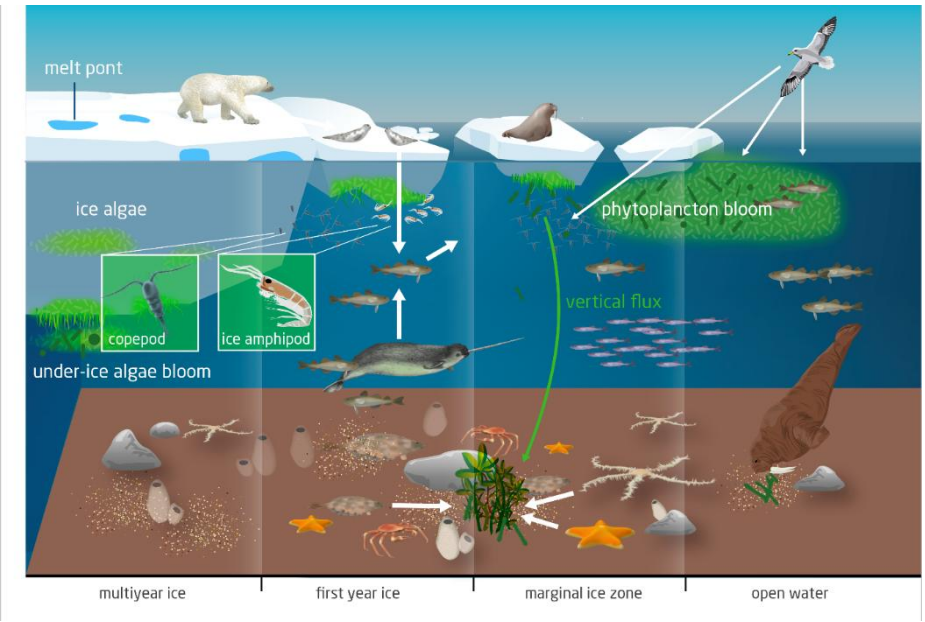

Figure 4: Scheme Arctic food web. From Sea-ice biology 05 Scheme Arctic food web [Infographic], by Alfred Wegener Institute & Sea Ice Portal, n.d. (https://www.meereisportal.de/fileadmin/user_upload/Infografiken/Meereisbiologie/Englisch/1._Meereis_als_Lebensraum/Sea-ice_biology_05_Scheme_Arctic_foodweb.png [27.10.2025].

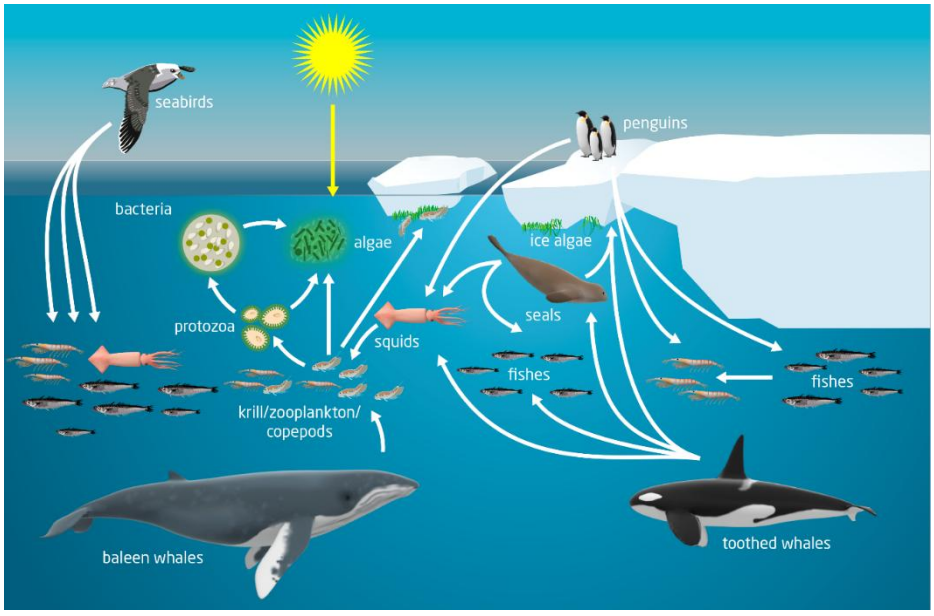

Figure 5: The Antarctic food web. From Sea-ice biology 06 Scheme Antarctic food-web [Infographic], by Alfred Wegener Institute & Sea Ice Portal, n.d. (https://www.meereisportal.de/fileadmin/user_upload/Infografiken/Meereisbiologie/Englisch/1._Meereis_als_Lebensraum/Sea-ice_biology_06_Scheme_Antarctic_foodweb.png) [27.10.2025].

To detect ecological changes and document seasonal and decadal trends, long-term observing programs in the polar regions are necessary. Currently, these monitoring programs are absent, and little is known about the distribution of phycotoxins in polar waters. For example, there are no offshore HAB monitoring programs in the US waters of the Chukchi Sea, despite it being known that seasonal blooms that pose risks to the ecosystem and food safety are occurring in this region (Fachon et al., 2024). Moreover, the limited data available are primarily from coastal regions, as they are easier to access,

especially in the polar regions, and are important for the local fishing industry. However, with continued ocean warming, HABs are expected to occur more often in offshore waters (Lefebvre et al., 2025), highlighting the necessity of long-term monitoring programs to understand and mitigate these emerging risks.

Research Aim

The aim of this study is to investigate the occurrence and distribution of phycotoxins in Arctic waters and in the Southern Ocean by collecting and analysing phytoplankton, zooplankton and water samples from polar coastal and oceanic regions. The main objective is to expand knowledge of phycotoxin presence in these understudied areas and improve our understanding of toxin exposure and transfer at the base of polar food webs, where studies remain scarce. It also aims to provide insight into the current status of phycotoxin occurrence in these regions, establishing a baseline to further assess phycotoxin expansion in response to environmental change.

To do so, the following specific objectives were considered as part of the thesis:

1. To identify and quantify phycotoxins produced by microalgae (phytoplankton) in Arctic coastal and open waters through the analysis of phytoplankton net samples and dissolved toxin samples collected during three research cruises, to establish data on their presence and diversity and determine whether toxins not previously described in these regions occur.
2. To investigate the transfer of phycotoxins through the lower trophic levels of the marine food web, from phytoplankton to zooplankton, considering both primary consumers (herbivorous zooplankton) and secondary consumers (carnivorous zooplankton feeding on other zooplankton), thereby providing novel information on toxin levels and pathways at the base of polar food webs.
3. To assess species-specific differences in phycotoxin exposure among zooplankton taxa, identifying those that are more prone to toxin uptake that may play a key role in transferring phycotoxins to higher trophic levels.
4. To expand knowledge on the occurrence and distribution of phycotoxins in the Southern Ocean, where current information is extremely limited, by analysing available samples from a single research cruise and a few dissolved toxin samples, and to compare these findings with Arctic systems.

4 Material and Methods

This section provides information on the study areas, field samples collected, and the procedures for toxin extraction and analysis. It included protocols for solid-phase adsorption toxin tracking (SPATT) and phycotoxin extraction for phytoplankton and zooplankton samples, as well as methods for their detection, identification, and quantification using liquid chromatography-tandem mass spectrometry (LC-MS/MS) and high-performance liquid chromatography fluorescence detection (HPLC-FLD). The protocols have been refined and updated over the years within the Phycotoxin group at the Alfred-Wegener-Institute (AWI), led by Dr. Bernd Krock.

4.1 Study Area

The study areas for this thesis were the two polar regions: the Arctic waters and the Southern Ocean around Antarctica. The samples were collected during three Arctic and one Antarctic expeditions, as well as at the German Antarctic Receiving Station (GARS)-O'Higgins (63°19'16.04"S - 57°54'4.31"W).
The LCC_NW (11th of September to the 5th of October 2023) started on the east coast of Greenland through the Northwest-Passage and ended in Seattle, USA, on board the cruise ship Le Commandant Charcot. A total of 285 samples were collected, including phytoplankton, zooplankton, AZA and dissolved toxin samples at 22 different stations (Fig. 6; Tab. S1).

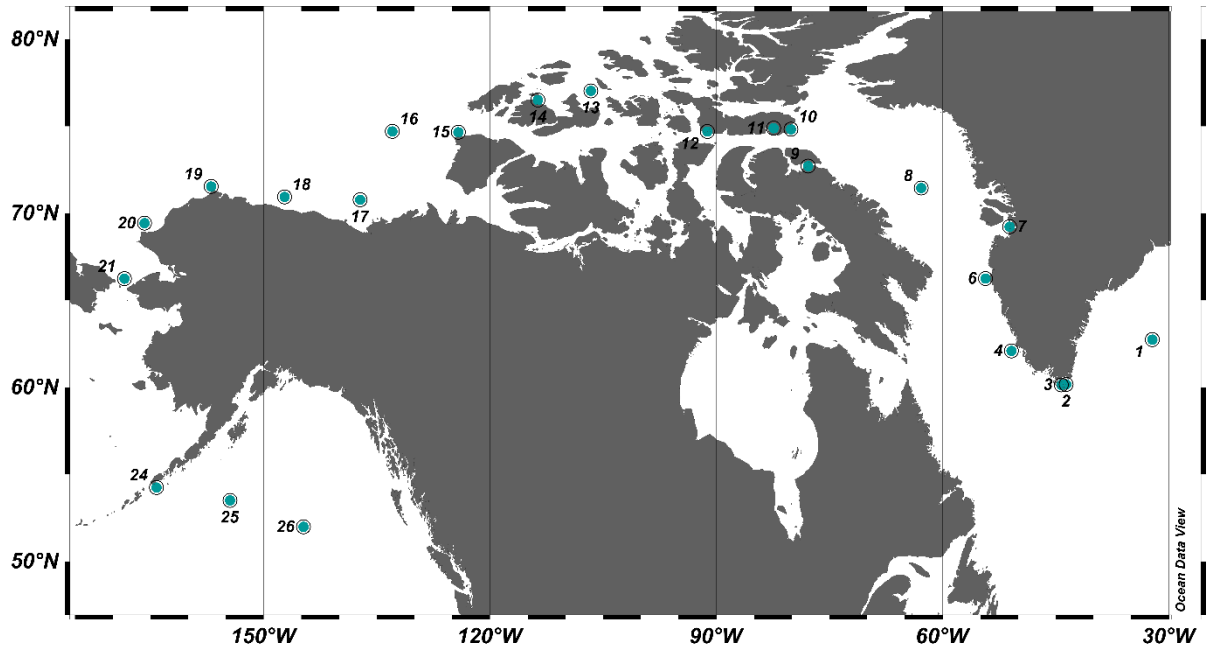

Figure 6: Map with the stations from the "Northwest-Passage" Expedition (LCC_NW) on Le Commandant Charcot in 2023.

The ARA15A expedition in the central Arctic, Chukchi Sea, Bering Sea and Strait was performed from the 30th of July to the 24th of August 2024 on board the RV Araon. A total of 41 stations with 565 field samples were collected, including phytoplankton, zooplankton and dissolved toxins (Fig. 7; Tab. S2).

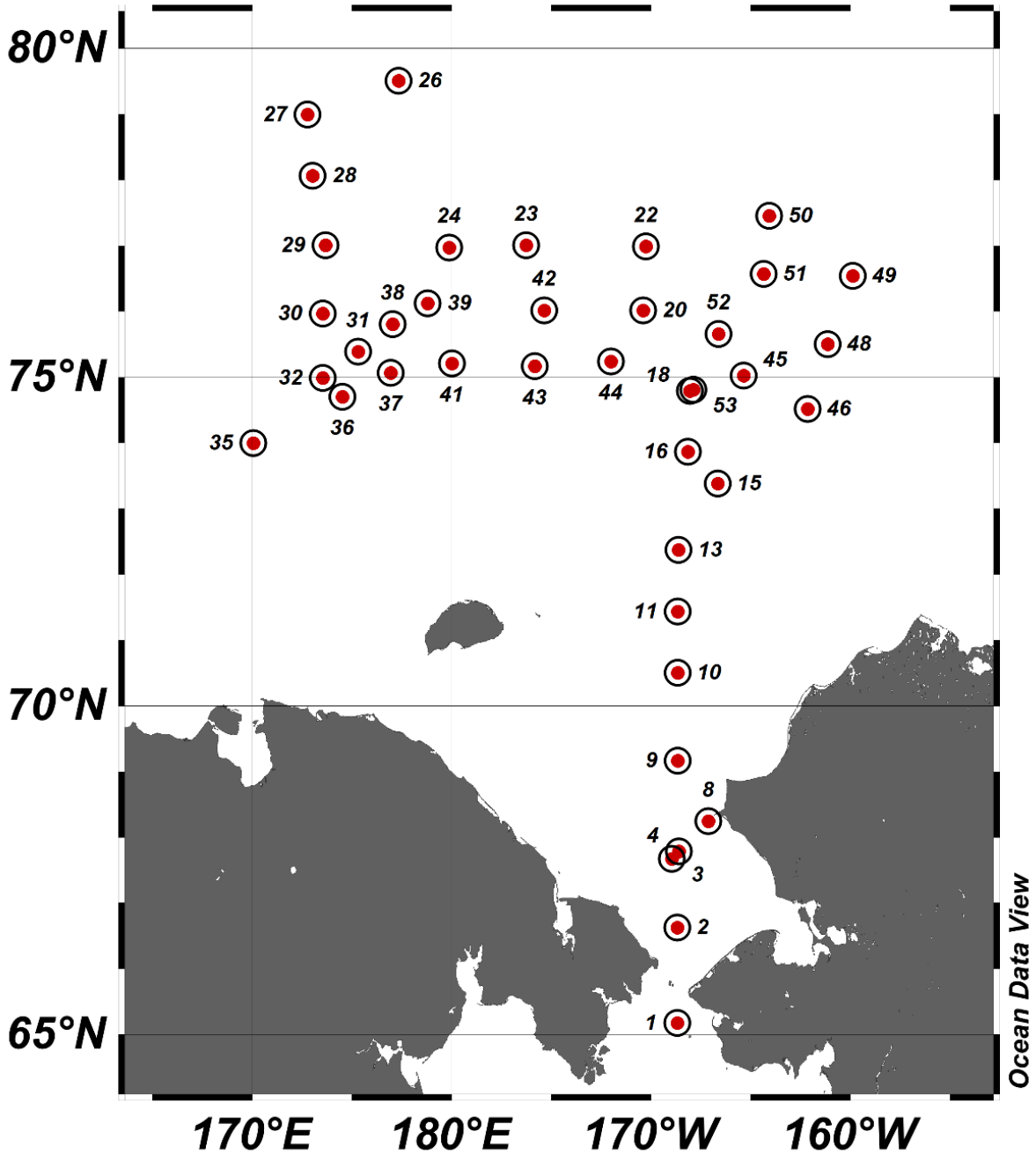

Figure 7: Map with the stations from the ARA15A expedition on the RV Araon in 2024.

The LCC_TA from the 8th to the 25th of September 2024, starting in Nome, Alaska, on the cruise ship Le Commandant Charcot, sampled at 13 stations and 183 samples (phytoplankton, zooplankton, AZA and dissolved toxin samples) were collected (Fig. 8; Tab. S3).

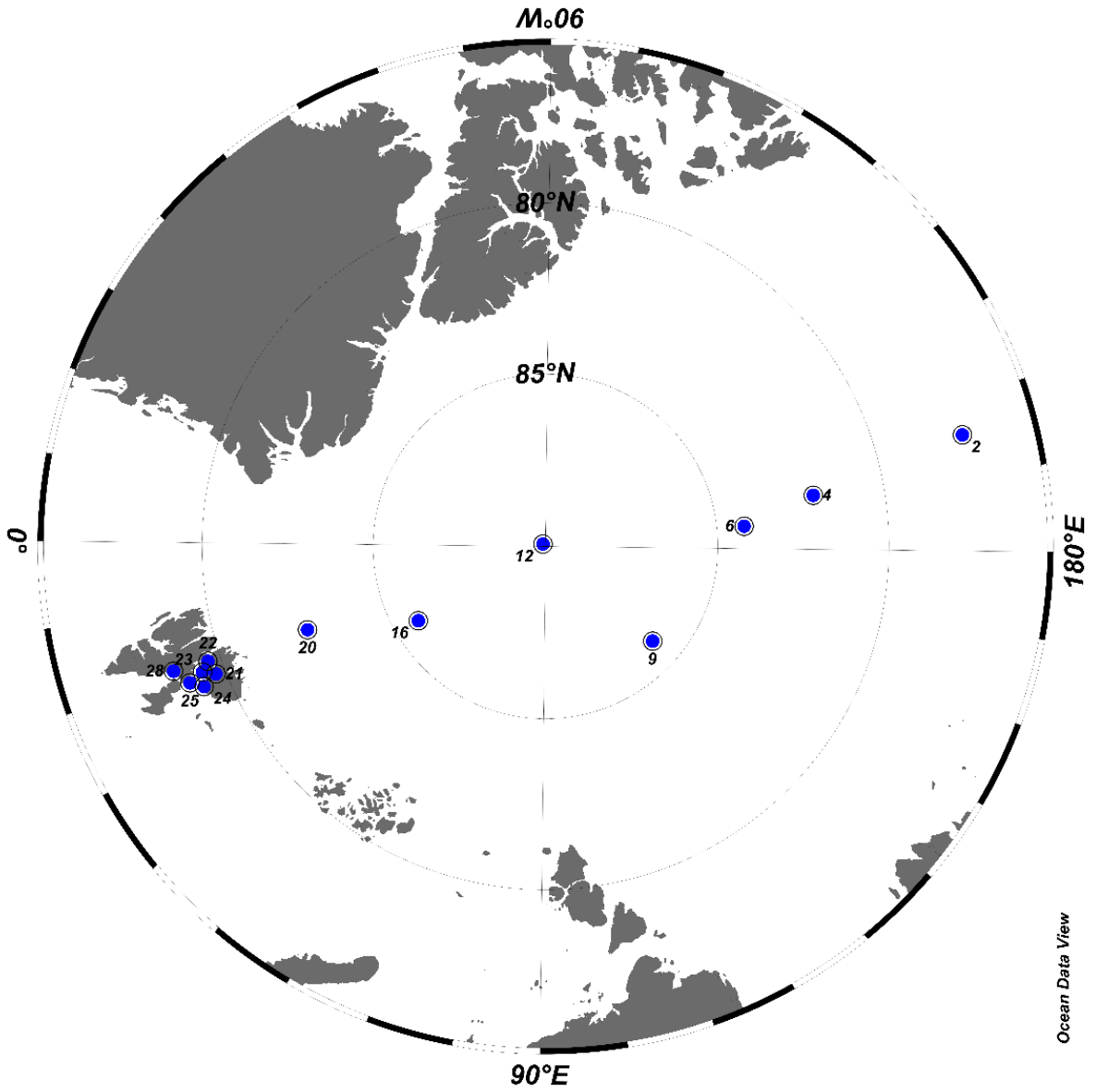

Figure 8: Map with stations from the "Transarctic" Expedition (LCC_TA) on the Commandant Charcot 2024.

In the Southern Ocean, samples were collected from the 10th to the 29th of January 2024, during an expedition (LCC_SO) along the west coast of the Antarctic Peninsula, also on board the French cruise ship Le Commandant Charcot (Fig. 9, Tab. S4). At the northern tip of the Antarctic Peninsula, in collaboration with the GARS-O'Higgins, dissolved toxins were collected with SPATT bags from April 2022 to April 2023 (Fig. 9).

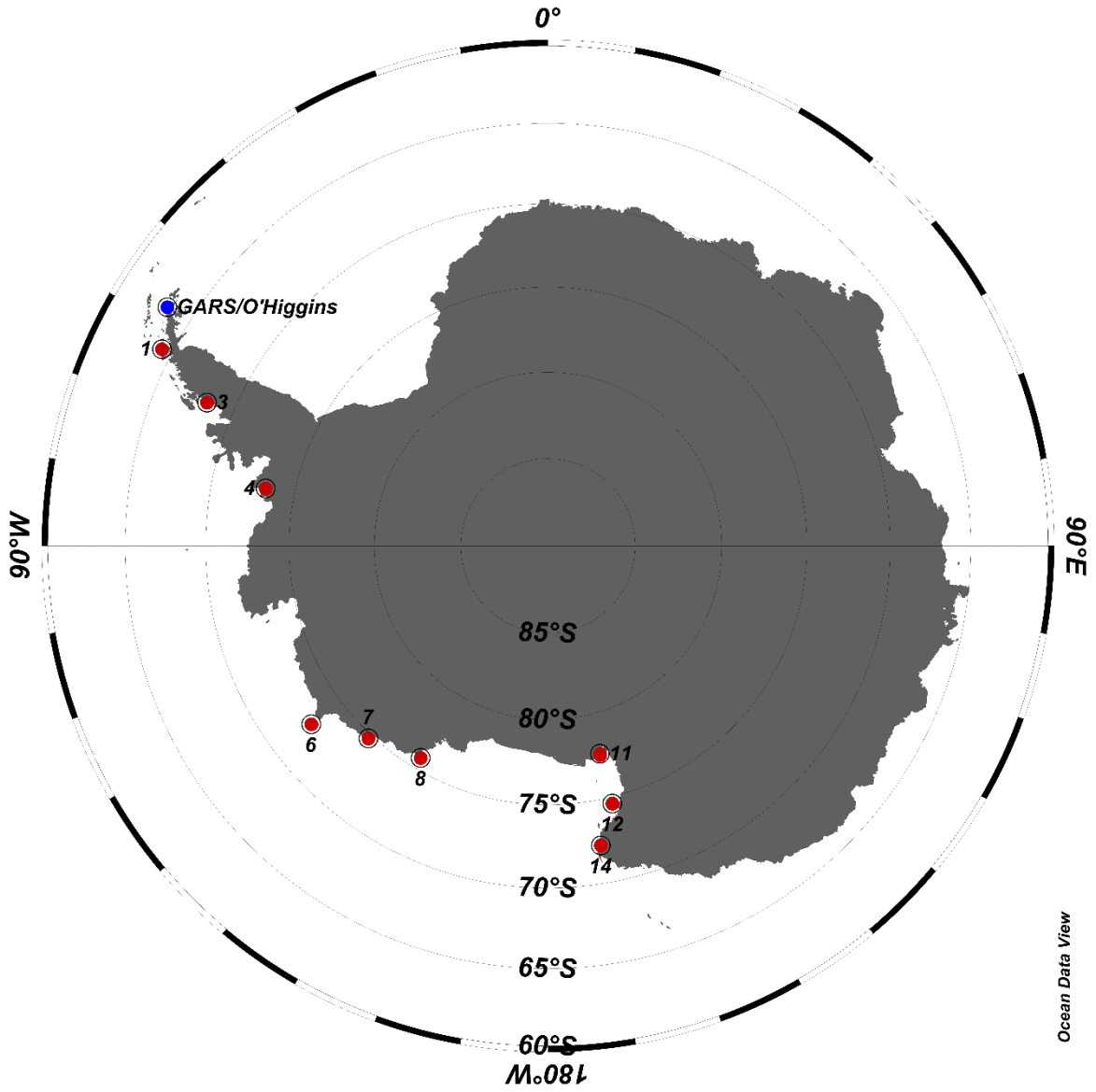

Figure 9: The ten Antarctic sampling stations collected during an Antarctic-Expedition 2024 on board Le Commandant Charcot (red) and the German Antarctic Receiving Station (GARS)-O'Higgins (blue).

4.2 Sample Collection

Phytoplankton, zooplankton, dissolved toxins and seawater samples were collected during the four expeditions.

4.2.1. Plankton samples

On board the cruise ship "Le Commandant Charcot"

During the LCC_NW, LCC_TA and LCC_SO expeditions on board Le Commandant Charcot, two nets were used for plankton sampling: one net with a 20 µm-mesh size to collect phytoplankton and a bigger net with a 150 µm-mesh size to collect zooplankton. The nets were lowered up to a depth of 30 m for phytoplankton and up to 50 m for zooplankton, collecting plankton from the water column (Tab. S1, 2,

4). A winch was used to deploy the nets at a speed of 0.5 $m \cdot s^{-1}$. From the net, the water collected in the net collector was transferred to a canister. With filtered seawater (FSW), the collector was flushed to ensure the collection of most of the sample and the volume was added to the canister (Fig. 10). The volumes collected from multiple tows were combined.

Figure 10: Cleaning of the net with filtered seawater (FSW) to ensure the collection of most of the biomass (Photo: Marina Arregui).

With FSW the volume of the samples was adjusted to a defined volume, depending on the amount of biomass collected. From the phytoplankton samples, 18 ml were transferred to a 20 ml glass vial, and 2 ml paraformaldehyde (PFA) [20 %], to a final concentration of 1 % PFA, were added to fix the samples for taxonomic studies. From the zooplankton samples, 160 ml were mixed with 40 ml PFA [20 %], and a final concentration of 4 % PFA was used to fix the samples. Moreover, at some stations in LCC_NW and LC_SO expeditions, zooplankton individuals belonging to certain taxonomic suborders or species were collected from the filter, identified under the stereomicroscope, and stored apart frozen [- 20 °C] to detect toxins in these specific organisms. These samples were put in 2 or 5 ml-tubes, depending on the size of the individual or the number of individuals collected.

The rest of the sample, both for phytoplankton and zooplankton, was filtered using filter towers with decreasing mesh sizes. For phytoplankton, three filters with mesh sizes of 200, 50 and 20 µm were used. As a result, three fractions were obtained for the phytoplankton: larger than 200 µm, between 200-50 µm, and between 50-20 µm. For the zooplankton samples, four filters were used to collect zooplankton fractions larger than 1000 µm, between 1000-500 µm, 500-250 µm, and 250-150 µm. Each fraction was rinsed with FSW from the tower filters and put into a 50 ml-tube. The volume was filled up to 45 ml and divided into three aliquots of 15 ml collected in 15-ml tubes (deoxyribonucleic acid (DNA), hydrophilic and lipophilic toxins together with DA). Then, the samples were centrifuged for 15 min at maximum speed, and the supernatant was discarded. The pellet and some remaining water (approximately 2 ml) were left and transferred to a 2 ml-tube. Before storage, the samples were centrifuged again for 15 min to separate the supernatant and the pellet. The supernatant was discarded with a pipette. The samples were stored at -20°C until the extraction at AWI.

