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DOCTORAL THESIS PRESENTED AS A COLLECTION OF THEMATICALLY RELATED SCIENTIFIC PUBLICATIONS

Carbon and nutrient cycling in Arctic fjord systems: water column and sediment interactions

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Obieg węgla i substancji biogenicznych w systemach fiordów Arktycznych: oddziaływania między tonią wodną a osadami

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You are not a drop in the ocean
You are the entire ocean in a drop

Attributed to Rumi

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List of Abbreviations and Symbols

Abbreviation	Definition
Cl^-	Chloride
CTD	Conductivity, Temperature, Depth
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DSi	Dissolved Silica
HCA	Hierarchical Cluster Analysis
LDA	Linear Discriminant Analysis
MFA	Multiple Factor Analysis
NH_4^+	Ammonium
N:P:Si	nitrogen-to-phosphorus-to-silicon molar ratio (Redfield–Brzeziński)
NO_3^-	Nitrate
PO_4^{3-}	Phosphate
SGD	Submarine Groundwater Discharge
$\delta^{13}C_{DIC}$	Stable Carbon Isotope Composition of Dissolved Inorganic Carbon

Wykaz skrótów i symboli

Skrót	Rozwinięcie
Cl^-	chlorki
CTD	sonda pomiarowa (przewodność, temperatura, głębokość)
DIC	rozpuszczony węgiel nieorganiczny
DOC	rozpuszczony węgiel organiczny
DSi	krzemionka rozpuszczona
HCA	hierarchiczna analiza skupień
LDA	liniowa analiza dyskryminacyjna
MFA	wieloraka analiza czynnikowa
NH_4^+	jony amonowy
N:P:Si	stosunek molowy azotu do fosforu i krzemu (Redfielda–Brzezińskiego)
NO_3^-	azotany
PO_4^{3-}	fosforany
SGD	podmorski dopływ wód podziemnych
$\delta^{13}C_{DIC}$	skład trwałych izotopów węgla rozpuszczonego węgla nieorganicznego

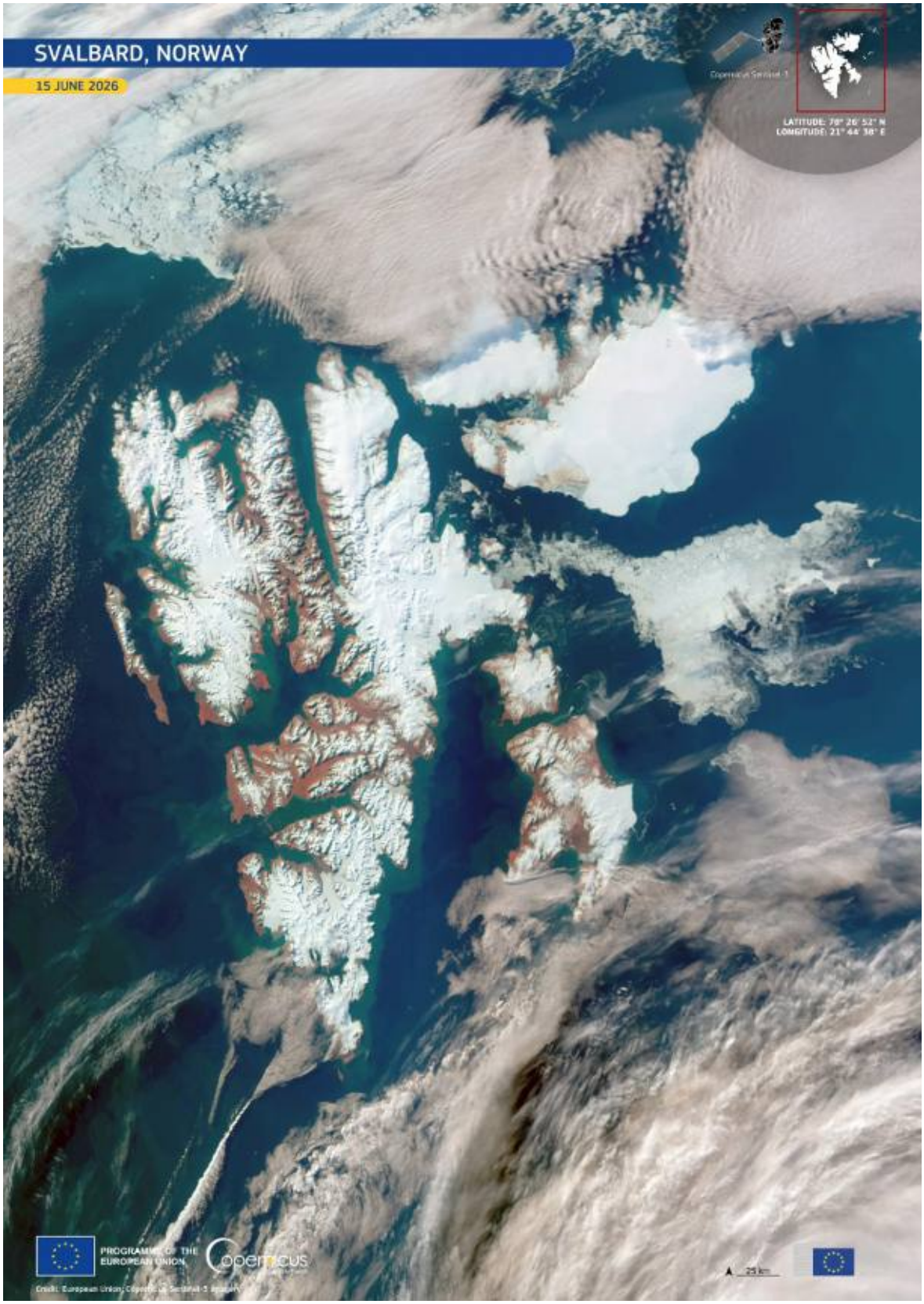

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Table of Contents

Acknowledgements i
Financial support / Wsparcie finansowe ii
List of Abbreviations and Symbols iii
Wykaz skrótów i symboli iv
Introduction (Summary in English) **1**
Purpose of Research 3
Objective 1 4
Objective 2 4
Objective 3 5
Study area 6
Methods 7
Synopsis of Research Works 8
Achievements 10
Wprowadzenie (Streszczenie w języku polskim) **12**
Cel badań 14
Cel szczegółowy 1 15
Cel szczegółowy 2 16
Cel szczegółowy 3 17
Obszar badań 18
Metody 18
Synteza prac badawczych 19
Osiągnięcia 22
References **24**
Research Articles (Artykuły naukowe) **30**
Research Article 1 - Saghravani et al. (2024), Earth System Science Data 31
Author Contribution Statements 45
Research Article 2 - Saghravani et al., under review in Oceanologia 52
Author Contribution Statements 77
Research Article 3 - Saghravani et al. (2026), Polish Polar Research 83
Author Contribution Statements 110

Introduction

The Arctic is experiencing rapid warming, at about two to four times the global average, mainly due to feedback mechanisms like sea ice and snow albedo loss, intensified poleward heat and moisture transport, along with shifts in cloud cover and atmospheric water vapor (Meredith et al., 2019; Bruhwiler et al., 2021). This accelerated warming has led to glacier retreat, shrinking and thinning of sea ice, permafrost thawing, and changes in oceanic and atmospheric circulation patterns (IPCC, 2019; Hugonnet et al., 2021; Dunse et al., 2022; Miner et al., 2022; Rantanen et al., 2022; Thoman et al., 2023). Arctic fjords are semi-enclosed coastal systems that receive freshwater, sediment, and organic and inorganic matter from land. These terrestrial inputs mix with marine waters and are transformed within the fjord (Svendsen et al., 2002; Bianchi et al., 2020; Hopwood et al., 2020). Meltwater from surface runoff or frontal ice loss, along with its solutes, influences the hydrography and biogeochemistry of fjord waters, affecting productivity both within the fjords and on the nearby shelf (Hopwood et al., 2016, 2020).

The fjords of western Spitsbergen are characterized by pronounced vertical hydrographic gradients and seasonal stratification. They serve as conduits for the transfer of heat, salt, nutrients, and dissolved carbon between glacier influenced waters and the coastal ocean (Hopwood et al., 2020). The hydrography of these fjords is primarily governed by two contrasting currents: the East Spitsbergen Current, which transports cold Arctic Water, and the West Spitsbergen Current, which carries warmer, more saline Atlantic Water, along with much of the region's heat, carbon, and plankton resources (Cottier et al., 2005; Menze et al., 2020). These source waters also differ in their nutrient and carbon composition; Atlantic Water becomes increasingly depleted in nutrients as it progresses northward (Smoła et al., 2017). Moreover, the relative proportions of Atlantic and Arctic waters influence nutrient supply and cycling on the shelf and within the fjords (Henley et al., 2020; Santos-Garcia et al., 2022; Tuerena et al., 2022). The extent to which Atlantic Water penetrates individual fjords depends on factors such as fjord morphology, sill depth, and circulation patterns, resulting in a gradient of Atlantification along the western coast of Spitsbergen (Oglethorpe et al., 2026). As a consequence, fjords range from Arctic-dominated systems, such as Hornsund, to those strongly influenced by Atlantic waters, such as Kongsfjorden (Cottier et al., 2005, 2007; Nilsen et al., 2008; Promińska et al., 2018; Tverberg et al., 2019). In this context, accelerating glacier retreat, permafrost thaw, and hydrological changes are modifying the delivery of nutrients and carbon to fjord waters and sediments. These alterations impact primary production, organic matter burial, and benthic recycling, processes vital to local ecosystem functionality and the broader

Arctic carbon cycle (Rysgaard et al., 1998; Smith et al., 2015; Tverberg et al., 2019; McGovern et al., 2020).

The interaction among terrestrial inputs, ocean circulation, and sedimentary processes makes Arctic fjords highly dynamic biogeochemical systems. Nutrient availability governs primary production, whereas the production, transformation, and burial of organic matter regulate carbon storage and recycling within the fjord ecosystem. Sediments are essential in these processes, functioning as repositories of organic matter and sites of intense microbial activity where mineralization, nutrient regeneration, and benthic exchange facilitate the return of carbon and nutrients to the overlying water column (Rysgaard et al., 1998; Glud et al., 2000; Koziorowska et al., 2018; Jørgensen et al., 2021; Szymczycha et al., 2025). Pore waters preserve the integrated imprint of sedimentary biogeochemical processes and offer important information on early diagenesis and the coupling between benthic and pelagic systems.

Freshwater reaches the fjords through several pathways, including glacial meltwater, river discharge, and submarine groundwater discharge (SGD), each delivering chemically distinct water and organic matter to the coastal zone and contributing to pronounced spatial heterogeneity in nutrient and carbon concentrations (McGovern et al., 2020; Santos et al., 2021; Kim et al., 2022; Diak et al., 2023; Szymczycha et al., 2025). The influence of these pathways is increasing as permafrost thaw and glacial retreat modify subsurface hydrology and open new routes for nutrient and carbon transport (Diak et al., 2023; Kleber et al., 2023). Where freshwater inputs coincide with restricted circulation and limited deep water renewal, nutrients and carbon may accumulate in bottom waters and pore waters; conversely, nearby, better-ventilated sites tend to remain comparatively depleted, resulting in enriched "hotspots" that may occur immediately adjacent to less enriched areas within the same fjord (Skogseth et al., 2005; Inall and Gillibrand, 2010). The origin of the carbon accumulating in pore waters can be identified isotopically, since inorganic carbon in pore waters may derive from organic matter remineralization, carbonate dissolution, or methane oxidation, each carrying a distinct stable carbon-isotope signature. Furthermore, because pore waters and near bottom waters are interconnected via benthic–pelagic exchange, their chemistry may covary spatially despite significant differences in absolute concentrations. In instances where such covariation exists, sedimentary biogeochemical conditions could be inferred, at least partially, from water column sampling alone (Kostka et al., 1999; Huettel et al., 2014).

Despite increasing understanding of Arctic fjord biogeochemistry, large scale studies that integrate observations across multiple fjords or sites are still rare, as most research has focused on individual systems (Codispoti et al., 2013; Kim et al., 2022). Firstly, water column nutrient and carbon distributions, along with their relation to

water mass structure, have seldom been characterized across several fjords using a consistent methodology (Promińska et al., 2017; McGovern et al., 2020). Secondly, although sediment–water nutrient exchange has been studied in a number of the Arctic fjords (Hulth et al., 1996; Rysgaard et al., 1998; Kostka et al., 1999; Glud et al., 2000; Koziorowska et al., 2018; Morata et al., 2020; Barrett et al., 2023), comparative analyses of how benthic fluxes vary among fjords with different glacial regimes and organic matter supply are limited. Thirdly, it remains unclear whether the chemical signatures in surface waters, deep waters, and sediment pore waters are driven by shared environmental factors or are affected by layer-specific processes (Huettel et al., 2014). Fourthly, pore water freshening caused by SGD has been observed in several Svalbard fjords (Hong et al., 2019; Kim et al., 2022; Diak et al., 2023; Kleber et al., 2023; Szymczycha et al., 2025) and in deeper Arctic margin settings (Saghravani, 2026), yet its spatial distribution and biogeochemical significance are not well understood. This thesis aims to fill these gaps in the fjord systems of western Spitsbergen, Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden, which span an Arctic-to-Atlantic influence gradient, presenting varying degrees of Atlantification and climate induced changes. Although these fjords lie along a common shelf gradient, they are treated separately in the research articles presented here, where their specific characteristics and local processes are examined.

Purpose of Research

The main purpose of this dissertation is to delineate the distribution and cycling of carbon and nutrients within the western Spitsbergen fjords, encompassing surface waters, the water column, and sediment pore waters. It aims to identify the physical and biogeochemical processes that govern their distribution, exchange, and stoichiometry in the context of ongoing Atlantification and cryospheric change. Key processes include water mass mixing and transformation, density stratification, organic matter remineralization and early diagenesis, diffusive benthic exchange, and pore water freshening. This investigation is guided by the hypothesis that nutrient and carbon distributions are influenced by water mass identity, basin morphology, and local environmental inputs, such as freshwater from SGD, rather than by geographic gradients like the proximity to glacier fronts. As a result, biogeochemical variability is anticipated to be organized at the level of individual basins and biogeochemical "hotspots" (areas of intense biogeochemical processing), rather than exhibiting uniform patterns across entire fjords. The research is structured around three main objectives.

Objective 1: Characterize the spatial variability of carbon and nutrient distributions in the water column of western Spitsbergen fjords

Hypothesis: The spatial distribution of nutrients and dissolved carbon in the western Spitsbergen fjords is mainly regulated by the mixing and transformation processes of Atlantic and Arctic water masses.

Research Questions:

- What are the concentration ranges of the key nutrients (nitrate: NO_3^-; ammonium: NH_4^+; phosphate: PO_4^{3-}; dissolved silica: DSi) and dissolved carbon species (dissolved inorganic carbon: DIC; dissolved organic carbon: DOC) present in the water column and sediment pore waters of the fjords?
- How do these constituents (NO_3^-, NH_4^+, PO_4^{3-}, DSi, DIC, DOC) vary among different fjords and among various water masses within individual fjords?
- Do the water masses identified from temperature-salinity properties carry statistically distinct nutrient and carbon signatures, both within and between fjords?
- Which water masses show the most distinctive nutrient and carbon composition, and how do locally formed and modified waters compare with those of Atlantic and Arctic origin?

Approach: Conduct a hydrographic and biogeochemical survey of the fjords during the summer melting season of 2021. Classify water masses based on established temperature–salinity criteria for Svalbard fjords, and analyze spatial variability among fjords and water masses employing nonparametric statistical methods (Kruskal-Wallis test). Interpret the observed biogeochemical patterns in relation to hydrographic structure and environmental gradients.

Objective 2: Quantify the exchange between sediment and water, as well as benthic nutrient recycling, and evaluate the impact of SGD

Hypothesis: Sediment pore water chemistry is interconnected with overlying bottom waters, and diffusive benthic fluxes represent a substantial source of regenerated nutrients to the water column. Nonetheless, benthic recycling deviates from the canonical Redfield-Brzeziński stoichiometry due to differential remineralization and retention of nitrogen, phosphorus, and silica. Furthermore, pore water freshening influences nutrient and carbon gradients, thereby modifying both the magnitude and stoichiometry of benthic exchange.

Research Questions:

- What are the magnitudes and directions of diffusive benthic fluxes for DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-}, and DSi across the sediment-water interface?
- Do the flux stoichiometries follow the Redfield-Brzeziński ratio of nitrogen to phosphorus to silicon (N:P:Si = 16:1:15, where Si denotes DSi), or are there systematic deviations?
- How do benthic fluxes and ratios of DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-}, and DSi vary among fjords with different oceanographic and glacial conditions?
- What are the dominant sources of pore water DIC, as inferred from the relationship between DIC concentration and stable carbon isotope composition of DIC ($\delta^{13}C_{DIC}$)?
- Where does SGD occur?

Approach: Sampling was conducted in 2022 aboard r/v Oceania during a research cruise to Svalbard, yielding 12 sediment cores up to about 1.5 m in length. Estimate diffusive fluxes from pore water concentration gradients utilizing Fick's first law (Berner, 1980), with diffusion coefficients corrected for temperature and converted to sediment conditions using measured porosity and tortuosity. Delineate sediment geochemical zones using hierarchical cluster analysis (HCA) and separate them using linear discriminant analysis (LDA). Trace pore water freshening and SGD by employing Chloride (Cl^-) as a conservative tracer. Attribute pore water DIC sources based on the relationship between DIC and $\delta^{13}C_{DIC}$. Finally, compare flux ratios to the Redfield–Brzeziński values (Redfield, 1963; Brzeziński, 1985).

Objective 3: Resolve vertical biogeochemical connectivity between the water column and sediment pore waters, and identify sites of pronounced subsurface enrichment

Hypothesis: The chemical composition of the water column and sediment pore waters is interconnected through hydrodynamic mixing, sedimentation, and early diagenetic processes. Although the absolute concentration disparities between the water column and pore waters can reach several orders of magnitude, it is anticipated that benthic-pelagic coupling will induce significant spatial covariation between the deep water and pore water layers. Nonetheless, summer stratification diminishes the coupling between surface and deeper waters, resulting in distinct biogeochemical signatures for each layer and fostering the emergence of local biogeochemical hotspots, areas where restricted circulation coincides with an increased supply of organic matter. If such covariation is present, the biogeochemical conditions of pore waters, including the locations of hotspots, should be at least partially inferable from water column sampling alone.

Research Questions:

- How do nutrient and carbon concentrations covary across the five vertical layers (surface water, bottom water, water above sediment, and upper and lower sediment pore water)?
- How are sedimentary biogeochemical signals connected to the overlying water column, and which layers show the strongest coupling?
- Which sites contribute disproportionately to subsurface variability, and what basin and environmental characteristics do they share?

Approach: Integrate the water column and sediment datasets from the 2021 and 2022 campaigns. Apply multiple factor analysis (MFA) on the six chemical variables measured across each of the five layers at the 19 stations where all layers were sampled, with hydrographic and site variables incorporated as supplementary information. Identify hotspot stations based on their contributions to the primary ordination axis, and evaluate whether bottom water chemistry reflects pore water conditions.