In most of the 26 stations of the LCC_NW, plankton samples were taken. No zooplankton samples could be taken in Canadian waters (stations 9 to 17) due to the lack of governmental permits. During the LCC_SO and LCC_TA phytoplankton and zooplankton samples were taken in international waters according to the prevailing laws.

<u>On board the Korean icebreaker RV Araon</u>

On the Korean icebreaker RV Araon, four nets were used for plankton sampling: a 20 µm-mesh size net to collect phytoplankton, two Bongo nets with 150 and 500/350 µm-mesh sizes, one Ring and a Frame Trawl net with 500 µm-mesh size to collect zooplankton (Fig. 11). The phytoplankton net was lowered up to a depth of 100 meters, and the zooplankton nets were deployed up to 1500 m from the stern of the ship. A winch was used to deploy the nets at a speed of 0.5 $m \cdot s^{-1}$ for phytoplankton and 0.8 $m \cdot s^{-1}$ for the zooplankton nets (Tab. S2). After deploying the nets, the collector was rinsed with FSW, and the biomass was collected in a 1 L-bottle.

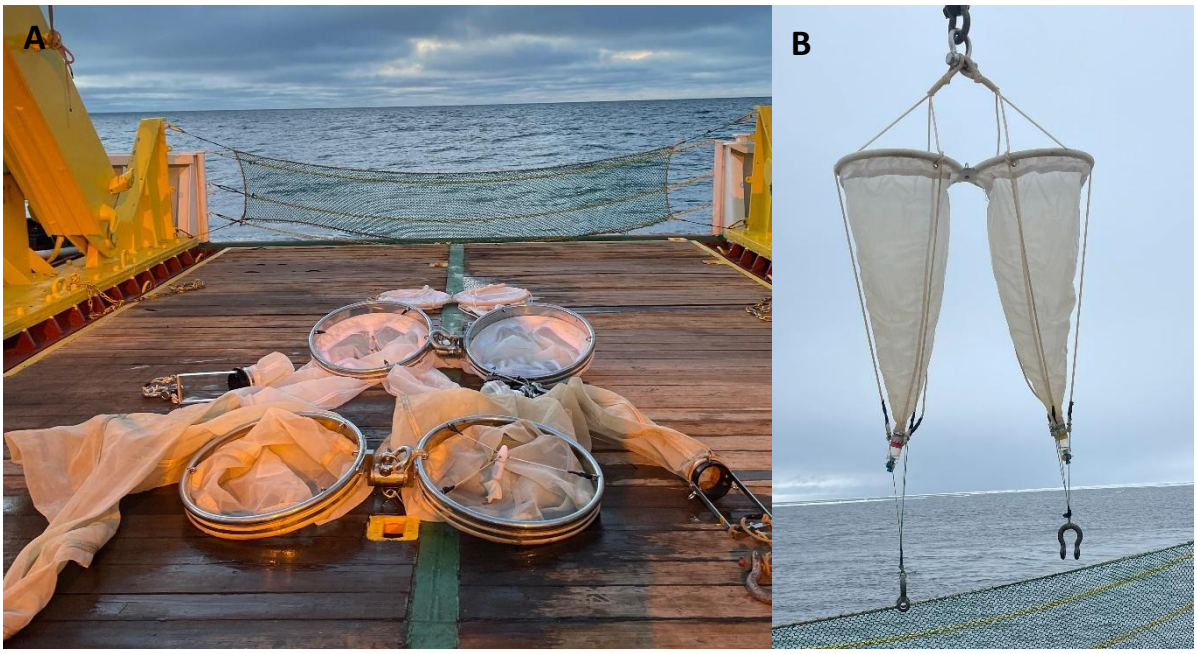

Figure 11: (A) Three plankton nets for sampling: 500 and 350 um Bongo net (bottom), 150 um Bongo (middle) and 20 um phytoplankton net (top); (B) Phytoplankton twin net (Photos: Franziska Linke).

For phytoplankton, similarly to the other expeditions, the sample was filtered using the same filters (200, 50 and 20 µm) to obtain the three fractions. As in the other expeditions, the filters were flushed, and three aliquots (DNA, hydrophilic and lipophilic toxins and DA samples) of 15 ml per fraction were obtained. Due to the lack of a centrifuge for this purpose onboard, samples were filtered through a filter system using a syringe to separate the liquid from the biomass on the filter. The 0.45 µm nylon filters (Merck KGaA, Darmstadt, Germany) were used for DNA samples and for the hydrophilic and lipophilic together with DA toxins glass-fiber filters (GF/F) (Whatman, Cytiva, Marlborough, USA) were used. The filter was folded and transferred to a 2 or 5 ml-tube (Fig. 12). At some stations, multiple filters

were used for one fraction to prevent the blockage of the filter. The samples were stored at -20°C until the extraction at AWI.

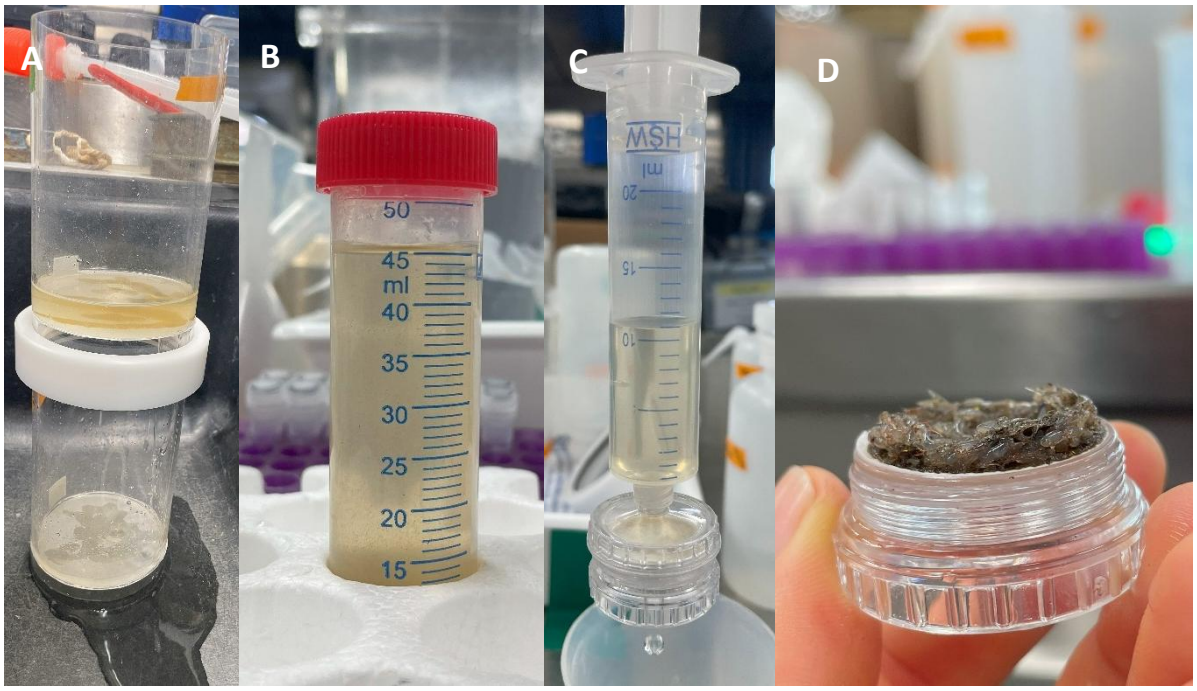

Figure 12: (A) Filter tower with mesh size 50 and 20 um; (B) 50 mL tube with 50 to 200 um fractions; (C) Syringe with filter system to filter phytoplankton samples; (D) Filter with biomass (filter cake) over 200 um fraction (Photos: Franziska Linke).

For the zooplankton samples, several individuals were collected from the nets, separated, and identified using a stereomicroscope during the expedition (Fig. 13). The number of individuals, species, depth, and the type of net used were noted. The individuals were put into 2 ml- or 5 ml-tubes, depending on the number and size of the individuals.

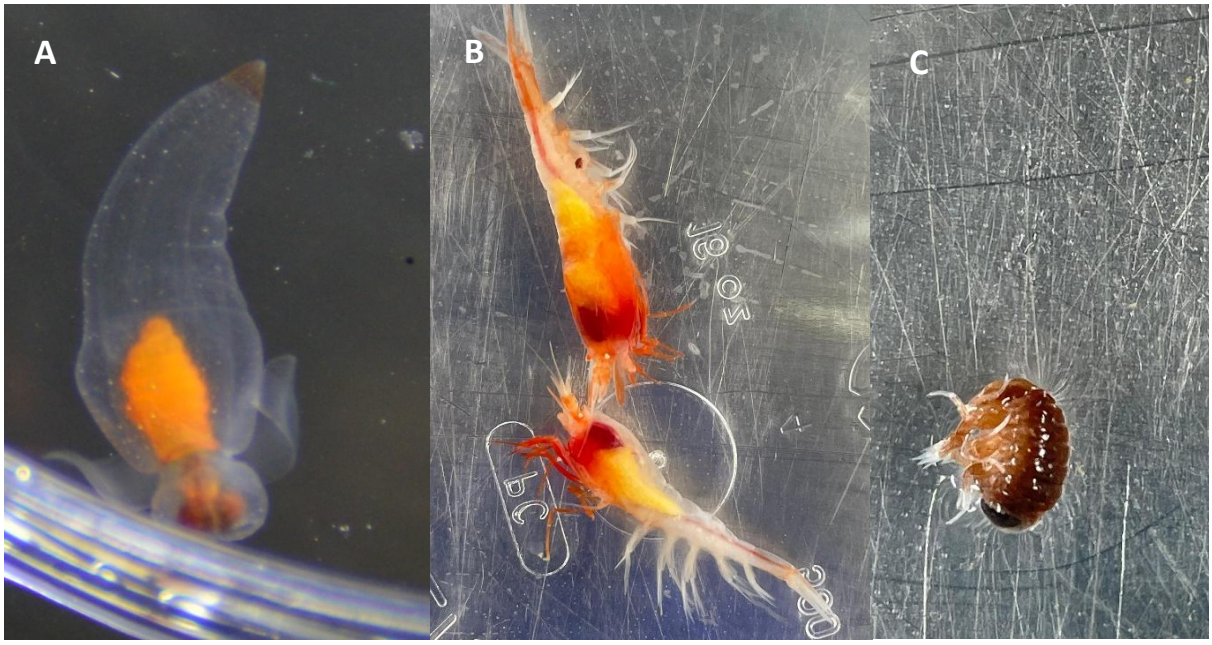

Figure 13: Zooplankton individuals from the ARA15A expedition: (A) Clione limacina; (B) Northern deep-sea shrimp; (C) Amphipod (Photos: Franziska Linke).

During the expedition, 53 stations were sampled. At 41 stations, phytoplankton and zooplankton nets were deployed at the other stations no nets were deployed. At station 6 only zooplankton and at station 30 only phytoplankton sampling was possible.

4.2.2 Azadinium

The dinoflagellate *Azadinium sp*. produces AZAs. Because these species are smaller than 20 µm, if present in the sample, they will not be retained by the filter towers, including the one with the lower mesh size (20 µm). Thus, to sample *Azadinium sp.* and its associated toxins, 8 L-Niskin bottles were deployed at LCC_NW, LCC_SO and LCC_TA. The bottles were lowered and closed to collect water samples at the surface, 10 m and 20 m depth (Fig. 14). A conductivity, temperature, and depth (CTD) - instrument was attached to the rope to collect data on depth, water temperature, salinity, and oxygen levels.

Figure 14: Sampling with the Niskin-Bottle and CTD-instrument (Photo: Marina Arregui).

Once collected, 2 to 4 L of mixed water from the three depths were filtered through a 5 µm polycarbonate filter (Merck KGaA, Germany) for AZA determination. The filtration was applied under low vacuum [max. 200 mbar].

After filtration, the filter was immediately put into a 50 ml-tube and washed with 1 ml MeOH [100 %] until complete decoloration was observed. Then, the MeOH was transferred to a spin filter for centrifugation for 1 min at maximum. speed. The filtrate obtained was put into a labelled HPLC-vial and stored frozen [-20 °C] until measurement for toxin AZA detection with the analytical equipment at AWI.

4.2.3 Solid-phase adsorption toxin tracking (SPATT) sampling

During all the expeditions (Tab. S5 and S6) and at GARS-O'Higgins (Tab. S7), toxins dissolved in the water were collected. For that, SPATT bags were used (MacKenzie et al. 2004). These are bags of 50-µm mesh gauze filled with 10 g Diaion HP20 (Sigma, Deisenhofen, Germany), activated before the expedition by putting them into MeOH [100 %] and stirring overnight. The activated SPATTs were washed with water

and then individually placed in a moist zip-lock bag. On board, the SPATTs were placed into a 2 L-bucket on the ships and a continuous flow of 400-500 ml·min^{-1} of seawater into the bucket was adjusted. After 2 to 4 days, the SPATT bag was replaced and put in a plastic bag (Krock et al., 2020). At the GARS-O'Higgins the bags were stationed in the harbour at the northern tip of the Antarctic Peninsula between 15 and 31 days. While for some months the sampling was not possible at GARS-O'Higgins because of the ice shield. In addition, some bags opened, and the sample was lost. As a result, for some months there has been no sample and data. Before and after usage, the SPATT bags were stored at 4 °C.

In total, 1167 field samples at 86 stations were collected in the polar waters: 516 phytoplankton, 579 zooplankton, 40 *Azadinium* and 32 dissolved toxin samples. A total of 135 samples were collected in the Southern Ocean near Antarctica, and 1,032 in Arctic waters (Tab. 1).

Table 1: Number of samples from the four expeditions and Antarctic station: LCC_NW (Northwest-Passage), GARS (GARS-O'Higgins), LCC_SO (Antarctic Expedition), ARA15A and LCC_TA (Transarctic); green: Southern Ocean, blue: Arctic waters.

Cruise/Project	Phytoplankton	Zooplankton	AZA	SPATTs	Total No. of samples	Stations
LCC_NW	138	127	17	3	285	22
GARS	-	-	-	8	8	1
LCC_SO	60	48	11	8	127	9
ARA15A	240	316	-	9	565	41
LCC_TA	78	88	12	4	182	13
Total No. of Samples	516	579	40	32	1167	86

The AZA samples were analysed for AZA and isomers. All other samples were analysed for lipophilic, hydrophilic toxins, DA and isomers.

4.3 Sample preparation

Phytoplankton and zooplankton

For phycotoxin extraction, phytoplankton and zooplankton samples collected from the different fractions were dried under a nitrogen (N_2) stream until all the liquid had evaporated. MeOH [100 %] was used for the extraction of lipophilic toxins and DA. The hydrophilic toxins were extracted using water acidified to 0.03 M acetic acid.

For the toxin extraction, between 250 to 1000 µm MeOH or aqueous acetic acid were added to the sample, depending on the pellet mass. Afterwards, lysis matrix D (1.4 mm ceramic spheres, MP Biomedicals, Eschwege, Germany) was added into the 2 ml-tubes and homogenized with the Bio101 FastPrep Instrument (MP Biomedicals, Germany) for 45 seconds (Fig. 15). During this step, the cells got

broken, and the intracellular toxins were released and got dissolved in. The next step was to centrifuge the samples for 15 min at 15,000 rounds per minute (rpm) at 10 °C. The remaining cell components settled to the bottom and formed a pellet. The supernatant was transferred to a spin filter and centrifuged at 15,000 rpm for one minute. The filtered supernatant was then transferred to an HPLC storage vial.

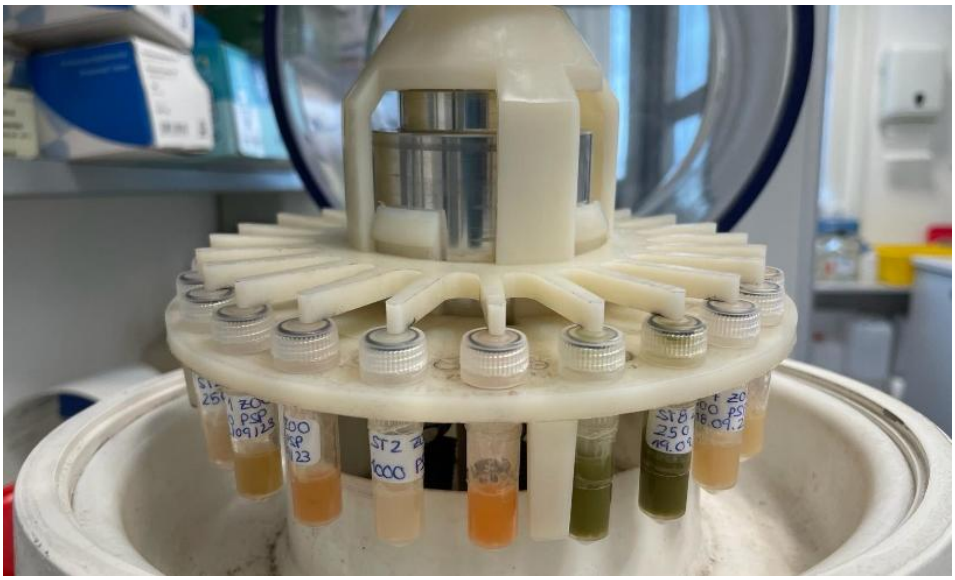

Figure 15: Zooplankton samples with Lysin beads get homogenized with the homogenizer to break the cells (Photo: Franziska Linke).

One extraction was carried out for the phytoplankton pellet samples. For the phytoplankton filter samples collected during ARA15A, and for all the zooplankton samples, the pellet was resuspended a second time in a volume equal to or lower than the first extraction, homogenized, and then filtered. The supernatant was added to the storage vial from the first extraction. The vials were sealed hermetically and stored in the freezer at - 20 °C (Fig. 16).

For the zooplankton samples composed of individuals identified using a stereomicroscope, the individuals were crushed with a mortar and dissolved in water. This was then divided evenly into two 2 ml-tubes. The samples were dried again under the N_2 stream and afterwards extracted as described previously.

Figure 16: Zooplankton extracts in storage vials (Photo: Franziska Linke).

Solid phase adsorption toxin tracking bags (SPATTs)

The SPATT bags were thoroughly washed with deionized water and dried for 24 h in an oven at 50 °C. The dry resin was transferred from the bag into a 50 ml-tube, and 30 ml MeOH of 100 % was added. To

dissolve the toxins attached to the resin the samples were shaken at 60-70 strokes per minute overnight. The resin with MeOH was poured into a glass chromatography column of 270 mm length, 13 mm internal diameter, filled with 20 mm glass wadding and 10 mm quartz sand, and 15 ml MeOH were added to rinse the tube. Dropwise, the eluate was eluted from the column. Then, 25 ml of MeOH were added to the column when the supernatant reached the top of the filling. The supernatant was added to the remaining sample. In a rotary evaporator, the sample was reduced to an approximately final volume of 1 ml. Subsequently, the sample was transferred to a 2 ml-tube and dried under a nitrogen stream at 35 °C. To resuspend the sample, 0.5 to 1 ml of MeOH were used, and samples were spin filtered through a 0.4 µm pore filter (Krock et al., 2020). Then samples were stored at -20 °C.

4.4 Toxin Analysis

Toxin detection and quantification were performed using various analytical equipment, which will be explained in the following paragraphs. Certified phycotoxin reference standards were obtained from the National Research Council (NRC) in Canada, and used to identify toxins, calculate their concentrations in the samples (Tab. 2) and the limit of detection (LoD). The LoDs for the different measurement were between $0.01 \cdot 10^{-3}$ and 0.97 $ng \cdot \mu l^{-1}$.

Final toxin concentrations for phytoplankton and zooplankton net samples were expressed in nanograms per meter of net tow (NT) ($ng \cdot m$ of NT^{-1}). The zooplankton individuals were expressed in nanograms per gram tissue ($ng \cdot g^{-1}$) because just some individuals from a NT were collected and not the whole NT/water column were analysed. The plankton net samples are analysed for intracellular and SPATT samples for dissolved phycotoxins in the water.

4.4.1 Lipophilic Toxins

Sample extracts for lipophilic toxin determination were measured with the API-Sciex 4000 QTrap triple quadrupole mass spectrometer coupled with an Agilent 1100 Series HPLC system (Agilent Technologies Pickering Laboratories, Waldbronn, Germany). Reversed-phase chromatography was performed on a C_8 column [50 x 2 mm] packed with 3 µm Hypersil beads (Phenomenex, Aschaffenburg, Germany) at 20 °C. The gradient elution was performed with two eluents, eluent A, which was water and eluent B, which was acetonitrile-water (95:5; v:v), both containing 50 mM formic acid and 2 mM ammonium format. The total run time for each sample was 31 min, consisting of 12 min of column equilibration with 5 % B, 10 min of linear gradient to 100 % B, 6 min of isocratic elution with 100 % B and a return to initial conditions during 3 min. The injection volume was 5 µl at a constant flow rate of 200 $\mu l \cdot min^{-1}$.

The chromatographic run was divided into three periods for the different toxins. The initial 8 min were for the detection of DA, followed by a 2.5-min-long period for the measurement of GYMs and SPXs and finally, a 5.5-minute-long period for goniodomin A (GDA), OA, DTXs, AZAs, PTXs and yessotoxins (YTX)

(Tab. 2). Parameters of the MS/MS were as follows: Ion-Spray-Voltage: 5500 V, temperature: 275 °C, nebulizer gas: 50 psi, auxiliary gas: 50 psi, declustering potential: 50; entrance potential: 10 V, exit potential:15 V, curtain gas: 20 psi during the first period and 10 psi during the second and third period.

Table 2: Lipophilic toxin standards with the transitions (precursor ion > fragment ion) selected for identification and quantification and their concentrations; DA=Domoic acid, GYM= Gymnodimine, SPX= Spirolide, GDA= Goniodomin, OA= Okadaic acid, DTX=Dinophysistoxin, AZA= Azaspiracid, PTX= Pectenotoxin, YTX=Yessotoxin.

Toxin	Mass transition [m/z]	Concentration [ρg/µl]
DA	312.1 > 266.1	500
SPX-1	692.6 > 164.1	500
GYM-A	508.3 > 490.1	100
PTX-2	876.6 > 213.1	215
YTX	1160.6 > 965.6	1000
OA	822.6 > 223.1	964
DTX-1	836.6 > 237.1	500
DTX-2	822.6 > 223.1	500
AZA-1	842.6 > 824.6	100
GDA	786.5 > 607.4	500

The measurements were carried out in positive-ion mode using the multiple reaction monitoring (MRM) technique. This technique only scans for specific molecule fragments obtained from the original molecule, also called transitions, within the periods specified in the method (Tab. 2) (Hoffmann & Stroobant, 2007).

A targeted LC-MS/MS method was applied for the detection of SPX- and GYM-analogues, distinct from the multi-toxin method. This specific method allowed the identification of derivatives not covered by the available reference standards. The samples were remeasured on the same equipment, but eluent B was replaced by MeOH:water (95:5; v:v), buffered with 50 mM formic acid and 2 mM ammonium formate. Measurements consisted of a linear gradient from 5 % B to 100 % B within 10 min, subsequent isocratic elution with 100 % B for 10 min, return to initial conditions within 1 min, and 9 min of column equilibration at 5 % B. The total runtime for the method was 30 min. The following parameters were used for the detection of CIs: Ion-Spray-Voltage: 5500 V, temperature: 650 °C, nebulizer gas: 40 psi, auxiliary gas: 70 psi, declustering potential: 121 V; entrance potential:10 V, exit potential: 22 V, curtain gas: 20 psi. Measurements were performed in the selected reaction monitoring (SRM) in the positive mode, measuring 45 different compounds. The concentrations of analogues were calculated with the related standard SPX-1 and GYM-A.

The software Analyst 1.5 from Sciex was used for toxin quantification. First, the standards' retention time (RT) and mass transition were compared to the peaks from the samples to identify the toxins.

Then, the area of the standards and toxins in the samples were defined using the program and used to calculate the toxin concentration in the sample. The LoD for each toxin was calculated (Equ. 1). The concentrations under the LoD were considered as zero and not shown in the graphs.

$$LoD = \frac{c \cdot 3 \cdot N}{S}$$

Equation 1: Formula to calculate limit of detection (LoD); c = concentration [pg/ul]; N = noise; S = signal.

4.4.2 Domoic Acid and Isomers with LC-MS/MS

DA and isomers were measured with the Waters XEVO TQ-XS tandem quadrupole atmospheric pressure mass spectrometer coupled to the ACQUITY ultra-high-performance liquid chromatography (UHPLC) (Waters, Eschborn, Germany) to scan for DA and isomers. The injection volume [0.5-1.5 µl] of the sample was adjusted to the signal from the first measurement of DA with the API-Sciex 4000 QTrap triple quadrupole mass spectrometer.

A high-strength silica (HSS) C18 column (100 x 2.1 mm, 1.8 µm, Acquity, Waters) heated to 40 °C was used for reversed-phase chromatography. Mobile phase A was water, and mobile phase B was acetonitrile, both acidified with 0.1 % (v:v) formic acid [26.5 µM]. Isocratic elution was performed over the total run time of 12 min with 6 % eluent B. The injection volume for standards was 0.5 µl. The UHPLC run at a constant flow rate of 0.4 ml·min^{-1}. Mass spectrometric measurements were performed in the positive mode of SRM, selecting the proton adduct $[M+H]^+$ of DA and the isomers (*m/z* 312>266). Further parameters of the mass spectrometer were: desolvation temperature: 600 °C, desolvation gas flow: 1,000 L·h^{-1}, cone gas flow: 150 L·h^{-1}, cone voltage: 40 V, source temperature: 150 °C, collision gas flow 0.15 ml·min^{-1}, and collision energy 15 eV. DA and the isomers were quantified against a separate external standard for iso-DA C and a standard mix containing DA, isodomoic acid (iso-DA) E, iso-DA D, iso-DA A, and epidomoic acid (epi-DA) (CRM-DA-h) (Tab. 3; Fig. 17), using the software MassLynx (Version 4.2, Waters) (Thomas et al., 2022).

*Table 3: Concentrations and retention times of the used standards. *=concentration not certified. $^+$=the combination of the concentrations is certified.*

Compound	Concentration [pg µl^{-1}]	Retention time [min]
Domoic acid	96600 $^+$	9.31
Isodomoic acid E	190 *	6.08
Isodomoic acid D	820 *	6.67
Isodomoic acid A	1100 *	7.68
Isodomoic acid C	400	10.52
Epi-domoic acid	550 $^+$	10.72

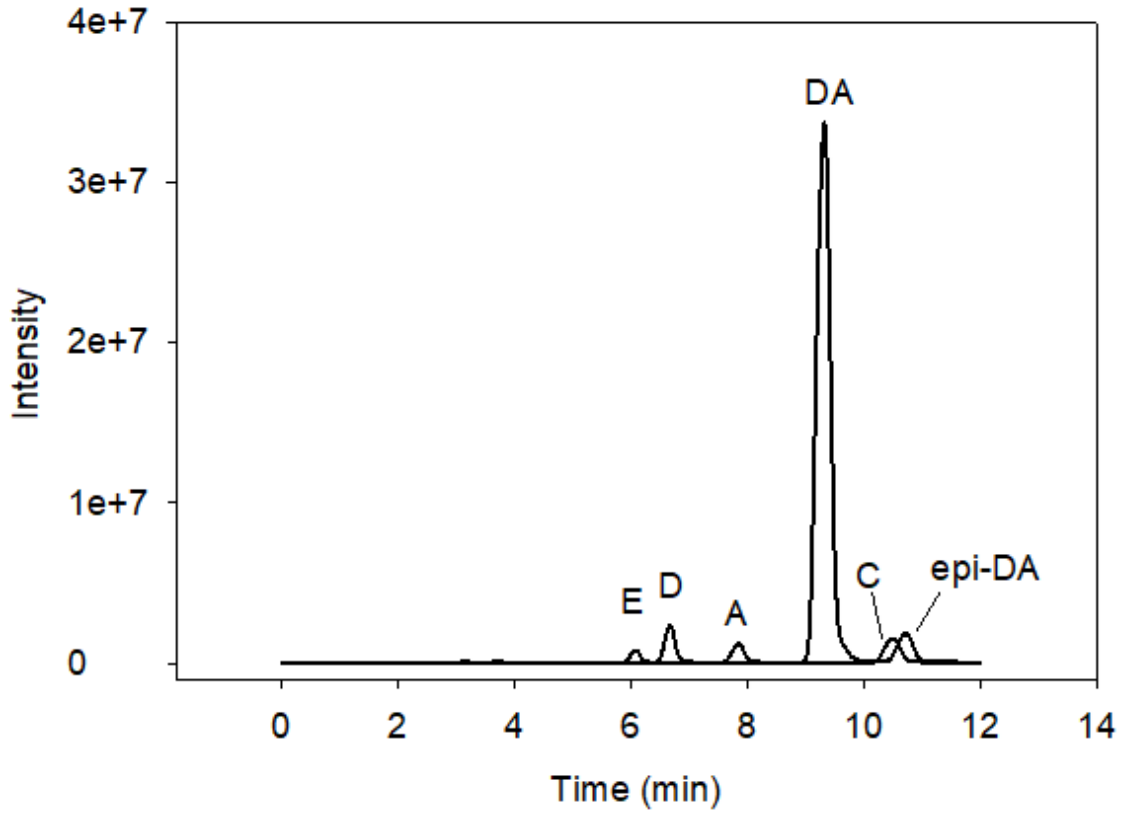

Figure 17: Total iron chromatogram of the standard for isodomoic acid C and the standard mix containing DA, epi-DA and the isodomoic acids E, D, and A (Thomas et al., 2022).

To calculate the DA concentrations in the samples from ARA15A and LCC_TA, a calibration curve was used (Tab. 4). The CRM-DA-h (Homogenity_2231, RPC210924, NRC Canada) standard was diluted 1:3 with solvent water: acetonitrile (95:5, v:v). For the calibration twelve dilutions were used and measured with the samples.

Table 4: Domoic acid (DA) calibration curve data for ARA15A with concentrations of the standard dilutions [pg/ul], areas, function f(x), R^2 and limit of detection (LoD) [pg/ul].

Sample	Conc. [pg/ul]	Area				
		ARA15A_Zoo_1	ARA15A_Zoo_2	ARA15A_Phyto_1	ARA15A_Phyto_2	LCC_TA_Zoo_Phyto
Cal-12-DA_04.12.24	1.82E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cal-11-DA_04.12.24	5.45E-01	1.03E+03	0.00E+00	6.62E+02	1.35E+03	0.00E+00
Cal-10-DA_04.12.24	1.64E+00	2.83E+03	3.74E+03	1.79E+03	2.33E+03	1.49E+03
Cal-9-DA_04.12.24	4.91E+00	6.34E+03	5.79E+03	5.69E+03	6.51E+03	3.62E+03
Cal-8-DA_04.12.24	1.47E+01	2.19E+04	2.31E+04	1.73E+04	1.96E+04	1.41E+04
Cal-7-DA_04.12.24	4.42E+01	7.36E+04	7.67E+04	5.13E+04	5.79E+04	5.68E+04
Cal-6-DA_04.12.24	1.33E+02	2.36E+05	2.44E+05	1.61E+05	1.73E+05	2.31E+05
Cal-5-DA_04.12.24	3.98E+02	7.72E+05	7.87E+05	5.02E+05	5.66E+05	7.60E+05
Cal-4-DA_04.12.24	1.19E+03	2.32E+06	2.38E+06	1.52E+06	1.69E+06	2.37E+06
Cal-3-DA_04.12.24	3.58E+03	7.01E+06	7.13E+06	4.64E+06	5.13E+06	7.37E+06
Cal-2-DA_04.12.24	1.07E+04	2.15E+07	2.17E+07	1.44E+07	1.61E+07	2.24E+07
Cal-1-DA_04.12.24	3.22E+04	6.35E+07	6.37E+07	4.61E+07	5.10E+07	6.64E+07
CRM DA-h	9.66E+04	2.29E+08	2.22E+08	1.48E+08	1.38E+08	1.67E+08
f(x)=		2322.4x	2262.5x	1522.9x	1448.6x	1763.6x
R^2		0.9972	0.9981	0.9994	0.9990	0.9964
LoD [pg/ul]		1.44	3.82	3.54	1.22	1.98

4.4.3 Hydrophilic Toxins

The HPLC-FLD Agilent LC1 100-FLD G1321A (Agilent Technologies Pickering Laboratories, Waldbronn, Germany) was used to measure hydrophilic toxins (STX and analogues). The HPLC-FLD detects the oxidation products derived from hydrophilic toxins, which are purine derivatives that can be detected via FLD.

Standards are measured for each run, and the retention times were used to identify compounds in the samples. To calculate the concentration of the detected toxin, standard mixes containing different concentrations of the hydrophilic toxins were used to construct a calibration curve. Afterwards, the absolute areas of the standards and the samples were determined with the OpenLab CDS Chem Station C01.10. Then, the equation obtained from the calibration curve was used to calculate the toxin concentration in the samples.

4.5 Data analysis and visualization

To generate bar plots the software R (RStudio, Version 2023.06.0) and packages dplyr (Wickham et al., 2014), ggplot2 (Wickham, 2016), ggsci (Xia0, 2016), readxl (Wickham & Bryan, 2015), knitr (Xie; 2012) and tidyr (Wickham et al., 2014) were used (R Core Team, 2024). The Ocean Data View (ODV) was used to generate maps with the stations and distribution of the different toxin classes (Schlitzer, 2025).

5 Results

5.1 Arctic waters

Three expeditions were performed in the Arctic waters: LCC_NW in 2023, LCC_TA in 2024 on the cruise ship Le Commandant Charcot and the Arctic expedition (ARA15A) on the Korean RV Araon in 2024. During the LCC_NW at 22 stations, 285 samples were collected. The following year, 565 samples at 41 stations during ARA15A and 182 samples at 13 stations during LCC_TA were sampled. In total, 1032 samples (phytoplankton, zooplankton, AZA and dissolved toxins with SPATTs) were collected, and 76 stations were performed during the three expeditions.

5.2 Arctic Phytoplankton

Lipophilic toxins

The lipophilic toxins PTX-2, SPX-1, SPX-A, SPX-B, SPX-C and 20- Methyl (Me)-SPX-G were found in phytoplankton net samples during the Arctic expeditions.

SPXs (SPX-1, SPX-A, SPX-B, SPX-C and 20-Me-SPX-G) were detected during the LCC_NW near the north-east coast of Baffin Island (station 9) in values up to 12.91 ng·m^{-1} of NT. SPX-B (10.56 ng·m^{-1} of NT) and SPX-1 (10.38 ng·m^{-1} of NT) were the most prevalent toxins and made up over 55 % of the total amount of detected lipophilic toxins in the phytoplankton. The 20-Me-SPX-G was found in the Atlantic-influenced region near the southern tip of Greenland (station 3, 0.97 ng·m^{-1} of NT), in Disko Bay, Baffin Bay (stations 6 to 8, up to 0.40 ng·m^{-1} of NT) and in small values in the Northwest Passage (station 12, 0.03 ng·m^{-1} of NT). PTX-2 was also found in much lower values between 0.04 and 0.26 ng·m^{-1} of NT, and was the least abundant toxin with a proportion of 1.3 % of the total lipophilic toxins (0.5 ng·m^{-1} of NT) (Fig. 18 and 19; Tab. S8).

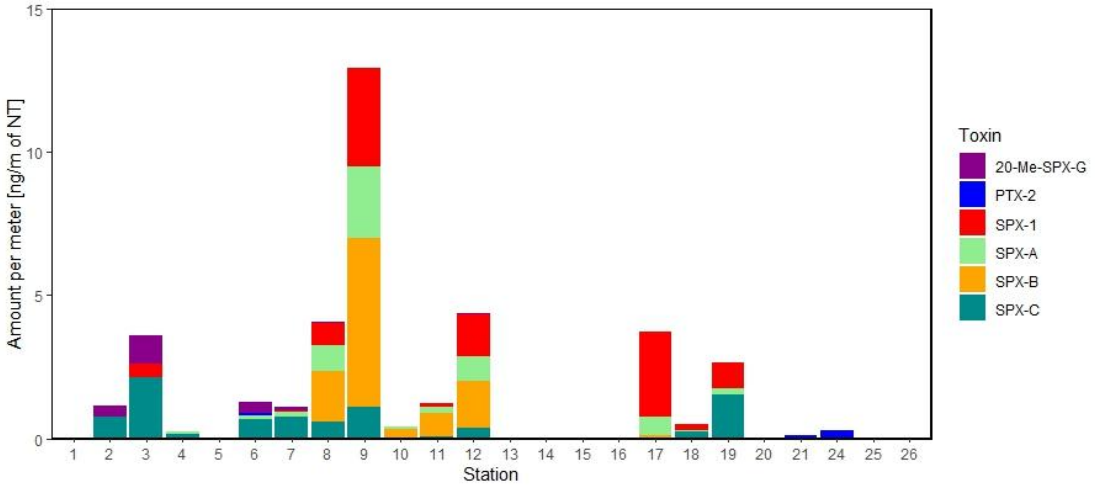

Figure 18: Amount of lipophilic phycotoxins: 20-methyl-spirolide G (20-Me-SPX-G, purple), pectenotoxin 2 (PTX-2, blue), spirolide 1 (SPX-1, red), spirolide A (SPX-A, light green), spirolide B (SPX-B, orange) and spirolide C (SPX-C, green) per meter of net tow (NT) [ng/m of NT] in phytoplankton per station from the LCC_NW expedition in the Arctic 2023.

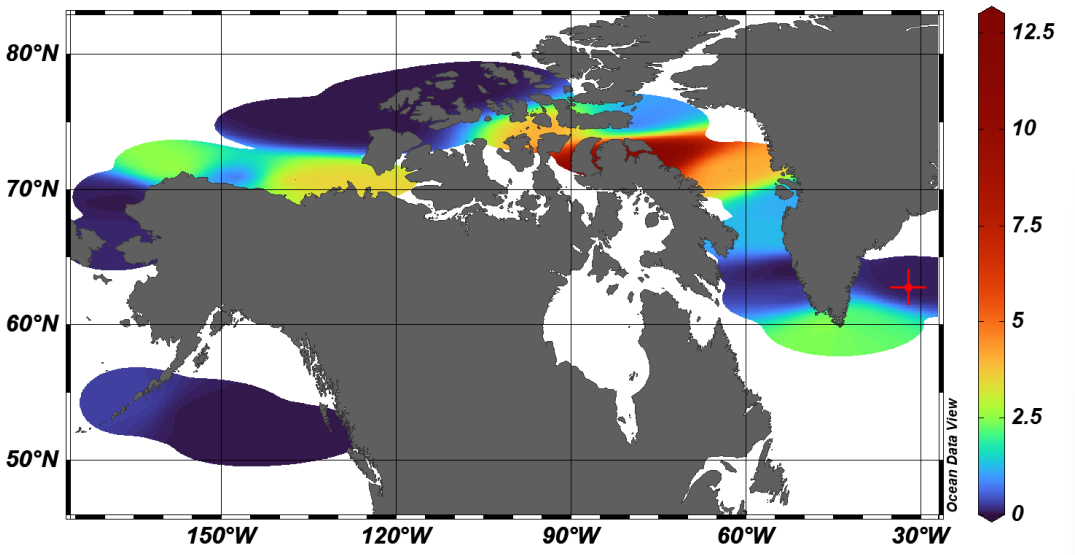

Figure 19: Distribution of lipophilic phycotoxins per meter of net tow (NT) [ng/m of NT] per station in phytoplankton from the LCC_NW Expedition in the Arctic 2023.

The following year, during the ARA15A expedition in the Pacific Arctic region, three lipophilic toxins, PTX-2, SPX-1 and SPX-C were found in amounts ranging from 0.07 up to 13.61 ng·m^{-1} of NT when considered together. The highest level recorded was for PTX-2 (12.27 ng·m^{-1} of NT) in the Chukchi Sea (station 11). In the Central Arctic Ocean (stations 20 to 44), only small amounts of PTX-2 (lower than 0.62 ng·m^{-1} of NT) were present as far as 79 °N (station 26). SPX-1 and SPX-C were detected up to amounts of 3.64 and 5.11 ng·m^{-1} of NT in the Chukchi Sea near the Alaskan west coast (station 4) in shallow waters. Lower amounts up to 0.84 ng·m^{-1} of NT could be detected in the Bering Strait and Central Arctic Ocean. Overall, PTX-2 was the most abundant phycotoxin (66.6 %) of the total amount of lipophilic toxins sampled, followed by SPX-C (18.9 %) and SPX-1 (14.5 %). No toxins or just small amounts were detected on the east side of the Arctic Central Ocean (Fig. 20; Tab. S9).

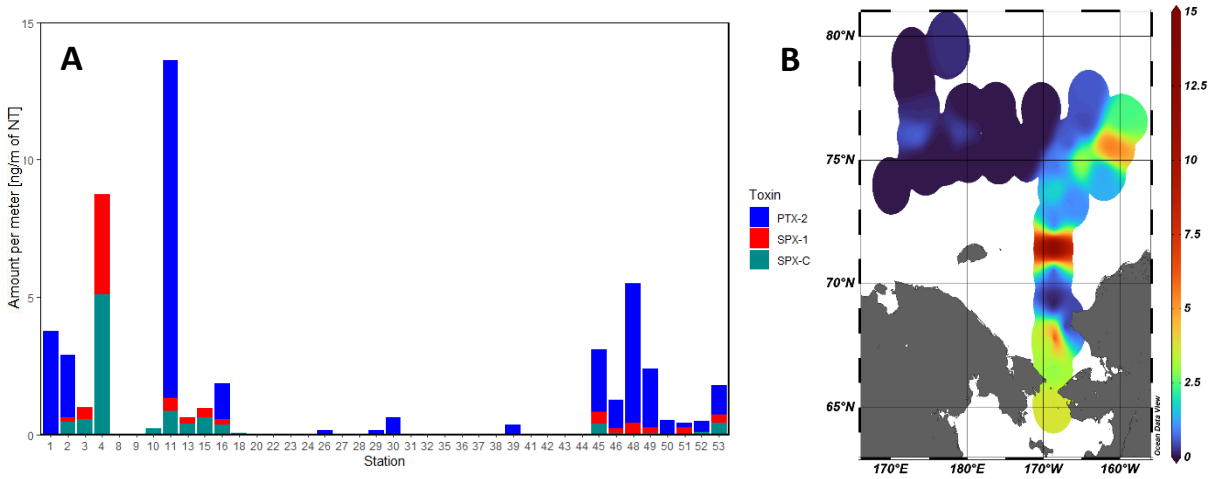

Figure 20: Amount of lipophilic toxins in phytoplankton per station per meter of net tow (NT) [ng/m of NT] during the ARA15A expedition in the Arctic 2024: (A) pectenotoxin 2 (PTX-2, blue), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, green) and (B) distribution of total lipophilic toxin amount.

In September 2024, during the LCC_TA expedition across the Central Arctic Ocean and around Svalbard, toxins were detected at seven of the thirteen sampling stations, including 20-Me-SPX-G, PTX-2, SPX-1, and SPX-C. No toxins were detected north of 80° N (stations 4, 6, 9, 12). PTX-2 was present in Atlantic-influenced waters near Svalbard (station 28) at a concentration of 0.07 ng·m^{-1} of NT, being the latest highest amount detected during the cruise. The most frequently occurring toxin was SPX-C in both the Pacific and Atlantic influenced regions. 20-Me-SPX-G was only detected in the Atlantic-influenced region, below 0.02 ng·m^{-1} of NT. In contrast, SPX-1 was detected at the beginning of the cruise on the Pacific-influenced side of the Arctic Central Ocean (station 2), with a concentration of 0.02 ng·m^{-1} of NT (Fig. 21; Tab. S10).

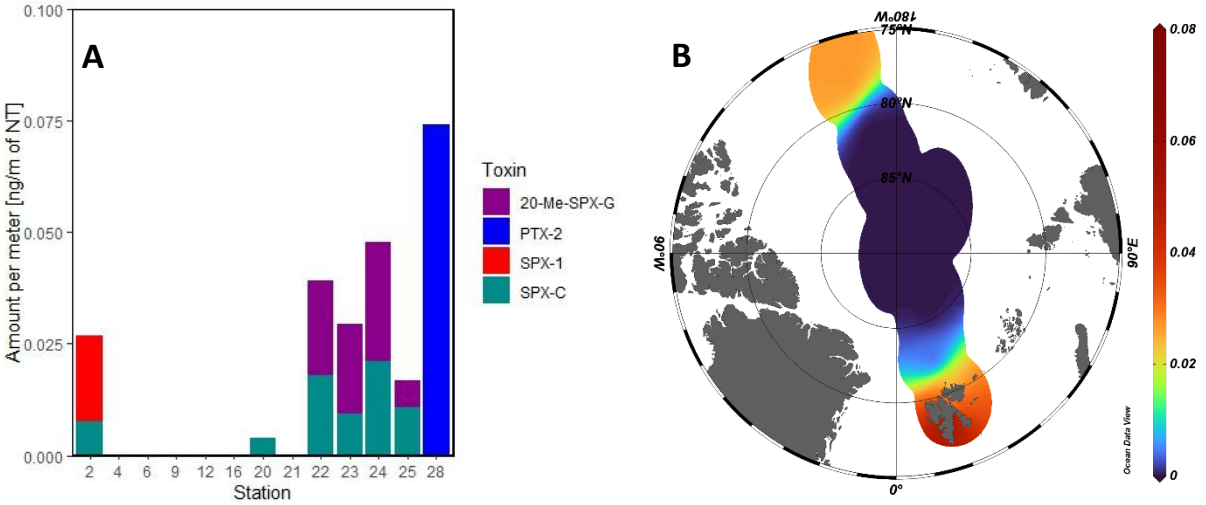

Figure 21: Amount of lipophilic toxins in phytoplankton per station per meter of net tow (NT) [ng/m of NT] during the LCC_TA expedition in the Arctic 2024 (A) 20-methyl-spirolide G (20-Me-SPX-G, purple), pectenotoxin 2 (PTX-2, blue), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, green) and (B) distribution of total lipophilic toxin amount.

DA and its isomers

DA, iso-DA A, C, D and E dominated the toxins found during the LCC_NW, with values up to 617.77 ng·m^{-1} of NT at the southern tip of Greenland (station 3). In addition, in the Northwest Passage (station 12), with a smaller value of 39.58 ng·m^{-1} of NT DA was detected (Fig. 22). In both stations, DA was the dominant toxin, with its isomers accounting for less than 1.86 % of the DA-related compounds (Tab. S11).

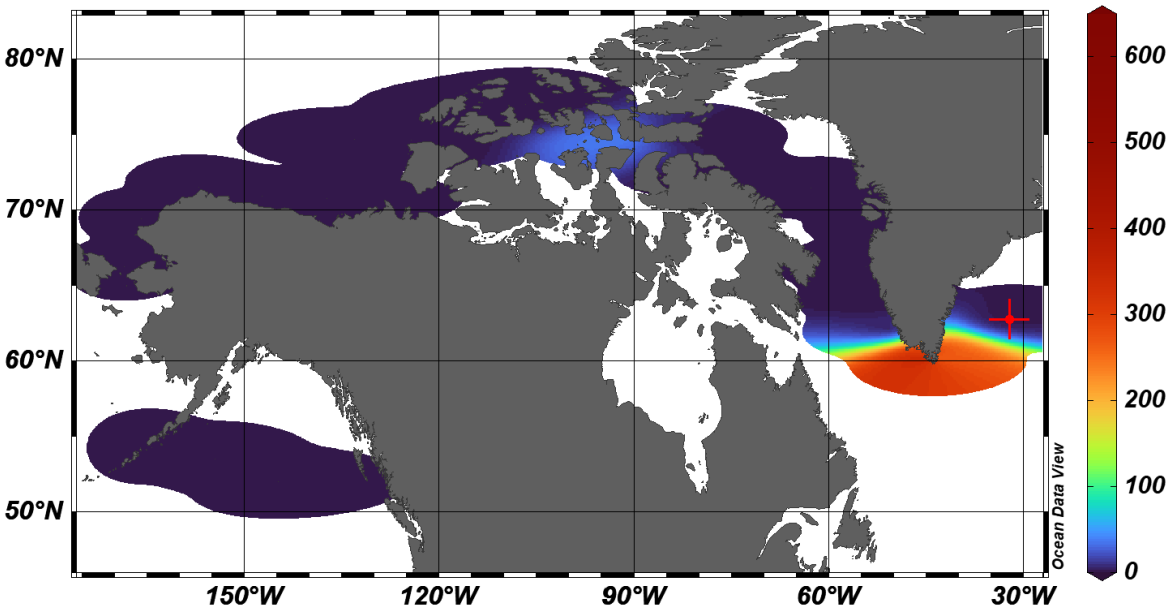

Figure 22: Distribution of domoic acid (DA) and isomers per meter of net tow (NT) [ng/m of NT] in phytoplankton from the LCC_NW Expedition in the Arctic 2023.

During the ARA15A expedition the following year, DA, epi-DA, and the iso-DA A, C, D and E were identified in 33 stations. Values up to 44.85 ng·m^{-1} of NT (station 50) could be measured in the Central Arctic Ocean (stations 23, 29, 30, 31, 50) north of 75° N. DA was the predominant form in all stations (94.7 %) in values between 0.01 (station 48) to 42.78 ng·m^{-1} of NT (station 50), and isomers and epimers ranging between 0.4 (iso-DA C) to 2.5 % (epi-DA) with amounts between 1 and <0.01 ng·m^{-1} of NT. DA and isomers were not present or just in values up to 0.30 ng·m^{-1} of NT near the Alaskan west coast (stations 8 to 10) and the east Arctic Central Ocean (stations 18 to 30 and 32 to 38) (Fig. 23; Tab. S12).

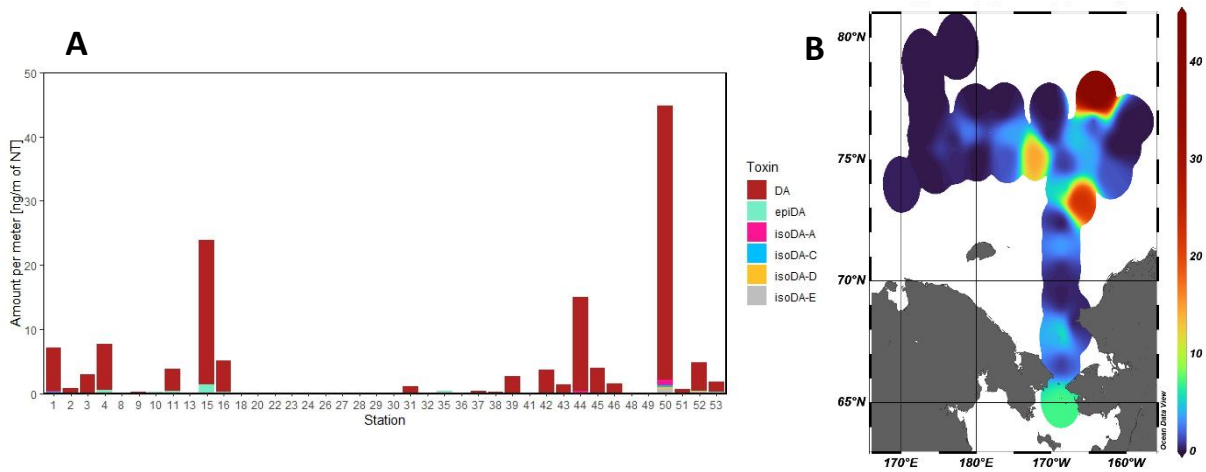

Figure 23: Amount of domoic acid isomers per meter of net tow (NT) [ng·m^{-1}of NT] per station in phytoplankton during the ARA15A expedition in the Arctic 2024: (A) domoic acid (DA, red), epimer (epi-DA, green) and isomers A (iso-DA A, pink), C (iso-DA C, blue), D (iso-DA D, yellow) and E (iso-DA E, grey) and (B) distribution *of total DA and isomers.*

In the Central Arctic Ocean during the LCC_TA cruise, low concentrations of DA (0.41 ng·m^{-1} of NT) and iso-DA A (0.02 ng·m^{-1} of NT) were detected only at station 2 (77 °N) (Tab. S13).