Study area

The fjords extend across the Arctic-to-Atlantic gradient of western Spitsbergen, along which the West Spitsbergen Current penetrates individual fjord systems to varying extents, contingent upon fjord morphology and sill depth (Cottier et al., 2005; Nilsen et al., 2008). Hornsund, situated in the south, is affected by cold Arctic and coastal waters (Włodarska-Kowalczuk et al., 1998; Promińska et al., 2018) and is separated by a shallow sill into a main basin and the inner Brepollen basin (Moskalik et al., 2014; Błaszczyk et al., 2019). Isfjorden, the largest Svalbard fjord system, consists of several secondary fjords with contrasting hydrographic characteristics, ranging from Atlantic-influenced outer regions to cold, silled inner basins such as Billefjorden (Szczuciński et al., 2009; Skogseth et al., 2020). The connected Kongsfjorden-Krossfjorden system in the north exhibits relatively open shelf connections that facilitate frequent intrusion of Atlantic Water (Hop et al., 2002; Svendsen et al., 2002; Tverberg et al., 2019). All fjords receive freshwater and sediment contributions from glaciers terminating in marine and land environments (Smith et al., 2015; Halbach et al., 2019; Hopwood et al., 2020), and rest upon diverse catchment geologies, ranging from the Precambrian crystalline basement of Hornsund (Görlich, 1986; Dallmann, 2015) to carbonate and sandstone sequences surrounding Kongsfjorden (Svendsen et al., 2002). These geological differences influence pore water chemistry through processes such as carbonate dissolution and silicate weathering (Wallmann et al., 2008; März et al., 2015). The fjords provide a natural environment for investigating biogeochemical responses to

varying degrees of Atlantification and glacial influence (Svendsen et al., 2002; Promińska et al., 2018).

Methods

Overview of the methodologies employed in the manuscripts presented herein, with comprehensive analytical and statistical details provided in the respective manuscripts.

Fieldwork was conducted aboard r/v Oceania during the 2021 and 2022 summer melting seasons, and the three studies draw on partially overlapping sets of stations and cores rather than a single combined dataset. Paper 1 is based on a 2021 multi-fjord water column survey, with three to five depths per station at 33 stations, measured with a conductivity, temperature, depth (CTD) rosette, together with Niemistö and/or GEMAX cores up to about 40 cm. Paper 2 is based on twelve deeper sediment cores, up to about 1.5 m long, recovered with gravity and GEMAX corers in 2022. Paper 3 combines water column and sediment data from both campaigns (2021–2022) at the 19 stations where all five vertical layers were available, using cores of variable length. Pore waters were extracted with Rhizon samplers, and station water depths across the three studies ranged from about 17 to 374 m. The measured variables include in situ temperature, salinity, and dissolved oxygen, together with the dissolved inorganic nutrients (NO_3^-, NH_4^+, PO_4^{3-}, DSi), dissolved inorganic and organic carbon (DIC, DOC), Cl^-, the major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), and, in sediment pore waters, the stable carbon-isotope composition of DIC ($\delta^{13}C_{DIC}$). All constituents were determined by standard analytical methods with quality control against certified reference materials.

Water masses were classified by their temperature-salinity properties using established Svalbard definitions (Cottier et al., 2005; Nilsen et al., 2008; Promińska et al., 2018), the standard approach for separating Atlantic, Arctic, and locally formed waters in these fjords. Diffusive benthic fluxes across the sediment–water interface were calculated from pore water concentration gradients using Fick's first law (Berner, 1980). This approach is appropriate for fine-grained, diffusion dominated fjord muds and yields fluxes directly from measured pore water profiles. Pore water freshening and SGD were traced with Cl^-, which behaves conservatively in marine sediments, and pore water DIC sources were characterized using $\delta^{13}C_{DIC}$, since remineralized organic matter, dissolving carbonates, and methane-derived carbon carry distinct isotopic signatures. Spatial patterns were analyzed using the non-parametric Kruskal-Wallis test with Dunn's post hoc comparisons (chosen because the concentration data are non-normally distributed and group sizes are unequal), HCA (Ward's method, which delineates geochemical zones without prescribing groups in advance), LDA (used to test the separability of the resulting clusters), and MFA (which weights each sampled

layer equally, so that covariation among layers can be assessed without any single layer dominating the ordination).

Synopsis of Research Works

The dissertation is organized into three interconnected studies, progressing from the characterization of spatial biogeochemical patterns, through the identification of fundamental sedimentary processes, to an integrated analysis of water column-sediment interactions in the fjords of western Spitsbergen. Together, these studies are a systematic evaluation of carbon and nutrient distribution and cycling throughout the vertical continuum of Arctic fjord ecosystems.

The first article, "*Distributions of in-situ parameters, dissolved (in)organic carbon, and nutrients in the water column and pore waters of Arctic fjords (western Spitsbergen) during a melting season*" (Saghravani et al., 2024), laid the observational groundwork for the thesis and addressed Objective 1. During the 2021 melting season, it characterized variables such as temperature, salinity, oxygen, inorganic nutrients, and dissolved carbon in the water columns and shallow pore waters of Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden. Seven distinct water masses were identified based on their temperature-salinity profiles, including surface, Arctic, winter-cooled, intermediate, local, transformed Atlantic, and Atlantic Water. The Kruskal-Wallis test indicated that most constituents differed significantly among fjords and between water masses. Hornsund, which was devoid of Atlantic or transformed Atlantic Water, emerged as the most nutrient- and DIC-enriched system, influenced primarily by Arctic and coastal waters (Włodarska-Kowalczuk et al., 1998), whereas Kongsfjorden exhibited the most pronounced Atlantic signature. The Local Water, exclusive to Isfjorden, displayed the highest concentrations of NO_3^-, PO_4^{3-}, DSi, and DIC among all water masses. Surface pore waters were enriched in NH_4^+, PO_4^{3-}, DSi, and DIC relative to the overlying bottom waters, at times exceeding an order of magnitude, indicating a substantial potential for benthic–pelagic exchange. By employing a uniform methodology across fjords and depositing the complete dataset into an open repository, the publication established a spatial and compositional baseline for subsequent process-based studies.

Building on these patterns, the second article, "*Nutrients and carbon cycling in marine sediments of Arctic fjords*" (Saghravani et al., under review), shifted from descriptive to mechanistic analysis, addressing Objective 2. In 2022, twelve sediment cores up to about 1.5 m long were collected and analyzed for pore water nutrients, dissolved carbon, Cl^-, and the stable carbon isotope composition of DIC. HCA identified five geochemical zones (HC1 to HC5) that mapped onto sediment depth: an oxygenated, nitrate-rich shallow zone interacting with bottom water; mid-depth zones enriched in

DSi, NH_4^+, DOC, and PO_4^{3-} where labile organic matter undergoes remineralization; and deeper zones with the highest DIC, DOC, PO_4^{3-}, and DSi, where low-permeability mud and mineral dissolution promote solute accumulation. The $\delta^{13}C_{DIC}$ values, ranging from approximately +1 to -14‰, along with the negative relationship between DIC and $\delta^{13}C_{DIC}$, indicate that carbonate dissolution and organic matter remineralization, rather than methane oxidation, dominate the carbon dynamics. Cl^- concentrations decrease with depth at two Hornsund sites, indicating pore water freshening consistent with SGD (Kim et al., 2022). Comparison between affected and unaffected deep clusters suggests that this freshwater source introduces inorganic nitrogen and dilutes DIC, phosphate, and silica. Diffusive benthic fluxes, calculated via Fick's first law, deviated from Redfield–Brzeziński stoichiometry: the nitrogen to phosphorus (N:P) flux ratios averaged 0.2 in Hornsund, 6.2 in Isfjorden, and 10.1 in Kongsfjorden, all below the expected 16:1. In Krossfjorden, negative fluxes into sediments indicated net uptake or accumulation, leading to their exclusion from ratio analysis. The N:DSi flux ratios were 2.9 in Hornsund, 6.5 in Isfjorden, and 43.4 in Kongsfjorden, all exceeding the expected ~1.1 (16:15), with the largest nitrogen excess over silica observed in Kongsfjorden. Hornsund exhibited noticeable phosphorus and silica release relative to nitrogen, but a low nitrogen flux, which does not necessarily indicate nitrogen limitation in the overlying waters. Conversely, Kongsfjorden showed the greatest nitrogen excess relative to silica. Overall, deviations from Redfield–Brzeziński stoichiometry varied across the fjords, reflecting regional heterogeneity (Koziorowska et al., 2018; Morata et al., 2020).

The third article, "*Covariation of dissolved nutrients and carbon in seawaters and sediment porewaters of western Svalbard fjords*" (Saghravani et al., 2026), combined water column and sediment data to address Objective 3. It investigates how sedimentary signals are connected to the overlying water column, and which sites contribute disproportionately to subsurface variability. MFA of six chemical variables across five layers, surface water, bottom water, water above sediment, and upper and lower pore water at nineteen stations showed that deep water and pore water form a single system: bottom water, water above sediment, and pore water strongly loaded on the first ordination axis (0.65–0.72), while surface water was decoupled, reflecting summer stratification. The close association between bottom water and pore water chemistry suggests that bottom water composition reflects underlying sediment signals, providing a practical way to detect benthic activity through water column sampling, thereby directly addressing Objective 3. Notably, three sites in silled Billefjorden and the deep main basin of Hornsund contributed disproportionately to this axis, accounting for roughly 73% of its variance, and appeared as enriched end-members compared to the lower concentration baseline from other sites. These hotspots shared restricted deep water renewal and organic matter input; where these

conditions did not overlap, as in inner Brepollen, hotspots were less developed, indicating that basin restriction alone is insufficient. Variability among basins within a fjord often surpassed differences between fjords, leading to the conclusion that western Spitsbergen fjords behave as a mosaic of distinct biogeochemical environments. A small number of locally controlled hotspots, rather than systematic fjord-scale gradients, primarily influence subsurface nutrient and carbon cycling (Cottier et al., 2005; Skogseth et al., 2020).

The three studies found that Arctic fjords operate as mosaics in which physical separation and organic matter supply, acting synergistically, concentrate carbon and nutrient cycling at specific sites. This spatial configuration is often overlooked in geographic or fjord-averaged descriptions and is anticipated to change as winter water formation, Atlantic water intrusion, and freshwater input continue to alter the environment (Tverberg et al., 2019; Diak et al., 2023).

Achievements

- Established a comprehensive observational dataset encompassing nutrients, dissolved inorganic and organic carbon, and hydrographic parameters in western Spitsbergen fjords. This dataset extends through the water column and sediment pore waters, and has been made publicly accessible for subsequent Arctic research [Research Articles 1, 2, 3].
- Demonstrated strong biogeochemical differentiation among water masses and fjord systems. Statistical analyses showed that nutrient and carbon concentrations differed significantly among fjords and water masses, revealing distinct biogeochemical signatures associated with Arctic- and Atlantic-influenced waters. Arctic Water was relatively enriched in nutrients (except NH_4^+) and DIC in Hornsund compared with Isfjorden, whereas Local Water in Isfjorden exhibited the highest concentrations of NO_3^-, PO_4^{3-}, DSi, and DIC among the investigated water masses [Research Article 1].
- Resolved five depth-related sediment geochemical zones using hierarchical clustering and LDA, and used the $\delta^{13}C_{DIC}$ relationship to attribute deep pore water carbon to carbonate dissolution and organic matter remineralization [Research Article 2].
- Identified pore water freshening at two Hornsund sites and demonstrated its influence on sediment biogeochemistry. Cl^- depletion in deep pore waters was interpreted as evidence of freshwater mixing consistent with SGD. Comparison of freshened and non-freshened pore waters showed higher inorganic nitrogen

but lower DIC, PO_4^{3-}, and DSi concentrations in the freshened waters [Research Article 2].

- Quantified spatially variable diffusive benthic fluxes of carbon and nutrients and demonstrated deviation from Redfield–Brzeziński stoichiometry. The results showed that sediments can act as either sources or sinks of nutrients depending on the site, with high phosphorus release in Hornsund and negative nitrogen and phosphorus fluxes at some Kongsfjorden sites. The observed N:P and N:DSi flux ratios differed from the Redfield–Brzeziński reference ratios (N:P of 0.2–10.1 versus 16:1; N:DSi of 2.9–43.4 versus ~1.1=16:15), demonstrating that benthic nutrient regeneration is strongly fjord- and site-specific [Research Article 2].
- Revealed strong basin scale heterogeneity and identified biogeochemical hotspots within western Spitsbergen fjords. Three stations accounted for approximately 73% of the variance along the dominant MFA dimension. These hotspots occurred in restricted basins characterized by limited deep-water renewal and a supply of labile organic matter. Differences among basins within individual fjord systems were often as large as or larger than those among fjord systems, supporting a mosaic rather than a fjord-wide gradient in subsurface biogeochemistry [Research Article 3].
- Demonstrated strong link between bottom water and sediment pore water biogeochemistry at the site scale. MFA showed that bottom water, water above sediment, and upper and lower pore waters covaried strongly, whereas surface waters were largely separated. This suggests that bottom water chemistry integrates spatial variability in the underlying sedimentary biogeochemical environment, allowing pore water hotspots to be identified, at least in part, from water column sampling [Research Article 3].

Wprowadzenie

Arktyka doświadcza gwałtownego ocieplenia - około dwu- do czterokrotnie szybszego niż średnia globalna - głównie wskutek mechanizmów sprzężeń zwrotnych, takich jak utrata albedo lodu morskiego i pokrywy śnieżnej, nasilony transport ciepła i wilgoci w kierunku bieguna oraz zmiany zachmurzenia i zawartości pary wodnej w atmosferze (Meredith i in., 2019; Bruhwiler i in., 2021). To przyspieszone ocieplenie prowadzi do cofania się lodowców, kurczenia się zasięgu i zmniejszania grubości lodu morskiego, rozmarzania wieloletniej zmarzliny oraz zmian w cyrkulacji oceanicznej i atmosferycznej (IPCC, 2019; Hugonnet i in., 2021; Dunse i in., 2022; Miner i in., 2022; Rantanen i in., 2022; Thoman i in., 2023). Fiordy arktyczne są półzamkniętymi systemami przybrzeżnymi, które otrzymują z lądu wodę słodką, osady oraz materię organiczną i nieorganiczną. Ten materiał pochodzenia lądowego miesza się z wodami morskimi i ulega przemianom w obrębie fiordu (Svendsen i in., 2002; Bianchi i in., 2020; Hopwood i in., 2020). Wody roztopowe pochodzące ze spływu powierzchniowego lub z ubytku lodu na czołach lodowców, wraz z niesionymi przez nie substancjami rozpuszczonymi, wpływają na hydrografię i biogeochemię wód fiordów, oddziałując na produktywność zarówno w samych fiordach, jak i na przyległym szelfie (Hopwood i in., 2016, 2020).

Fiordy zachodniego Spitsbergenu charakteryzują się wyraźnymi pionowymi gradientami hydrograficznymi oraz sezonową stratyfikacją. Stanowią one drogi przenoszenia ciepła, soli, substancji biogenicznych i rozpuszczonego węgla między wodami pozostającymi pod wpływem lodowców a oceanem przybrzeżnym (Hopwood i in., 2020). Hydrografia tych fiordów jest kształtowana głównie przez dwa kontrastujące ze sobą prądy: Prąd Wschodniospitsbergeński, transportujący zimną wodę arktyczną, oraz Prąd Zachodniospitsbergeński, niosący cieplejszą i bardziej zasoloną wodę atlantycką wraz ze znaczną częścią ciepła, węgla i zasobów planktonu docierających do regionu (Cottier i in., 2005; Menze i in., 2020). Wody te różnią się także składem substancji biogenicznych i węgla; Woda atlantycka ulega postępującemu zubożeniu w biogeny w miarę przemieszczania się na północ (Smoła i in., 2017). Ponadto wzajemne proporcje wód atlantyckich i arktycznych wpływają na dostawę i obieg związków biogenicznych na szelfie i w fiordach (Henley i in., 2020; Santos-Garcia i in., 2022; Tuerena i in., 2022). Stopień, w jakim woda atlantycka wnika do poszczególnych fiordów, zależy od takich czynników jak morfologia fiordu, głębokość progu i cyrkulacja, co prowadzi do powstania gradientu atlantyfikacji wzdłuż zachodniego wybrzeża Spitsbergenu (Oglethorpe i in., 2026). W konsekwencji fiordy tworzą kontinuum od systemów zdominowanych przez wody arktyczne, takich jak Hornsund, po systemy silnie kształtowane przez wody atlantyckie, takie jak Kongsfjorden (Cottier i in., 2005, 2007; Nilsen i in., 2008; Promińska i in., 2018;

Tverberg i in., 2019). W tym kontekście przyspieszające cofanie się lodowców, rozmarzanie wieloletniej zmarzliny oraz zmiany hydrologiczne modyfikują dostawę związków biogenicznych i węgla do wód i osadów fiordów. Zmiany te wpływają na produkcję pierwotną, zagrzebywanie materii organicznej w osadach oraz recykling bentosowy - procesy kluczowe dla funkcjonowania lokalnych ekosystemów i dla arktycznego obiegu węgla w szerszej skali (Rysgaard i in., 1998; Smith i in., 2015; Tverberg i in., 2019; McGovern i in., 2020).

Wzajemne oddziaływanie dopływu materii z lądu, cyrkulacji oceanicznej i procesów zachodzących w osadach sprawia, że fiordy arktyczne są wysoce dynamicznymi systemami biogeochemicznymi. Dostępność związków biogenicznych warunkuje produkcję pierwotną, natomiast produkcja, przemiany i zagrzebywanie materii organicznej regulują magazynowanie i recykling węgla w ekosystemie fiordu. Osady odgrywają w tych procesach kluczową rolę, będąc zarówno rezerwuarem materii organicznej, jak i miejscem intensywnej aktywności mikrobiologicznej, gdzie mineralizacja, regeneracja związków biogenicznych i wymiana bentosowa umożliwiają powrót węgla i związków biogenicznych do toni wodnej (Rysgaard i in., 1998; Glud i in., 2000; Koziorowska i in., 2018; Jørgensen i in., 2021; Szymczycha i in., 2025). Wody porowe zachowują zintegrowany zapis procesów biogeochemicznych zachodzących w osadach i dostarczają cennych informacji o wczesnej diagenezie oraz o sprzężeniu między systemem bentosowym a pelagicznym.

Woda słodka dociera do fiordów kilkoma drogami - jako wody roztopowe lodowców, spływ rzeczny oraz podmorski dopływ wód podziemnych (SGD) - a każda z nich dostarcza do strefy przybrzeżnej wodę i materię organiczną o odmiennym składzie chemicznym, przyczyniając się do wyraźnej przestrzennej heterogeniczności stężeń związków biogenicznych i węgla (McGovern i in., 2020; Santos i in., 2021; Kim i in., 2022; Diak i in., 2023; Szymczycha i in., 2025). Znaczenie tych dróg rośnie, ponieważ rozmarzanie wieloletniej zmarzliny i cofanie się lodowców przekształcają hydrologię podpowierzchniową i otwierają nowe szlaki transportu związków biogenicznych i węgla (Diak i in., 2023; Kleber i in., 2023). Tam, gdzie dopływ wód słodkich zbiega się z ograniczoną cyrkulacją i ograniczonym odnawianiem wód głębokich, biogeny i węgiel mogą gromadzić się w wodach przydennych i porowych; z kolei pobliskie, lepiej wentylowane stanowiska pozostają zwykle stosunkowo zubożone, w wyniku czego wzbogacone „hotspoty" mogą występować w bezpośrednim sąsiedztwie obszarów mniej wzbogaconych w obrębie tego samego fiordu (Skogseth i in., 2005; Inall i Gillibrand, 2010). Pochodzenie węgla gromadzącego się w wodach porowych można określić izotopowo, ponieważ rozpuszczony węgiel nieorganiczny w wodach porowych może pochodzić z remineralizacji materii organicznej, rozpuszczania węglanów lub utleniania metanu, a każdy z tych procesów charakteryzuje się odrębną

sygnaturą trwałych izotopów węgla. Ponadto, ponieważ wody porowe i wody przydenne są ze sobą powiązane poprzez wymianę bentosowo-pelagiczną, ich skład chemiczny może wykazywać przestrzenną współzmienność pomimo znacznych różnic w wartościach bezwzględnych stężeń. Jeżeli taka współzmienność występuje, warunki biogeochemiczne panujące w osadach można by wnioskować, przynajmniej częściowo, wyłącznie na podstawie opróbowania toni wodnej (Kostka i in., 1999; Huettel i in., 2014).