Hydrophilic toxins

Three different hydrophilic toxins were identified in phytoplankton during the LCC_NW and ARA15A: STX, N-sulfocarbamoyl toxin (C1/C2), and GTX-2/GTX-3. C1/C2 and GTX-2/GTX-3 are listed together, as each pair can interconvert.

In LCC_NW in 2023, STX was the only hydrophilic toxin detected at the west coast of Greenland (station 6, 0.13 ng·m^{-1} of NT) and north of the Bering Strait (station 21, 5.72 ng·m^{-1} of NT) (Tab. S8).

At the ARA15A cruise in 2024, STX and some of its analogues, including C1/C2 and GTX-2/GTX-3 were present north of the Bering Strait (station 2). This is the only station where STX-analogues were detected, some of them, like GTX-1/GTX-4 and neoSTX, were detected only at trace levels near the LoD. STX was further detected at several different stations in small amounts, up to 1.52 ng·m^{-1} of NT in the Chukchi Sea (Fig. 24, Tab. S9).

In the cruise LCC_TA in September 2024, no hydrophilic toxins were detected.

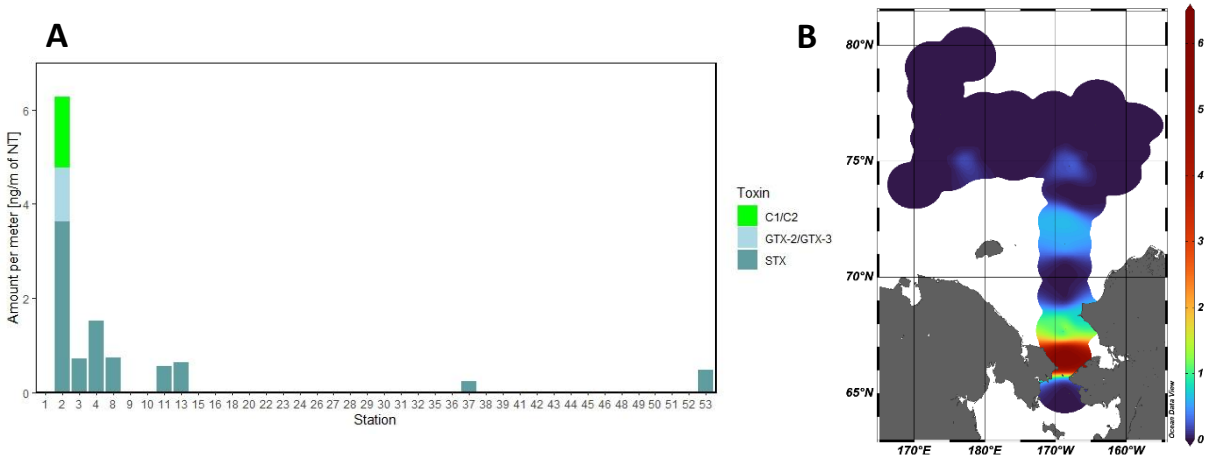

Figure 24: Concentration of hydrophilic toxins *per meter of net tow (NT) [ng/m of NT] per station in phytoplankton during the ARA15A expedition in the Arctic 2024: (A) N-sulfocarbamoyl toxin (C1/C2, lime green), gonyautoxin 2/3 (GTX-2/GTX-3, light blue) and saxitoxin (STX, green) and (B) map with distribution of total hydrophilic toxin concentration.*

Dissolved Toxins

No lipophilic toxins nor DA and isomers could be detected in the LCC_NW SPATT samples. In the ARA15A (V199) and LCC_TA (V201) expeditions, PTX-2 was detected dissolved in the water with a peak in the Bering Strait and Chukchi Sea at the beginning of both cruises. No other toxins were detected during the ARA15A expedition (Fig. S1).

However, the sample V201-179 from the LCC_TA was the only sample where five different toxins (DTX-1, OA, PTX-2, SPX-1 and SPX-C) could be detected with a total amount over 250 ng (Fig. S1). This SPATT bag sampled dissolved toxins at the beginning of the expedition through the Bering Strait in the direction of the North Pole(Fig. S1).

5.3 Arctic Zooplankton

In zooplankton, the next level in the Arctic marine food web after phytoplankton, several hydrophilic, lipophilic and DA toxins were detected (Tab. 5).

Table 5: Detected phycotoxins during the three Arctic expeditions LCC_NW, ARA15A and LCC_TA; detected in phytoplankton (green), in zooplankton (orange), in both (yellow), was not detected (grey); spirolide 1 (SPX-1), spirolide A (SPX-A), spirolide B (SPX-B), spirolide C (SPX-C), 20-methyl-spirolide G (20-Me-SPX-G), 27-hydroxy-spirolide C (27-hydroxy-SPX-C), pectenotoxin 2 (PTX-2), domoic acid (DA) and isomers A (iso-DA A), C (iso-DA C), D (iso-DA D), E (iso-DA E) and epimer (epi DA), saxitoxin (STX), neosaxitoxin (neoSTX), decarbamoylneosaxitoxin (dcSTX).

	Toxin	Expedition LCC_NW	ARA15A	LCC_TA
lipophilic	SPX-1			
	SPX-A			
	SPX-B			
	SPX-C			
	20-Me-SPX-G			
	27-hydroxy-SPX-C			
	CP-4			
	PTX-2			
DA and isomers	DA			
	iso-DA A			
	iso-DA C			
	iso-DA D			
	iso-DA E			
	epi DA			
hydrophilic	STX			
	neoSTX			
	dcSTX			
	GTX-2/-3			
	C1/C2			

Lipophilic toxins

In the cruise LCC_NW, 27-hydroxy-SPX-C, SPX-1, SPX-B and SPX-C were identified. At 12 of the 14 different stations where zooplankton sampling was possible, hydrophilic toxins were found. At the stations 1 in the Denmark Strait and 26 in the Bering Sea, no toxins were found. The highest value with 2.18 ng·m^{-1} of NT was measured near the Alaskan coast, close to Point Barrow (station 19). In this region, SPX-C (1.18 ng·m^{-1} of NT), SPX-1 (0.91 ng·m^{-1} of NT) and a small amount of 27-hydroxy-SPX-C (0.07 ng·m^{-1} of NT) were found. SPX-C accounts for the largest part of the total measured lipophilic toxins with 58.68 % and showed the widest distribution. Only in the Denmark Strait (station 1), the Labrador Sea (station 8), and in the Pacific Ocean south of the Bering Strait (stations 24 to 26) it could not be detected. 27-hydroxy-SPX-C was more present in the Atlantic-influenced waters and in waters

just beyond the Northwest Passage. Exactly the opposite is the case for SPX-1, which was found in the Labrador Sea before entering the Northwest Passage (station 8) and in all the stations sampled after the Northwest Passage until the Aleutian Islands (station 24). SPX-B was only found in offshore regions with values under 1 ng·m^{-1} of NT (Fig. 25 and 26; Tab. S14).

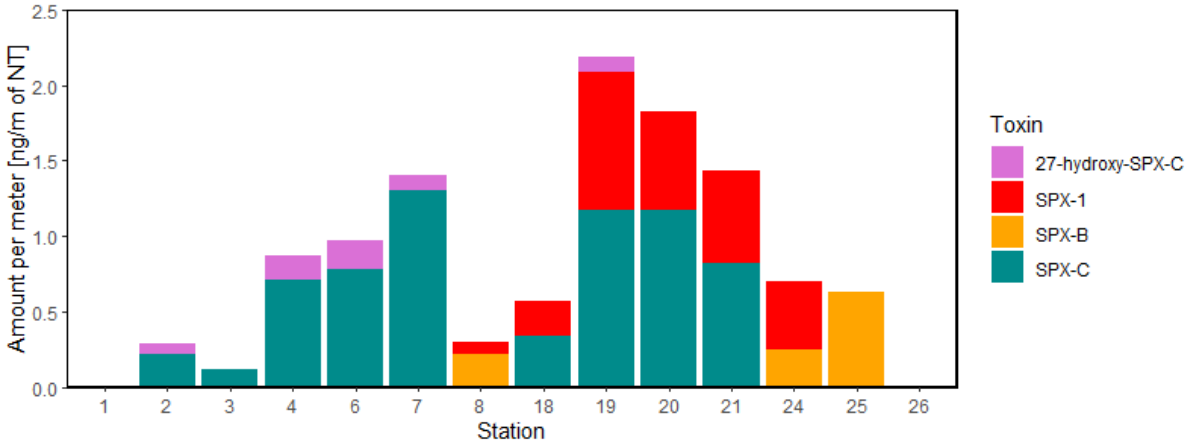

Figure 25: Amount of lipophilic phycotoxins per meter of net tow (NT) [ng/m of NT] per station: 27-hydroxyl-spirolide C (20-hydroxy-SPX-C, light purple), spirolide 1 (SPX-1, red), spirolide B (SPX-B, orange) and spirolide C (SPX-C, green) in zooplankton from the LCC_NW expedition in the Arctic 2023.

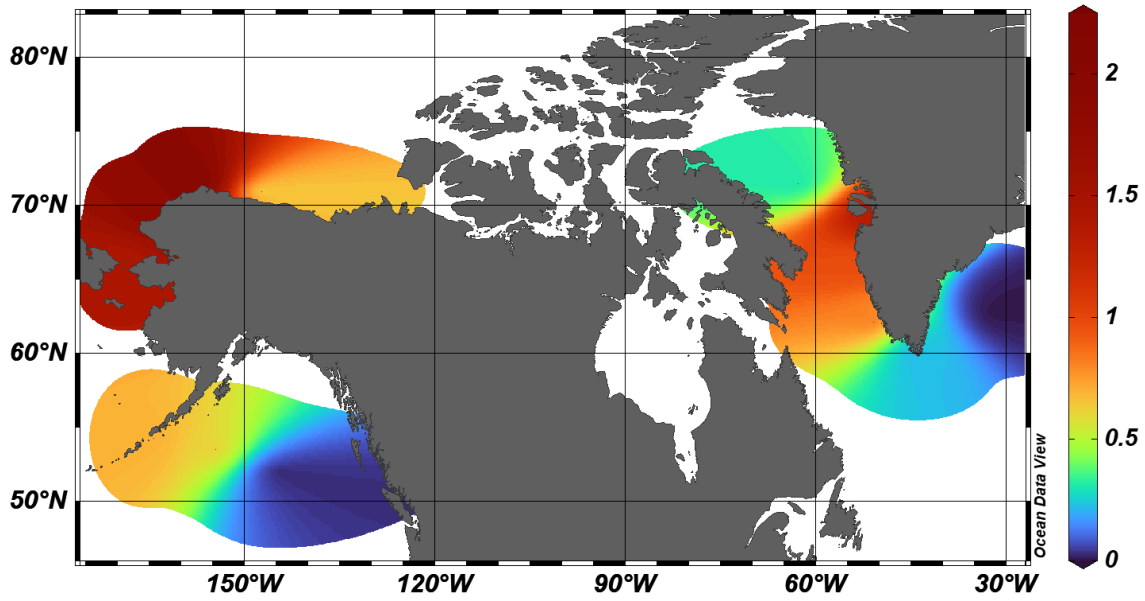

Figure 26: Distribution of lipophilic phycotoxins per meter of net tow (NT) [ng/m of NT] in zooplankton from the LCC_NW expedition in the Arctic in 2023.

Three SPX-analogues, SPX-1, SPX-C and an undescribed SPX-related compound referred to as compound 4 (CP-4) with a *m/z* 720/164 (Nieva et al., 2020), were detected. However, the highest total toxin concentration, including all SPX-analogues, was recorded in the northern part of the Chukchi Sea with 145.05 ng·g^{-1} (station 18). SPX-C was the most represented toxin with 61.9 %, followed by SPX-1 and CP-4, which made up 3.0 % of the total lipophilic toxins. The highest amount of SPX-C was detected

in the Central Arctic Ocean at 79 °N (station 26) with 116.72 ng·g^{-1}. SPX-1 and SPX-C were mainly found at the Bering Strait and Chukchi Sea (stations 1 to 18) (Fig. 27; Tab. S15).

During the LCC_TA cruise, no lipophilic toxins were detected in zooplankton samples.

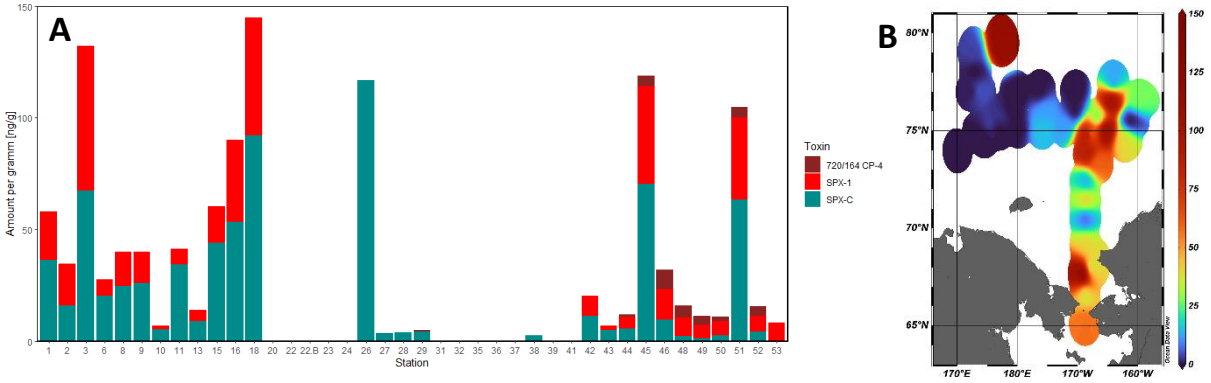

Figure 27: Amount of lipophilic toxins per gram of tissue [ng/g] per station in zooplankton from the ARA15A expedition in the Arctic 2024: (A) compound 4 (720/164 CP-4, dark red), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, cyan) and (B) total distribution of lipophilic toxins.

DA and isomers

DA, epi-DA and isomers iso-DA A, C, D, and E were found in zooplankton during the three cruises.

In 2023, during LCC_NW, the highest amount was detected at the southern tip of Greenland (59.76 ng·m^{-1} of NT). In addition, lower concentrations were measured at the two surrounding stations, ranging from 0.79 to 11.46 ng·m^{-1} of NT. In all the cases, DA was the most common toxin, and the other isomers (iso-DA A, C, D and E) only made up a proportion of 6.4 % (Tab. S16).

The highest value in 2024 (ARA15A) was found in the Central Arctic Ocean (station 20, 1545.2 ng·g^{-1}). Additionally, two other stations in the Central Arctic Ocean showed elevated values exceeding 900 ng·g^{-1} (stations 44 and 50). Only small amounts (< 134.09 ng·g^{-1}) or no detectable toxins were measured in the north part of the Chukchi Sea (stations 6 to 18) and the west part of the Central Arctic Ocean (22B to 39). DA made up the largest proportion with over 93 % and were present as far north as 79 °N (station 26). The remaining isomers and epimers represented between 0.4 (iso-DA E) to 2.0% (iso-DA D) (Fig. 28; Tab. S17).

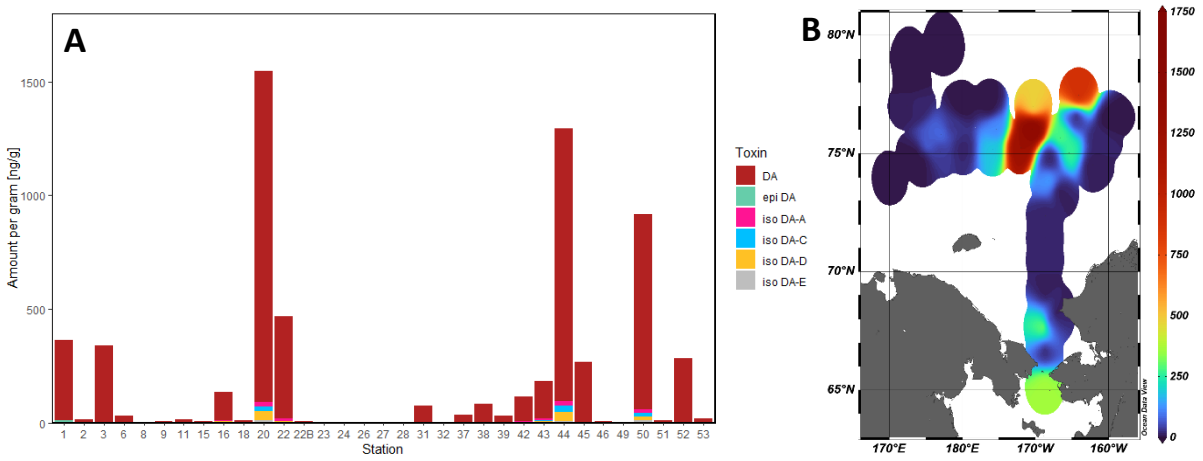

Figure 28: Amount of domoic acid and isomers per gram of tissue [ng/g] in the zooplankton per station from the ARA15A expedition in the Arctic, 2024: (A) domoic acid (DA, red), epimer (epi-DA , green) and isomers A (iso DA-A, pink), C (iso DA-C, blue), D (iso DA-D, yellow) and E (iso DA-E, grey) and (B) map with the distribution.

During the LCC_TA, DA and iso-DA A, C, D and E were also detected in the Central Arctic Ocean up to 14.03 ng·m^{-1} of NT (station 2) at 77 °N. Furthermore, in a lower concentration, DA could be detected at station 6, which is at 84 °N, with 0.12 ng·m^{-1} (Tab. S18). At the more northern stations and on the Atlantic site, neither DA nor its isomers were detected.

Hydrophilic toxins

During LCC_NW in zooplankton STX (0.06 ng·m^{-1}), decarbamoylsaxitoxin (dcSTX) (<0.01 ng·m^{-1} of NT) and neosaxitoxin (neoSTX) (0.02 ng·m^{-1} of NT) were present near the Bering Strait (station 21) with the highest value of 0.08 ng·m^{-1} of NT. Additionally, small amounts of STX (<0.01 ng·m^{-1} of NT) were detected further north near the Alaskan west coast (stations 19 and 20) (Fig. 29; Tab. S14).

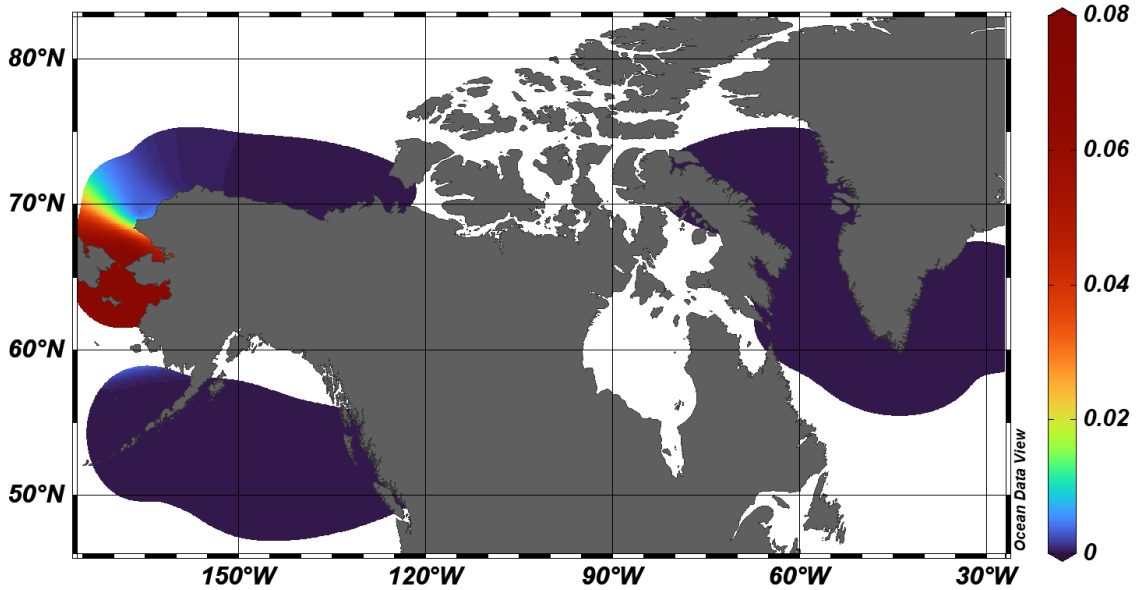

Figure 29: Distribution of hydrophilic toxins [ng/m of NT] in zooplankton from the LCC_NW expedition in the Arctic 2024.

In the zooplankton samples from ARA15A, STX and neoSTX were present at several stations. The highest total concentration was measured in the Arctic Central Ocean (stations 16 and 18) with over

3000 ng·g^{-1}, when STX and neoSTX were considered together. In general, STX was measured at all stations in the Bering Strait, Chukchi Sea and the first stations in the Arctic Central Ocean (stations 1 to 22) up to values of 2499.40 ng·g^{-1}. Similarly, neoSTX was present in most of the same stations but in smaller amounts (up to 594.98 ng·g^{-1}). NeoSTX was only present when STX was also detected. In the second half of the cruise, STX could only be found, but not frequently, and in smaller concentrations (Figs. 30 and 31). However, STX could also be detected up to 79°N (station 26; 34. 83 ng·g^{-1}) (Tab. S15).

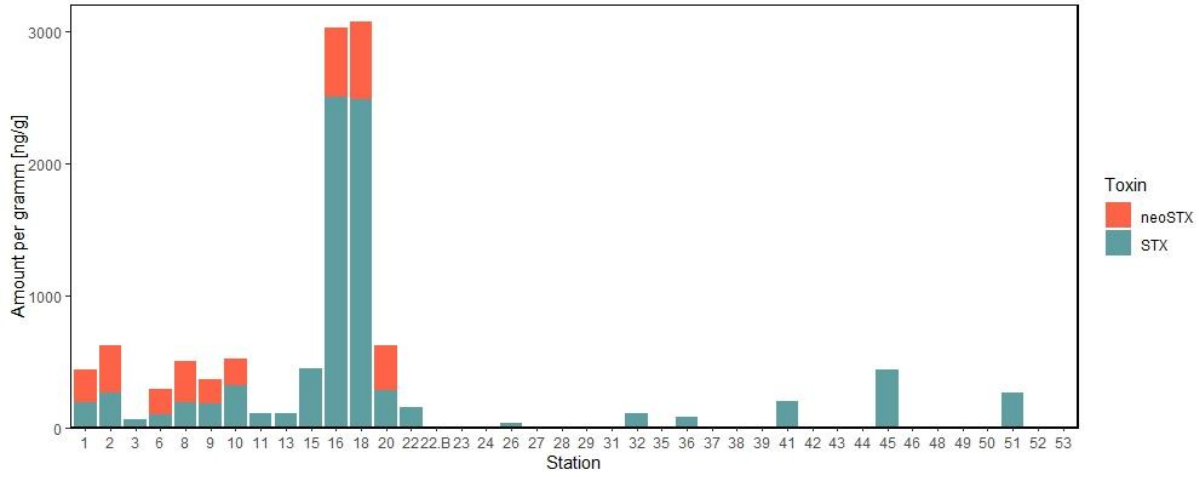

Figure 30: Amount of hydrophilic toxin per gram of tissue [ng/g] in the zooplankton per station: neosaxitoxin (neoSTX, orange) and saxitoxin (STX, green) from ARA15A in the Arctic 2024.

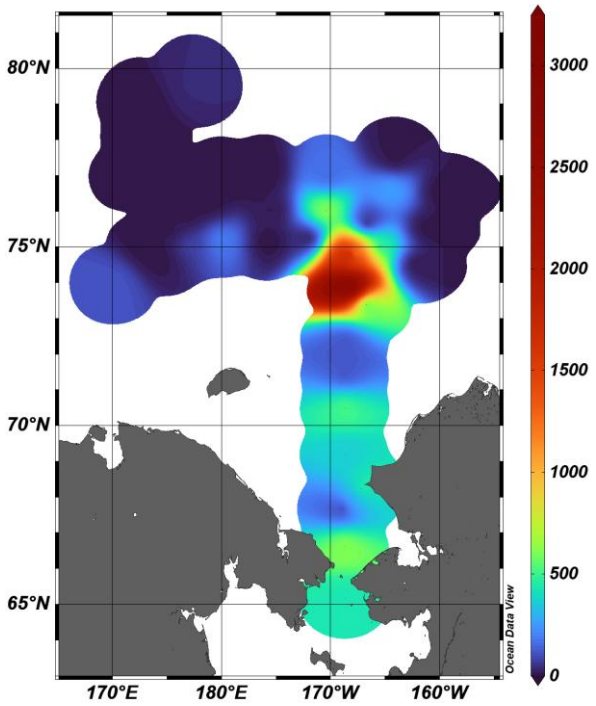

Figure 31: Distribution of hydrophilic toxins [ng/g] in zooplankton from the ARA15A expedition in the Arctic 2024.

During LCC_TA, STX was detected only at station 4, with a concentration of 0.68 ng·m^{-1} of NT (Tab. S19).

Individuals

Several individuals were collected and identified during the LCC_NW and the ARA15A expeditions. The species *Clione limacina* feeds directly on *Limacina helicina* (Arshavsky et al., 1993). In samples from both expeditions the lipophilic (SPX-1 and SPX-C) and hydrophilic (neoSTX, dcSTX and STX) toxins could be detected in these two species. In 2024 (ARA15A) also DA, isoDA-C and -D were mainly present in some individuals in the Bering Strait (station 1 to 3) and in the northern part of Chukchi Sea. SPX-C was present at more stations and higher values up to 20234 ng (LCC_NW) and 116.72 ng·g^{-1} (ARA15A) than SPX-1. In all samples STX was measured. NeoSTX was in several individuals from both expeditions, but dcSTX could only be detected in the two samples from the LCC_NW present in smaller amounts but not 2024 during ARA15A (Tab. 6).

Table 6: Phycotoxins (neoSTX: neosaxitoxin; dcSTX: ; STX: saxitoxin; SPX-1: spirolide 1; SPX-C: spirolide C; iso-DA D: isodomic acid D; DA: domoic acid; iso-DA C: isodomoic acid C) in the zooplankton species Clione limacina (C. limacina, grey) and Limacina helicina (L. helicina, white) from the Arctic expeditions LCC_NW in ng and ARA15A in ng/g.