Pomimo rosnącej wiedzy o biogeochemii fiordów arktycznych badania na dużą skalę, integrujące obserwacje z wielu fiordów, wciąż należą do rzadkości, ponieważ większość prac koncentrowała się na pojedynczych systemach (Codispoti i in., 2013; Kim i in., 2022). Po pierwsze, rozmieszczenie związków biogenicznych i węgla w toni wodnej oraz ich związek ze strukturą mas wodnych rzadko charakteryzowano w kilku fiordach jednocześnie przy użyciu spójnej metodyki (Promińska i in., 2017; McGovern i in., 2020). Po drugie, chociaż wymianę związków biogenicznych między osadem a wodą badano w pojedynczych fiordach arktycznych (Hulth i in., 1996; Rysgaard i in., 1998; Kostka i in., 1999; Glud i in., 2000; Koziorowska i in., 2018; Morata i in., 2020; Barrett i in., 2023), analizy porównawcze zmienności strumieni bentosowych między fiordami o różnych reżimach lodowcowych i różnej dostawie materii organicznej są nieliczne. Po trzecie, nadal nie jest jasne, czy skład chemiczny wód powierzchniowych, wód głębokich i wód porowych osadów jest kształtowany przez wspólne czynniki środowiskowe, czy też podlega procesom specyficznym dla poszczególnych warstw (Huettel i in., 2014). Po czwarte, wysładzanie wód porowych powodowane przez SGD stwierdzono w kilku fiordach Svalbardu (Hong i in., 2019; Kim i in., 2022; Diak i in., 2023; Kleber i in., 2023; Szymczycha i in., 2025), lecz jego przestrzenne rozmieszczenie i znaczenie biogeochemiczne pozostają słabo poznane (Saghravani, 2026). Niniejsza rozprawa ma na celu wypełnienie tych luk w fiordach zachodniego Spitsbergenu - Hornsund, Isfjorden, Kongsfjorden i Krossfjorden - które obejmują gradient od warunków arktycznych po atlantyckie, odzwierciedlając zróżnicowany stopień atlantyfikacji i zmian wywołanych zmianą klimatu. Chociaż fiordy te leżą wzdłuż wspólnego gradientu szelfowego, w prezentowanych tu artykułach naukowych rozpatrywane są osobno, z uwzględnieniem ich specyficznych cech i lokalnych procesów.

Cel badań

Głównym celem niniejszej rozprawy jest scharakteryzowanie rozmieszczenia i obiegu węgla oraz substancji biogenicznych w fiordach zachodniego Spitsbergenu - od wód powierzchniowych, poprzez toń wodną, po wody porowe. Rozprawa zmierza do zidentyfikowania procesów fizycznych i biogeochemicznych, które kształtują ich

rozmieszczenie, wymianę i stechiometrię w kontekście postępującej atlantyfikacji i zmian kriosfery. Do kluczowych procesów należą: mieszanie i przekształcanie mas wodnych, stratyfikacja gęstościowa, remineralizacja materii organicznej i wczesna diageneza, dyfuzyjna wymiana bentosowa oraz wysładzanie wód porowych. Badania oparto na hipotezie, że rozkłady związków biogenicznych i węgla są kształtowane przez typ masy wodnej, morfologię basenu i lokalne dopływy środowiskowe, takie jak woda słodka pochodząca z SGD, a nie przez gradienty geograficzne, takie jak odległość od czół lodowców. W konsekwencji oczekuje się, że zmienność biogeochemiczna będzie zorganizowana na poziomie poszczególnych basenów i biogeochemicznych „hotspotów" (obszarów intensywnych procesów), a nie w postaci jednolitych wzorców obejmujących całe fiordy. Badania ustrukturyzowano wokół trzech celów szczegółowych.

Cel szczegółowy 1: Charakterystyka przestrzennej zmienności rozmieszczenia węgla i substancji biogenicznych w toni wodnej fiordów zachodniego Spitsbergenu

Hipoteza: Przestrzenne rozmieszczenie związków biogenicznych i rozpuszczonego węgla w fiordach zachodniego Spitsbergenu jest regulowane przede wszystkim przez procesy mieszania i przekształcania atlantyckich i arktycznych mas wodnych.

Pytania badawcze:

- Jakie są zakresy stężeń kluczowych związków biogenicznych (azotany: NO_3^-; jon amonowy: NH_4^+; fosforany: PO_4^{3-}; krzemionka rozpuszczona: DSi) oraz rozpuszczonych form węgla (rozpuszczony węgiel nieorganiczny: DIC; rozpuszczony węgiel organiczny: DOC) w toni wodnej i wodach porowych osadów badanych fiordów?
- Jak składniki te (NO_3^-, NH_4^+, PO_4^{3-}, DSi, DIC, DOC) różnią się między fiordami oraz między masami wodnymi w obrębie poszczególnych fiordów?
- Czy masy wodne wyodrębnione na podstawie właściwości termohalinowych (temperatura–zasolenie) charakteryzują się statystycznie odrębnymi sygnaturami związków biogenicznych i węgla, zarówno w obrębie poszczególnych fiordów, jak i między nimi?
- Które masy wodne wykazują najbardziej wyróżniający się skład związków biogenicznych i węgla oraz jak wody uformowane i przekształcone lokalnie wypadają na tle wód pochodzenia atlantyckiego i arktycznego?

Podejście badawcze: Przeprowadzenie badań hydrograficznych i biogeochemicznych fiordów w letnim sezonie topnienia 2021 r. Klasyfikacja mas wodnych na podstawie ustalonych kryteriów temperatury i zasolenia dla fiordów Svalbardu oraz analiza przestrzennej zmienności między fiordami i masami wodnymi z zastosowaniem

nieparametrycznych metod statystycznych (test Kruskala–Wallisa). Interpretacja obserwowanych wzorców biogeochemicznych w odniesieniu do struktury hydrograficznej i gradientów środowiskowych.

Cel szczegółowy 2: Ilościowa ocena wymiany między osadem a wodą oraz bentosowego recyklingu związków biogenicznych, a także ocena wpływu SGD

Hipoteza: Skład chemiczny wód porowych osadów jest powiązany ze składem wód przydennych, a dyfuzyjne strumieni powrotnych stanowią istotne źródło zregenerowanych związków biogenicznych dla toni wodnej. Niemniej jednak recykling bentosowy odbiega od kanonicznej stechiometrii Redfielda–Brzezińskiego wskutek zróżnicowanej remineralizacji i retencji azotu, fosforu i krzemu. Ponadto wysładzanie wód porowych wpływa na stężenia związków biogenicznych i węgla, modyfikując zarówno wielkość, jak i stechiometrię wymiany bentosowej.

Pytania badawcze:

- Jakie są wielkości i kierunki strumieni powrotnych DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-} i DSi przez granicę osad–woda?
- Czy stechiometria strumieni odpowiada stosunkowi Redfielda–Brzezińskiego azotu do fosforu i krzemu (N:P:Si = 16:1:15, gdzie Si oznacza krzemionkę rozpuszczoną, DSi), czy też występują systematyczne odchylenia?
- Jak strumieni powrotnych DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-} i DSi oraz ich stosunki różnią się między fiordami o odmiennych warunkach oceanograficznych i lodowcowych?
- Jakie są dominujące źródła DIC w wodach porowych, wnioskowane z zależności między stężeniem DIC a składem trwałych izotopów węgla DIC ($\delta^{13}C_{DIC}$)?
- Gdzie występuje SGD?

Podejście badawcze: Opróbowanie przeprowadzono w 2022 r. podczas rejsu badawczego na Svalbard na pokładzie r/v Oceania, w trakcie którego pobrano 12 rdzeni osadów o długości do około 1,5 m. Oszacowanie strumieni dyfuzyjnych na podstawie gradientów stężeń w wodach porowych z zastosowaniem pierwszego prawa Ficka (Berner, 1980), przy użyciu współczynników dyfuzji skorygowanych o temperaturę i przeliczonych na warunki panujące w osadzie na podstawie zmierzonej porowatości i krętości. Wyznaczenie geochemicznych stref osadów za pomocą hierarchicznej analizy skupień (HCA) i ich rozdzielenie metodą liniowej analizy dyskryminacyjnej (LDA). Śledzenie wysładzania wód porowych i SGD z wykorzystaniem chlorków (Cl^-) jako znacznika konserwatywnego. Określenie źródeł DIC w wodach porowych na podstawie zależności między DIC a $\delta^{13}C_{DIC}$. Wreszcie

porównanie stosunków strumieni z wartościami Redfielda–Brzezińskiego (Redfield, 1963; Brzeziński, 1985).

Cel szczegółowy 3: Rozpoznanie pionowej łączności biogeochemicznej między tonią wodną a wodami porowymi osadów oraz zlokalizowanie miejsc wyraźnego wzbogacenia podpowierzchniowego

Hipoteza: Skład chemiczny toni wodnej i wód porowych osadów jest powiązany poprzez mieszanie hydrodynamiczne, sedymentację i procesy wczesnej diagenezy. Chociaż różnice bezwzględnych stężeń między tonią wodną a wodami porowymi mogą sięgać kilku rzędów wielkości, oczekuje się, że sprzężenie bentosowo-pelagiczne wywoła istotną przestrzenną współzmienność między warstwami wód głębokich i wód porowych. Letnia stratyfikacja osłabia jednak sprzężenie między wodami powierzchniowymi a głębszymi, prowadząc do powstania odrębnych sygnatur biogeochemicznych poszczególnych warstw i sprzyjając tworzeniu się lokalnych hotspotów biogeochemicznych - obszarów, w których ograniczona cyrkulacja zbiega się ze zwiększoną dostawą materii organicznej. Jeżeli taka współzmienność występuje, warunki biogeochemiczne wód porowych, w tym lokalizacja hotspotów, powinny być przynajmniej częściowo możliwe do wywnioskowania wyłącznie na podstawie opróbowania toni wodnej.

Pytania badawcze:

- Jak stężenia związków biogenicznych i węgla współzmieniają się w pięciu pionowych warstwach (woda powierzchniowa, woda przydenna, woda nad osadem oraz górna i dolna warstwa wód porowych osadów)?
- W jaki sposób sygnały biogeochemiczne pochodzące z osadów są powiązane z leżącą nad nimi tonią wodną i które warstwy wykazują najsilniejsze sprzężenie?
- Które stacje badawcze mają nieproporcjonalnie duży udział w zmienności podpowierzchniowej i jakie wspólne cechy basenów oraz warunki środowiskowe je charakteryzują?

Podejście badawcze: Zintegrowanie zbiorów danych z toni wodnej i osadów z kampanii 2021 i 2022 r. Zastosowanie wielorakiej analizy czynnikowej (MFA) do sześciu zmiennych chemicznych mierzonych w każdej z pięciu warstw na 19 stacjach, na których opróbowano wszystkie warstwy, z włączeniem zmiennych hydrograficznych i charakteryzujących stanowiska jako zmiennych uzupełniających. Identyfikacja stacji stanowiących hotspoty na podstawie ich udziału w głównej osi ordynacyjnej oraz ocena, czy skład chemiczny wód przydennych odzwierciedla warunki panujące w wodach porowych.

Obszar badań

Badane fiordy rozciągają się wzdłuż gradientu arktyczno-atlantyckiego zachodniego Spitsbergenu, wzdłuż którego Prąd Zachodniospitsbergeński wnika do poszczególnych systemów fiordowych w różnym stopniu, zależnie od morfologii fiordu i głębokości progu (Cottier i in., 2005; Nilsen i in., 2008). Hornsund, położony na południu, pozostaje pod wpływem zimnych wód arktycznych i przybrzeżnych (Włodarska-Kowalczuk i in., 1998; Promińska i in., 2018) i jest podzielony płytkim progiem na basen główny i wewnętrzny basen Brepollen (Moskalik i in., 2014; Błaszczyk i in., 2019). Isfjorden, największy system fiordowy Svalbardu, składa się z kilku fiordów bocznych o kontrastujących cechach hydrograficznych - od zewnętrznych obszarów pozostających pod wpływem wód atlantyckich po zimne, oddzielone progami baseny wewnętrzne, takie jak Billefjorden (Szczuciński i in., 2009; Skogseth i in., 2020). Połączony system Kongsfjorden–Krossfjorden na północy ma stosunkowo otwarte połączenie z szelfem, co ułatwia częste wnikanie wody atlantyckiej (Hop i in., 2002; Svendsen i in., 2002; Tverberg i in., 2019). Wszystkie fiordy otrzymują wodę słodką i osady z lodowców uchodzących do morza oraz kończących się na lądzie (Smith i in., 2015; Halbach i in., 2019; Hopwood i in., 2020) i leżą na zróżnicowanym geologicznie podłożu zlewni - od prekambryjskiego podłoża krystalicznego Hornsundu (Görlich, 1986; Dallmann, 2015) po sekwencje węglanowe i piaskowcowe otaczające Kongsfjorden (Svendsen i in., 2002). Te różnice geologiczne wpływają na skład chemiczny wód porowych poprzez takie procesy jak rozpuszczanie węglanów i wietrzenie krzemianów (Wallmann i in., 2008; März i in., 2015). Fiordy te stanowią naturalne środowisko do badania biogeochemicznych reakcji na zróżnicowany stopień atlantyfikacji i wpływu lodowców (Svendsen i in., 2002; Promińska i in., 2018).

Metody

Przedstawiono tu przegląd metod zastosowanych w prezentowanych publikacjach; szczegółowe informacje analityczne i statystyczne zamieszczono w poszczególnych pracach.

Badania terenowe prowadzono na pokładzie r/v Oceania podczas letnich sezonów topnienia w latach 2021 i 2022, a trzy prace opierają się na częściowo pokrywających się zbiorach stacji i rdzeni, a nie na jednym połączonym zbiorze danych. Praca 1 opiera się na przeprowadzonym w 2021 r. przeglądzie toni wodnej w wielu fiordach - po trzy do pięciu głębokości na każdej z 33 stacji opróbowanych za pomocą rozety CTD - uzupełnionym o rdzenie o długości do około 40 cm pobrane próbnikami Niemistö i/lub GEMAX. Praca 2 opiera się na dwunastu głębszych rdzeniach osadów o długości do około 1,5 m, pobranych w 2022 r. rdzeniówką grawitacyjną i próbnikiem GEMAX.

Praca 3 łączy dane z toni wodnej i osadów z obu kampanii (2021–2022) na 19 stacjach, na których dostępne były wszystkie pięć warstw pionowych, z wykorzystaniem rdzeni o różnej długości. Wody porowe ekstrahowano próbnikami Rhizon, a głębokość wody na stacjach w trzech badaniach wynosiła od około 17 do 374 m. Mierzone zmienne obejmowały temperaturę, zasolenie i tlen rozpuszczony mierzone in situ, a także rozpuszczone nieorganiczne biogeny (NO_3^-, NH_4^+, PO_4^{3-}, DSi), rozpuszczony węgiel nieorganiczny i organiczny (DIC, DOC), Cl^-, główne kationy (Na^+, K^+, Ca^{2+}, Mg^{2+}) oraz - w wodach porowych osadów - skład trwałych izotopów węgla DIC ($\delta^{13}C_{DIC}$). Wszystkie składniki oznaczono standardowymi metodami analitycznymi z kontrolą jakości opartą na certyfikowanych materiałach odniesienia.

Masy wodne sklasyfikowano na podstawie ich właściwości termohalinowych (temperatura–zasolenie) zgodnie z ustalonymi definicjami dla Svalbardu (Cottier i in., 2005; Nilsen i in., 2008; Promińska i in., 2018), co stanowi standardowe podejście do rozdzielenia wód atlantyckich, arktycznych i lokalnie uformowanych w tych fiordach. Strumieni powrotnych przez granicę osad–woda obliczono na podstawie gradientów stężeń w wodach porowych z zastosowaniem pierwszego prawa Ficka (Berner, 1980). Podejście to jest odpowiednie dla drobnoziarnistych, zdominowanych przez dyfuzję mułów fiordowych i pozwala wyznaczyć strumienie bezpośrednio ze zmierzonych profili wód porowych. Wysładzanie wód porowych i SGD śledzono za pomocą Cl^-, który zachowuje się konserwatywnie w osadach morskich, a źródła DIC w wodach porowych scharakteryzowano na podstawie $\delta^{13}C_{DIC}$, ponieważ zremineralizowana materia organiczna, rozpuszczające się węglany i węgiel pochodzący z metanu mają odmienne sygnatury izotopowe. Wzorce przestrzenne analizowano nieparametrycznym testem Kruskala–Wallisa z porównaniami post hoc Dunna (wybranym ze względu na brak rozkładu normalnego danych i nierówną liczebność grup), HCA (metodą Warda, która wyznacza strefy geochemiczne bez z góry narzuconego podziału na grupy), LDA (użytą do sprawdzenia rozdzielności uzyskanych skupień) oraz MFA (która nadaje jednakową wagę każdej opróbowanej warstwie, dzięki czemu współzmienność między warstwami można ocenić bez dominacji którejkolwiek z nich w ordynacji).

Synteza prac badawczych

Rozprawa składa się z trzech powiązanych ze sobą prac, prowadzących od charakterystyki przestrzennych wzorców biogeochemicznych, poprzez identyfikację podstawowych procesów zachodzących w osadach, po zintegrowaną analizę oddziaływań między tonią wodną a osadami w fiordach zachodniego Spitsbergenu. Łącznie prace te dają całościowy obraz rozmieszczenia i obiegu węgla oraz związków biogenicznych w pionowym kontinuum ekosystemów fiordów arktycznych.

Pierwsza praca, „Distributions of in-situ parameters, dissolved (in)organic carbon, and nutrients in the water column and pore waters of Arctic fjords (western Spitsbergen) during a melting season" (Saghravani i in., 2024), stworzyła podstawę obserwacyjną rozprawy i realizowała Cel szczegółowy 1. W sezonie topnienia 2021 r. scharakteryzowano w niej temperaturę, zasolenie, tlen, nieorganiczne biogeny i rozpuszczony węgiel w toni wodnej i płytkich wodach porowych fiordów Hornsund, Isfjorden, Kongsfjorden i Krossfjorden. Na podstawie właściwości termohalinowych wyróżniono siedem mas wodnych: wodę powierzchniową, arktyczną, schłodzoną zimą, pośrednią, lokalną, przekształconą atlantycką oraz atlantycką. Test Kruskala–Wallisa wykazał, że większość składników różniła się istotnie między fiordami i między masami wodnymi. Hornsund, w którym nie stwierdzono wody atlantyckiej ani przekształconej wody atlantyckiej, okazał się systemem najbardziej wzbogaconym w biogeny i DIC, pozostającym głównie pod wpływem wód arktycznych i przybrzeżnych (Włodarska-Kowalczuk i in., 1998), podczas gdy Kongsfjorden wykazywał najwyraźniejszą sygnaturę atlantycką. Woda Lokalna, występująca wyłącznie w fiordzie Isfjorden, charakteryzowała się najwyższymi stężeniami NO_3^-, PO_4^{3-}, DSi i DIC spośród wszystkich mas wodnych. Powierzchniowe wody porowe były wzbogacone w NH_4^+, PO_4^{3-}, DSi i DIC względem wód przydennych, miejscami o ponad rząd wielkości, co wskazuje na znaczny potencjał wymiany bentosowo-pelagicznej. Dzięki zastosowaniu jednolitej metodyki we wszystkich fiordach i zdeponowaniu pełnego zbioru danych w otwartym repozytorium publikacja ta ustanowiła przestrzenny i składowy punkt odniesienia dla kolejnych badań procesowych.