Cruise	Station	Species	neoSTX	dcSTX	STX	SPX-1	SPX-C	iso-DA D	DA	iso-DA C
LCC_NW	**21**	*L. helicina*	180.70	8.76	698.62	4996.56	7336.55	0.00	0.00	0.00
[ng]	**21**	*C. limacina*	1244.35	18.49	4659.08	14452.86	20234.00	0.00	0.00	0.00
ARA15A	**1**	*C. limacina*	241.74	-	192.17	18.35	36.42	0.00	99.42	0.00
[ng/g]	**2**	*L. helicina*	360.41	-	260.74	13.97	14.88	0.00	11.36	2.32
	3	*L. helicina*	0	-	58.56	48.13	49.58	0.00	287.12	0.00
	6	*C. limacina*	188.86	-	96.86	7.27	20.17	-	-	-
	10	*C. limacina*	202.27	-	316.21	1.51	5.23	-	-	-
	11	*C. limacina*	0	-	108.10	0	17.08	-	-	-
	13	*C. limacina*	0	-	109.44	0	0	-	-	-
	15	*C. limacina*	0	-	442.41	16.20	32.44	0.00	5.69	0.00
	16	*C. limacina*	525.64	-	2427.81	15.10	24.46	-	-	-
	16	*C. limacina*	0	-	71.59	21.75	28.41	1.64	13.71	0.00
	18	*C. limacina*	594.98	-	2479.24	46.60	87.92	0.00	4.79	0.00
	20	*L. helicina*	341.10	-	277.09	0	0	16.00	575.62	0.00
	22	*L. helicina*	0	-	156.20	0	0	0.00	106.32	0.00
	26	*C. limacina*	0	-	34.83	0	116.72	-	-	-
	35	*C. limacina*	0	-	109.49	0	0	-	-	-
	37	*C. limacina*	0	-	82.06	0	0	-	-	-
	41	*L. helicina*	0	-	197.09	0	0	-	-	-
	45	*C. limacina*	0	-	435.95	26.67	59.53	0.00	33.79	0.00
	51	*C. limacina*	0	-	259.82	26.97	57.83	0.00	7.00	0.00

Nine different genera were collected during ARA15A in 2024 (Tab. S20 and S21). In pteropods like *L. helicina* or *C. limacina*, mainly lipophilic (SPX-1 and -C) and hydrophilic toxins (neoSTX, dcSTX and STX) were found. Additionally, the lipophilic toxins SPX-1, SPX-C and CP-4 could also be detected in the copepod and amphipod groups (Fig. S2 and S4). In contrast, DA and its isomers were mostly present in copepods. Lower amounts of DA and the iso-DA C were measured in pteropods. In chaetognatha, amphipods and krill only DA was detected (Fig. S3).

5.4 Southern Ocean (Antarctica)

In total, 135 samples from the Southern Ocean were analysed: 60 phytoplankton, 48 zooplankton and 16 SPATT samples from nine stations.

Phytoplankton

In the LCC_SO expedition, PTX-2 was the only phycotoxin found in the phytoplankton samples from the net tows (stations 6 to 11). The highest amount per meter was found in the Amundsen Sea in front of Marie Byrd Land, with 1.70 ng·m^{-1} of NT (Fig. 32). No toxins could be detected in samples from other regions in phytoplankton (Tab. S22).

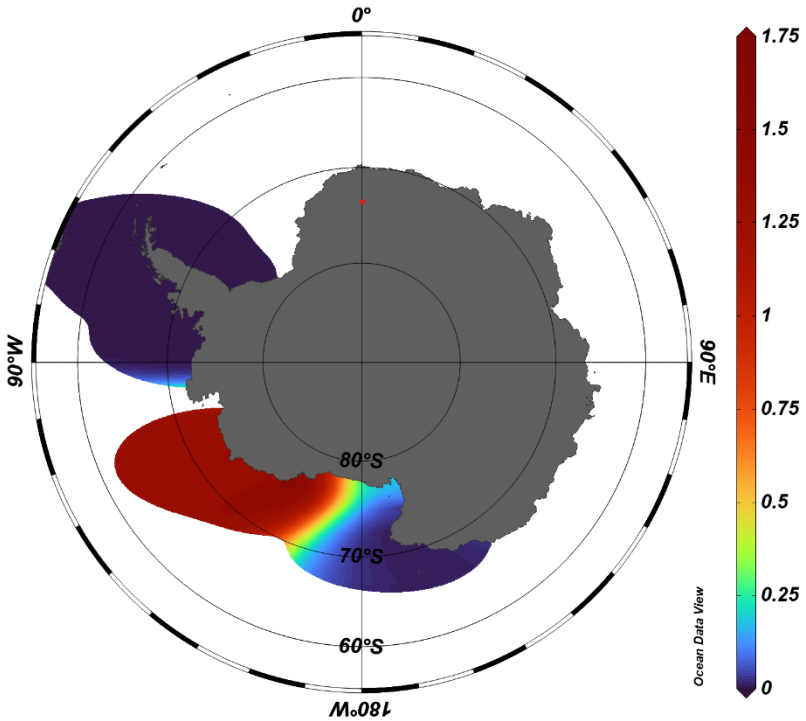

*Figure 32: Map with the total amount of PTX-2 per meter of net tow (NT) [*ng/m of NT*] in phytoplankton samples from the LCC_SO in the Southern Ocean (Antarctica).*

Hydrophilic toxins and DA and its isomers were not detected in the phytoplankton samples.

Dissolved Toxins

In the LCC_SO samples, PTX-2 was also found dissolved in the water, as in phytoplankton, and it was detected in six of the seven SPATT samples. Just in the Ross Sea (SPATT sample 165) no PTX-2 were detected (Tab. S6).

The same phycotoxin, PTX-2, could be measured in the samples from GARS-O'Higgins (Tab. S7).

Zooplankton

In zooplankton from LCC_SO, neither hydrophilic nor lipophilic toxins, nor DA and isomers could be detected.

5.5 Azadinium

No AZA toxins could be detected in the extracted samples for AZAs analysis, either in the Arctic waters or in the Southern Ocean.

6 Discussion

In recent years, regular monitoring programs for phycotoxins have been established worldwide, with the exception of the polar regions. The Arctic and the Southern Ocean remain largely unexplored in this regard, with a significant lack of data on phycotoxin occurrence. Both regions are heating up at faster rates than the rest of the world (Rantanen et al., 2022; Ding et al., 2025), and additionally, 2024 was the warmest year recorded to date (Bevacqua et al., 2025). The chemical, physical and biological conditions are changing in these regions, and this is expected to have an impact on phytoplankton communities (Moritz et al., 2002; Mauritsen, 2016; Lannunzel et al., 2020), potentially leading to more frequent HABs in the most northern or southern regions of the planet (Kremp et al., 2012; Kim et al., 2018).

In this study, several phycotoxins, including DA and its isomers, lipophilic (SPX-analogues, PTX-2, OA, DTX-1) and hydrophilic toxins (STX and analogues), were detected in phytoplankton and within the lower trophic levels of the trophic web, including primary consumers (zooplankton feeding on phytoplankton) and secondary consumers (zooplankton preying on other zooplankton species), and dissolved in polar waters. While some research has focused on understanding phycotoxins in Arctic phytoplankton, data remain scarce for zooplankton and higher trophic levels and are even more limited for the Antarctic region. These findings therefore expand current knowledge by providing new evidence of phycotoxin occurrence in Antarctic food webs and beyond the primary producers in Arctic ecosystems, providing a baseline as environmental conditions in these regions continue to change.

6.1 Arctic waters

In Arctic waters, six toxin classes, including PTX-2, SPXs, STXs, OA, DTX-1, and DA, comprising a total of 17 analogues, were identified in this study. No toxins in phytoplankton were detected north of 80 °N in the Atlantic side or on the Pacific side of the Central Arctic Ocean. Regarding zooplankton, phycotoxins were detected at latitudes as high as 84 °N. Similarly, no published data have confirmed the presence of phycotoxins at such a high latitude. When comparing the findings in phytoplankton with the ice shield cover of the Central Arctic Ocean, the cover on the Atlantic site extends farther south than on the Pacific site (Fig. S5-7). The ice cover limits light availability and restricts the mixing of the water column and nutrient exchange with surrounding waters (Lannunzel et al., 2020). These factors inhibit phytoplankton growth and phycotoxin production more north. In phytoplankton phycotoxins were mostly found in ice-free areas. This leads to the hypothesis that toxic phytoplankton species have not immigrate into the ice-covered regions and the conditions under the ice shield inhibit their growth.

6.1.1 Phytoplankton

Six different lipophilic phycotoxins were detected in the net samples taken during the three cruises, including one analogue of PTX (PTX-2) and five of SPXs (SPX-1, SPX-A, SPX-B, SPX-C, and 20-Me-SPX-G).

These lipophilic toxins were detected in both coastal waters (LCC_NW) and offshore regions (ARA15A and LCC_TA). The phytoplankton species producing these lipophilic toxins are commonly found in Arctic coastal waters. Studies from Tillmann et al. (2014) and Rodriguez-Marconi et al. (2024) discovered these species in coastal areas around Disko Bay in 2012 and 2017.

The lipophilic toxin PTX-2 was widely distributed at the west coast of Greenland, the Bering Strait, the Chukchi Sea, near Svalbard and the Central Arctic Ocean. Near Disko Bay, the presence of the PTX-2 producing species *D. acuta* has been reported (Rodriguez-Marconi et al., 2024). During LCC_NW (2023) and ARA15A (2024), PTX-2 was found in the Bering Strait. Additionally, in 2024, high amounts were measured further north in the Chukchi Sea and as far as 79 °N in the Central Arctic Ocean (ARA15A, station 26). The most northerly record up to date was in shellfish at 74°N (Gao et al., 2019) in the Chukchi Sea. To the best of our knowledge, there are no studies about PTX-producing species or PTX-2 in the Pacific site of the Arctic Ocean that far north. The high values in 2024 in the Chukchi Sea show the abundance of the dinoflagellate species *Dinophysis sp.* (Krock et al., 2008) or an undescribed species in this region.

The findings of SPXs agree with previous studies and with the presence of the phytoplankton species *A. ostenfeldii*, which is the only known producer of these compounds (Cembella et al., 2000; Touzet et al., 2008). The SPX-analogue SPX 20-Me-SPX-G was detected only in Atlantic-influenced regions in both years, but was not detected at the Pacific-influenced sites. Previous studies have likewise reported the presence of 20-Me-SPX-G in Atlantic polar waters (Tillmann et al., 2017). This distribution pattern is likely influenced by the Gulf Stream, which transports warm Atlantic water up north, resulting in higher sea-surface temperatures near Greenland compared to the Pacific side (Palter, 2015). This might favour the appearance and phycotoxin production of *A. ostenfeldii* on the Atlantic side.

In the case of the analogue SPX-1, the opposite pattern occurred; it was only found in the Pacific-influenced regions, such as the Chukchi Sea and the Northwest Passage. Moreover, the analogue SPX-B was recorded in the Northwest Passage in 2023. Samples collected from 1980 to 1993 already confirmed the presence of *A. ostenfeldii* in the Chukchi Sea (Okolodkov & Dodge, 1996). Since no species is known to produce exclusively SPX-1 and SPX-B so far, an unknown species or a distinct strain of *A. ostenfeldii*, which produces the two SPX-analogues, could have been present in 2023 in the Northwest Passage.

Consistently, DA was the toxin showing the highest concentrations across all expeditions. DA and the presence of toxigenic microalgae species that produce DA and isomers, like the diatom *Pseudo-nitzschia spp.*, have already been reported in Arctic regions (Farabegoli et al., 2018; Huntington et al., 2020). In the west coast of Greenland, blooms of *Pseudo-nitzschia spp.* have been described in Baffin Bay (Bruhn et al., 2021), and the DA-producing *Pseudo-nitzschia delicatissima* was already isolated in Disko Bay in April 2012, June 2013 and June 2014 (Lundholm et al., 2018). Other species producing DA,

such as some macroalgae species, including *Chondria armata* and *Digenea simplex*, or the diatom *Pseudo-nitzschia seriata,* are also known to be present in this area (Farabegoli et al., 2018; Weber et al., 2021). During the LCC_NW cruise, in September 2023, a remarkably high value of DA was measured at the southern tip of Greenland, with over 600 $ng \cdot m^{-1}$ of NT. This high value was more than 10-times higher than at other stations in phytoplankton and indicates a high abundance of a DA-producing species in this region on the 13th of September 2023. Sea surface temperature during this month were relatively high compared to previous decades (Fig. S8). *Pseudo-nitzschia spp.* has a greater growth rate with rising water temperatures, as shown by Lefebvre et al. (2025). This could have positively influenced the proliferation of DA-producing species near Greenland. To confirm a high abundance of DA-producing cells in the area, data on cell counts would be necessary.

In 2024 during the ARA15A and LCC_TA, DA was reported in smaller amounts (<50 $ng \cdot m^{-1}$ of NT) in the Chukchi Sea and the Central Arctic Ocean and as far north as 77 °N. This represents the northernmost record of DA in phytoplankton to date. In the literature, DA has already been reported in water samples from the Bering Strait, the Chukchi Sea and the Beaufort Sea, up to 69 °N in 2018 (Huntington et al., 2020). These new findings suggest that DA-producing species are expanding further north, likely in response to changing Arctic environmental conditions.

The DA isomers and epimers accounted for only a portion of less than 10 % of the total amount during all cruises, and none of them were detected in the absence of DA. In strains like *P. seriata,* the production of DA and iso-DA A has been proven (Weber et al., 2021), while the transformation of DA into epi-DA can occur through long-term storage or heating (Quilliam et al., 1989; Quilliam, 2003). Although studies about DA and its isomers are available in the literature, the biochemical pathways and mechanisms underlying their formation remain poorly understood.

In the Bering Strait, the Chukchi Sea and on the west coast of Greenland, three hydrophilic toxins (STX, C1/C2, GTX-2/GTX-3) were detected during LCC_NW (2023) and ARA15A (2024) cruises. The presence of STX on the west coast of Greenland agrees with previous findings. Between 2018 and 2023, *A. ostenfeldii* and *A. catenella,* both producers of STX, dominated the phytoplankton community in Disko Bay (Hoerstmann et al., 2025), supporting the hypothesis that these species are the likely source of STX in waters near Greenland. Furthermore, in the last years, the region around the Bering Strait has been sampled increasingly, revealing an increasing frequency of STX detections and occurrences of *A. catenella* (Lefebvre et al., 2022; Fachon et al., 2024; Lefebvre et al., 2025). The present study confirmed this continued presence, suggesting that STX-producing species are now established in the Bering Strait and the Chukchi Sea. The high abundance of STX and analogues could be explained by the presence of *A. catenella* cysts in the sediment, which germinate seasonally as water temperatures rise and environmental conditions shift, favouring HAB development (Gobler et al. 2017; Boivin-Rioux et al. 2021; Fachon et al., 2024). The overall hydrophilic toxin composition found in phytoplankton samples

in this area resembled that reported by Fachon et al. (2024) for the same region. They identified STX, neoSTX, GTX-1/GTX-4, GTX-2/GTX-3, B1, and C1/C2 in phytoplankton, which agrees with the detection of STX, C1/C2, GTX-2/GTX-3 and trace amounts of GTX-1/GTX-4 and neoSTX in the present study. Toxin B1 could not be detected during ARA15A, likely due to concentrations below the analytical detection limit.

In 2023, during the LCC_NW cruise, no toxins were detected in the SPATT samples. In contrast, during the ARA15A and LCC_TA cruises in 2024, PTX-2 was found in all samples. During LCC_TA in 2024, SPX-1, SPX-C, DTX-1 and OA were also detected in SPATTs in the Pacific-influenced site. OA and DTX-1 were neither in phytoplankton nor zooplankton samples. The lipophilic toxins PTX-2, OA, and DTX-1 are chemically related and are often produced by the same dinoflagellate species, such as *D. acuminata* and *D. acuta* (Bruhn et al., 2021; Möller et al., 2022). OA is among the most lipophilic toxins and adsorbs well to the resin in the SPATTs; therefore, even trace amounts of dissolved OA below the detection limit in phytoplankton may be concentrated in the SPATTs. Although SPATTs cannot be used to quantify toxin concentrations, as adsorption efficiency varies with environmental and methodological factors, they provide indirect yet valuable evidence of phycotoxin occurrence (Möller et al., 2022) and the presence of a PTX-2, DTX-1 and OA toxin-producing phytoplankton species in the Chukchi Sea. The finding of PTX-2 in the ARA15A samples confirms the finding in the phytoplankton. The absence of PTX-2 in the LCC_NW, where much lower levels of PTX-2 were detected in phytoplankton, samples validates the results of the phytoplankton samples.

6.1.2 Phycotoxins along the Arctic Food Chain

While many studies have focused on phycotoxins in phytoplankton, much less is known about their transfer through the food web and the distribution in zooplankton. Zooplankton can be exposed to phycotoxins primarily through feeding on phytoplankton, although some species may also accumulate toxins indirectly through trophic transfer (e.g., by preying on smaller, toxin-containing zooplankton) (Fenchel, 1988). In this study, a total of 15 phycotoxins, including analogues from different toxin classes, were found in zooplankton.

In relation to lipophilic toxins, five analogues were detected in zooplankton samples during LCC_NW and ARA15A: SPX-1, SPX-B, SPX-C, 27-hydroxy-SPX-C, and CP-4. The SPX analogues CP-4 (ARA15A, in copepods and amphipods) and 27-hydroxy-SPX-C (LCC_NW, in net samples) were only detected in zooplankton, not in phytoplankton. In contrast, the other SPX analogues were detected in both trophic levels. In phytoplankton samples, PTX-2 (LCC_NW, ARA15A, LCC_TA), SPX-A (LCC_NW) and 20-Me-SPX-G (LCC_NW and LCC_TA) were present but absent in zooplankton.

When considering zooplankton individuals collected separately, during LCC_NW (2023), high concentrations of two lipophilic toxins, SPX-1 and SPX-C, were measured in the pteropods *L. helicina* and *C. limacina* in the Bering Strait. *L. helicina* is a filter-feeding pteropod that serves as the main prey

for the pteropod *C. limacina* in polar waters (Conover & Lalli, 1972; Hopkins, 1985; Hopkins, 1987; Arshavsky et al., 1993). Both pteropod species were also sampled during ARA15A (2024), but at different locations in the Bering Strait, Chukchi Sea, and Central Arctic Ocean. Similar to LCC_NW results, SPX-1 and SPX-C were detected in both species, suggesting that pteropods were the main vectors of lipophilic toxins in these regions. In some polar and subpolar waters, pteropods can replace krill as the dominant zooplankton group (Fabry et al., 2008). Pteropods are an important food source for several fish, like the North Pacific salmon, mackerel, herring and cod (LeBrasseur, 1996). Although SPXs have also been reported in mussels from Nova Scotia (Canada) (Hu et al. 1996), in the Sognefjord (Norway) (Aasen et al., 2005), and in Spain (Parades-Banda et al., 2018). In other studies copepods have been considered the main vectors for the transfer of phycotoxins in the food web (Turner et al., 2000; Lincoln et al., 2001; D'Agostino et al., 2019). Turriff et al. (1995) showed the accumulation of SPXs produced by *A. ostenfeldii* in copepods, but only in small quantities. In Golfo San José (Argentina), D'Agostino et al. (2019) found 20-Me-SPX-G and PTX-2 in the copepods *Calanus carinatus* and *Calanus australis*, but only in trace levels. For SPX-A, no records in zooplankton could be found in the literature what agrees with our findings just in phytoplankton.

Although SPXs were detected in zooplankton (SPX-1, SPX-B, SPX-C, 27-hydroxy-SPX-C, and CP-4) during these cruises, it is not proven why different analogues are found compared to phytoplankton (SPX-1, SPX-A, SPX-B, SPX-C, and 20-Me-SPX-G). These differences may result from predator-related metabolic transformations during trophic transfer. *C. limacina* is able to survive three months without food and can slow the metabolism around 20 times (Lee, 1974, Conover & Lalli, 1972) This metabolic differences may also explain why pteropods accumulate higher amounts of SPXs, whereas copepods do not incorporate these toxins or do so only in trace amounts below detection limits. Further experimental work is needed to clarify toxin uptake and transformation processes in Arctic zooplankton.

Regarding hydrophilic toxins, STX was the only hydrophilic toxin present in both phytoplankton and zooplankton samples. STX and neoSTX were found in net samples in LCC_NW and mainly in pteropods during ARA15A, while dcSTX could only be detected in zooplankton net samples from LCC_NW. STX and its analogues have been recurrently detected in the Bering Strait and Chukchi Sea in recent years (Lefebvre et al., 2016; Fachon et al., 2024), a pattern also reflected in the zooplankton analysed in this study. In Massachusetts Bay, Turner et al. (2000) found that PSP toxins accumulate mainly in large copepods (> 500 µm). STX-analogues have also been previously reported in shellfish, marine mammals, and seabirds that feed on zooplankton (Baggesen et al., 2012; Landsberg et al., 2014; Van Hemert et al., 2021; Lefebvre et al., 2022; Fachon et al., 2024; Lefebvre et al., 2025).

The STX-analogues can interconvert due to predators' metabolism or low pH conditions (Krock et al., 2007). It is often suggested that this transformation occurs in higher organisms, which is supported by

the findings of dcSTX and neoSTX, which are exclusively found in zooplankton and not in phytoplankton in the present study.

In this study, the highest concentrations of hydrophilic toxins (neoSTX, dcSTX, and STX) were described in the Bering Strait both in net samples and in the pteropods *C. limacina* and *L. helicina* in 2023 (LCC_NW). STX and neoSTX were also measured in *C. limacina* individuals collected in ARA15A (2024). Maoka et al. (2014) described the accumulation of carotenoids, which originate from phytoplankton, in *L. helicina, C. limacina* and finally in salmon, illustrating the trophic linkage among these species.

Together with the SPX results, these findings suggest that *L. helicina* and its predator, *C. limacina*, serve as important vectors facilitating the transfer of both hydrophilic and lipophilic (SPXs) phycotoxins within Arctic food webs.

DA and isomers were found in zooplankton net samples at the southern tip of Greenland (LCC_NW) and in the Central Arctic Ocean (ARA15A, LCC_SO), in agreement with studies showing the accumulation of phycotoxins in copepods (Lincoln et al.,2001; Maneiro et al.,2005). The highest concentrations were observed in copepods when sampled individually during the ARA15A cruise, consistent with earlier observations. Feeding experiments conducted by Lincoln et al. (2001) with *Acartia tonsa* and *Temora longicornis*, and by Maneiro et al. (2005) with *Acartia clausi*, demonstrated that copepods accumulate DA, although the toxin does not act as a feeding deterrent and appears to have no adverse effects on them. In the Arctic marine ecosystem, copepods from the family *Calanus spp.* play a crucial role in transferring energy from primary producers (phytoplankton) to higher organisms and serve as a potential vector for DA in the trophic web (Falk-Petersen et al., 2009; Kosobokova & Hirche, 2009). This shows the potential of transferring DA and isomers to higher levels of the Arctic food web, including marine mammals (Hendrix et al., 2021). Further experimental studies are needed to identify key species or genera that might be crucial in DA transfer up the marine food web.

In addition to DA, all known isomers (in net samples and individuals) and epi-DA (in individuals) were detected in this study, suggesting that DA isomers can also accumulate in higher trophic levels. Unfortunately, no data is available in the literature for isomers in zooplankton. This can be explained by the focus of monitoring only on DA and not on the isomers, as these are considered less toxic. As a result, many aspects of the isomers are still unknown (Olsen et al., 2021).

The comparison of toxin distributions across the three expeditions showed that toxin patterns between phytoplankton and zooplankton were not aligned. In general, high toxin concentrations in phytoplankton did not correspond to elevated levels in zooplankton, nor vice versa. High toxin levels in zooplankton are expected to occur after the phytoplankton peak, as time is required for zooplankton to be exposed to and accumulate sufficient toxin concentrations through feeding, resulting in a temporal offset between the occurrence of toxins in phytoplankton and their detection in zooplankton.

Moreover, zooplankton can contain toxins even when those toxins are no longer detected in the phytoplankton (Teegarden & Cembella., 1996; Turner et al., 2000; Leandro et al., 2010). Leandro et al. (2010) conducted an experiment in which they fed *Calanus finmarchicus* a toxic strain (*Pseudo-nitzschia multiseries*) and a non-toxic strain of the same species, demonstrating that copepods can accumulate DA and retain it for up to 48 hours. The results obtained in this work, along with the time lag in toxin detection between phytoplankton and zooplankton, highlight the importance of sampling both groups to assess phycotoxin dynamics, as relying on a single trophic level could result in incomplete information.

Still, many aspects of the Arctic waters remain unknown (Smith et al., 2007; Armbrust, 2009; David & Saucède, 2015; Lundholm et al., 2024), and additional data are needed to better predict future changes. Therefore, regular monitoring programs and systematic sampling of both phytoplankton and zooplankton are needed.

6.2 Southern Ocean (Antarctica)

In the Southern Ocean during LCC_SO, PTX-2 was the only phycotoxin detected in phytoplankton near Marie Byrd Land, as well as dissolved in the water during the LCC_SO and from GARS-O'Higgins. Krock et al. (2020) identified the toxic dinoflagellate species *Dinophysis norvegica,* a known producer of PTX-2, DTX-1, and OA (Nagai et al., 2023), in seawater near King George Island (KGI) between 2013 and 2015. However, PTX-2 was not detected in phytoplankton net samples at that time. In contrast, in the SPATT samples collected from coastal waters during the same period, the lipophilic phycotoxins PTX-2, pectenotoxin-2 seco acid (PTX-2sa) and YTX were found (Krock et al., 2020). Remarkably, 2024 was characterized by unusually high temperatures in Marie Byrd Land (Ding et al., 2025), which could have enhanced the growth and metabolic activity of *Dinophysis* populations (e.g., *D. norvegica*), explaining the findings of PTX-2 in phytoplankton net samples during LCC_SO. To our knowledge, this represents the first detection of PTX-2 in phytoplankton net samples from the Southern Ocean.