Druga praca, „Nutrients and carbon cycling in marine sediments of Arctic fjords" (Saghravani i in., w recenzji), opierając się na tych wzorcach, przeszła od analizy opisowej do mechanistycznej, realizując Cel szczegółowy 2. W 2022 r. pobrano dwanaście rdzeni osadów o długości do około 1,5 m i przeanalizowano w nich biogeny, rozpuszczony węgiel, Cl^- oraz skład trwałych izotopów węgla DIC w wodach porowych. Metodą HCA wyodrębniono pięć stref geochemicznych (HC1–HC5) odpowiadających głębokości w osadzie: natlenioną, bogatą w azotany strefę płytką pozostającą w wymianie z wodą przydenną; strefy pośrednie wzbogacone w DSi, NH_4^+, DOC i PO_4^{3-}, w których remineralizacji ulega labilna materia organiczna; oraz strefy głębsze o najwyższych stężeniach DIC, DOC, PO_4^{3-} i DSi, w których słabo przepuszczalne muły i rozpuszczanie minerałów sprzyjają akumulacji substancji rozpuszczonych. Wartości $\delta^{13}C_{DIC}$, mieszczące się w zakresie od około +1 do −14‰, wraz z ujemną zależnością między DIC a $\delta^{13}C_{DIC}$ wskazują, że w dynamice węgla dominują rozpuszczanie węglanów i remineralizacja materii organicznej, a nie utlenianie metanu. Stężenia Cl^- maleją z głębokością na dwóch stanowiskach w Hornsundzie, co wskazuje na wysładzanie wód porowych zgodne z SGD (Kim i in., 2022). Porównanie objętych i nieobjętych wysładzaniem głębokich skupień sugeruje,

że to źródło wody słodkiej wprowadza azot nieorganiczny, a jednocześnie rozcieńcza DIC, fosforany i krzemionkę. Strumieni powrotnych, obliczone według pierwszego prawa Ficka, znacząco odbiegały od stechiometrii Redfielda–Brzezińskiego: stosunki strumieni azotu do fosforu (N:P) wynosiły średnio 0,2 w Hornsundzie, 6,2 w fiordzie Isfjorden i 10,1 w fiordzie Kongsfjorden, a więc poniżej oczekiwanej wartości 16:1. W fiordzie Krossfjorden ujemne strumienie (skierowane do osadów) wskazywały na pobieranie netto lub akumulację, w związku z czym wyłączono je z analizy stosunków. Stosunki strumieni N:DSi wynosiły 2,9 w Hornsundzie, 6,5 w fiordzie Isfjorden i 43,4 w fiordzie Kongsfjorden, we wszystkich przypadkach przekraczając oczekiwaną wartość ~1,1 (16:15), przy czym największy nadmiar azotu względem krzemu stwierdzono w Kongsfjorden. Hornsund cechował się wyraźnym uwalnianiem fosforu i krzemu względem azotu przy niskim strumieniu azotu, co jednak niekoniecznie oznacza limitację azotem w wodach nadległych. Kongsfjorden z kolei wykazywał największy nadmiar azotu względem krzemu. Ogólnie odchylenia od stechiometrii Redfielda–Brzezińskiego różniły się między fiordami, odzwierciedlając regionalną heterogeniczność (Koziorowska i in., 2018; Morata i in., 2020).

Trzecia praca, „Covariation of dissolved nutrients and carbon in seawaters and sediment porewaters of western Svalbard fjords" (Saghravani i in., 2026), połączyła dane z toni wodnej i osadów w celu realizacji Celu szczegółowego 3. Bada ona, w jaki sposób sygnały pochodzące z osadów są powiązane z leżącą nad nimi tonią wodną oraz które stanowiska mają nieproporcjonalnie duży udział w zmienności podpowierzchniowej. MFA sześciu zmiennych chemicznych w pięciu warstwach - wodzie powierzchniowej, wodzie przydennej, wodzie nad osadem oraz górnej i dolnej warstwie wód porowych - na dziewiętnastu stacjach wykazała, że wody głębokie i wody porowe tworzą jeden system: woda przydenna, woda nad osadem i wody porowe wykazywały silne ładunki na pierwszej osi ordynacyjnej (0,65–0,72), podczas gdy woda powierzchniowa była od nich odseparowana, co odzwierciedla letnią stratyfikację. Ścisły związek między składem chemicznym wody przydennej a wód porowych sugeruje, że skład wody przydennej odzwierciedla sygnały pochodzące z leżących poniżej osadów, co daje praktyczny sposób wykrywania aktywności bentosowej poprzez opróbowanie toni wodnej i bezpośrednio odpowiada na Cel szczegółowy 3. Co istotne, trzy stanowiska - w oddzielonym progiem Billefjorden oraz w głębokim basenie głównym Hornsundu - miały nieproporcjonalnie duży udział w tej osi, odpowiadając za około 73% jej wariancji, i wyróżniały się jako wzbogacone człony skrajne na tle poziomu odniesienia o niższych stężeniach, wyznaczonego przez pozostałe stanowiska. Hotspoty te łączyło ograniczone odnawianie wód głębokich oraz dopływ materii organicznej; tam, gdzie warunki te nie występowały łącznie, jak w wewnętrznym basenie Brepollen, hotspoty były słabiej rozwinięte, co wskazuje, że samo ograniczenie wymiany wód w basenie nie jest wystarczające. Zmienność między

basenami w obrębie jednego fiordu często przewyższała różnice między fiordami, prowadząc do wniosku, że fiordy zachodniego Spitsbergenu funkcjonują jako mozaika odrębnych środowisk biogeochemicznych. To niewielka liczba lokalnie kontrolowanych hotspotów, a nie systematyczne gradienty w skali fiordu, w głównej mierze kształtuje podpowierzchniowy obieg związków biogenicznych i węgla (Cottier i in., 2005; Skogseth i in., 2020).

Łącznie trzy prace wykazały, że fiordy arktyczne funkcjonują jak mozaiki, w których fizyczna izolacja i dostawa materii organicznej, działając synergicznie, koncentrują obieg węgla i związków biogenicznych w określonych miejscach. Ta przestrzenna konfiguracja jest często pomijana w opisach geograficznych lub uśrednionych dla całego fiordu i należy oczekiwać, że będzie ewoluować w miarę, jak tworzenie się wód zimowych, wnikanie wód atlantyckich i dopływ wód słodkich będą nadal przekształcać środowisko (Tverberg i in., 2019; Diak i in., 2023).

Osiągnięcia

- Utworzono kompleksowy zbiór danych obserwacyjnych obejmujący związki biogeniczne, rozpuszczony węgiel nieorganiczny i organiczny oraz parametry hydrograficzne w fiordach zachodniego Spitsbergenu. Zbiór ten obejmuje toń wodną i wody porowe osadów i został udostępniony publicznie na potrzeby dalszych badań arktycznych [Artykuły naukowe 1, 2, 3].
- Wykazano silne zróżnicowanie biogeochemiczne między masami wodnymi i systemami fiordowymi. Analizy statystyczne wykazały, że stężenia związków biogenicznych i węgla różniły się istotnie między fiordami i masami wodnymi, ujawniając odrębne sygnatury biogeochemiczne związane z wodami pozostającymi pod wpływem arktycznym i atlantyckim. Woda arktyczna w Hornsundzie była względnie wzbogacona w biogeny (z wyjątkiem NH_4^+) i DIC w porównaniu z fiordem Isfjorden, natomiast woda lokalna w fiordzie Isfjorden charakteryzowała się najwyższymi stężeniami NO_3^-, PO_4^{3-}, DSi i DIC spośród badanych mas wodnych [Artykuł naukowy 1].
- Wyodrębniono pięć związanych z głębokością stref geochemicznych osadów za pomocą hierarchicznej analizy skupień i LDA oraz wykorzystano zależność DIC-$\delta^{13}C_{DIC}$ do przypisania węgla w głębokich wodach porowych rozpuszczaniu węglanów i remineralizacji materii organicznej [Artykuł naukowy 2].
- Zidentyfikowano wysładzanie wód porowych na dwóch stanowiskach w Hornsundzie i wykazano jego wpływ na biogeochemię osadów. Zubożenie w Cl^- w głębokich wodach porowych zinterpretowano jako świadectwo domieszki wody słodkiej zgodnej z SGD. Porównanie wysłodzonych i niewysłodzonych

wód porowych wykazało wyższe stężenia azotu nieorganicznego, lecz niższe stężenia DIC, PO_4^{3-} i DSi w wodach wysłodzonych [Artykuł naukowy 2].

- Ilościowo określono przestrzennie zmienne strumieni powrotnych węgla i związków biogenicznych oraz wykazano odchylenia od stechiometrii Redfielda–Brzezińskiego. Wyniki pokazały, że osady mogą pełnić rolę źródła lub pochłaniacza związków biogenicznych w zależności od stanowiska, przy wysokim uwalnianiu fosforu w Hornsundzie i ujemnych strumieniach azotu i fosforu na niektórych stanowiskach w fiordzie Kongsfjorden. Zaobserwowane stosunki strumieni N:P i N:DSi (średnie dla fiordów N:P od 0,2 do 10,1 wobec 16:1; N:DSi od 2,9 do 43,4 wobec ~1.1=16:15) odbiegały od referencyjnych stosunków Redfielda–Brzezińskiego, wskazując, że bentosowa regeneracja związków biogenicznych jest silnie specyficzna dla poszczególnych fiordów i stanowisk [Artykuł naukowy 2].
- Ujawniono silną heterogeniczność w skali basenów i zidentyfikowano hotspoty biogeochemiczne w fiordach zachodniego Spitsbergenu. Trzy stacje odpowiadały za około 73% wariancji wzdłuż dominującego wymiaru MFA. "Hotspoty" te występowały w basenach o ograniczonej wymianie wód, cechujących się ograniczonym odnawianiem wód głębokich oraz dostawą labilnej materii organicznej. Różnice między basenami w obrębie poszczególnych systemów fiordowych były często równie duże lub większe niż różnice między systemami fiordowymi, co przemawia za mozaikowym, a nie gradientowym w skali fiordu, charakterem podpowierzchniowej biogeochemii [Artykuł naukowy 3].
- Wykazano silne sprzężenie między biogeochemią wód przydennych a wód porowych osadów w skali stacji pomiarowej. MFA wykazała, że woda przydenna, woda nad osadem oraz górna i dolna warstwa wód porowych silnie się współzmieniały, podczas gdy wody powierzchniowe były w dużej mierze od nich odseparowane. Sugeruje to, że skład chemiczny wody przydennej integruje przestrzenną zmienność leżącego poniżej środowiska biogeochemicznego osadów, umożliwiając identyfikację hotspotów w wodach porowych - przynajmniej częściowo - na podstawie opróbowania toni wodnej [Artykuł naukowy 3].

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Research Articles

The doctoral dissertation is based on the three original research articles reproduced in full below. They are arranged in a logical rather than chronological sequence, progressing from a descriptive characterization of spatial biogeochemical patterns, through a mechanistic quantification of benthic sediment–water exchange, to an integrated assessment of vertical connectivity and the identification of biogeochemical hotspots across the water column and sediment of western Spitsbergen fjords.

Artykuły naukowe

Niniejsza rozprawa doktorska opiera się na trzech oryginalnych artykułach naukowych, zamieszczonych poniżej w pełnym brzmieniu. Zostały one uporządkowane w kolejności logicznej, a nie chronologicznej – od opisowej charakterystyki przestrzennych wzorców biogeochemicznych, poprzez mechanistyczną ocenę ilościową wymiany bentosowej między osadem a wodą, po zintegrowaną analizę pionowej łączności i identyfikację hotspotów biogeochemicznych w toni wodnej i osadach fiordów zachodniego Spitsbergenu.

RESEARCH ARTICLE 1

EARTH SYSTEM SCIENCE DATA

Distributions of in situ parameters, dissolved (in)organic carbon, and nutrients in the water column and pore waters of Arctic fjords (western Spitsbergen) during a melting season

Rozmieszczenie parametrów in situ, rozpuszczonego węgla (nie)organicznego oraz substancji biogenicznych w toni wodnej i wodach porowych fiordów arktycznych (zachodni Spitsbergen) w sezonie topnienia

Seyed Reza Saghravani, Michael Ernst Böttcher, Wei-Li Hong, Karol Kuliński, Aivo Lepland, Arunima Sen, Beata Szymczycha

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Open Access Earth System Science Data

Distributions of in situ parameters, dissolved (in)organic carbon, and nutrients in the water column and pore waters of Arctic fjords (western Spitsbergen) during a melting season

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Abstract. A nutrient distribution, such as that of phosphate (PO_4^{3-}), ammonium (NH_4^+), nitrate (NO_3^-), dissolved silica (Si), total dissolved nitrogen (TN), and dissolved organic nitrogen (DON), together with dissolved organic carbon (DOC) and inorganic carbon (DIC), was investigated during a high-melting season in 2021 in the western Spitsbergen fjords (Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden). Both the water column and the pore water were investigated for nutrients and dissolved carbon distribution and gradients. The water column concentrations of most measured parameters, such as PO_4^{3-}, NH_4^+, NO_3^-, Si, and DIC, showed significant changes among fjords and water masses. In addition, pore water gradients of PO_4^{3-}, NH_4^+, NO_3^-, Si, DIC, and DOC revealed significant variability between fjords and are likely substantial sources of the investigated elements for the water column. The reported dataset reflects differences in hydrography and biogeochemical ecosystem functions of the investigated western Spitsbergen fjords and may form the base for further modeling of physical oceanographic and biogeochemical processes within these fjords. All data discussed in this communication are stored in the Zenodo online repository at https://doi.org/10.5281/zenodo.11237340 (Szymczycha et al., 2024).

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1 Introduction

The Arctic is facing significant and rapid transformations due to Arctic amplification accelerating climate change in the region (Dunse et al., 2022). The warming of the climate causes a change in oceanic and atmospheric circulation patterns, permafrost degradation, and decrease in the thickness and extent of sea ice, as well as shrinkage of glaciers (IPCC, 2022; Dunse et al., 2022). Freshwater released from glacial meltwater runoff or frontal ablation and accompanying fluxes of solutes is a significant factor that changes the hydrographic pattern and biogeochemistry of water masses, which in turn affects the biological productivity in the ocean and fjords (Hopwood et al., 2016, 2020).

Many studies have investigated the biogeochemistry of nutrients in the Barents Sea and Arctic region (Henley et al., 2020; Gundersen et al., 2022; Tuerena et al., 2022). Substantial efforts have been made in existing Arctic monitoring programs, research initiatives, and scientific projects to describe, explain, and predict environmental changes due to diverse pressures on the Arctic ecosystem (Townhill et al., 2022). Studies indicate that net primary production in open Arctic waters is mainly sustained by the upwelling of nutrients and light availability (Henley et al., 2020; Stroeve et al., 2021), while nitrogen is considered to be the key limiting nutrient in the Arctic Ocean (Mills et al., 2018; Ko et al., 2020). In addition, Henley et al. (2020) indicated that, with ongoing sea ice losses due to Atlantification, the expected shift from more Arctic-like ice-impacted conditions to more Atlantic-like ice-free conditions is projected to increase nutrient availability and the duration of the vegetation period in the Arctic shelf region.

Arctic fjords have not gained similar attention, and investigations were usually focused on individual fjord systems (Codispoti et al., 2013; Henley et al., 2020; Kim et al., 2022; Pogojeva et al., 2022). Spatially wide studies of fjords and investigations focusing on the hydrography and biogeochemical functioning of the Arctic shelf seafloor are still lacking. To address the existing knowledge gaps, we studied the water masses and pore waters together with their biogeochemical composition in the western Spitsbergen fjords. The selected area is an excellent research site for investigating the effects of both rapidly occurring climate change and varied levels of Atlantification, as different fjords are under the diverse impact of the East Spitsbergen Current, bringing cold Arctic water (ArW), and the West Spitsbergen Current, carrying warmer and more saline Atlantic water (AtW). This was also our motivation for releasing this macronutrient dataset, which we believe may constitute a biogeochemical reference for other experimental and modeling research in the region.

2 Materials and methods

2.1 Study area description

The west coast of the Svalbard archipelago (76–80° N) consists of different fjords and sub-fjords (Fig. 1). All investigated fjords (Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden) are influenced by the East Spitsbergen Current, carrying cold ArW from the Barents Sea, and the West Spitsbergen Current, with warmer and more saline AtW from the Norwegian Sea (Promińska et al., 2018) (Fig. 1, Table 1). When AtW mixes with ArW, the warmer transformed Atlantic water (TAW) forms (Table 1, Cottier et al., 2005). Surface water (SW) (Table 1) is formed locally from glacial melt and river runoff and occupies the surface layer of the fjord. Intermediate water (IW) forms as a result of mixing AtW or TAW with overlying fresher SW. Local water (LW) and winter-cooled water (WCW) usually form during autumn and winter (Cottier et al., 2005; Hop et al., 2006; Cantoni et al., 2020) in depressions within the inner fjords.

Hornsund is located on the southern end of Spitsbergen and is about 30 km long and 15 km wide (Fig. 1). The fjord is divided into the main basin and inner basin (Brepollen) by a shallow sill located in the center of the fjord (Błaszczyk et al., 2019). The average depth is approximately 90 m, while the deepest section reaches 250 m (Moskalik et al., 2014). Sediments consist of mud and sandy mud, laminated mud, homogeneous to bioturbated mud, and sandy gravel (Drewnik et al., 2016). Freshwater discharge to the fjord was estimated to be approximately 1.8 km^3 annually (Węsławski et al., 1991), mainly due to glacier melting (64 %), with the fastest retreating rate being in Svalbard (with an average rate of between 100 and $> 200\,m\,yr^{-1}$; Grabiec et al., 2018). Other freshwater sources, such as frontal ablation and river runoff, primarily influence the upper water column (Zaborska et al., 2020). Hornsund exhibits high nutrient enrichment and experiences a strong influence from the ArW and colder coastal water (Włodarska-Kowalczuk et al., 1998). These conditions contribute to greater productivity in Hornsund compared to the warmer and saline fjords (Santos-Garcia et al., 2022).

Isfjorden stands as the largest fjord system on Spitsbergen, with about 100 km in length from the mouth to the head and up to 425 m in depth (Table 1). Isfjorden has several sub-fjords and bays. Studies conducted in Isfjorden have provided evidence of the significant impact of freshwater on the water column (McGovern et al., 2020; Finne et al., 2022). Seasonal stratification has been responsible for the retention of terrestrial carbon and nutrients within the euphotic zone and a decrease in vertical mixing during the most productive season (McGovern et al., 2020; Finne et al., 2022). The enhanced freshwater input contributes to the overall nutrient loading in the system, affecting the biogeochemical processes and ecosystem functioning.