Previous studies have also shown the presence of other toxic species and phycotoxins in Antarctic waters. In 2002, Silver et al. (2010) detected DA in the Southern Ocean. Moreover, in 2021, strains of the toxic species *Pseudo-nitzschia subcurvata* were isolated from these waters for the first time, confirming the presence of DA and iso-DA C in them (Olesen et al., 2021). The toxins are expected to be transferred up through the food chain, and the Southern Ocean is an important feeding ground for many seabirds and marine mammals like the humpback whale (*Megaptera novaeangliae*) and the southern right whale (*Eubalena australis*) (Riekkola et al., 2018). DA has already been detected in the specie *E. australis* in Argentinian waters (D'Agostino et al., 2017). Further studies are needed to understand and close the knowledge gab regarding the development of the phytoplankton communities, distribution of phycotoxins and the impact on the food chain in the Southern Ocean.

6.3 Limitations

This study provides a baseline of data about phycotoxins in the Arctic waters and the Southern Ocean, but it is subject to several limitations. Sampling was conducted opportunistically, often depending on cruise schedules and logistical constraints. For example, during LCC cruises (LCC_NW, LCC_SO and LCC_TA), net samples were collected only once per day, providing only a single sample over large spatial areas. In contrast, during the ARA15A expedition, on board a research vessel, shorter distances and more closely spaced locations were sampled, providing a greater coverage of toxins. Sampling procedure, e.g., depths of the NTs were different at the different expeditions, ranging from 10 to 100 m for phytoplankton and from 30 to over 1,500 m for zooplankton. In addition, during ARA15A, only individuals were picked from the zooplankton nets and not whole net tows were used, like in the other expeditions.

Additionally, a comparison between the Arctic and Southern Oceans in this study is challenging, as the sampling effort has been unequal: over 1,000 samples were analysed from Arctic waters, whereas less than 150 samples were analysed from the Southern Ocean. This difference reflects the logistical challenges of accessing Antarctic waters and the historically greater research focus on the Arctic. Thus, data on phycotoxins in the Southern Ocean remain scarce. Nevertheless, findings in the Arctic waters could indicate what will happen in the Southern Ocean due to global warming, as shifts in phytoplankton community composition and bloom timings are expected.

7 Conclusion

This study provides the first assessment of phycotoxin occurrence and distribution in the base of polar food webs, both in the Arctic and Southern Ocean. Phycotoxins were detected in water, phytoplankton, and zooplankton samples in Arctic waters, demonstrating their presence at the base of the Arctic food web. These findings indicate that phycotoxin-producing species and their associated toxins are present in Arctic waters, suggesting a potential risk of harmful algal events.

In the Pacific Arctic, phycotoxins (PTX-2, SPX-C, DA and STX) were found in open waters at higher latitudes than previously reported (up to 84 °N), suggesting that toxic phytoplankton species are expanding further north in Arctic waters.

The formation of toxin isomers due to the metabolism of the animals ingesting them, together with the time delay between phytoplankton and zooplankton, endorses the necessity of sampling at various trophic levels for proper phycotoxin assessment.

In this study, PTX-2 was detected for the first time in Antarctic phytoplankton. The Southern Ocean seems to be less exposed to blooms and the production of phycotoxins. However, lower sampling effort and limited data available for Antarctic waters prevent definitive conclusions.

In summary, these results provide a data baseline regarding phycotoxin occurrence and distribution in polar waters. Further studies are necessary to better understand the distribution and dynamics of phycotoxins in these regions. Moreover, establishing long-term monitoring programs is essential to understand the initiation of HABs and the transfer of phycotoxins through the food web. These efforts will also allow us to make predictions about how the distribution of toxigenic species and the occurrence of their associated toxins might change in a future scenario of eutrophication and global warming.

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9 Appendix

9.1 Supplementary Tables

Table S1: Station information for LCC_NW expedition September and October 2023: GPS Coordinates, Latitude and Longitude in Deg., Date, UTC time, Temperature in °C, phytoplankton (PP) and zooplankton (ZP) net tows (NT) with depth in m, Niskin bottle and CTD data.

Station	GPS Coordinates	Lat. [Deg]	Long. [Deg]	Date	Time (UTC)	Temp. (°C)	PP-NT	ZP-NT	Niskin	CTD
1	62°44’29,01’’N 32°12’45,01’’W	62.74	-32.21	12.09.23	19:30	10.09	2 (30m)	2 (30m)	No	Yes
2	60°10’24,10’’ N 43°37’37,53’’W	60.17	-43.63	13.09.23	19:42	2.31	2 (30m)	2 (30m)	No	Yes
3	60°8’43,10’’N 44°16’29,19’’W	60.15	-44.28	14.09.23	11:25	2.57	2 (30m)	2 (30m)	No	Yes
4	62°5’36,51’’N 50°52’54,66’’W	62.09	-50.88	15.09.23	20:05	3.05	2 (30m)	2 (30m)	No	Yes
6	66°14’51,73’’N 54°19’2,88’’W	66.25	-54.32	17.09.23	10:30	4.78	2 (30m)	2 (30m)	Yes	Yes
7	69°13’45,37’’N 51°6’55,46’’W	69.23	-51.12	18.09.23	12:15	2.70	2 (30m)	2 (30m)	No	Yes
8	71°27’0,86’’N 62°50’14,36’’W	71.45	-62.84	19.09.23	13:15	6.50	2 (30m)	2 (30m)	No	Yes
9	72°42’22,84’’N 77°50’18,10’’W	72.71	-77.84	20.09.23	13:25	nd	2 (30m)	No	No	Yes
10	74°49’37,84’’N 80°6’26,52’’W	74.83	-80.11	21.09.23	13:55	-0.37	2 (30m)	No	Yes	Yes
11	74.84°N 80.219°W	74.89	-82.40	22.09.23	13:35	0.40	2 (30m)	No	No	Yes
12	74°41’32,79’’N 91°10’27,12’’W	74.69	-91.17	23.09.23	15:45	1.98	2 (30m)	No	Yes	Yes
13	77°1’40,99’’N 106°36’56,16’’W	77.03	-106.62	25.09.23	07:00	nd	1 (30m)	No	No	Yes
14	76°30’0,16’’N 113°39’1,32’’W	76.50	-113.65	26.09.23	23:05	-0.30	2 (30m)	No	Yes	Yes
15	74°39’22,72’’N 124°10’59,38’’W	74.66	-124.18	27.09.23	17:25	-0.57	2 (30m)	No	Yes	Yes
16	74°42’6,80’’N 132°56’25,54’’W	74.70	-132.94	28.09.23	21:30	-0.58	2 (30m)	No	Yes	Yes
17	70°46’21,18’’N 137°12’31,95’’W	70.77	-137.21	29.09.23	18:30	3.58	2 (30m)	No	Yes	Yes
18	70°56’31,56’’N 147°13’20,40’’W	70.94	-147.22	01.10.23	21:15	4.57	2 (30m)	2 (30m)	Yes	Yes
19	71°32’19,11”N 156°57’41,73”W	71.54	-156.96	02.10.23	17:58	2.51	2 (30m)	2 (30m)	Yes	Yes
20	69°26’5,30’’N 165°47’31,88”W	69.44	-165.79	03.10.23	19:54	7.23	2 (30m)	2 (30m)	Yes	Yes
21	66°14’35,41’’N 168°26’56,08’’W	66.24	-168.45	04.10.23	19:15	5.97	2 (30m)	2 (30m)	Yes	Yes
24	54°14’47,62”N 164°11’51,53”W	54.25	-164.20	07.10.23	19:45	9.57	1 (30m)	1 (30m)	No	Yes
25	53°30’18,73”N 154°27’19,37”W	53.51	-154.46	08.10.23	18:20	10.72	2 (30m)	2 (30m)	Yes	Yes
26	51°59’27,81”N 144°43’22,27”W	51.99	-144.72	09.10.23	18:20	12.33	2 (30m)	2 (30m)	Yes	Yes

Table S2: Station information for ARA15A expedition in August 2024: GPS Coordinates, Latitude and Longitude in Deg., Date, UTC time, Temperature in °C, phytoplankton (PP) and zooplankton (ZP) net tows with depth in m; nd = no data.

									Depth net tows [m]			
									ZP-Nets			
Station	**GPS Coordinates**		**Lon [Deg]**	**Lat [Deg]**	**Date**	**Time (UTC)**	**Temp. [°C]**	**PP-NT**	**Ring**	**500 um**	**150 um**	**FTN**
1	65° 10.41511' N	168° 41.42582' W	-168.690	65.173	01.08.2024	00:58	3.12	40	45			
2	66° 37.79605' N	168° 41.25496' W	-168.687	66.629	01.08.2024	10:48	7.07	35		35		
3	67° 40.19986' N	168° 57.59987' W	-168.960	67.670	01.08.2024	18:19	2.79	40		40		
4	67° 46.97878' N	168° 36.14424' W	-168.602	67.783	01.08.2024	20:38	2.00	40		40		
6	68° 0.7806' N	167° 52.0152' W	-167.867	68.013	02.08.2024	00:15	5.33	-		45		
8	68° 14.49438' N	167° 07.32176' W	-167.122	68.242	02.08.2024	05:29	6.85	35			40	
9	69° 10.01089' N	168° 40.00276' W	-168.667	69.167	02.08.2024	12:47	5.53	45		45		
10	70° 30.00351' N	168° 40.01077' W	-168.667	70.500	02.08.2024	21:27	-0.69	35	35	35		
11	71° 25.80138' N	168° 40.01336' W	-168.667	71.430	03.08.2024	03:52	1.75	45		45		
13	72° 22.40899' N	168° 37.45580' W	-168.624	72.373	03.08.2024	12:15	-1.27	43	48	43		
15	73° 22.70254' N	166° 39.64881' W	-166.661	73.378	03.08.2024	22:02	-1.44	65		65		
16	73° 51.67138' N	168° 08.84156' W	-168.147	73.861	04.08.2024	04:35	-1.28	100		162	165	
18	74° 47.26130' N	168° 03.39479' W	-168.057	74.788	04.08.2024	13:34	-1.29	100	175			
20	76° 00.75201' N	170° 24.16603' W	-170.403	76.013	05.08.2024	03:05	-1.42	100		200		
22	76° 59.07830' N	170° 15.90999' W	-170.265	76.985	05.08.2024	16:44	-1.51	100		200		
22.B	77° 01.41439' N	172° 26.86015' W	-172.448	77.024	05.08.2024	21:33	nd	-				986
23	77° 00.05913' N	176° 16.24869' W	-176.271	77.001	06.08.2024	06:30	-1.46	100			200	
24	76° 58.10506' N	179° 52.99700' E	179.883	76.968	06.08.2024	14:28	-1.45	100				461
26	79° 30.13498' N	177° 20.09851' E	177.335	79.502	11.08.2024	23:12	-1.53	100	500			
27	78° 59.66142' N	172° 46.87769' E	172.781	78.994	12.08.2024	12:12	-1.61	100	500	200		
28	78° 03.80374' N	173° 02.32827' E	173.039	78.063	12.08.2024	23:02	-1.59	100		200		
29	77° 00.34899' N	173° 40.99490' E	173.683	77.006	13.08.2024	08:29	-1.31	100		200		200
30	75° 57.83632' N	173° 32.20470' E	173.537	75.964	13.08.2024	22:05	-1.16	100				
31	75° 23.10411' N	175° 18.47304' E	175.308	75.385	14.08.2024	03:32	-1.31	100		200		

32	74° 59.28568' N	173° 32.79420' E	173.547	74.988	14.08.2024	08:49	-1.22	100		131	
35	73° 59.61753' N	170° 03.44684' E	170.057	73.994	14.08.2024	19:42	-1.13	40		40	
36	74° 42.03305' N	174° 31.15119' E	174.519	74.701	15.08.2024	07:45	-1.37	65		65	
37	75° 03.76842' N	176° 57.27582' E	176.955	75.063	15.08.2024	23:32	-1.37	100		190	
38	75° 48.09038' N	177° 03.12404' E	177.052	75.802	16.08.2024	09:25	-1.29	100	500		
39	76° 07.34484' N	178° 47.86751' E	178.798	76.122	17.08.2024	02:56	-1.35	100		200	
41	75° 12.43673' N	179° 59.11565' W	-179.985	75.207	17.08.2024	16:03	-1.29	100		200	
42	76° 00.87414' N	175° 21.91717' W	-175.365	76.015	18.08.2024	12:04	-1.45	100		200	
43	75° 09.82527' N	175° 50.23663' W	-175.837	75.164	18.08.2024	20:21	-1.39	100	100	200	
44	75° 14.32232' N	172° 00.85278' W	-172.014	75.239	19.08.2024	07:23	-1.20	100	150		
45	75° 01.42379' N	165° 21.73762' W	-165.362	75.024	20.08.2024	05:23	-0.69	100	500	200	
46	74° 30.98371' N	162° 09.09349' W	-162.152	74.516	20.08.2024	21:47	0.43	100	500		
48	75° 29.90933' N	161° 08.79197' W	-161.147	75.498	21.08.2024	17:16	0.00	100		200	
49	76° 32.37852' N	159° 53.37643' W	-159.89	76.54	22.08.2024	04:25	-1.12	100	100, 1200		
50	77° 27.20180' N	164° 05.23737' W	-164.087	77.453	22.08.2024	19:37	-1.48	100		200	
51	76° 34.04320' N	164° 21.61430' W	-164.36	76.567	23.08.2024	09:31	-1.27	100			545
52	75° 39.34011' N	166° 37.04657' W	-166.617	75.656	23.08.2024	19:39	-1.29	100			268
53	74° 48.32423' N	167° 52.91484' W	-167.882	74.805	24.08.2024	03:30	-1.09	100		182	

Table S3: Station information for LCC_TA expedition in the Arctic waters in September 2024; GPS Coordinates, Latitude and Longitude in Deg., Date, UTC time, Temperature in °C, phytoplankton (PP) and zooplankton (ZP) net tows (NT) with depth in m, Niskin bottle and CTD data.

Station	GPS Coordinates	Lat. [Deg]	Long. [Deg]	Date	Time (UTC)	Temp. [°C]	PP-net	ZP-net	Niskin	CTD
2	77°24'4.23''N 164°22'31.04''W	77.401	-164.375	09.09.24	08:00	1.09	2 NT (30 m)	2 NT (50 m)	No	No
4	82°4'37.87''N 168°33'9.62''W	82.077	-168.553	10.09.24	16:30	-1.42	2 NT (30 m)	2 NT (50 m)	Yes	No
6	84°12'31.54''N 173°35'8.77''W	84.209	-173.586	11.09.24	09:20	-1.80	2 NT (30 m)	2 NT (50 m)	No	Yes
9	85°51'9.85''N 139°8'44.92''E	85.853	139.146	13.09.24	05:45	-1.19	2 NT (30 m)	2 NT (50 m)	Yes	Yes
12	89°53'57.12''N 44°8'0.81''W	89.899	-44.134	15.09.24	11:04	-1.47	2 NT (30 m)	2 NT (50 m)	Yes	Yes
16	85°43'42.68''N 30°55'27.85''E	85.729	30.924	18.09.24	11:29	-1.66	2 NT (30 m)	2 NT (50 m)	Yes	Yes
20	82°40'31.00''N 19°54'43.42''E	82.675	19.912	20.09.24	09:56	-1.62	2 NT (30 m)	2 NT (50 m)	Yes	Yes
21	79°42'35.64''N 21°46'7.94''E	79.710	21.769	21.09.24	09:02	2.62	2 NT (30 m)	2 NT (50 m)	Yes	Yes
22	79°36'52.39''N 19°26'20.99''E	79.615	19.439	21.09.24	22:32	2.36	2 NT (30 m)	2 NT (50 m)	Yes	Yes
23	79°21'14.46''N 20°45'16.15''E	79.354	20.754	22.09.24	09:32	2.28	2 NT (30 m)	No	Yes	Yes
24	79°14'51.07''N 22°57'6.09''E	79.248	22.952	22.09.24	15:44	1.65	2 NT (30 m)	No	Yes	Yes
25	78°54'8.65''N 21°38'24.73''E	78.902	21.640	22.09.24	22:38	2.46	2 NT (30 m)	2 NT (50 m)	Yes	Yes
28	78°33'30.44''N 19°10'44.25''E	78.558	19.179	24.09.24	09:12	2.49	2 NT (30 m)	2 NT (50 m)	Yes	Yes

Table S4: Station information for LCC_SO expedition in the Southern Ocean (Antarctica) in January 2024; GPS Coordinates, Latitude and Longitude in Deg., Date, UTC time, Temperature in °C, phytoplankton (PP) and zooplankton (ZP) net tows (NT) with depth in m, Niskin bottle and CTD data; nd = no data.

Station	GPS Coordinates	Lat. [Deg]	Long. [Deg]	Date	Time (UTC)	Temp. [°C]	PP-NT	ZP-NT	Niskin	CTD
1	64°20’ 29,01’’S 32°12’ 45,01’’W	-64.35	-63.03	10.01.2024	19:18	-1	1 NT (20m)	No	Yes	Yes
2	66°53’ 38,63’’S 67°11’ 35,81’’W	-66.89	-67.19	11.01.2024	21:36	-0.4	No	No	Yes	Yes
3	68°18’ 32.86’’S 67°12’ 38,51’’W	-68.31	-67.21	12.01.2024	14:06	nd	3 NT (20m)	1 NT (30m)	Yes	Yes
4	73°15’ 55,53’’S 78°31’ 7,86’’W	-73.27	-78.52	14.01.2024	19:55	nd	3 NT (20m)	2 NT (30m)	Yes	Yes
5	71°26’ 53,50’’S 117°50’ 33,05’’W	-71.45	-117.84	17.01.2024	20:42	-2.2	No	No	Yes	Yes
6	72°46’ 11,02’’S 127°10’ 23,44’’W	-72.77	-127.17	18.01.2024	23:53	-3.7	3 NT (20m)	2 NT (30m)	Yes	Yes
7	74°44’ 53,24’’S 136°51’ 46,05’’W	-74.75	-136.86	20.01.2024	17:32	-0.8	3 NT (20m)	2 NT (30m)	Yes	Yes
8	75°41’ 12,36’’S 148°44’ 39,12’’W	-75.69	-148.74	21.01.2024	18:55	-1.3	2 NT (20 m)	2 NT (30m)	Yes	Yes
9	78°34’ 25,29’’S 163°50’ 20,41’’W	-78.57	-163.84	24.01.2024	01:35	-7.4	No	No	Yes	Yes
10	77°32’ 36,11’’S 166°3,3’ 6,3’’E	-77.54	166.39	25.01.2024	20:00	nd	3 NT (20m)	2 NT (30m)	Yes	Yes
11	77°38’ 2,05’’S 166°23’ 31,41’’E	-77.63	166.39	26.01.2024	20:30	-4.5	3 NT (10m)	No	No	No
12	74°36’ 33,96’’S 165°31’ 47,86’’E	-74.61	165.53	27.01.2024	22:00	nd	3 NT (10m)	No	No	No
13	74°22’ 52,76’’S 165°33,51’ 20’’E	-74.38	165.56	28.01.2024	05:00	nd	No	No	Yes	Yes
14	72°18’ 6,82’’S 170°11’ 29,50’’E	-72.30	170.19	28.01.2024	20:30	-2.3	3 NT (20m)	2 NT (30m)	No	No
15	72°18’ 16,38’’S 170°3,3’ 91’’E	-72.30	170.08	29.01.2024	02:00	nd	No	No	Yes	Yes

Table S5: Information about Solid phase adsorption toxin tracking (SPATT) bags sampling from the LCC_NW, ARA15A and LCC_TA: Samplenumber (No.)., start and end date, time (UTC), coordinates.

Cruise	No.	Start	Time	Initial coordinates	End	Time	End coordinates
LCC_NW	110	12.09.2023	18:00	62°44’29,01’’N 32°12’45,01’’W	14.09.2023	17:55	60°30’23,37’’N 45°18’38,76’’W
LCC_NW	111	14.09.2023	17:55	60°30’23,37’’N 45°18’38,76’’W	17.09.2023	14.20	67°13’22’’N 55°10’11,8’’W
LCC_NW	159	17.09.2023	14:22	67°13’22’’N 55°10’11,8’’W	19.09.2023	10:00	71°27’0,86’’N 62°50’14,36’’W
ARA15A	557	31.07.2024	17:56	64° 33.1619' N 167° 8.0354' W	02.08.2024	22:13	70° 30.2498' N 168° 40.2221' W
ARA15A	558	02.08.2024	22:13	70° 30.2498' N 168° 40.2221' W	05.08.2024	20:38	77° 0.2503' N 172° 4.1885' W
ARA15A	559	05.08.2024	20:38	77° 0.2503' N 172° 4.1885' W	08.08.2024	04:55	79° 12.5322' N 177° 30.3466' W
ARA15A	560	08.08.2024	05:00	79° 12.5322' N 177° 30.3466' W	10.08.2024	20:55	79° 28.2518' N 178° 0.0649' E
ARA15A	561	12.08.2024	18:25	78° 12.6763' N 173° 12.6009' E	16.08.2024	03:01	75° 17.2990' N 177° 13.5946' E
ARA15A	562	16.08.2024	03:01	75° 17.2990' N 177° 13.5946' E	18.08.2024	20:27	75° 9.8252' N 175° 50.2370' W
ARA15A	563	18.08.2024	20:27	75° 9.8252' N 175° 50.2370' W	20.08.2024	22:28	74° 30.9833' N 162° 9.0933' W
ARA15A	564	20.08.2024	22:28	74° 30.9833' N 162° 9.0933' W	23.08.2024	01:05	77° 26.4689' N 164° 1.6660' W
ARA15A	565	23.08.2024	01:05	77° 26.4689' N 164° 1.6660' W	24.08.2024	21:14	73° 47.9973' N 164° 42.0143' W
LCC_TA	42	06.09.2024	22:35	64º40.571'N 167º29.760'W	09.09.2024	08:52	76º41'8.82''N 163º56'0.20''W
LCC_TA	44	15.09.2024	13:04	89º54'34.28''N 51º30'49.27''W	16.09.2024	17:55	89º54'34.28''N 51º30'49.27''W
LCC_TA	48	20.09.2024	20:00	82º13'46.47''N 18º51'41.44''E	22.09.2024	20:50	78º54'16.29''N 21º38'8.80''E
LCC_TA	49	22.09.2024	20:35	78º54'16.29''N 21º37'12.13''E	25.09.2024	8:30	77º4'24.13''N 15º59'6.96''E

Table S6: Information about Solid phase adsorption toxin tracking (SPATT) bags sampling from LCC_SO in the Southern Ocean: Sample., start and end date, time (UTC) and amount of pectenotoxin 2 (PTX-2).

Sample	Start	Time	Initial coordinates	End	Time	End coordinates	PTX-2 [ng]
160	15.01.24	01:51	73°15’20.9’’S 78°31’52,9’’W	20.01.24	01:18	73°50’57.7’’S 128°8’51,4’’W	3.44
162	20.01.24	01:18	73°50’57.7’’S 128°8’51,4’’W	22.01.24	00:57	75°41’11,7’’S 150°36’40,1’’W	17.54
163	22.01.2024	19:15	77°0’47.6’’S 154°27’35,8’’W	25.01.24 (skipped 24.01.24)	20:15	77°23’42,6’’S 174°35’34,6’’E	4.63
164	26.01.24	20:15	77°23’42.6’’S 174°35’34,6’’E	28.01.24	2:48	74°36’34’’S 165°31’47,9’’E	8.08
165	28.01.24	2:48	74°36’34’’S 165°31’47,9’’E	30.01.24	3:10	70°40’9,04’’S 170°31’44,9’E	0.00
166	30.01.24	3:10	70°40’9,04’’S 170°31’44,9’E	01.02.24	2:51	58°58’47,3’’S 171°46’30,3’’E	21.15
167	01.02.24	2:51	58°58’47,3’’S 171°46’30,3’’E	03.02.24	04:10	46°19’38,3’’S 170°30’14,5’’E	3.85

Table S7: Amount of dissolved toxins in ng collected with Solid phase adsorption toxin tracking (SPATT) bags at the German Antarctic Receiving Station (GARS) – O’Higgins (63°19'16.04"S - 57°54'4.31"W) from February 2022 to April 2023: pectenotoxin 2 (PTX-2).

Sample	Beginning	End	Days	PTX-2 [ng]
Feb 22	13.02.2022	28.02.2022	15	17.25
Mar 22	02.03.2022	30.03.2022	28	17.09
Apr 22	01.04.2022	29.04.2022	28	17.25
May 22	02.05.2022	28.05.2022	26	13.09
Jul 22	02.07.2022	29.07.2022	27	10.23
Oct 22	02.10.2022	02.11.2022	29	13.85
Dec 22	05.12.2022	05.01.2023	31	6.94
Apr 23	05.04.2023	05.05.2023	30	38.87

Table S8: Amount of lipophilic (DSP) and hydrophilic (PSP) toxins in phytoplankton: 20-methyl-spirolide G (20-Me-SPX-G), pectenotoxin 2 (PTX-2), spirolide 1 (SPX-1), spirolide A (SPX-A), spirolide B (SPX-B), spirolide C (SPX-C) and saxitoxin (STX) per meter of net tow (NT) [ng/m of NT] per station from the LCC_NW in the Arctic 2023.

Station	DSP [ng/m of NT]						Total DSP [ng/m of NT]	PSP [ng/m of NT]
	SPX-1	SPX-C	20-Me-SPX-G	SPX-A	SPX-B	PTX-2		STX
1	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.00
2	0.00	0.78	0.36	0.00	0.00	0.00	1.14	0.00
3	0.49	2.13	0.97	0.00	0.00	0.00	3.58	0.00
4	0.01	0.16	0.00	0.06	0.00	0.00	0.22	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.67	0.40	0.10	0.01	0.10	1.28	0.13
7	0.02	0.75	0.16	0.19	0.00	0.00	1.12	0.00
8	0.77	0.58	0.04	0.91	1.78	0.00	4.08	0.00
9	3.43	1.10	0.00	2.50	5.89	0.00	12.91	0.00
10	0.00	0.04	0.00	0.09	0.27	0.00	0.40	0.00
11	0.09	0.06	0.00	0.22	0.84	0.00	1.21	0.00
12	1.48	0.35	0.03	0.84	1.67	0.00	4.37	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.00
17	2.94	0.02	0.00	0.66	0.09	0.00	3.71	0.00
18	0.23	0.25	0.00	0.03	0.00	0.00	0.50	0.00
19	0.88	1.53	0.00	0.23	0.01	0.00	2.64	0.00
20	0.02	0.01	0.00	0.00	0.00	0.00	0.03	0.00
21	0.00	0.02	0.00	0.00	0.00	0.10	0.11	5.72
24	0.00	0.00	0.00	0.03	0.00	0.26	0.30	0.00
25	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**10.38**	**8.43**	**1.96**	**5.86**	**10.56**	**0.50**	**37.70**	**5.85**
[%]	**27.5**	**22.4**	**5.2**	**15.6**	**28.0**	**1.3**		

Table S9: Amount of lipophilic (DSP) and hydrophilic (PSP) toxins in phytoplankton: pectenotoxin 2 (PTX-2,), spirolide 1 (SPX-1), spirolide C (SPX-C), saxitoxin (STX), gonyautoxin 2/3 (GTX-2/GTX-3) and N-sulfocarbamoyl toxin 1/2 (C1/C2) per meter of net tow (NT) [ng/m of NT] per station from the ARA15A in the Arctic 2024.

Station	DSP [ng/m of NT]			Total DSP [ng/m of NT]	PSP [ng/m of NT]			Total PSP [ng/m of NT]
	PTX-2	SPX-1	SPX-C		C1/C2	GTX-2/GTX-3	STX	
1	3.77	0.00	0.00	3.77	0.00	0.00	0.00	0.00
2	2.28	0.17	0.44	2.89	1.51	1.15	3.62	6.28
3	0.00	0.46	0.55	1.00	0.00	0.00	0.72	0.72
4	0.00	3.64	5.11	8.75	0.00	0.00	1.52	1.52
8	0.00	0.00	0.00	0.00	0.00	0.00	0.73	0.73
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.22	0.22	0.00	0.00	0.00	0.00
11	12.27	0.50	0.84	13.61	0.00	0.00	0.56	0.56
13	0.00	0.23	0.38	0.61	0.00	0.00	0.62	0.62
15	0.00	0.33	0.61	0.95	0.00	0.00	0.00	0.00
16	1.28	0.20	0.36	1.84	0.00	0.00	0.00	0.00
18	0.00	0.00	0.07	0.07	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.17	0.00	0.00	0.17	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.15	0.00	0.00	0.15	0.00	0.00	0.00	0.00
30	0.62	0.00	0.00	0.62	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.23
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.36	0.00	0.00	0.36	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	2.27	0.44	0.38	3.08	0.00	0.00	0.00	0.00
46	1.02	0.16	0.06	1.25	0.00	0.00	0.00	0.00
48	5.10	0.41	0.00	5.51	0.00	0.00	0.00	0.00
49	2.16	0.19	0.05	2.40	0.00	0.00	0.00	0.00
50	0.53	0.00	0.00	0.53	0.00	0.00	0.00	0.00
51	0.18	0.26	0.00	0.43	0.00	0.00	0.00	0.00
52	0.42	0.00	0.07	0.49	0.00	0.00	0.00	0.00
53	1.05	0.32	0.41	1.78	0.00	0.00	0.48	0.48
Total	**33.64**	**7.30**	**9.55**	**50.48**	**1508.28**	**1151.67**	**8493.45**	**11153.40**
[%]	**66.63**	**14.46**	**18.91**		**13.52**	**10.33**	**76.15**	

Table S10: Amount of lipophilic toxins in phytoplankton: pectenotoxin 2 (PTX-2), spirolide 1 (SPX-1), spirolide C (SPX-C) and 20-Methyl-spirolide G (20-Me-SPX-G) per meter of net tow [ng/m of NT] per station from the LCC_TA in the Arctic 2024.

Station	Amount per meter of NT [ng/m of NT]				Total [ng/m of NT]
	PTX-2	SPX-1	SPX-C	20-Me-SPX-G	
2	0.00	0.02	0.01	0.00	0.03
4	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.02	0.02	0.04
23	0.00	0.00	0.01	0.02	0.03
24	0.00	0.00	0.02	0.03	0.05
25	0.00	0.00	0.01	0.01	0.02
28	0.07	0.00	0.00	0.00	0.07
Total	**0.07**	**0.02**	**0.07**	**0.07**	**0.24**
[%]	**31.2**	**8.0**	**29.7**	**31.0**	

Table S11: Amount of domoic acid (DA) and isomers A (iso-DA A), C (iso-DA C), D (iso-DA D) and E (iso-DA E) per meter of net tow (NT) [ng/m of NT] in phytoplankton per station from LCC_NW in the Arctic 2023.

Station	Amount per meter of NT [ng/m of NT]					Total [ng/m of NT]
	iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	
2	0.00	0.00	0.00	0.00	0.00	0.00
3	3.56	1.63	16.95	583.86	11.77	617.77
10	0.00	0.00	0.00	0.00	0.00	0.00
12	0.29	0.00	1.17	38.13	0.00	39.58
Total	**3.85**	**1.63**	**18.12**	**621.99**	**11.77**	**657.35**
[%]	**0.6**	**0.2**	**2.8**	**94.6**	**1.8**	

Table S12: Amount of domoic acid (DA) and isomers A (iso-DA A), C (iso-DA C), D (iso-DA D), E (iso-DA E) and epimer (epi DA) per meter of net tow (NT) [ng/m of NT] in phytoplankton per station from ARA15A in the Arctic 2024.

Station	Amount per meter of NT [ng/m of NT]						Total [ng/m of NT]
	iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	epi DA	
1	0.00	0.13	0.13	6.76	0.08	0.00	7.10
2	0.00	0.00	0.00	0.76	0.00	0.00	0.76
3	0.00	0.00	0.00	2.82	0.00	0.11	2.93
4	0.00	0.00	0.15	7.14	0.00	0.40	7.69
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.16	0.00	0.00	0.16
10	0.00	0.00	0.00	0.12	0.00	0.18	0.29
11	0.00	0.00	0.00	3.41	0.00	0.36	3.77
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	22.50	0.00	1.44	23.94
16	0.00	0.00	0.10	4.89	0.00	0.11	5.10
18	0.00	0.00	0.00	0.03	0.00	0.04	0.08
20	0.00	0.00	0.00	0.05	0.00	0.00	0.05
22	0.00	0.00	0.00	0.08	0.00	0.00	0.08
23	0.00	0.00	0.00	0.04	0.00	0.00	0.04
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.04	0.00	0.00	0.00	0.00	0.04
29	0.00	0.00	0.00	0.03	0.00	0.00	0.03
30	0.00	0.00	0.00	0.02	0.00	0.00	0.02
31	0.00	0.04	0.00	1.00	0.00	0.00	1.03
32	0.00	0.00	0.00	0.05	0.00	0.00	0.05
35	0.00	0.05	0.00	0.00	0.00	0.25	0.30
36	0.00	0.00	0.00	0.04	0.00	0.00	0.04
37	0.00	0.03	0.00	0.37	0.00	0.00	0.40
38	0.00	0.02	0.00	0.22	0.00	0.00	0.24
39	0.00	0.08	0.05	2.56	0.00	0.00	2.70
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.04	3.68	0.00	0.00	3.73
43	0.00	0.00	0.00	1.40	0.00	0.00	1.40
44	0.00	0.07	0.30	14.49	0.07	0.00	14.93
45	0.00	0.00	0.08	3.81	0.00	0.06	3.95
46	0.04	0.00	0.03	1.45	0.00	0.00	1.52
48	0.00	0.00	0.00	0.01	0.00	0.00	0.01
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.72	0.18	0.80	42.78	0.33	0.04	45.11
51	0.02	0.00	0.00	0.55	0.00	0.03	0.59
52	0.13	0.03	0.09	4.35	0.00	0.14	4.80
53	0.00	0.00	0.04	1.58	0.00	0.13	1.76
Total	**0.91**	**0.65**	**1.83**	**127.16**	**0.48**	**3.29**	**134.33**
[%]	**0.68**	**0.49**	**1.36**	**94.67**	**0.36**	**2.45**	

Table S13: Amount of domoic acid (DA) and isomers A (iso-DA A) per meter of net tow (NT) [ng/m of NT] of phytoplankton per station from LCC_TA in the Arctic 2024.

Station	Amount per meter of NT [ng/m of NT]		Total [ng/m of NT]
	iso-DA A	DA	
2	0.02	0.41	0.43
4	0.00	0.00	0.00
6	0.00	0.00	0.00
9	0.00	0.00	0.00
20	0.00	0.00	0.00
21	0.00	0.00	0.00
22	0.00	0.00	0.00
23	0.00	0.00	0.00
24	0.00	0.00	0.00
Total	**0.02**	**0.41**	**0.43**
[%]	**4.0**	**96.0**	

Table S14: Amount of lipophilic (DSP) and hydrophilic (PSP) toxins in zooplankton: spirolid 1 (SPX-1), 27-hydroxy-spirolid C (27-hydroxy-SPX-A), spirolide B (SPX-B), spirolide C (SPX-C), neosaxitoxin (neoSTX), decarbamoylneosaxitoxin (dcSTX) and saxitoxin (STX) per meter of net tow (NT) [ng/m of NT] per station from the LCC_NW in the Arctic 2023.

Station	DSP [ng/m of NT]				Total DSP [ng/m of NT]	PSP [ng/m of NT]			Total PSP [ng/m of NT]
	SPX-1	SPX-C	27-hydroxy-SPX-C	SPX-B		neoSTX	dcSTX	STX	
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.22	0.07	0.00	0.29	0.00	0.00	0.00	0.00
3	0.00	0.12	0.00	0.00	0.12	0.00	0.00	0.00	0.00
4	0.00	0.71	0.15	0.00	0.87	0.00	0.00	0.00	0.00
6	0.00	0.78	0.19	0.00	0.97	0.00	0.00	0.00	0.00
7	0.00	1.31	0.10	0.00	1.40	0.00	0.00	0.00	0.00
8	0.08	0.00	0.00	0.22	0.30	0.00	0.00	0.00	0.00
18	0.23	0.34	0.00	0.00	0.57	0.00	0.00	0.00	0.00
19	0.91	1.18	0.09	0.00	2.18	0.00	0.00	0.00	0.00
20	0.65	1.17	0.00	0.00	1.82	0.00	0.00	0.00	0.00
21	0.62	0.82	0.00	0.00	1.44	0.02	0.00	0.06	0.08
24	0.45	0.00	0.00	0.25	0.70	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.63	0.63	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**2.95**	**6.64**	**0.61**	**1.09**	**11.29**	**0.02**	**0.00**	**0.06**	**0.08**
[%]	**26.1**	**58.8**	**5.4**	**9.7**		**19.8**	**0.9**	**79.2**	

Table S15: Amount of lipophilic (DSP) and hydrophilic (PSP) toxins in zooplankton: compound 4 (720/164 CP-4), spirolide 1 (SPX-1), spirolide C (SPX-C), neosaxitoxin (neoSTX) and saxitoxin (STX) per gram of tissue [ng/g] per station from ARA15A in the Arctic 2024.

Station	DSP: Total amount per gram of tissue [ng/g]			Total DSP	PSP: Total amount per gram of tissue [ng/g]		Total PSP
	SPX-1	SPX-C	720/164 CP-4	[ng/g]	neoSTX	STX	[ng/g]
1	21.46	36.42	0.00	57.88	241.74	192.17	433.91
2	18.71	15.98	0.00	34.68	360.41	260.74	621.15
3	65.06	67.26	0.00	132.33	0.00	58.56	58.56
6	7.27	20.17	0.00	27.44	188.86	96.86	285.72
8	15.56	24.47	0.00	40.03	310.88	188.30	499.17
9	14.05	26.03	0.00	40.08	180.22	180.40	360.61
10	1.51	5.23	0.00	6.74	202.27	316.21	518.48
11	7.03	34.35	0.00	41.38	0.00	108.10	108.10
13	4.96	8.78	0.00	13.74	0.00	109.44	109.44
15	16.20	44.09	0.00	60.29	0.00	442.41	442.41
16	36.85	53.21	0.00	90.06	525.64	2499.40	3025.04
18	52.97	92.08	0.00	145.05	594.98	2479.24	3074.22
20	0.00	0.00	0.00	0.00	341.10	277.09	618.19
22	0.00	0.00	0.00	0.00	0.00	156.20	156.20
22.B	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	116.72	0.00	116.72	0.00	34.83	34.83
27	0.00	3.58	0.00	3.58	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	4.58	0.74	5.32	0.00	0.00	0.00
31	0.00	3.46	0.00	3.46	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	109.49	109.49
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	82.06	82.06
38	0.00	2.38	0.00	2.38	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	197.09	197.09
42	5.38	6.60	0.00	11.98	0.00	8.76	8.76
43	5.54	9.77	0.00	15.31	0.00	0.00	0.00
44	5.42	5.50	0.95	11.87	0.00	0.00	0.00
45	35.80	70.44	4.63	110.86	0.00	435.95	435.95
46	21.81	9.46	8.45	39.72	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	14.38	3.38	9.57	27.33	0.00	0.00	0.00
50	6.47	2.55	1.80	10.83	0.00	0.00	0.00
51	35.65	62.80	4.65	103.11	0.00	259.82	259.82
52	16.35	4.71	4.34	25.40	0.00	0.00	0.00
53	8.30	0.00	0.00	8.30	0.00	0.00	0.00
Total	**416.73**	**734.00**	**35.14**	**1185.87**	**2946.09**	**8493.12**	**11439.21**
[%]	**0.35**	**0.62**	**0.03**		**25.75**	**74.25**	

Table S16: Amount of domoic acid (DA) and isomers A (iso-DA A), C (iso-DA C), D (iso-DA D) and E (iso-DA E) per meter of net tow (NT) [ng/m of NT] in zooplankton per station from LCC_NW in the Arctic 2023.

Station	Amount per meter of NT [ng/m of NT]					Total [ng/m of NT]
	iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	
1	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.79	0.00	0.79
3	0.25	1.21	1.83	55.58	0.89	59.76
4	0.00	0.00	0.35	11.11	0.00	11.46
6	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00
Total	**0.25**	**1.21**	**2.17**	**67.49**	**0.89**	**72.01**
[%]	**0.4**	**1.7**	**3.0**	**93.7**	**1.2**	

Table S17: Amount of domoic acid (DA), epimer (epi DA) and isomers A (iso-DA A), C (iso-DA C), D (iso-DA D) and E (iso-DA E) per gram of tissue [ng/g] of zooplankton per station from ARA15A in the Arctic 2024.

Station	Amount per gram of tissue [ng/g]						Total
	iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	epi DA	[ng/g]
1	0.00	0.00	0.00	354.31	0.00	10.37	364.69
2	0.00	0.00	0.00	11.36	2.32	0.00	13.69
3	0.00	0.00	0.00	337.58	0.00	0.00	337.58
6	1.32	2.17	0.00	28.23	0.00	0.00	31.72
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	5.46	0.00	0.00	5.46
10	0.00	1.00	2.00	3.00	4.00	5.00	15.00
11	0.00	0.00	0.00	12.84	0.00	0.00	12.84
13	0.00	1.00	2.00	3.00	4.00	5.00	15.00
15	0.00	0.00	0.00	5.69	0.00	0.00	5.69
16	0.00	4.45	5.34	124.30	0.00	0.00	134.09
18	0.00	0.00	0.00	8.38	0.00	0.00	8.38
20	10.28	38.93	19.10	1454.27	22.64	0.00	1545.23
22	0.00	6.75	12.05	449.87	0.00	0.00	468.67
22.B	2.60	0.00	0.00	4.70	0.00	0.00	7.30
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.59	0.00	0.00	0.59
26	0.00	0.00	0.00	0.78	0.00	1.26	2.04
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	1.00	2.00	3.00	4.00	5.00	15.00
31	0.00	0.00	0.00	68.90	0.00	3.85	72.75
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	34.33	0.00	0.00	34.33
38	0.00	0.00	3.66	78.00	0.00	0.00	81.66
39	0.00	0.00	0.00	28.81	0.00	0.00	28.81
41	0.00	1.00	2.00	3.00	4.00	5.00	15.00
42	0.00	0.00	3.61	109.65	2.54	0.00	115.80
43	0.00	6.56	5.78	164.50	5.09	0.00	181.94
44	4.91	40.58	22.37	1199.22	28.59	0.00	1295.67
45	0.00	0.00	0.94	266.44	0.00	0.00	267.38
46	0.00	0.00	0.00	6.20	0.00	0.00	6.20
48	0.00	1.00	2.00	3.00	4.00	5.00	15.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	8.62	19.63	14.28	859.55	15.73	0.00	917.81
51	0.00	0.00	0.00	11.80	0.00	0.00	11.80
52	0.00	2.10	0.00	281.75	0.00	0.00	283.85
53	0.00	0.00	0.00	16.62	0.00	0.00	16.62
Total	**27.72**	**126.17**	**97.13**	**5939.15**	**96.93**	**40.48**	**6327.58**
[%]	**0.44**	**1.99**	**1.54**	**93.86**	**1.53**	**0.64**	

Table S18: Amount of domoic acid (DA) and isomers E (iso-DA E), D (iso-DA D), A (iso-DA A) and C (iso-DA C) per meter of net tow (NT) [ng/m of NT] of zooplankton per station from LCC_TA in the Arctic 2024.

Station	Amount per meter of NT [ng/m of NT]					Total [ng/m of NT]
	iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	
2	0.23	0.08	0.27	13.38	0.08	14.03
4	0.00	0.00	0.00	0.02	0.00	0.03
6	0.00	0.00	0.00	0.12	0.00	0.13
9	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00
Total	**0.23**	**0.08**	**0.27**	**13.53**	**0.08**	**14.19**
[%]	**1.6**	**0.6**	**1.9**	**95.3**	**0.6**	

Table S19: Amount of saxitoxin (STX) in zooplankton per m of net tow [ng/m of NT] per station from LCC_TA in the Arctic 2024.

Station	STX [ng/m of NT]
2	0.00
4	0.68
6	0.00
9	0.00
12	0.00
16	0.00
20	0.00
21	0.00
22	0.00
23	0.00
24	0.00
25	0.00
28	0.00

Table S20: Amount of lipophilic and hydrophilic toxins in zooplankton: compound 4 (CP-4), spirolide 1 (SPX-1), spirolide C (SPX-C), neosaxitoxin (neoSTX) and saxitoxin (STX) per gram of tissue [ng/g] in the different genus (Pteropods, Copepod, Amphipod, Krill, Fish, Chaetognatha, Geatinouse Zooplankton, Tunicata) and species from ARA15A in the Arctic 2024.

			[ng/g]				
Station	**Species**	**Genus**	**neoSTX**	**STX**	**SPX-1**	**SPX-C**	**CP-4**
1	C. limacina	Pteropod	241.74	192.17	18.35	36.42	0.00
1	Calanus glacialis	Copepod	0.00	0.00	3.11	0.00	0.00
1	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
1		Amphipod	0.00	0.00	0.00	0.00	0.00
1	Larvae	Krill	0.00	0.00	0.00	0.00	0.00
2	Thynoessa sp.	Krill	0.00	0.00	0.00	1.10	0.00
2	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
2	Limacina helicina	Pteropod	360.41	260.74	13.97	14.88	0.00
2		Amphipod	0.00	0.00	0.00	0.00	0.00
2	Calanus spp.	Copepod	0.00	0.00	4.73	0.00	0.00
3		Amphipod	0.00	0.00	0.00	0.00	0.00
3	Calanus spp.	Copepod	0.00	0.00	10.71	17.68	0.00
3	Sagitta sp.	Chaetognatha	0.00	0.00	6.22	0.00	0.00
3	L. helicina	Pteropod	0.00	58.56	48.13	49.58	0.00
6	C. limacina	Pteropod	188.86	96.86	7.27	20.17	0.00
6	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
8	Calanus spp.	Copepod	0.00	0.00	15.56	22.90	0.00
8	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
8		Pteropod	310.88	188.30	0.00	0.00	0.00
8	Jelly fish (bell shape)	Gelatineous Zooplankton	0.00	0.00	0.00	1.57	0.00
9		Amphipod	0.00	0.00	0.00	0.00	0.00
9	Calanus spp.	Copepod	0.00	0.00	6.25	19.40	0.00
9		Pteropod	180.22	180.40	7.80	6.63	0.00
9	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
10	C. limacina	Pteropod	202.27	316.21	1.51	5.23	0.00
10	Larvae	Krill	0.00	0.00	0.00	0.00	0.00
10		Amphipod	0.00	0.00	0.00	0.00	0.00
10	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
11		Krill	0.00	0.00	0.00	0.00	0.00
11	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
11	C. limacina	Pteropod	0.00	108.10	0.00	17.08	0.00
11	Calanus spp.	Copepod	0.00	0.00	7.03	17.28	0.00
13	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
13	C. limacina	Pteropod	0.00	109.44	0.00	0.00	0.00
13	Calanus spp.	Copepod	0.00	0.00	4.96	8.78	0.00
15	C. limacina	Pteropod	0.00	442.41	16.20	32.44	0.00
15	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
15	Calanus spp.	Copepod	0.00	0.00	0.00	11.65	0.00
15	Fish egg	Fish	0.00	0.00	0.00	0.00	0.00
16	C. limacina	Pteropod	525.64	2427.81	15.10	24.46	0.00
16	C. limacina	Pteropod	0.00	71.59	21.75	28.41	0.00
16	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.34	0.00
16	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00

16		Amphipod	0.00	0.00	0.00	0.00	0.00
18	C. limacina	Pteropod	594.98	2479.24	46.60	87.92	0.00
18	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
18	Calanus spp.	Copepod	0.00	0.00	6.37	4.16	0.00
20	L. helicina	Pteropod	341.10	277.09	0.00	0.00	0.00
20	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
20	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
20		Amphipod	0.00	0.00	0.00	0.00	0.00
22	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
22		Amphipod	0.00	0.00	0.00	0.00	0.00
22	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
22	L. helicina	Pteropod	0.00	156.20	0.00	0.00	0.00
22.B	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
22.B	(5cm)	Krill	0.00	0.00	0.00	0.00	0.00
22.B	Larvae	Krill	0.00	0.00	0.00	0.00	0.00
23	Themisto sp.	Amphipod	0.00	0.00	0.00	0.00	0.00
23	Sagitta sp	Chaetognatha	0.00	0.00	0.00	0.00	0.00
23	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
24		Amphipod	0.00	0.00	0.00	0.00	0.00
24	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
24	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
26		Amphipod	0.00	0.00	0.00	0.00	0.00
26	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
26	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
26	C. limacina	Pteropod	0.00	34.83	0.00	116.72	0.00
26	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
27	Themisto libellula (small)	Amphipod	0.00	0.00	0.00	0.00	0.00
27	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00
27	Calanus hyperboreus	Copepod	0.00	0.00	0.00	3.58	0.00
27	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	0.00	0.00
27	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
27	Themisto libellula (4cm)	Amphipod	0.00	0.00	0.00	0.00	0.00
28		Amphipod	0.00	0.00	0.00	0.00	0.00
28	Calanus hyp.	Copepod	0.00	0.00	0.00	0.00	0.00
28	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	3.85	0.00
29	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
29		Krill	0.00	0.00	0.00	0.00	0.00
29	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00
29	Calanus hyp.	Copepod	0.00	0.00	0.00	0.73	0.74
29	Themisto libellula (5cm)	Amphipod	0.00	0.00	0.00	0.00	0.00
29	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	3.46	0.00

31	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
31	Themisto libellula (3cm)	Amphipod	0.00	0.00	0.00	0.00	0.00
31	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	0.00	0.00
31		Krill	0.00	0.00	0.00	0.00	0.00
31	Calanus hyp.	Copepod	0.00	0.00	0.00	0.00	0.00
31		Amphipod	0.00	0.00	0.00	0.00	0.00
32	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
32	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
32	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
32	C. limacina	Pteropod	0.00	109.49	0.00	0.00	0.00
35	Appendicularia	Tunicata	0.00	0.00	0.00	0.00	0.00
36	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
36		Amphipod	0.00	0.00	0.00	0.00	0.00
36	C. limacina	Pteropod	0.00	82.06	0.00	0.00	0.00
37	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
37	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	0.00	0.00
37	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
37		Amphipod	0.00	0.00	0.00	0.00	0.00
38	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
38	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
38		Krill	0.00	0.00	0.00	0.00	0.00
38	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00
38	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	2.38	0.00
38	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
39	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00
39	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00
39		Krill	0.00	0.00	0.00	0.00	0.00
41	Calanus hyp.	Copepod	0.00	0.00	0.00	0.00	0.00
41	L. helicina	Pteropod	0.00	197.09	0.00	0.00	0.00
41	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00
42	Themisto abyssorum	Amphipod	0.00	8.76	0.00	0.00	0.00
42	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
42	Copepod unkn. (red)	Copepod	0.00	0.00	5.38	6.60	0.00
42	Calanus spp.	Copepod	0.00	0.00	3.56	4.74	0.00
43	Calanus spp.	Copepod	0.00	0.00	0.00	3.19	0.00
43	Themisto libellula (4cm)	Amphipod	0.00	0.00	1.98	1.84	0.00
43	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
44	Calanus hyp.	Copepod	0.00	0.00	2.96	1.81	0.95
44	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00

44	Copepod unkn. (red)	Copepod	0.00	0.00	2.46	3.69	0.00
44	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
45	Themisto abyssorum	Amphipod	0.00	0.00	1.79	1.76	0.00
45	Themisto sp. (small)	Amphipod	0.00	0.00	7.33	9.15	4.63
45	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
45	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00
45	C. limacina	Pteropod	0.00	435.95	26.67	59.53	0.00
45	Calanus spp.	Copepod	0.00	0.00	7.86	0.00	0.00
46	Themisto abyssorum	Amphipod	0.00	0.00	3.53	3.41	0.00
46	Themisto libellula	Amphipod	0.00	0.00	0.80	0.60	0.00
46	Calanus spp.	Copepod	0.00	0.00	7.33	3.80	6.65
46	Themisto sp. (small)	Amphipod	0.00	0.00	2.28	1.64	1.80
46	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	0.00	0.00
48	Calanus hyp.	Copepod	0.00	0.00	8.63	2.07	5.35
49	Calanus hyp.	Copepod	0.00	0.00	1.92	0.00	1.99
49	Themisto abyssorum	Amphipod	0.00	0.00	1.44	0.00	0.00
49	Themisto libellula	Amphipod	0.00	0.00	2.39	1.30	1.39
49	Deep Sea Shrimp	Pandalus	0.00	0.00	0.00	0.00	0.85
49	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
50	Calanus spp.	Copepod	0.00	0.00	6.47	2.55	1.80
50	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	0.00	0.00
51	Calanus hyp.	Copepod	0.00	0.00	6.35	2.75	4.07
51	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
51	Themisto abyssorum	Amphipod	0.00	0.00	0.88	0.75	0.00
51	Themisto libellula	Amphipod	0.00	0.00	1.44	1.46	0.58
51	C. limacina	Pteropod	0.00	259.82	26.97	57.83	0.00
51	Copepod unkn. (red)	Copepod	0.00	0.00	0.99	0.65	0.00
52	Calanus spp.	Copepod	0.00	0.00	7.06	2.25	4.34
52	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
52	Themisto sp. (small)	Amphipod	0.00	0.00	0.00	1.82	0.00
52	Themisto libellula (big)	Amphipod	0.00	0.00	0.00	0.00	0.00
52		Amphipod	0.00	0.00	0.00	0.00	0.00
52	Deep Sea Krill (white)	Krill	0.00	0.00	0.00	0.00	0.00
53	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	0.00	0.00
53	Calanus spp.	Copepod	0.00	0.00	8.30	0.00	0.00

Table S21: Amount of domoic acid (DA), isomers (iso-DA A, C, D, E) and epimer (epi-DA) in zooplankton per gram of tissue [ng/g] in the different genus (Pteropods, Copepod, Amphipod, Krill, Chaetognatha) and species from ARA15A in the Arctic 2024.