Kongsfjorden is about 20 km long and up to 10 km wide, with an orientation from the southeast to the northwest

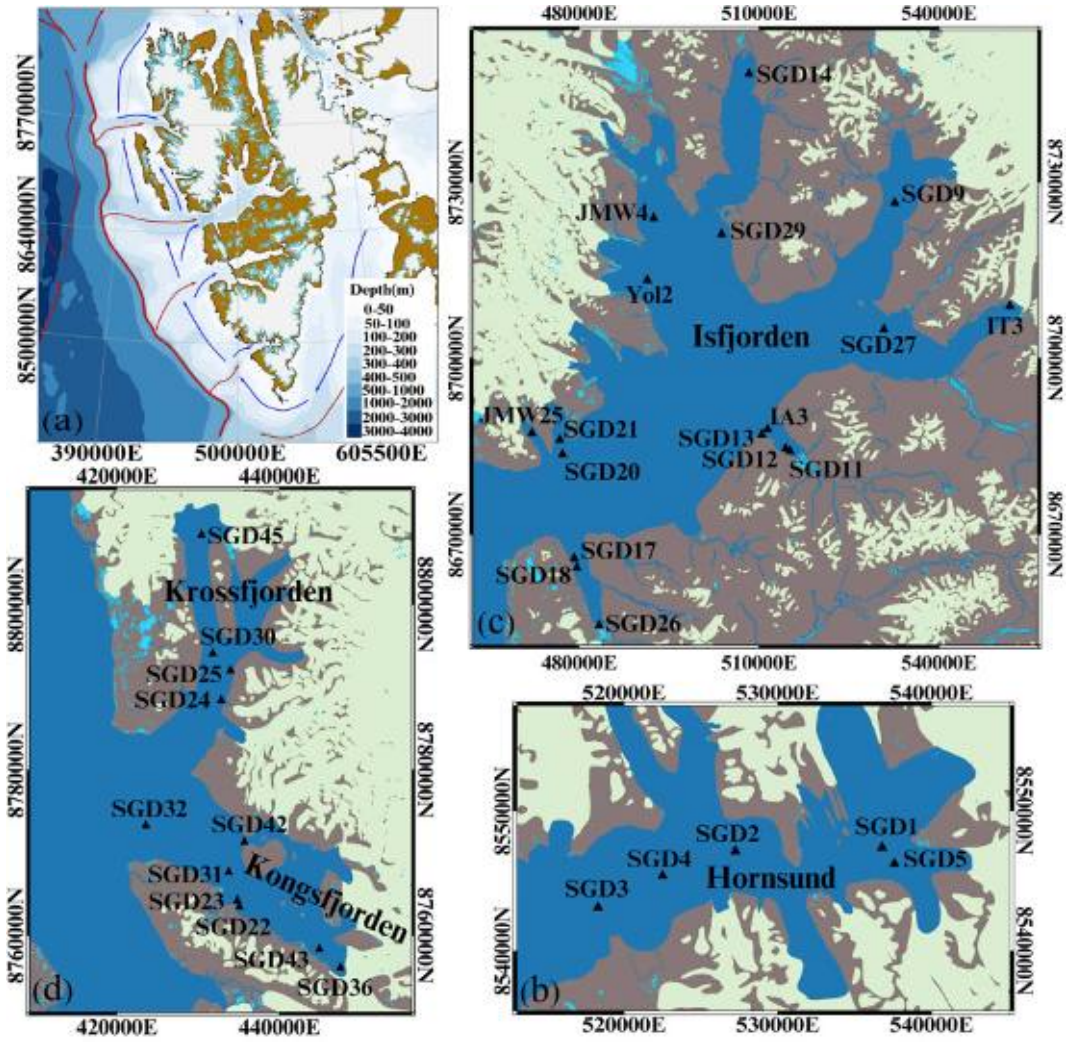

Figure 1. **(a)** The study area, including the general map of Spitsbergen, highlighting the depths of the fjords and the surrounding Svalbard shelf **(a)**. The warm West Spitsbergen Current and cold East Spitsbergen Current are indicated by red and blue arrows, respectively (Vihtakari, 2024, 2019). Study sites located in **(b)** Hornsund, **(c)** Isfjorden, and **(d)** Kongsfjorden and Krossfjorden are presented as black triangles.

(Promińska et al., 2017, Table 1). The depth at the mouth of the fjord is about 360 m and decreases towards the inner part, where it does not exceed 100 m (Svendsen et al., 2002). Kongsfjorden has remained sea-ice-free since 2011, invoking profound biogeochemical transformations (Hop and Wiencke, 2019; Pavlova et al., 2019). Unlike other Arctic fjords, it experiences a distinct influence of the intrusion of warm and saline waters (Hodal et al., 2012). The inflow of AtW and ArW from one side and glacier meltwater from another (Halbach et al., 2019) leads to amplified nutrients and carbon cycling, enhanced net primary productivity, and oxygen depletion in deeper waters (Santos-Garcia et al., 2022).

Krossfjorden exhibits a northeast-to-southwest orientation, stretching approximately 30 km in length and reaching widths from 3 to 6 km (Table 1). The total volume of Krossfjorden is 25 km^3, and its maximum depth is 373 m (Svendsen et al., 1992). Krossfjorden, characterized by a colder spring and less intrusion of AtW, shares similar conditions with the inner part of Kongsfjorden. However, it experiences a shorter period of glacier retreat compared to Kongsfjorden (Gamboa-Sojo et al., 2022). Studies on chlorophyll and other pigment distribution in surface sediments suggest that Krossfjorden is more productive than Kongsfjorden (Singh and Krishnan, 2019).

2.2 Sampling and analyses

Sampling was carried out from 25 July to 20 August 2021 on board the R/V *Oceania*, belonging to the Institute of Oceanology, Polish Academy of Sciences (IOPAN). A towed CTD profiling system (rosette) equipped with 10 L Niskin bottles was used to collect water samples from three to five depths at each location (selected based on salinity and oxy-

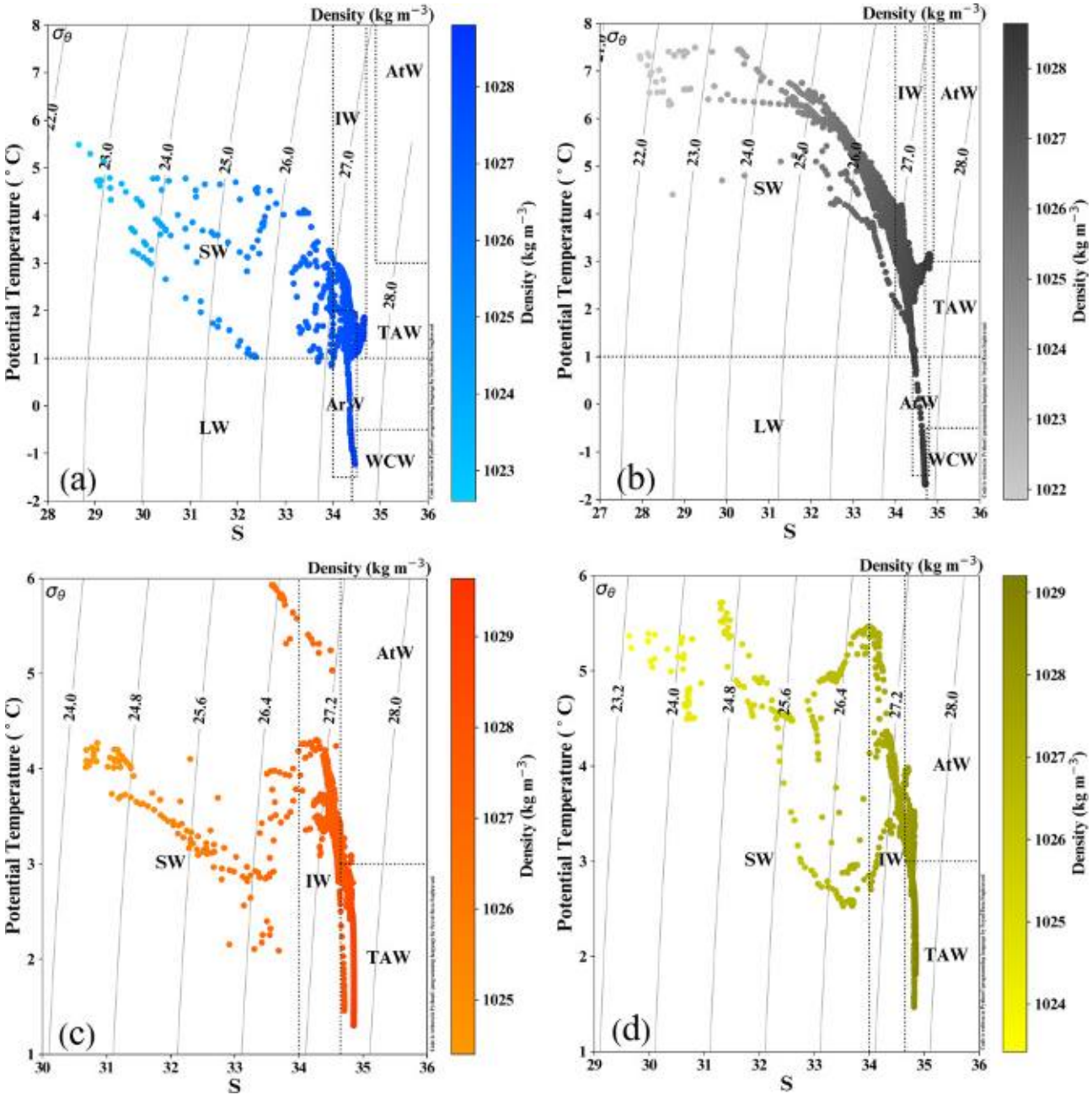

Figure 2. The water mass distribution, including surface water (SW), Arctic water (ArW), winter-cooled water (WCW), intermediate water (IW), local water (LW), transformed Atlantic water (TAW), and Atlantic water (AtW) in **(a)** Hornsund, **(b)** Isfjorden, **(c)** Kongsfjorden, and **(d)** Krossfjorden.

gen profiles). Temperature (T), salinity (S), and oxygen (O_2) concentration were measured in situ using a Sea-Bird Scientific SBE 911plus CTD profiler equipped with oxygen module SBE 43 (calibrated prior to the cruise). The accuracy of T, S, and O_2 is equal to ± 0.002 °C, ± 1 %, and ± 0.015 %, respectively. The results of averaged data for 0.5 m intervals are presented in the database. Temperature and salinity from layers where discrete samples were collected were used for an oceanographic classification of water masses.

2.2.1 Seawater sampling

Exactly 10 mL of seawater was filtered (cellulose acetate filters with a pore size of 0.45 µm), frozen in a pre-cleaned high-density polyethylene (PE) bottle, and stored at −20 °C for further nutrient analysis. The seawater for DIC analysis

was transferred into the pre-cleaned 250 mL glass bottle and poisoned with 100 µL saturated $HgCl_2$. Furthermore, 20 mL of seawater for DOC and TN analysis was filtered through pre-combusted 0.45 µm MN GF-5 filters, transferred into the pre-combusted glass bottle, and acidified to pH ∼ 2 with $HCl_{conc.}$ to stop mineralization and remove carbonates.

2.2.2 Pore water sampling

GEMAX and Nemisto gravity corers were used to collect up to approximately 40 cm long sediment cores. However, the retrieval of the cores in some locations was not possible due to the consolidated seafloor. Additionally, the pore water extracted from some sediment cores was insufficient to perform all analyses. Pore water was extracted from sediments through pre-drilled holes in the core liners via Rhizon® samplers (Rhizosphere; diameter of 2.5 mm and mean pore size of 0.15 µm) directly after extracting the cores. Up to 5 mL of pore water was frozen in a pre-cleaned high-density polyethylene bottle and stored at −20 °C for further nutrient analysis, and approximately 2 mL of pore water was kept in PE vials for further Cl^- analysis. For further DIC, DOC, and TN analysis, 12 mL of pore water was transferred into the pre-combusted glass bottle and poisoned with 50 µL saturated $HgCl_2$. Seawater pH was measured with a WTW 3400i multi-parameter field meter that yielded an accuracy of ±0.1. The pH results are given for a reference temperature of 25 °C.

2.2.3 Chemical analyses

Nutrient concentrations were determined using a SEAL AA500 AutoAnalyzer (Seal Analytical) and applying standard photometric methods (Grasshoff et al., 2009). Quality control consists of repeated measurements of two different CRMs (QC3179 by Sigma Aldrich and HAMIL by Environment Canada). Method detection limits are 0.33 µmol L^{-1} for nitrate (NO_3^-), 0.27 µmol L^{-1} for NH_4^+, 0.1 µmol L^{-1} for phosphate (PO_4^{3-}), and 0.3 µmol L^{-1} for dissolved silicates (Si). The accuracy of NO_3^-, NH_4^+, PO_4^{3-}, and Si measurements was 98.8 %, 98.8 %, 99.0 %, and 100.1 %, respectively, while the precision was 0.01, 0.02, 0.01, and 0.03 µmol L^{-1}, respectively. Chloride (Cl^-) was determined by titration (Mohr's method), with a precision of 0.1 mmol L^{-1}. The DIC analyses were carried out based on sample acidification with Apollo SciTech's AS-C6L DIC analyzer, equipped with the laser-based CO_2 detector (LI-7815; Li-Cor, USA). The accuracy of DIC measurements was ensured using certified reference materials (CRMs; batch nos. 190 and 195) by Andrew Dickson (Scripps Institution of Oceanography, USA), and the precision was obtained from triplicate measurements of individual samples and was not worse than ±3 µmol L^{-1}, with an average recovery of 99.0 %. The DOC and TN analyses were done in a TOC-L analyzer (Shimadzu) using a high-temperature (680 °C) oxidation method with Pt as the catalyst. The precision of the DOC measurements was ±4 µmol L^{-1}; the accuracy was determined by repeated measurements of the certified reference materials (CRMs) provided by the laboratory of Dennis A. Hansell (University of Miami, USA), and the recovery was 99 %. The accuracy of the TN measurements was guaranteed using the same CRMs used to determine DOC, ad average recovery was 97 %. DON was determined by subtracting the sum of NO_3^- and NH_4^+ from TN results.

2.3 Statistics and data analysis

All statistical analyses were carried out using Statistica (version 13), while the evaluation of the statistical significance was made using the Kruskal–Wallis test. Figure 1 was prepared using the map of Svalbard. Temperature–salinity (TS) diagrams were made using the Python programming language, while box plots were made by means of Statistica.

3 Data description

3.1 Water mass distribution

Different water masses were distinguished within the investigated fjords (Fig. 2; Szymczycha et al., 2024). The classification was done based on Cottier et al. (2005), Nilsen et al. (2008), and Promińska et al. (2018) separately for each fjord (Table 1). All the identified water masses align with those previously recognized in Arctic regions (Rudels et al., 2000), with some interesting differences found between the fjords. In Hornsund, SW, ArW, WCW, and IW were found. In Isfjorden, SW, ArW, IW, LW, and TAW occurred. In Kongsfjorden and Krossfjorden, IW, TAW, and AT were observed. It is worth noticing that Hornsund did not show any impact of TAW and AtW.

3.2 Water column data

The distribution of T, S, pH, O_2, NO_3^-, NH_4^+, PO_4^{3-}, Si, DIC, DOC, TN, and DON in summer 2021 in western Spitsbergen fjords was investigated. The obtained results were divided into fjords such as Hornsund (marked blue), Isfjorden (marked grey), Kongsfjorden (marked red), and Krossfjorden (marked yellow) (Fig. 3; Szymczycha et al., 2024). In all studied fjords, similar trends were observed, such as a decrease in T and pH and an increase in S, NO_3^-, NH_4^+, PO_4^{3-}, Si, DIC, and TN with depth, while O_2, DOC, and DON were variable with depth and did not show any patterns. To show the variability in measured parameters between fjords and separate the most freshened surface waters, the results were divided into the surface water layer (the uppermost layer up to 5 m based on salinity and temperature) and the bottom water (the lowermost layer in the water column) in each fjord (Fig. 4). Generally, the temperature of the surface water was warmer than that of the bottom water and shows a significant difference between the

Table 1. Salinity and temperature of various water masses in fjords. The classification was done based on Cottier et al. (2005), Nilsen et al. (2008), and Promińska et al. (2018) separately for each fjord.

	Hornsund (Nilsen et al., 2008)		Isfjorden (Nilsen et al., 2008)		Kongsfjorden–Krossfjorden (Cottier et al., 2005)	
	Temperature [°C]	Salinity	Temperature [°C]	Salinity	Temperature [°C]	Salinity
Arctic water (ArW)	$-1.5 > T > 2$	$34 < S < 34.5$*	$-1.5 > T > 1$	$34.4 < S < 34.8$	$-1.5 > T > 1$	$34.30 < S < 34.80$
Atlantic water (AW)	$T > 3$	$S > 34.9$	$T > 3$	$S > 34.9$	$T > 3$	$S > 34.65$
Intermediate water (IW)	$T > 1$	$34 < S < 34.7$	$T > 1$	$34 < S < 34.7$	$T > 1$	$34.00 < S < 34.65$
Local water (LW)	$T < 1$		$T < 1$		$-1.5 > T > 1$	$34.30 < S < 34.85$
Surface water (SW)	$T > 1$	$34 < S$	$T > 1$	$34 < S$	$T > 1$	$S < 34$
Transformed Atlantic water (TAW)	$T > 1$	$34.7 < S < 34.9$	$T > 1$	$S > 34.7$	$1 > T > 3$	$S > 34.65$
Winter-cooled water (WCW)	$T < -0.5$	$S > 34.4$	$T < -0.5$	$S > 34.74$	$T < -0.5$	$34.40 < S < 35$

* Promińska et al. (2018).

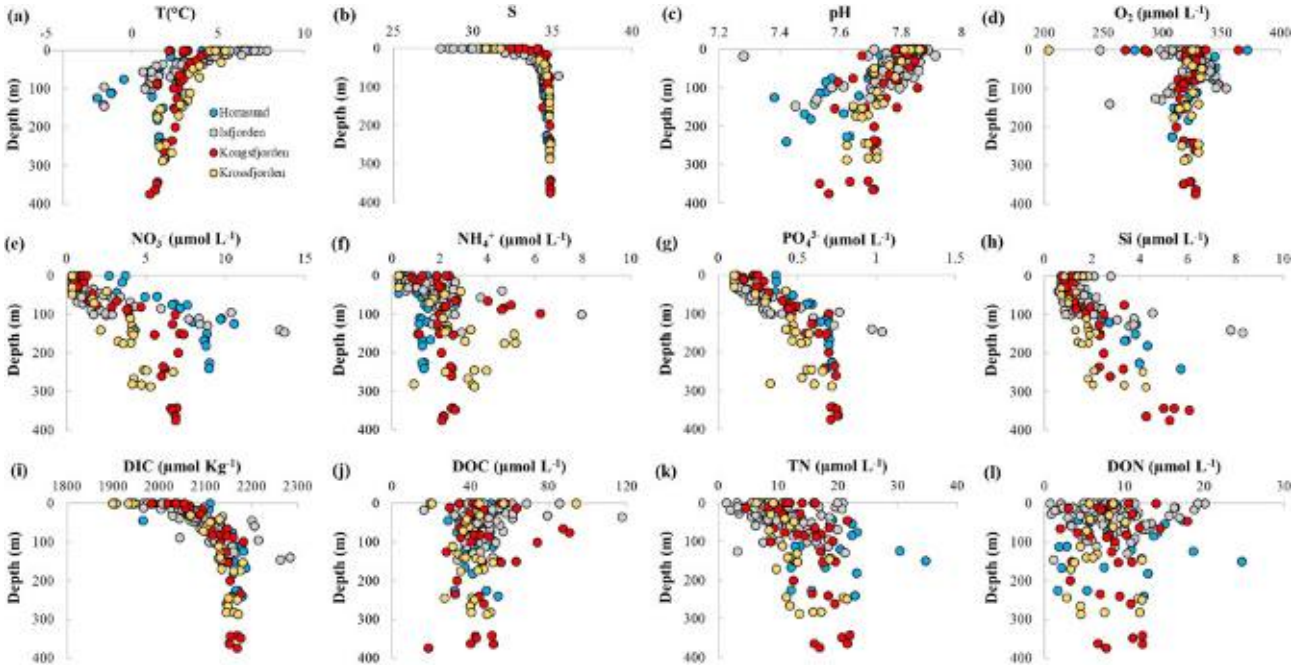

Figure 3. The distribution of **(a)** temperature (T), **(b)** salinity (S), **(c)** pH, **(d)** oxygen (O_2), **(e)** nitrate (NO_3^-), **(f)** ammonium (NH_4^+), **(g)** phosphate (PO_4^{3-}), **(h)** dissolved silica (Si), **(i)** dissolved inorganic carbon (DIC), **(j)** dissolved organic carbon (DOC), **(k)** total dissolved nitrogen (TN), and **(l)** dissolved organic nitrogen (DON) in Hornsund (marked blue), Isfjorden (marked grey), Kongsfjorden (marked red), and Krossfjorden (marked yellow).

fjords ($p = 0.00005$), with the highest being in Isfjorden and the coldest in Kongsfjorden. The bottom water temperature was similar in all fjords ($p = 0.1732$), however, only reaching negative values in Hornsund. Salinity was much higher in bottom water (median > 34) than in surface water (median < 33.5) and did not show significant differences between fjords ($p < 0.05$) in both surface and bottom water. The pH of the surface water was high (median > 7.8) and did not vary significantly between the fjords, while the pH of the bottom water was lower than the pH of the surface water and differed significantly between the fjords ($p = 0.0109$). The median concentration of O_2 in both surface and bottom water was comparable and ranged from 308.8 to 333.8 µmol L^{-1}. NO_3^-, NH_4^+, PO_4^{3-}, and DIC showed a significant difference in the median concentration between surface and bottom water and significantly varied between fjords in both water types ($p < 0.05$). Si showed a pattern similar to that of the other nutrients; however, in Isfjorden, no significant change was observed between the surface and bottom water. DOC did not change substantially between fjords and between water types. Interestingly, DOC, TN, and DON showed similar behavior in all fjords.

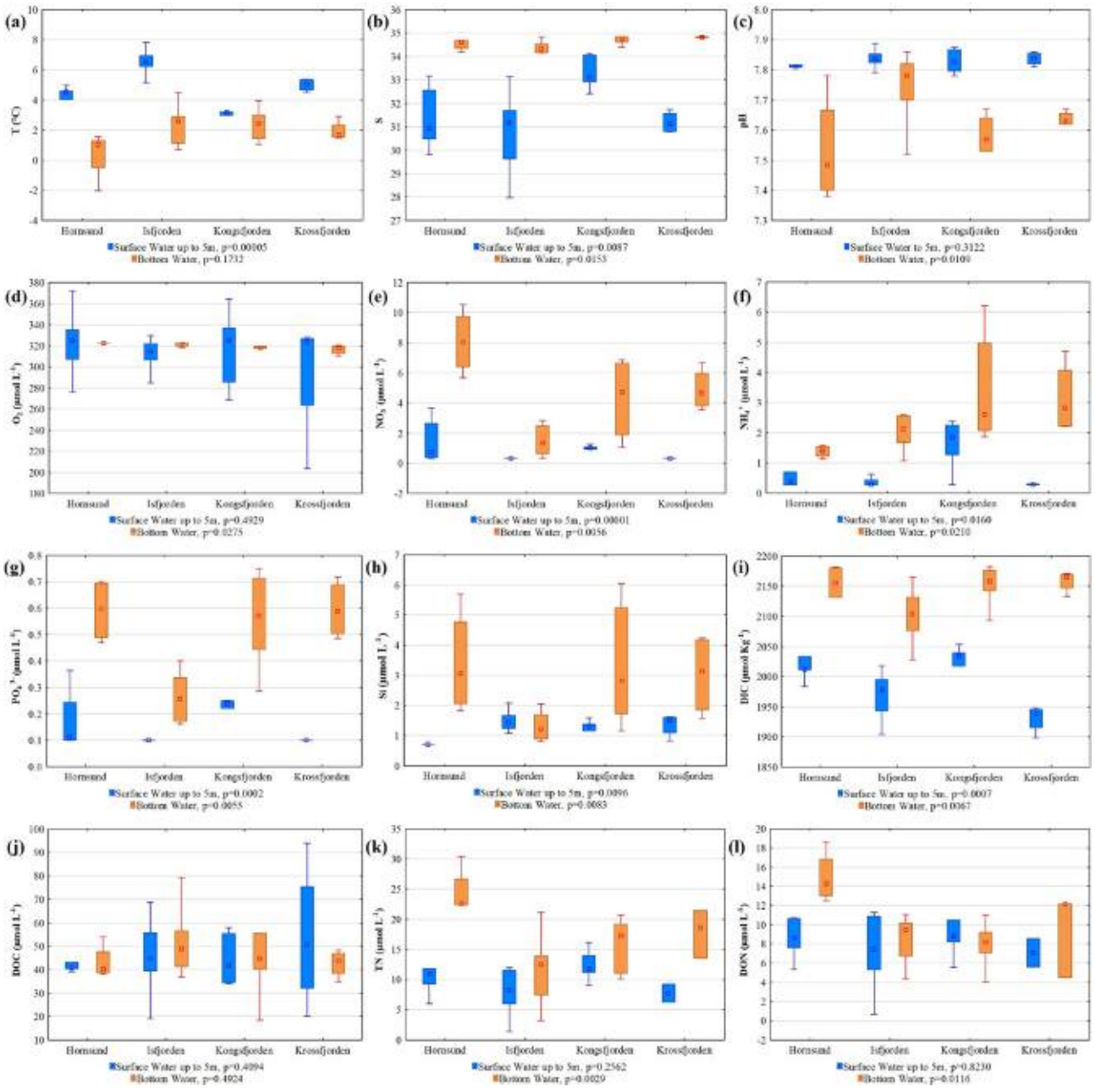

Figure 4. Box plots of **(a)** temperature (T), **(b)** salinity (S), **(c)** pH, **(d)** oxygen (O_2), **(e)** nitrate (NO_3^-), **(f)** ammonium (NH_4^+), **(g)** phosphate (PO_4^{3-}), **(h)** dissolved silica (Si), **(i)** dissolved inorganic carbon (DIC), **(j)** dissolved organic carbon (DOC), **(k)** total dissolved nitrogen (TN), and **(l)** dissolved organic nitrogen (DON) in surface water (marked blue) and bottom water (marked orange) in Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden. The p values indicate significant differences in the median concentration of the parameter between the investigated fjords.

3.3 Biogeochemistry of the water masses

In general, all fjord systems are transition zones between land and sea, resulting in complex and dynamic environments (Schlegel et al., 2023). The west Spitsbergen fjords are highly stratified (Fig. 3) and provide a pathway for the exchange of heat, salt, nutrients, and dissolved carbon between near-glacier waters and adjacent coastal regions (Hopwood et al., 2020). These coastal regions are additionally under varying influence of the East Spitsbergen Current and the West Spitsbergen Current, which bring cold ArW and warmer and more saline AtW, respectively. It is worth mentioning that the West Spitsbergen Current, in addition to transporting the majority of heat, also transports carbon that supplies plan

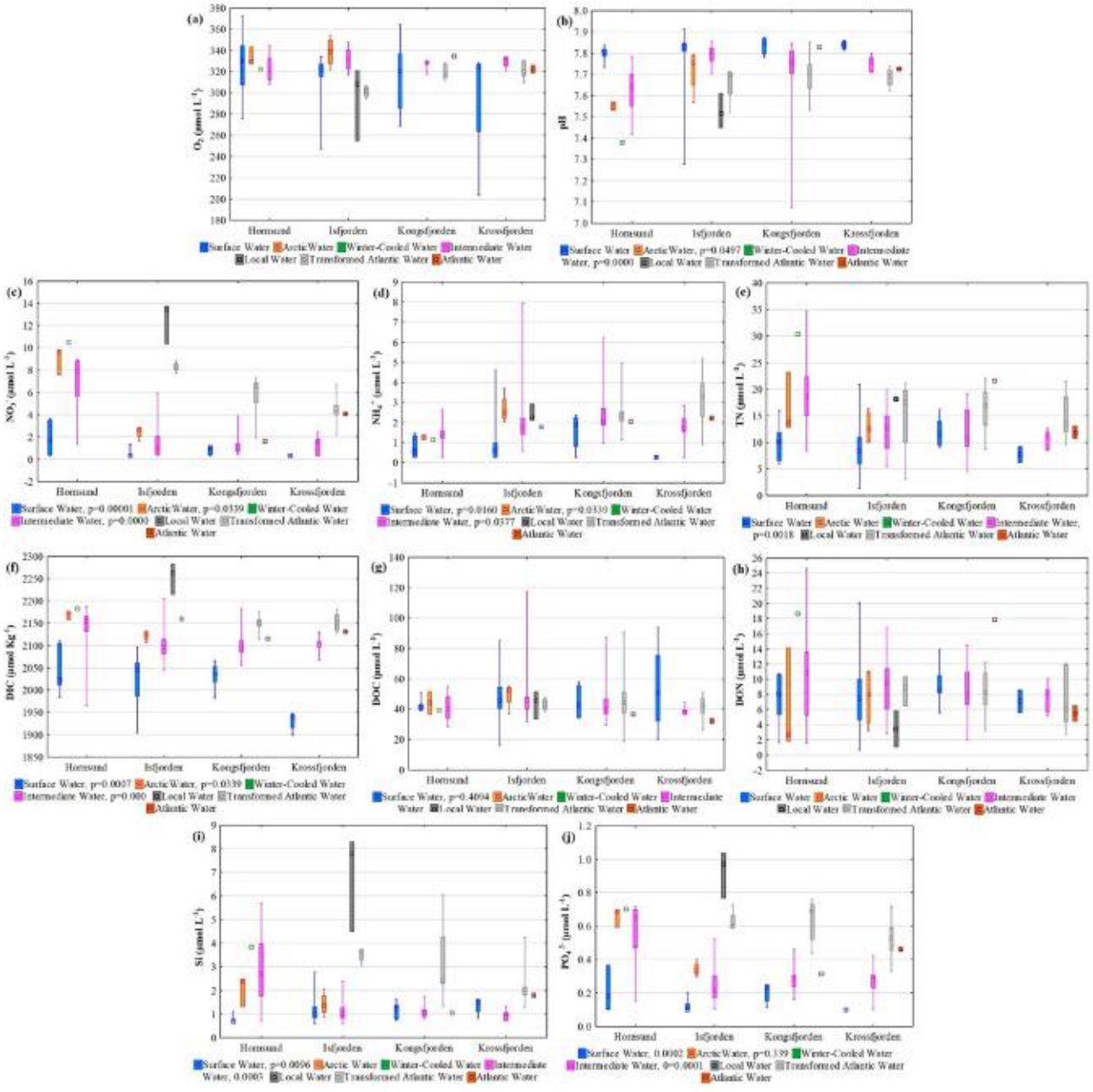

Figure 5. **(a)** Oxygen (O_2), **(b)** pH, **(c)** nitrate (NO_3^-), **(d)** ammonium (NH_4^+), **(e)** total dissolved nitrogen (TN), **(f)** dissolved inorganic carbon (DIC), **(g)** dissolved organic carbon (DOC), **(h)** dissolved organic nitrogen (DON), **(i)** dissolved silica (Si), and **(j)** phosphate (PO_4^{3-}) in surface water (marked as blue), Arctic water (marked orange), winter-cooled water (marked green), intermediate water (marked pink), local water (marked dark grey), transformed Atlantic water (marked light grey), and Atlantic water (marked red) in Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden. The p values indicate significant differences in the median concentration of the parameter between the investigated fjords, presented only if statistically significant.

(Menze et al., 2020). However, the West Spitsbergen Current along its way up to Kongsfjorden depletes in nutrients (Smoła et al., 2017), and, therefore, its influence on Kongsfjorden will be different from that on the Isfjorden. Thus, understanding the biogeochemical processes in the fjords and characterizing the differences among them is not possible without a detailed understanding of the water circulation. To characterize the distribution of T, S, pH, O_2, NO_3^-, NH_4^+, PO_4^{3-}, Si, DIC, DOC, TN, and DON in the investigated fjords, we used the Kruskal–Wallis test to characterize the differences in the concentrations of these constituents between different water masses within and between investi-

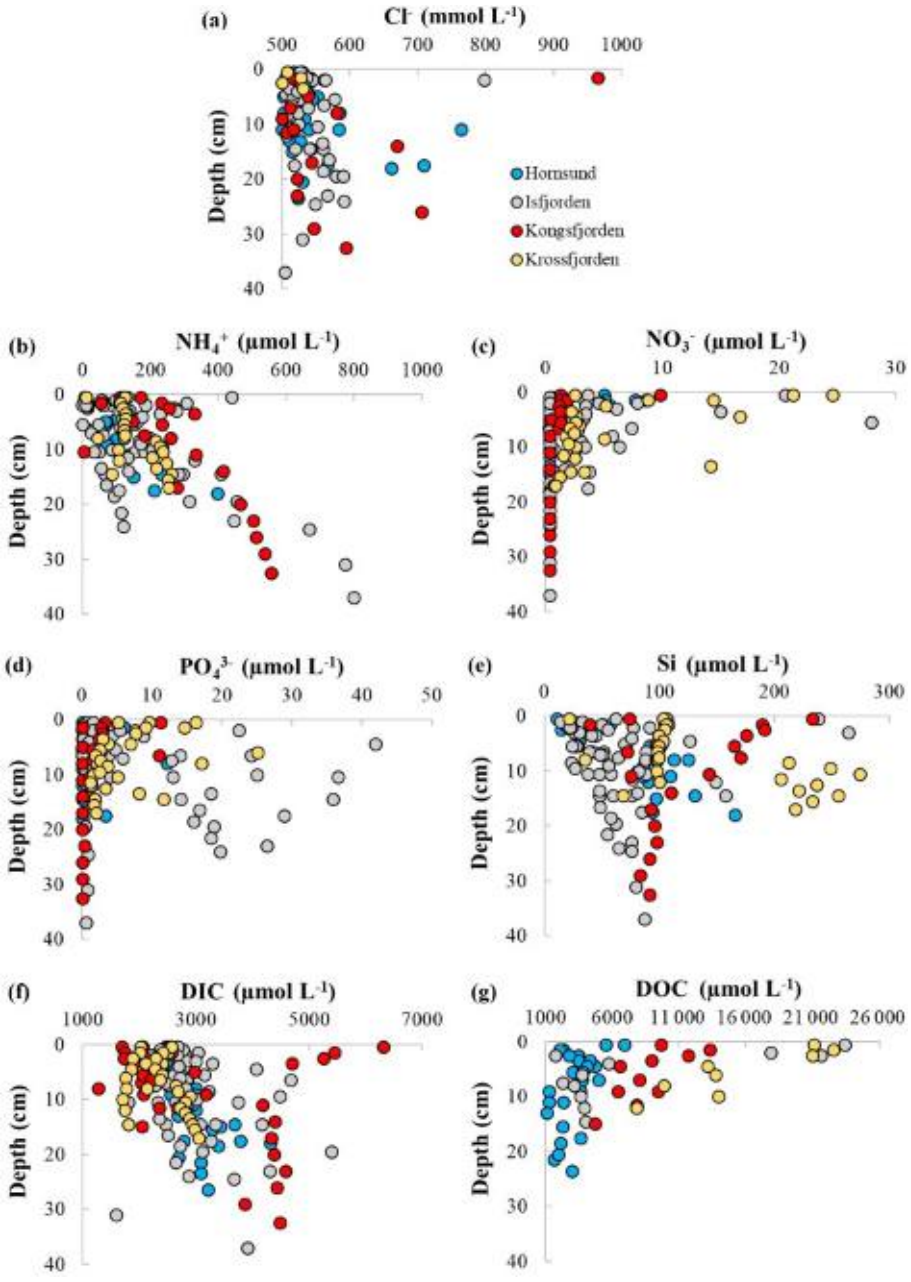

Figure 6. Distribution of **(a)** chloride (Cl^-), **(b)** nitrate (NO_3^-), **(c)** ammonium (NH_4^+), **(d)** phosphate (PO_4^{3-}), **(f)** dissolved silica (Si), **(g)** dissolved inorganic carbon (DIC), and **(h)** dissolved organic carbon (DOC) in pore water in Hornsund (marked blue), Isfjorden (marked grey), Kongsfjorden (marked red), and Krossfjorden (marked yellow).

gated fjords (Fig. 5). The *p* value is presented only if there was a significant difference in the median concentration of the parameter considered between the investigated fjords. SW, ArW, and IW were characterized by different compositions of most of the measured parameters, such as NO_3^-, NH_4^+, PO_4^{3-}, Si, and DIC between fjords. Besides NH_4^+, Arctic water is richer in nutrients and DIC in Hornsund in comparison to Isfjorden. However, LW, which was only observed in Isfjorden, was characterized by the highest concentration of NO_3^-, PO_4^{3-}, Si, and DIC between all water masses.

3.4 Pore water data

The distribution and gradients of Cl^-, NO_3^-, NH_4^+, PO_4^{3-}, Si, DIC, and DOC in pore waters in the investigated fjords are presented in Fig. 6 (Szymczycha et al., 2024). Generally, Cl^-, NH_4^+, PO_4^{3-}, Si, and DIC increased with depth and

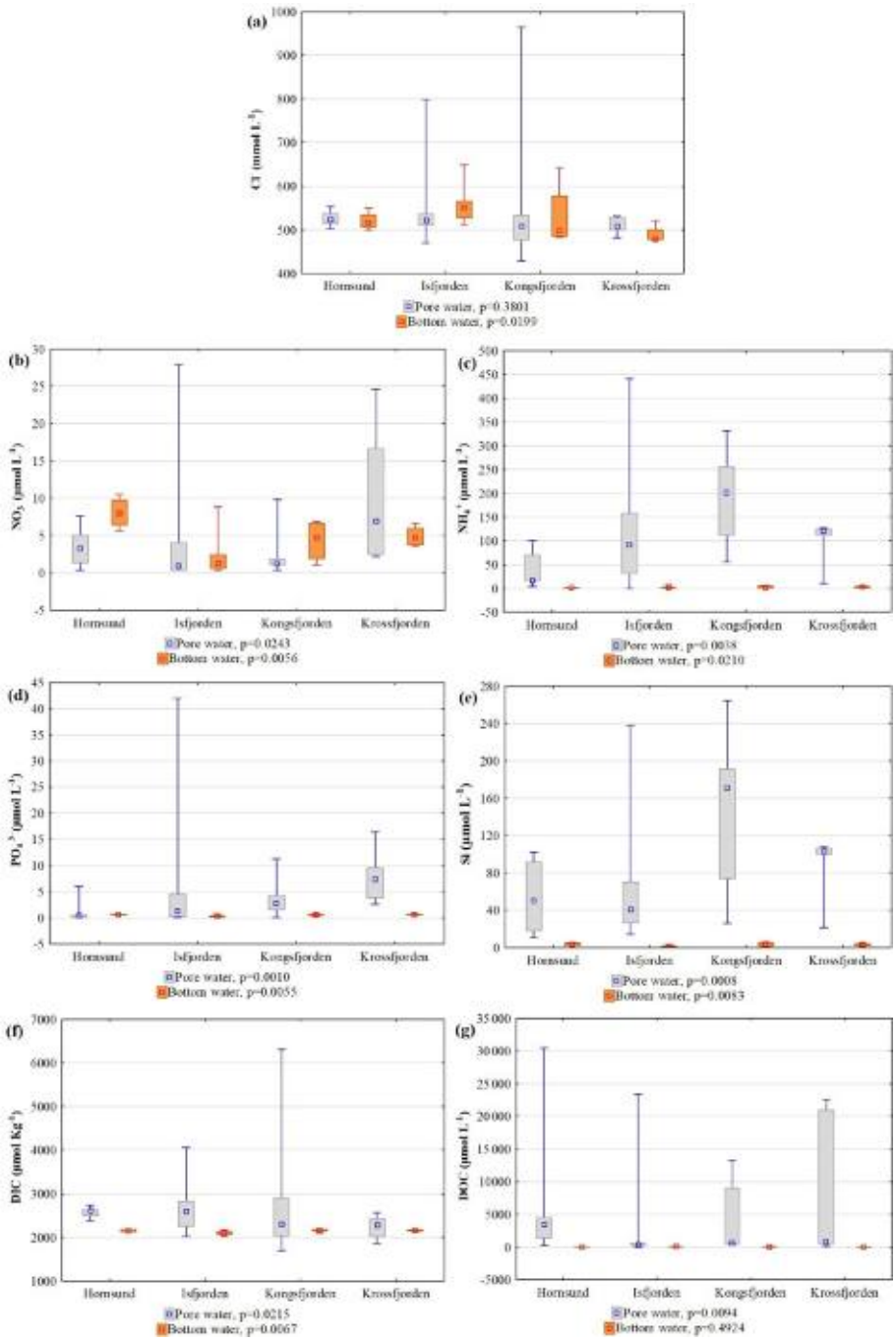

Figure 7. Box plots of **(a)** chloride (Cl^-), **(b)** nitrate (NO_3^-), **(c)** ammonium (NH_4^+), **(d)** phosphate (PO_4^{3-}), **(e)** dissolved silica (Si), **(f)** dissolved inorganic carbon (DIC), and **(g)** dissolved organic carbon (DOC) in pore water (marked grey) and bottom water (marked orange) in Hornsund, Isfjorden, Kongsfjorden, and Krossfjorden. The p values indicate significant differences in the median concentration of the parameter between the investigated fjords.