Station	Species	Genus	[ng/g]					
			iso-DA E	iso-DA D	iso-DA A	DA	iso-DA C	epi DA
1	C. limacina	Pteropod	0.00	0.00	0.00	99.42	0.00	0.00
1	Calanus glacialis	Copepod	0.00	0.00	0.00	241.06	0.00	10.37
1	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	9.29	0.00	0.00
1		Amphipod	0.00	0.00	0.00	4.55	0.00	0.00
2	L. helicina	Pteropod	0.00	0.00	0.00	11.36	2.32	0.00
3		Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
3	Calanus spp.	Copepod	0.00	0.00	0.00	287.12	0.00	0.00
3	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	13.34	0.00	0.00
3	L. helicina	Pteropod	0.00	0.00	0.00	37.12	0.00	0.00
6	C. limacina	Pteropod	1.32	2.17	0.00	18.43	0.00	0.00
6	Calanus spp.	Copepod	0.00	0.00	0.00	9.80	0.00	0.00
8	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
9	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
9	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	5.46	0.00	0.00
11	Calanus spp.	Copepod	0.00	0.00	0.00	12.84	0.00	0.00
15	C. limacina	Pteropod	0.00	0.00	0.00	5.69	0.00	0.00
15	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
16	C. limacina	Pteropod	0.00	1.64	0.00	13.71	0.00	0.00
16	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	24.31	0.00	0.00
16	Calanus spp.	Copepod	0.00	2.81	5.34	82.70	0.00	0.00
16		Amphipod	0.00	0.00	0.00	3.58	0.00	0.00
18	C. limacina	Pteropod	0.00	0.00	0.00	4.79	0.00	0.00
18	Calanus spp.	Copepod	0.00	0.00	0.00	3.58	0.00	0.00
20	L. helicina	Pteropod	0.00	16.00	0.00	575.62	0.00	0.00
20	Calanus spp.	Copepod	0.00	22.93	19.10	782.93	22.64	0.00
20	Sagitta sp.	Chaetognatha	10.28	0.00	0.00	95.72	0.00	0.00
22	Sagitta sp.	Chaetognatha	0.00	0.00	5.12	85.66	0.00	0.00
22		Amphipod	0.00	0.00	0.00	29.86	0.00	0.00
22	Calanus spp.	Copepod	0.00	6.75	6.93	228.03	0.00	0.00
22	L. helicina	Pteropod	0.00	0.00	0.00	106.32	0.00	0.00
22B	(5cm)	Krill	2.60	0.00	0.00	3.69	0.00	0.00
22B	Larvae	Krill	0.00	0.00	0.00	1.01	0.00	0.00
23	Sagitta sp	Chaetognatha	0.00	0.00	0.00	0.00	0.00	0.00
23	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
24	Calanus spp.	Copepod	0.00	0.00	0.00	0.59	0.00	0.00
26	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
26	Themisto libellula	Amphipod	0.00	0.00	0.00	0.78	0.00	1.26
27	Calanus hyp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
28	Calanus hyp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
31	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	11.89	0.00	0.00

31	Themisto libellula (3cm)	Amphipod	0.00	0.00	0.00	16.36	0.00	0.00
31	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	17.72	0.00	0.00
31	Calanus hyp.	Copepod	0.00	0.00	0.00	22.93	0.00	3.85
32	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
37	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	5.38	0.00	0.00
37	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	15.19	0.00	0.00
37	Calanus spp.	Copepod	0.00	0.00	0.00	13.77	0.00	0.00
38	Themisto libellula	Amphipod	0.00	0.00	0.00	14.70	0.00	0.00
38		Krill	0.00	0.00	0.00	4.20	0.00	0.00
38	Themisto abyssorum	Amphipod	0.00	0.00	0.00	4.10	0.00	0.00
38	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	26.56	0.00	0.00
38	Calanus spp.	Copepod	0.00	0.00	3.66	28.45	0.00	0.00
39	Themisto abyssorum	Amphipod	0.00	0.00	0.00	13.85	0.00	0.00
39		Krill	0.00	0.00	0.00	14.96	0.00	0.00
42	Themisto abyssorum	Amphipod	0.00	0.00	0.00	14.40	0.00	0.00
42	Themisto libellula	Amphipod	0.00	0.00	0.00	3.38	0.00	0.00
42	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	29.79	0.00	0.00
42	Calanus spp.	Copepod	0.00	0.00	3.61	62.08	2.54	0.00
43	Calanus spp.	Copepod	0.00	6.56	5.78	152.10	5.09	0.00
43	Themisto libellula (4cm)	Amphipod	0.00	0.00	0.00	12.41	0.00	0.00
44	Calanus hyp.	Copepod	4.91	40.58	22.37	1020.23	28.59	0.00
44	Themisto libellula	Amphipod	0.00	0.00	0.00	74.62	0.00	0.00
44	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	21.67	0.00	0.00
44	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	82.70	0.00	0.00
45	Themisto abyssorum	Amphipod	0.00	0.00	0.00	3.76	0.00	0.00
45	Themisto (small)	Amphipod	0.00	0.00	0.00	8.69	0.00	0.00
45	Sagitta sp.	Chaetognatha	0.00	0.00	0.00	220.20	0.00	0.00
45	Themisto libellula	Amphipod	0.00	0.00	0.94	0.00	0.00	0.00
45	C. limacina	Pteropod	0.00	0.00	0.00	33.79	0.00	0.00
45	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
46	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
46	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
46	Calanus spp.	Copepod	0.00	0.00	0.00	0.00	0.00	0.00
46	Themisto sp. (small)	Amphipod	0.00	0.00	0.00	6.20	0.00	0.00
49	Themisto abyssorum	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
49	Themisto libellula	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
50	Calanus spp.	Copepod	8.62	19.63	14.28	834.42	15.73	0.00
50	Copepod unkn. (red)	Copepod	0.00	0.00	0.00	25.13	0.00	0.00
51	Themisto abyssorum	Amphipod	0.00	0.00	0.00	3.64	0.00	0.00
51	Themisto libellula	Amphipod	0.00	0.00	0.00	1.16	0.00	0.00
51	C. limacina	Pteropod	0.00	0.00	0.00	7.00	0.00	0.00
52	Sagitta sp.	Chaetognatha	0.00	2.10	0.00	281.75	0.00	0.00
52	Themisto sp. (small)	Amphipod	0.00	0.00	0.00	0.00	0.00	0.00
52	Deep Sea Krill (white)	Krill	0.00	0.00	0.00	0.00	0.00	0.00
53	Calanus spp.	Copepod	0.00	0.00	0.00	16.62	0.00	0.00

Table S22: Amount of lipophilic toxins in phytoplankton: pectenotoxin 2 (PTX-2) per meter of net tow [ng/m of NT] per station from LCC_SO in the Southern Ocean (Antarctica) 2024.

Station	PTX-2 [ng/m of NT]
1	0.00
3	0.00
4	0.00
6	1.40
7	1.19
8	1.70
10	0.09
11	0.26
12	0.00
14	0.00
Total	**4.64**

9.2 Supplementary Figures

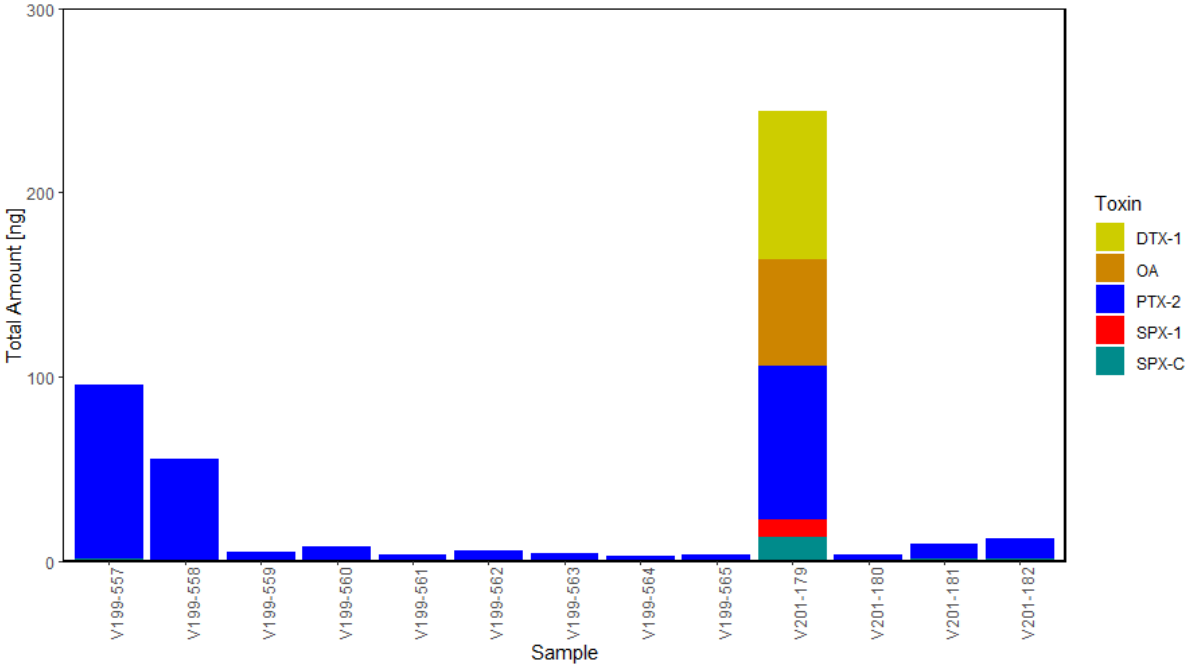

Figure S1: Dissolved toxin samples from the ARA15A and LCC_TA expedition in the Arctic: Total amount [ng] of dinophysistoxin 1 (DTX-1, yellow), okadaic acid (OA, orange), pectenotoxin 2 (PTX-2, blue), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, green) collected with SPATT-bags.

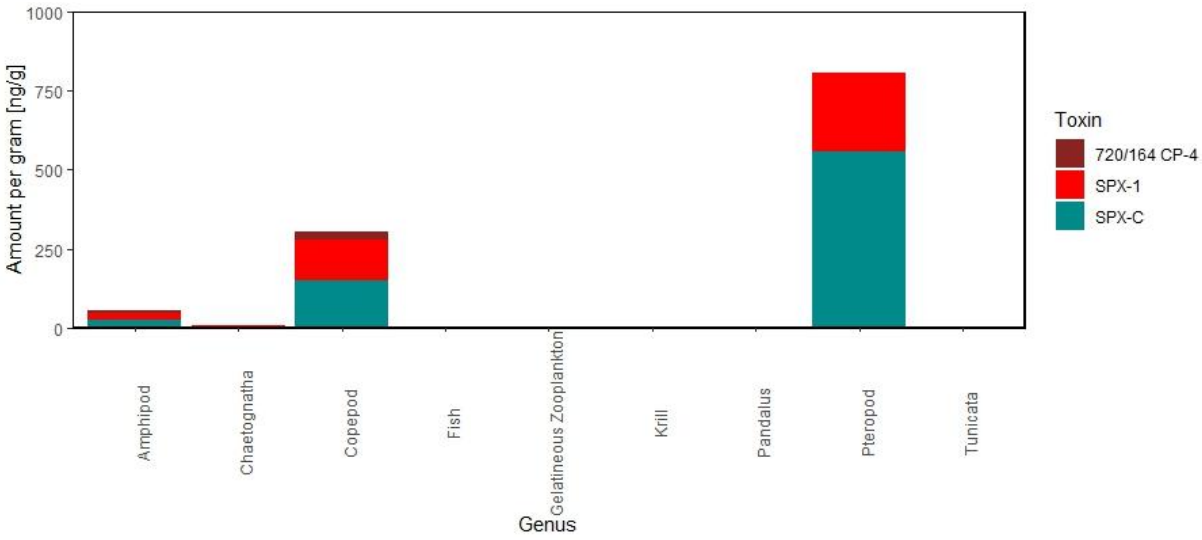

Figure S2: Amount per gram of tissue [ng/g]of lipophilic toxins: compound 4 (CP-4, dark red), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, cyan) *in different genus of zooplankton from ARA15A in the Arctic 2024.*

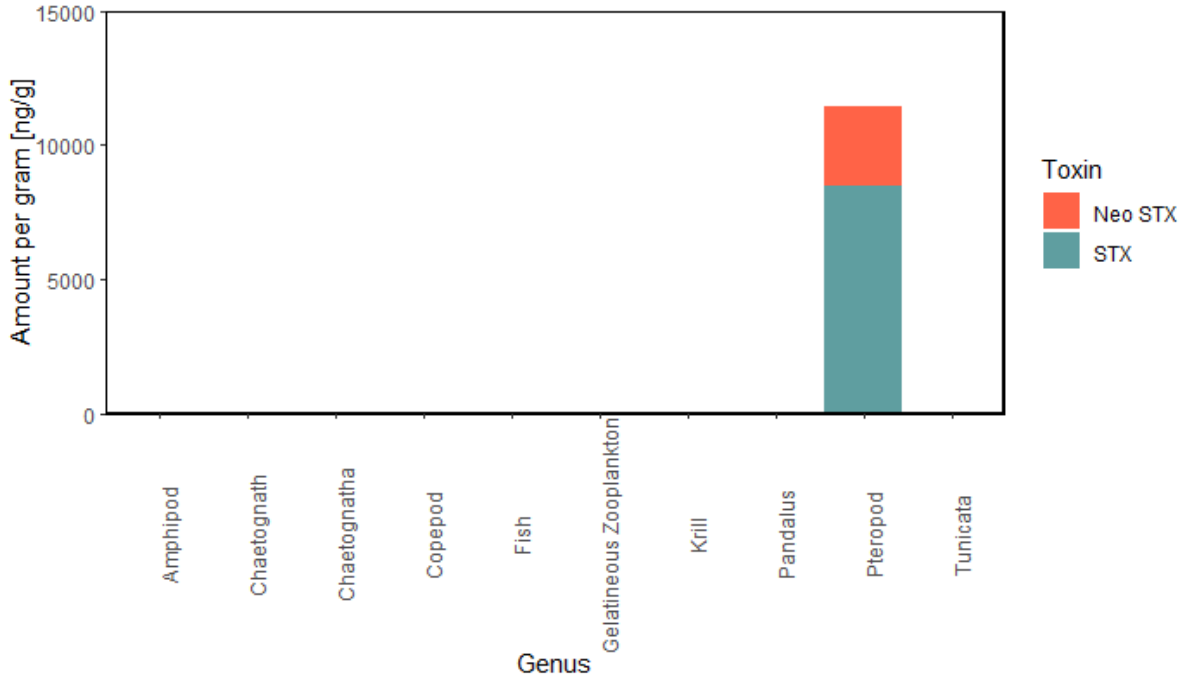

Figure S3: Amount per gram of tissue [ng/g] of hydrophilic toxins: compound 4 (CP-4, dark red), spirolide 1 (SPX-1, red) and spirolide C (SPX-C, cyan) *in different genus of zooplankton from ARA15A in the Arctic 2024*

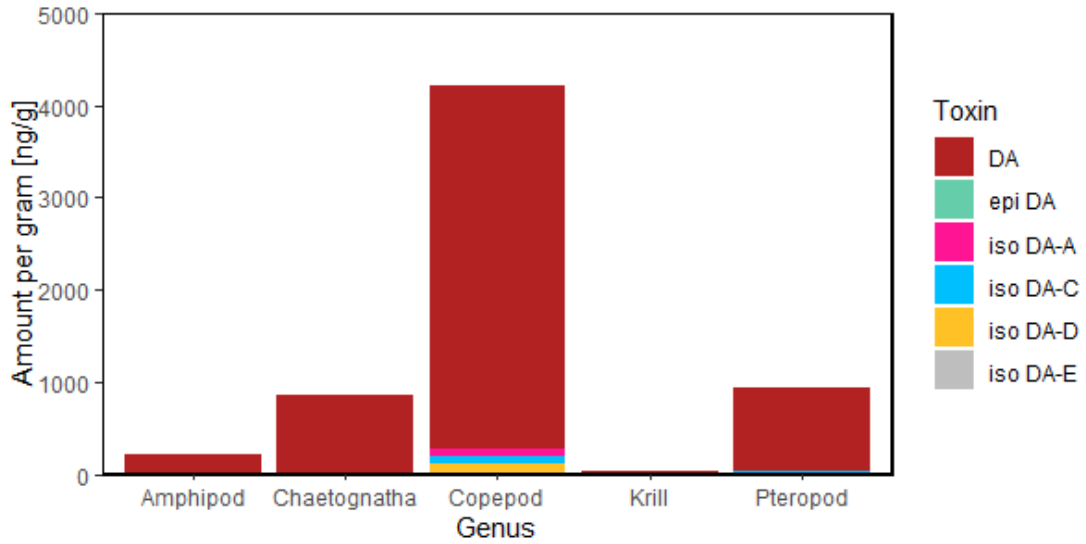

Figure S4: Amount per gram of tissue [ng/g] of domoic acid (DA, red), epimer (epi DA, green) and isomers A (iso DA-A, pink), C (iso DA-C, blue), D (iso DA-D, yellow) and E (iso DA-E, grey) in genus of the zooplankton from ARA15A in the Arctic 2024.

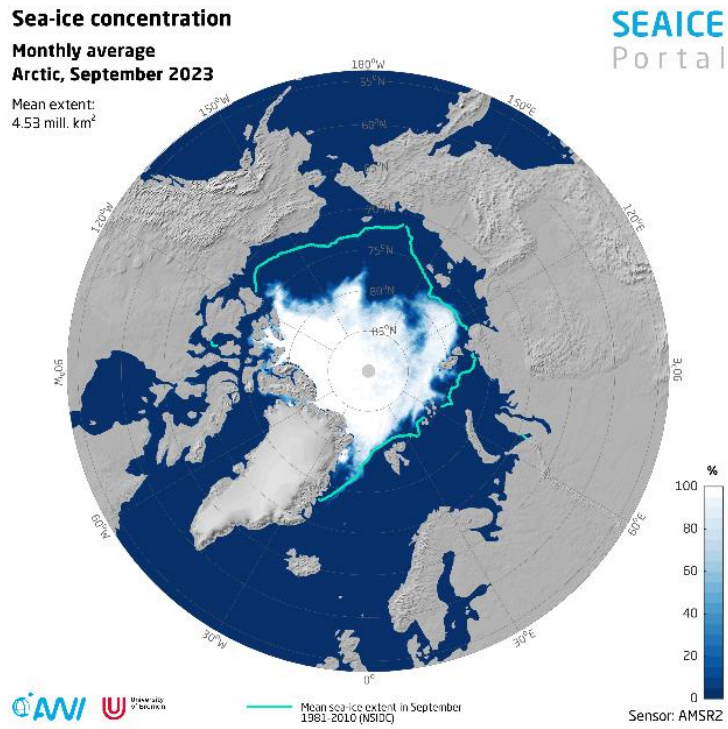

Figure S5: Arctic Sea-ice data from 01.09.2023 to 30.09.2023 from www.meereisportal.de (funding: REKLIM-2013-04) (Spreen at al., 2008).

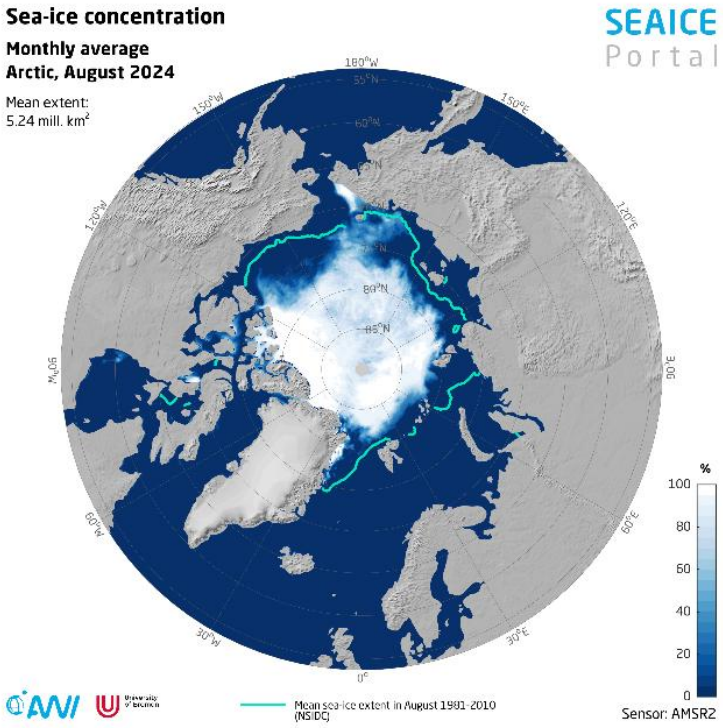

Figure S6: Arctic Sea-ice data from 01.08.2024 to 31.08.2024 from www.meereisportal.de (funding: REKLIM-2013-04) (Spreen at al., 2008).

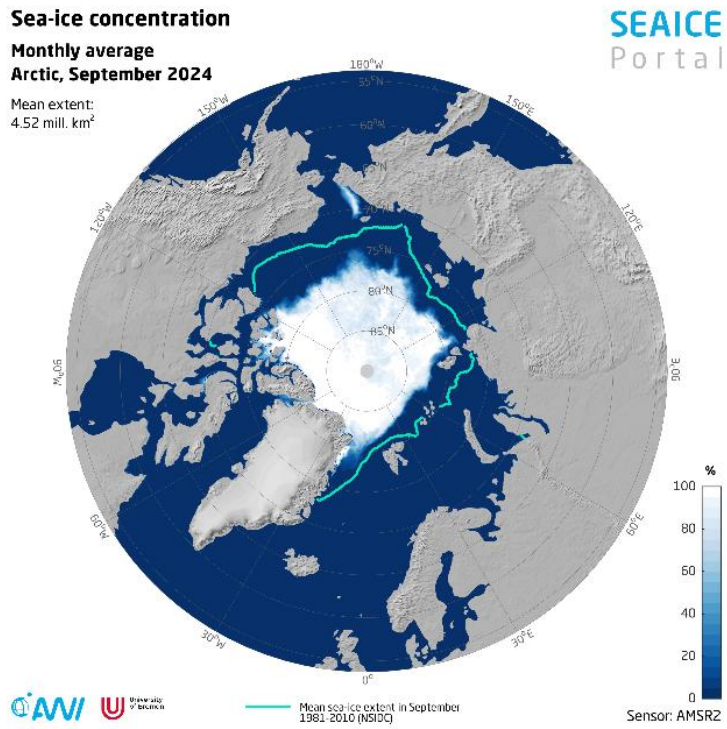

Figure S7: Arctic Sea-ice data from 01.08.2024 to 31.08.2024 from www.meereisportal.de (funding: REKLIM-2013-04) (Spreen at al., 2008).

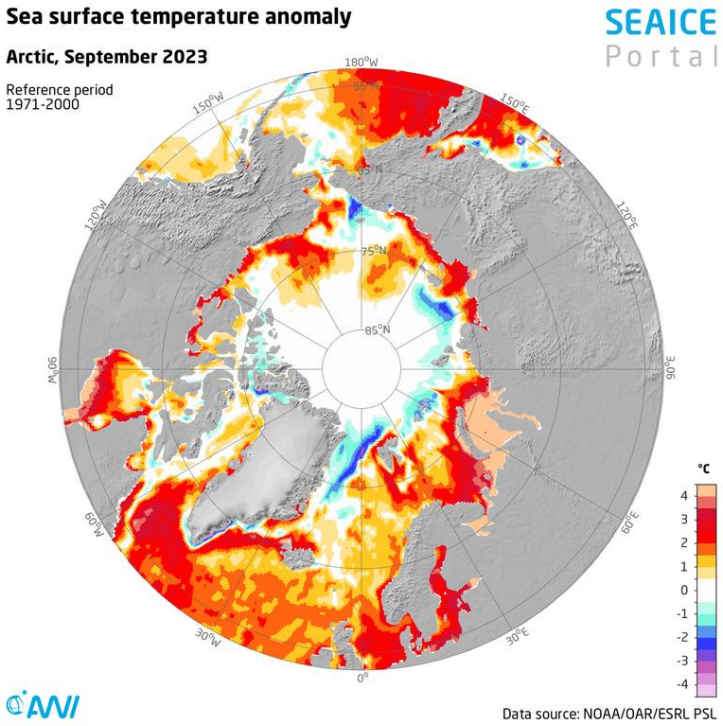

Figure S8: Sea surface temperature anomaly in the Arctic in September 2023 from www.meereisportal.de (Grosfeld et al. 2016).