NO_3^- and DOC decreased with depth. PO_4^{3-} decreased in every fjord except Isfjorden. To highlight the potential of the pore waters dataset for further assessment and interpretation by data users, the concentrations of investigated parameters in pore water up to 5 cm depth and the concentrations in bottom water are compared in Fig. 7.

The median concentrations of Cl^- in pore water did not differ significantly among fjords and were comparable to those of bottom water, apart from at Isfjorden, where the

median concentrations of Cl^- in pore water were smaller than those of bottom water. In all fjords, NO_3^- was higher in bottom water compared to pore water, while NH_4^+, PO_4^{3-}, Si, and DIC were significantly higher in pore water in comparison to bottom water. The median concentration of NO_3^-, NH_4^+, PO_4^{3-}, Si, and DIC was significantly different in both water types ($p < 0.05$). The median concentration of DOC was slightly higher in pore water than in bottom water. However, it is worth noticing that the concentration ranges for all of the measured parameters differ between and within the investigated fjords.

4 Data availability

All data described in this paper are stored in the Zenodo online repository (https://doi.org/10.5281/zenodo.11237340, Szymczycha et al., 2024).

5 Applications of the dataset

This dataset is beneficial for the broad scientific community that is interested in Arctic physical oceanography and marine biogeochemistry. In addition, the presented dataset provides evidence for the spatial distribution of nutrients and the dissolved carbon species in the investigated Arctic fjords. The data are made accessible as a basis for a wider dissemination that will lead to an enhanced understanding and new scientific insights into the nutrient cycles in the Arctic fjords. Possible applications may include (1) being a reference and allowing for comparison of the current measurements of the nutrients and dissolved carbon distribution in both the water column and sediments in the same region with future studies; (2) the determination of C : N : P : Si ratios in different water masses and their comparison between fjords as an assessment of the environmental controls and limiting factors for the primary production; and (3) parameterization, validation, and improvement of existing and future biogeochemical models.

Author contributions. SRS: conceptualization, data interpretation, preparation of figures, investigation, and writing (original draft, reviewing, and editing). MEB, WLH, KK, AL, AS, and BS: reviewing and editing.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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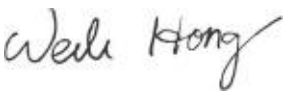

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RESEARCH ARTICLE 2

OCEANOLOGIA

Nutrients and carbon cycling in marine sediments of Arctic fjords

Obieg substancji biogenicznych i węgla w osadach morskich fiordów arktycznych

Seyed Reza Saghravani, Michael Ernst Böttcher, Wei-Li Hong, Magdalena Diak, Arunima Sen, Beata Szymczycha

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Nutrients and carbon cycling in marine sediments of Arctic fjords

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Highlights

1. HCA identified chemically distinctive clusters assigned to the shallow, middle, and deep sediment layers.
2. Pore water freshening was identified in Hornsund.
3. Freshwater in sediments is the source of NO_3^- and NH_4^+ while diluting DIC, $PO_4^{3-}$and DSi.
4. Marine sediments are primarily source of DIP.
5. The measured benthic fluxes significantly deviate from the Redfield-Brzeziński molar ratios.

Abstract

We investigated pore water chemistry in twelve marine sediment cores (up to 1.5 m in length) collected from distinct fjord systems: Hornsund, Isfjord, Kongsfjord, and Krossfjord. We identified five clusters corresponding to shallow, middle, and deep sediment layers, shaped by factors such as seawater circulation, local geology, organic matter (OM) degradation, and pore water freshening. Additionally, we quantified diffusive benthic fluxes of DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-}, and DSi and observed significant deviations from the Redfield-Brzezinski molar ratio with excess DIP and DSi release relative to nitrogen.

Keywords

Spitsbergen, Svalbard, pore water freshening, Submarine groundwater discharge, Freshwater-saltwater interface, carbon system, stable isotopes, machine learning

List of abbreviations, symbols, and acronyms

CA	cellulose acetate
Cl^-	chloride
CRM	certified reference material
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DIP	dissolved inorganic phosphate

DOC dissolved organic carbon
DSi dissolved silicates
HCA hierarchical cluster analysis
HDPE high density polyethylene
LDA linear discriminant analysis
NH_4^+ ammonium
NO_3^- nitrate
OM organic matter
POM particulate organic matter
PET polyethylene terephthalate
PO_4^{3-} phosphate
SGD submarine groundwater discharge
$\delta^{13}C_{DIC}$ δ^{13}C-DIC

1. Introduction

Over the past decades, the Arctic's mean annual surface temperature has increased more than twice the global average rate (Meredith et al., 2019). The warming trend is driven by a combination of surface albedo feedbacks, including the loss of snow and sea ice cover, cloud-sea ice interactions, changes in the lapse rate, increased northward transport of heat and moisture, and rising levels of atmospheric water vapor and cloudiness (Bruhwiler et al., 2021). Ongoing climate change, and the resulting reduction of the cryosphere - through ice melt, glacier retreat, and permafrost thaw - has led to increased discharge and deposition of terrestrial material in Arctic fjords (Hopwood et al., 2020).

The fjords along the western coast of Svalbard host dynamic marine sedimentary environments influenced by ocean currents, bedrock geochemistry, cryospheric conditions, and seasonal variations (winter vs. spring/summer melt)(Loeng, 1991; Saghravani et al., 2024; Ślubowska et al., 2005). Fjord sediments consist of a mixture of terrestrial and marine inputs, while the geological diversity of western Svalbard ranges from Precambrian basement rocks to Quaternary sediments, primarily composed of shales and organic carbon-rich formations (Krajewska et al., 2023). Bedrock mineralogy plays a key role in shaping fjord sedimentation by trapping terrestrial material and limiting extensive organic carbon remineralization (Bourgeois et al., 2017).

The oceanographic setting of Svalbard fjords is characterized by the intrusion of distinct water masses (Cottier et al., 2005; Nilsen et al., 2008; Promińska et al., 2018). Hornsund is primarily influenced by Arctic and colder coastal waters (Włodarska-Kowalczuk et al., 1998), while fjords such as Isfjord, Kongsfjord, and Krossfjord experience inflows of both Arctic and warmer, more saline Atlantic waters (Saghravani et al., 2024). The convergence of the water masses affects nutrient availability, water column stratification, and light penetration, all of which are crucial factors influencing primary productivity (Piwosz et al., 2009) and the flux of OM deposition to the sediments (Meyjes et al., 2024; Schubert and Calvert, 2001).

Previous studies on Svalbard fjords have investigated the spatial variability of OM composition and the contribution of ancient (petrogenic) OM (Kim et al., 2023; Krajewska et al., 2023; Ruben et al., 2023). Recent findings suggest a considerable input of petrogenic and aged soil-derived OM to present-day sedimentary OM in these fjords (Kim et al., 2023). However, the processes driving the discharge of ancient carbon, which is potentially mediated by sediment porewater dynamics, remain poorly understood. Furthermore, less attention has been given to the pore water

biogeochemistry of Arctic sediments, their heterogeneity, and their influence on the marine environment, particularly regarding how these factors may facilitate ancient carbon mobilization. Pore water profiles provide valuable insights into depositional processes (van der Weijden, 1993), diagenetic OM degradation and associated element (nutrient, sulfate, carbon species, trace element) cycling (Wehrmann et al., 2013), and the postglacial history of the region (Husum et al., 2019). For instance, oxygen availability decreases with sediment depth, while nitrate (NO_3^-) and dissolved organic carbon (DOC) concentrations shift due to the transition from aerobic degradation to anaerobic processes (Serpetti et al., 2016). Similarly, increased concentrations of ammonium (NH_4^+) and dissolved inorganic carbon (DIC) at specific depths indicate intensified OM degradation and nutrient cycling under anoxic conditions (Pescimoro et al., 2019). However, environmental factors such as glacial melt, which drive consistent sedimentary processes (Orita et al., 2015), geochemical variations (Hodson et al., 2005), and increased freshwater input (Rasmussen and Thomsen, 2013), can result in a steady nutrient supply, reducing vertical differentiation in OM degradation pathways and leading to more homogeneous pore water profiles (Bourgeois et al., 2017).

Vertical gradients in pore water composition also serves as an indicator of various geochemical processes, including gas hydrate formation (Betlem et al., 2021), authigenic mineral precipitation and dissolution (Loyd and Smirnoff, 2022), and the diffusive or advective transport of major and minor chemical substances (Zabel and Schulz, 2000). Hulth et al. (1996) demonstrated that pore water distributions of total dissolved nitrogen and DOC, along with OM reactivity, reflect hydrographic factors such as ice coverage and the production/import of particulate organic matter (POM) influenced by dominant water masses in the Svalbard region.

In addition, freshening of pore water has been observed in fjords such as Isfjord (Tempelfjord), Van Mijenfjord, and Hornsund, and has been attributed to fresh groundwater discharge. One feature was the positive covariation between the water isotope composition and Cl^- concentrations (Kim et al., 2022). On the land side, methane-rich groundwater springs have been found in the forefields of 78 land-terminating glaciers across central Svalbard, transporting deep-seated methane gas to the surface (Kleber et al., 2023). Additionally, shallow and deep groundwater influence methane dynamics in Svalbard's glacial catchments (Kleber et al., 2025, 2024).

Although the West Spitsbergen fjords have been the subject of extensive scientific research, no large-scale study has comprehensively examined pore water chemistry across regions with distinct hydrological and biogeochemical conditions. This study addresses that gap by characterizing the distribution of nutrients and dissolved organic and inorganic carbon in marine sediments from Arctic fjords. We combined pore water chemistry data with machine learning techniques to identify spatial patterns and underlying controls. Furthermore, we quantified the diffusive benthic fluxes of DIC, DOC, NO_3^-, NH_4^+, PO_4^{3-}, and DSi from sediments, used the stable isotope composition of DIC for source characterization, and evaluated the stoichiometric balance of N:P:Si to assess nutrient cycling dynamics.

2. Materials and methods

We investigated four different fjord systems along West Spitsbergen (Fig. 1), including Hornsund (SGD1, SGD2), Isfjord (TRYM, SGD14, SGD11, SGD21), Kongsfjord (SGD32, SGD42, SGD23, V1), and Krossfjord (SGD25, KL1). Sampling was carried out in 2022 during a research cruise to Svalbard aboard the r/v Oceania.

2.1 Sampling

Sediment cores were collected using a gravity corer and a Gemax corer. Prior to deployment, core liners were pre-drilled with holes every 1 cm and sealed with tape. Immediately after core retrieval, pore water was extracted from sediments using Rhizon® samplers (Rhizosphere, Ø 2.5 mm, and mean pore size 0.15 µm). Up to 5 mL of pore water was transferred into pre-cleaned high density polyethylene (HDPE) bottles and stored at −20°C for nutrient analysis. Approximately 2 mL was placed in polyethylene terephthalate (PET) vials for chloride (Cl^-) analysis. For DIC and DOC analysis, 12 mL of pore water was collected in pre-combusted glass bottles and preserved with 50 µL of saturated $HgCl_2$ solution. For δ^{13}C-DIC ($\delta^{13}C_{DIC}$) analysis, 3 mL of pore water was transferred to Exetainer® glass vials without headspace and preserved with 25 µL of saturated $HgCl_2$.

Bottom water samples were carefully collected from the seawater overlying the sediment in cores obtained with the Gemax corer. Temperature is determined immediately after collecting the samples with a calibrated handheld pH meter. For nutrient analysis, 10 mL of bottom water was filtered using cellulose acetate filters (0.45 µm), placed in pre-cleaned HDPE bottles, and stored at −20°C. For Cl^- analysis, approximately 2 mL was transferred to PET vials. For DIC analysis, bottom water was placed in pre-cleaned 250 mL glass bottles and poisoned with 100 µL of saturated $HgCl_2$. For DOC analysis, 20 mL of water was filtered through MN GF-5 filters (0.45 µm), transferred to pre-combusted glass bottles, and acidified to pH ~2 using concentrated HCl to prevent biological activity and remove carbonate. For $\delta^{13}C_{DIC}$, 12 mL of bottom water was placed in Exetainer® glass vials without headspace and preserved with 50 µL of saturated $HgCl_2$. All Cl^-, DIC, DOC, and $\delta^{13}C_{DIC}$ samples were stored at 4°C until analysis.

River water samples were collected during land-based expeditions directly from river channels (see Fig.1 for location). Rainwater was sampled using pre-cleaned buckets, which were rinsed with MilliQ water and then with rainwater from the same event (see Fig.1 for location). Open ocean water samples were collected using a Rosette sampler equipped with 10 L Niskin bottles. Subsampling protocols for rainwater, river water, and open ocean water followed the same procedures for bottom water samples described above.

2.2 Chemical analyses

Nutrient concentrations were quantified using the SEAL AA500 AutoAnalyzer (Seal Analytical) following standard photometric methods (Grasshoff et al., 2009). Quality control was ensured through repeated measurements of two certified reference materials (CRMs): QC3179, Sigma-Aldrich, and HAMIL, Environment Canada. Method detection limits were 0.27 µmol L^{-1} for NH_4^+, 0.1 µmol L^{-1} for PO_4^{3-}, and 0.3 µmol L^{-1} for DSi. Measurement accuracy for NH_4^+, PO_4^{3-}, and Si was 98.8%, 99.0%, and 100.1%, respectively, with corresponding precision values of 0.02, 0.01, and 0.03 µmol L^{-1}. Cl^- concentrations were determined via ion titration using Mohr's Method (Kłostowska et al., 2020). DIC analysis was conducted using the Apollo SciTech AS-C6L DIC Analyzer with a high-precision laser-based CO_2 detector (LI-7815, Li-Cor, USA). Accuracy was verified using CRMs (#190, #195) from A.G. Dickson (Scripps Inst. of Oceanography, USA), ensuring precision ≤ ±3 µmol L^{-1}. DOC was analyzed via high-T oxidation (680°C) with a Pt catalyst using a TOC-L analyzer (Shimadzu). Calibration was performed using CRMs from the D. Hansell Lab (Univ. of Miami, USA). $\delta^{13}C_{DIC}$ was measured using a high-precision gas IRMS (Thermo GasBench II coupled to a Thermo Finnigan MAT 253 via a Thermo Conflo IV interface) in the Geochem. & Isotope Biogeochem. Group at IOW, following Winde et al. (2014) and Ehlert von Ahn et al. (2023). $\delta^{13}C$ values were calculated as the $^{13}C/^{12}C$ ratio relative to the VPDB standard and reported in mUr (Brand and Coplen, 2012) as:

$\delta^{13}C = [(Rsa / Rstd) - 1] \times 1000$

2.3 Benthic flux of C, N, P

The diffusion of dissolved N, P, and Si species from the sediments into the overlying bottom seawater were calculated based on Fick's first law of diffusion using Eq. (1) (Berner, 1980):

$$J_x = \varphi D_{Sed} \frac{\Delta C}{\Delta x} \quad (1)$$

where Jx is the diffusion flux of x [NH_4^+, NO_3^-, PO_4^{3-}, DSi, DIC, DOC (µmol m^{-2} d^{-1})]; φ is the surface sediment porosity, D_{Sed} is the specific sediment diffusion coefficient for x in sediments [cm^{-2} s^{-1}], and $\frac{\Delta C}{\Delta x}$ is concentration gradient of the analysed substance between the pore fluid of the surface-most sediment layer and the seawater overlying the sediments [mg cm^{-3} cm^{-1}]. Sediment porosity, which refers to the proportion of void spaces in the sediment, is pivotal in determining the ease with which solutes can diffuse through the sediment matrix. Porosity was calculated as shown in Eq. (2):

$$\varphi = w[(100 - w)d^{-1} - 1 + w]^2 \quad (2)$$

Where w is the sediment-water content percentage ($\frac{\text{mass of sediment} - \text{dry mass}}{\text{dry mass}} * 100$) and d is the bulk density of sediment which is obtained based on sediment-water content. The D_{Sed} (cm^2 s^{-1}) values were calculated based on D_{Sw} diffusion coefficient in free solutions of seawater and tortuosity (θ):

$$D_{Sed} = \frac{D_{Sw}}{\theta^2} \quad (3)$$

D_{Sw} values were derived from existing literature and corrected for temperature according to the Stokes-Einstein equations (Li and Gregory, 1974). The diffusion coefficient for DOC and Si was adopted from Burdige (2007). The values were estimated for each station based on Eq. (4):

$$D_{Sw} = (m_0 + m_1 . T_{BW}) * 10^{-6} \quad (4)$$

Where m_0 and m_1 are linear coefficients (Boudreau, 1996) and T_{BW} is the bottom water's temperature. Tortuosity was calculated as a function of porosity based on the following Eq. (5):

$$\theta^2 = 1 - \ln(\varphi^2) \quad (5)$$

2.4 Statistical analysis

Statistical significance was evaluated using the Kruskal-Wallis analysis of variance (ANOVA) test to compare chemical elements of the whole profiles in terms of groups (i.e., fjords or clusters). When the Kruskal-Wallis test indicated significant differences, Dunn's post-hoc test was employed to identify which specific groups differed significantly for each chemical element (McKight and Najab, 2010).

Hierarchical cluster analysis (HCA) was performed using Ward's method (Saxena et al., 2017), which minimizes the total within-cluster variance by considering the Euclidean distances between data points (Strauss and von Maltitz, 2017; Székely and Rizzo, 2014). Before clustering, the data were standardized with a mean of zero and a standard deviation of one (Jolliffe and Cadima, 2016). Following HCA, Linear Discriminant Analysis (LDA) was applied to the clustered data to find a linear combination of features that best separated the clusters identified by the HCA. The dataset was divided into training and test sets using the train_test_split function from the sci-kit-learn library in Python (Pedregosa et al., 2011), and the LDA model was fitted on the training set's features with the HCA cluster labels as the target variable (Borcard et al., 2018; Legendre and

Legendre, 2012). The optimal number of clusters was determined by analyzing the dendrogram and evaluating the distances at which clusters were merged (Everitt and Hothorn, 2011).

3. Results

Three main pore water trends could be observed within the investigated fjord systems (Hornsund, Isfjord, Kongsfjord, and Krossfjord, Fig. 1): decrease, increase, or no change of chemical parameters with pore water depth (Fig. 2). NO_3^- had higher concentrations in surface pore water up to 6.86 µmol L^{-1} and decreased with depth, reaching 0.061 µmol L^{-1}. DIC increased with pore water depth from 1878.85 to 10395.36 µmol Kg^{-1} in all fjords, and the increase with depth was particularly pronounced at sites SGD11 and SGD21, where DIC reached substantially higher values in comparison to other sites, exceeding 20 mmol Kg^{-1}. DOC, similar to DIC, increased with pore water depth in all sites and was in the range of 16.10 to 780.28 µmol L^{-1}. In all fjords, NH_4^+ and DSi increased with pore water reaching 169.78 and 99.25 µmol L^{-1}, respectively. Cl^- was constant in all pore water profiles with depths ranging from 467.42 to 601.59 mmol L^{-1}, apart from Hornsund, where Cl^- decreased with pore water depth from 536.35 to 399.91 mmol L^{-1}. Similarly, PO_4^{3-} remained constant or slightly increased with pore water depth and was in the range between 0.029 and 30.04 µmol L^{-1} apart from sites DCK and SGD25, where PO_4^{3-} reached 76.57 and 74.69 µmol L^{-1}, respectively$\delta^{13}C_{DIC}$ showed variable distribution with pore water depth in all sites and ranged from -13.67 to 1.24 mUr.

DIN (NO_3^- + NH_4^+) concentrations were relatively high in river water (average 16.73 µmol L^{-1}) and surface open ocean (average 15.64 µmol L^{-1}), while bottom water (average 5.86 µmol L^{-1}) and rainwater (average 3.75 µmol L^{-1}) showed considerably lower values. DSi concentrations in river water and surface open ocean were equal to average values of 15.05 µmol L^{-1} and 12.21 µmol L^{-1}, respectively, while rainwater and bottom water exhibited much lower concentrations of 0.47 µmol L^{-1} and 3.02 µmol L^{-1}, respectively. In contrast, PO_4^{3-} showed a different trend: river water contains the lowest PO_4^{3-} concentration (0.002 µmol L^{-1}), whereas the open ocean sample was highest (0.96 µmol L^{-1}), with intermediate values found in rainwater and bottom water (0.45 µmol L^{-1} and 0.46 µmol L^{-1}, respectively).

To identify patterns in pore water chemistry, the HCA clustering technique was employed to group the samples based on their similarity in elemental concentrations and separate geochemical zones within the sediment profiles (Tfaily et al., 2018). The HCA identified five clusters: HC1, HC2, HC3, HC4, and HC5 (Fig. 3 and Fig. 4).

HC1 was assigned to bottom water and shallow pore waters (mainly up to 7 cmbsf with one exception in SGD23 with 20.5 cmbsf depth) across all sites and fjords (Fig. 4). HC4 and HC5 were associated with the mid-depth pore water layers (averaging around 39.86 cmbsf and 29.12 cmbsf, respectively), while HC3 and HC2 were primarily found in the deepest pore water layers (averaging around 78 cmbsf) (Fig. 4).

In Hornsund, the mid-depth pore water profiles of both sites (SGD1 and SGD2) were assigned to HC4, while deep pore water layers were assigned to HC3. In Isfjord, mid-depth pore water profiles were allocated to HC5 (sites: DCK and TRYM) and HC4 (sites: SGD11 and SGD21), while deep pore water layers were grouped in HC2 (sites: DCK, TRYM, SGD11, and SGD21). Kongsfjord had a very similar pattern to Isfjord, where mid-depth pore water profiles were allocated to HC5 (site: SGD23, SGD32, and SGD42) and HC4 (site: V1) while deep pore water layers were grouped in HC2 (sites: SGD23, SGD32, SGD42, and SGDV1). Interestingly, in Krossfjord, mid-depth pore water profiles were mainly allocated to HC5 (sites: SGD25 and KL1), while deep pore water layers were grouped in HC2 (sites: SGD25 and KL1). Therefore, Krossfjord shows characteristics similar

to Hornsund in the shallower sediments, while its deeper sediment composition is similar to that of Kongsfjord and Isfjord.

4. Discussion

4.1 Spatial variability

The statistical analysis indicates significant variability of investigated parameters in pore water among the studied fjords. The Kruskal-Wallis test shows significant differences among the fjords for four variables: Cl^- ($p = 8.36863E-12$), PO_4^{3-} ($p = 3.35E-9$), DSi ($p = 1.85E-10$), and NO_3^- ($p = 0.0014$) (Fig. 3). Particularly, Hornsund shows lower Cl^-, PO_4^{3-}, and DSi concentrations compared to the other fjords ($p < 0.001$) but higher NO_3^- ($p < 0.001$), as revealed by Dunn's post-hoc tests (Fig. 3). Spatial variability in pore water chemistry was also reported in previous studies in Arctic fjords of Greenland (Rysgaard et al., 1998), the east Siberian Sea (Miller et al., 2017), the Svalbard fjords (Wehrmann et al., 2014). The variability was explained by sea ice dynamics and glacial inputs, which influence hydrography, nutrient availability, and carbon chemistry in Arctic regions (Koziorowska-Makuch et al., 2023).

4.2 Bottom water and shallow pore water chemistry

In all fjords, HC1 showed higher average NO_3^- (3.27 µmol L^{-1}) and less negative $\delta^{13}C_{DIC}$ signatures (-0.89 mUr) compared to other clusters, while average concentrations of DIC (2229.88 µmol Kg^{-1}), DOC (109.37 µmol L^{-1}), PO_4^{3-} (0.43 µmol L^{-1}), DSi (6.85 µmol L^{-1}), and NH_4^+ (18.17 µmol L^{-1}) were found depleted in the HC1 in comparison to other clusters. Consequently, these results indicate possible active exchange with overlying waters and OM degradation under aerobic conditions (Hulth et al., 2005) (Fig. 2,3, and 4).

4.3 Mid-depth pore water chemistry

Mid-depth pore water profiles were grouped into two clusters: (1) HC5, comprising sites from Isfjord (DCK and TRYM), Kongsfjord (SGD23, SGD32, and SGD42), and Krossfjord (SGD25 and KLl); and (2) HC4, which included sites from Hornsund (SGD1 and SGD2), Isfjord (SGD11 and SGD21), and Kongsfjord (V1) (Fig. 4).

HC5 was characterized by the highest PO_4^{3-} concentrations among all clusters, likely resulting from phosphorus release via iron oxyhydroxide dissolution under suboxic conditions (Hong et al., 2020), inputs of phosphorus-rich glacial meltwater (Hodson et al., 2004), or sediment composition that promotes enhanced phosphorus regeneration (Rittenberg et al., 1955). Surface-adsorbed phosphate may be remobilized into pore water and transported upwards to surface sediments and bottom waters (Sundby et al., 1992). Elevated concentrations of DSi (average 49.97 µmol L^{-1}), DOC (average 278.02 µmol L^{-1}), and NH_4^+ (average 82.45 µmol L^{-1}), along with depleted $\delta^{13}C_{DIC}$ values (average -5.23 mUr), suggest the presence of more labile, marine-derived OM and its active decomposition (Sundby et al., 1992). Notably, within HC5, sites TRYM and SGD25 exhibited significantly higher PO_4^{3-} and DIC concentrations compared to other sites (Fig. 2). In contrast, site SGD23, located in the central part of Kongsfjord, showed considerably lower PO_4^{3-} but higher DSi and DOC concentrations than TRYM and SGD25. The pattern may indicate that glacial meltwater, often enriched in terrestrial DOC and DSi from siliceous rock erosion, contributes to surface sediment composition, while deeper, more homogeneous pore waters may contain a mixture of older terrestrial OM and biogenic silica from diatom degradation - typically undergoing slower breakdown under anoxic conditions (Ruben et al., 2023).

Sites classified within HC4 were generally located closest to tidewater or land-based glaciers. The average $\delta^{13}C_{DIC}$ value of -4.09 mUr in HC4 indicates a mix of marine and terrestrial OM. Glacial meltwater introduces terrestrial carbon to the sediments, likely enhancing microbial respiration and carbonate dissolution (Arndt et al., 2013). This is supported by elevated DIC (average 4340.94 µmol L^{-1}) and DOC (average 343.55 µmol L^{-1}) concentrations compared to HC5. Additionally, high NH_4^+ concentrations (average 130.55 µmol L^{-1}) and low NO_3^- (average 1.455 µmol L^{-1}) suggest active ammonification in OM-rich sediments near glacial sources (Hodson et al., 2005; Schmidt et al., 2025).

4.4 Deep pore water chemistry

HC2 comprises pore water samples from Isfjord, Kongsfjord, and Krossfjord and is characterized by the highest Cl^- concentrations among all clusters, averaging 537.85 mmol L^{-1}. These elevated values likely reflect historical cryogenic squeezing during submarine permafrost formation (Charkin et al., 2017), which may have concentrated dissolved species (Rotem et al., 2023) and contributed to the current geochemical profiles (Ottesen et al., 2005). The LDA shows that HC2 is clearly distinct from HC1 and other clusters (Fig. 5), with the highest concentrations of DIC (average 8,704.66 µmol Kg^{-1}), DOC (average 450.32 µmol L^{-1}), PO_4^{3-} (average 18.01 µmol L^{-1}), and DSi (average 61.20 µmol L^{-1}). The elevated concentrations can be attributed to the presence of low-permeability mud in the deep sediment layers, which restricts diffusion and promotes the accumulation of OM and solutes (Li et al., 2016; Ruttenberg and Goñi, 1997).

The observed $\delta^{13}C$-DIC values, ranging from +2 to –14 mUr, combined with DIC concentrations between 2,000 and 10,000 µmol Kg^{-1} —and reaching up to 20,000 µmol Kg^{-1} at some sites— suggest a mixture of carbon sources and biogeochemical processes. The more enriched $\delta^{13}C$ values (near +2 mUr) likely reflect carbonate dissolution or seawater DIC, typical of marine systems. In contrast, the gradually depleted $\delta^{13}C$ values (down to –14 mUr) at elevated DIC concentrations indicate significant contributions from organic matter remineralization, particularly of terrestrial (C_3 plant-derived) or marine organic matter, which show a lighter isotopic signature. The negative correlation between DIC and $\delta^{13}C$-DIC supports the addition of ^{12}C-enriched CO_2 to pore waters via microbial degradation processes, such as aerobic respiration, sulfate reduction, or methanogenesis in its early stages. The absence of more strongly depleted $\delta^{13}C$ values (< –20 mUr) suggests that methane oxidation plays a limited role, and that carbonate corrosion and organic matter remineralization dominate the carbon dynamics across the sediment profiles studied.

Furthermore, the high levels of DIC, DSi, and PO_4^{3-} likely result from mineral dissolution and weathering of silicate-rich rocks, red sandstones, and carbonate-rich formations (März et al., 2015; Wallmann et al., 2008; Yidana et al., 2012). The geology of Isfjord features mud and sandy mud with scattered clasts and ice-rafted debris (Levitan et al., 2008), while Kongsfjord is dominated by Devonian red sandstone with Carboniferous-Permian dolostone and limestone (Svendsen et al., 2002). Krossfjord's catchment consists of varied lithologies, including mica-schist, marble, dolomite, quartzite, granite, gneiss, and Mesoproterozoic migmatite basement rocks (Dallmann, 2015). The low-permeability conditions in these deep sediments restrict fluid transport, facilitating the retention and accumulation of solutes. These findings are consistent with previous studies on Svalbard's phosphogenic facies, where reduced fluid movement in fine-grained sediments preserved organic and inorganic components (Krajewski, 2000a). Additionally, microbial processes such as sulfate reduction and methanogenesis in oxygen-depleted zones likely contribute to these geochemical patterns through the accumulation of degradation products and methane release (Krajewski, 2000b).

4.5 Deep pore water freshening

Cl^- concentrations, as reported by Schlüter et al., (2004) and Szymczycha et al., (2012), are recognized as tracers for distinguishing between freshwater and saline water in marine environments. Cl^- is naturally abundant in seawater and significantly depleted in groundwater, making it an effective indicator for identifying submarine groundwater discharge (SGD). Unlike many other major ions, Cl^- does not form insoluble compounds and is not subject to adsorption processes. Furthermore, its concentration is generally unaffected by the chemical or biochemical properties of marine sediments. As a result, Cl^- concentration levels in pore water typically reflect those of the overlying seawater. Deviations from the equilibrium often point to processes such as molecular diffusion, compaction-driven migration, or pore water freshening.

In Arctic environments, pore water freshening can result from several mechanisms, including SGD, cryospheric meltwater inflow, gas hydrate dissociation, and dehydration reactions (Dimova et al., 2015; Lecher et al., 2017). SGD is particularly notable for its capacity to mobilize OM previously stabilized in sediments, while gas hydrate dissociation can release significant amounts of methane and inorganic carbon into the ocean. Both processes may influence sedimentary OM dynamics, with implications for the carbon cycle and climate change.

Evidence of pore water freshening was observed at only two sites in Hornsund (SGD1 and SGD2), both assigned to the HC3 cluster (deep pore water). Interestingly, the freshening did not correlate with water depth or distance from the shoreline. It is more likely that local subsurface hydrogeology, including aquifer properties, the extent of permafrost, and subsurface connectivity, plays a crucial role in governing the occurrence and intensity of pore water freshening (Hong et al., 2019). Thawing permafrost, for example, may open pathways for groundwater infiltration into marine sediments, altering their geochemical profiles (Frederick and Buffett, 2015). Hornsund's complex bedrock and hydrogeology that ranges from Proterozoic metamorphic rocks to Paleogene sedimentary formations, including Mesozoic phyllite, shale, and sandstone can further support the interpretation (Dallmann, 2015).

To assess the impact of pore water freshening, we compared geochemical parameters between deep pore water clusters affected by freshwater (HC3) and those not affected (HC2). Slightly elevated concentrations of NH_4^+ ($p = 0.0491$) and NO_3^- ($p = 0.053$) were found in HC3 compared to HC2, while DOC concentrations were similar in both clusters. In contrast, DIC ($p = 0.0001$), PO_4^{3-} ($p = 0.0000$), and DSi ($p = 0.0000$) were significantly higher in HC2. These results suggest that freshwater inputs in Arctic sediments may serve as a source of inorganic nitrogen, while simultaneously diluting DIC, PO_4^{3-}, and DSi concentrations.

4.6 Benthic fluxes and nutrient stoichiometry

In order to obtain the benthic fluxes, the profiles were analyzed using mathematical functions best-fitted to the vertical concentration distributions of the solutes under investigation (Denis and Grenz, 2003; Lengier et al., 2021). In general, dissolved carbon (DC=DIC+DOC) benthic fluxes were comparable in all fjords ($p > 0.05$), apart from sites DCK and SGD42 where DC reached 0.37 and 0.34 µmol m^{-2} d^{-1}, respectively (Fig. 6). Benthic fluxes of DIN ($NO_3^- + NH_4^+$) showed only positive values in Hornsund, while in other fjords negative and positive fluxes were indicated. DIP benthic fluxes showed positive fluxes reaching 39.47 µmol m^{-2} d^{-1} in all fjords apart from site SGD23 in Kongsfjord. DSi benthic fluxes were constantly positive across all fjords and ranged from 0.28 to 1.41 µmol m^{-2} d^{-1}. Our results align with Morata et al., (2020) indicated that DSi fluxes were consistently positive across all seasons and stations with higher values in summer which is in agreement with diatom-derived biogenic silica degradation.

In Hornsund, DIP fluxes were significantly higher (0.154–0.320 g m^{-2} y^{-1}; standardized to g m^{-2} y^{-1} for direct comparison with other studies) than previous study (0.001 g m^{-2} y^{-1}) by Koziorowska et al., (2018) most probably due different location of earlier sites and impact of pore water freshening. Conversely, stations in Kongsfjord (e.g., SGD23, V1) exhibited negative fluxes for both DIP (−0.504 g m^{-2} y^{-1}) and DIN (−0.145 and −0.036 g m^{-2} y^{-1}) indicate nutrient uptake by sediments most probably due to phosphorus sorption or nitrification and denitrification processes (Morata et al., 2020).

Benthic fluxes of DC, DIN, and DSi were significantly lower than those reported for the Bering and Chukchi Seas based on radon-222 (^{222}Rn) measurements, however, DIP fluxes were approximately four times higher (Barrett et al., 2023).

The Redfield-Brzeziński ratio (N:P:Si=16:1:15) represents the typical composition of marine phytoplankton biomass (Brzeziński, 1985; Redfield, 1963). Variations from the stoichiometric balance in seawater can lead to shifts in community composition, potentially promoting harmful algal blooms and associated eutrophication (Justić et al., 1995).

The N:P benthic flux ratios indicate spatial variability in nutrient regeneration patterns across fjords, with averaged 0.2, 6.2, and 10.1 for Hornsund, Isfjord, and Kongsfjord, respectively (Fig. 7). Similarly, N:DSi flux ratios followed the same trend, with average values of 2.9 in Hornsund, 6.5 in Isfjord, and a distinctly high 43.4 in Kongsfjord. In contrast, Krossfjord exhibited negative fluxes for both sites, which is relevant to accumulation rather than release to the water column, and thus was excluded from comparative analysis. The observed flux ratios based on the Redfield-Brzeziński ratio (N:P:Si = 16:1:15) suggest a potential imbalance in nutrient availability. Significant deviations from the Redfield-Brzeziński ratio were observed in Hornsund, where both N:P and N:DSi ratios were far below the ratio values, and in Kongsfjord, where N:DSi greatly exceeded the expected ratio. Therefore, Hornsund experiences nitrogen limitation or high release of phosphate and silica, while Kongsfjord may be characterized by an excess of nitrogen compared to silica.

In Hornsund, DIP fluxes were significantly higher (0.154–0.320 g m^{-2} y^{-1}; standardized to g m^{-2} y^{-1} for direct comparison with other studies) than previous study (0.001 g m^{-2} y^{-1}) by Koziorowska et al., (2018) most probably due to enhanced phosphorus regeneration or benthic release which are possibly driven by seasonal differences or climate change not captured in the earlier work. Koziorowska et al., (2018) reported DIP fluxes ranging from 0.001 to 0.043 g m^{-2} y^{-1} and DIN fluxes from 0.05 to 0.55 g m^{-2} y^{-1} in Kongsfjord. Conversely, our results in Kongsfjord (e.g., SGD23, V1) exhibited negative fluxes for DIP (−0.504 g m^{-2} y^{-1}) and DIN (−0.145 and −0.036 g m^{-2} y^{-1}) indicate nutrient uptake by sediments due to phosphorus sorption or nitrification and denitrification processes. It can be due to seasonally enhanced remineralization or OM degradation in warmer months, a likely explanation for the net DIP and DIN release (Morata et al., 2020).

The observed spatial variability in NH_4^+ in our findings emphasizes the role of seasonal dynamics in influencing NH_4^+ release (Vipindas et al., 2021) and the rate of nitrification in sediments, as highlighted by Devol (2015). Seasonal NH_4^+ variability has also been observed in Svalbard sediments by Kostka et al. (1999). Although our study did not directly calculate the total nitrogen (TN) flux, the measured benthic fluxes of NO_3^- and NH_4^+ indicate that the N:P benthic flux ratios deviate from the Redfield-Brzeziński ratio (16:1:15). In several sites such as Hornsund (SGD1 and SGD2), Isfjord (SGD11), and Kongsfjord (SGD32) we observed excess P release relative to N (Fig. 6). Recent studies show that in Arctic regions such as the Fram Strait and Barents Sea, vertical export of POM leads to more efficient phosphorus retention in the water column, resulting in lower

benthic of P to sediments. However, in our porewater results, the opposite trend of enhanced P release at some sites may indicate efficient OM degradation at the sediment-water interface or limited P adsorption to iron phases under reducing conditions. Koziorowska et al., (2018) observed that changes in phosphate concentrations were likely driven by its release from iron and manganese oxyhydroxides and carbonates, to which it had previously been adsorbed. The process could have resulted from the anaerobic degradation of organically bound phosphorus within the sediment's solid phase and/or the reduction of insoluble Fe(III) and Mn(IV) oxyhydroxides to their more soluble Fe(II) and Mn(II) forms. These transformations facilitated the release of adsorbed nitrogen- and phosphorus-containing organic compounds into pore waters. In anoxic marine settings, the precipitation of iron-phosphate minerals, notably vivianite, serves as a substantial P sink. However, under oxic conditions, dissolution of these minerals can release significant quantities of PO_4^{3-} in the water column (Husum et al., 2019). Seasonal hypoxia and thermal fluctuations lead to P release from sediments and start algal proliferations (Yang et al., 2021).

5. Conclusion

The study investigates spatial and vertical variability in pore water biogeochemistry across Arctic fjords, revealing significant differences in nutrient concentrations and carbon species between fjords and depth layers. Shallow pore water (HC1) was characterized by higher NO_3^- and less negative $\delta^{13}C_{DIC}$ than other clusters. Middle layers (HC4, HC5) showed elevated DSi, DOC, NH_4^+, and PO_4^{3-}. Deep pore waters (HC2, HC3) revealed high DIC, DOC, and nutrient accumulation. Freshening at two Hornsund sites (HC3) was identified. Benthic flux calculations demonstrated that sediments act as sources or sinks depending on site, with the highest fluxes for DIP in Hornsund. Nutrient ratios (N:P, N:DSi) deviated from Redfield-Brzezinski values, indicating nitrogen limitation in Hornsund, Isfjord, and Kongsfjord, while Krossfjord exhibited negative fluxes, which is relevant to accumulation rather than release to the water column.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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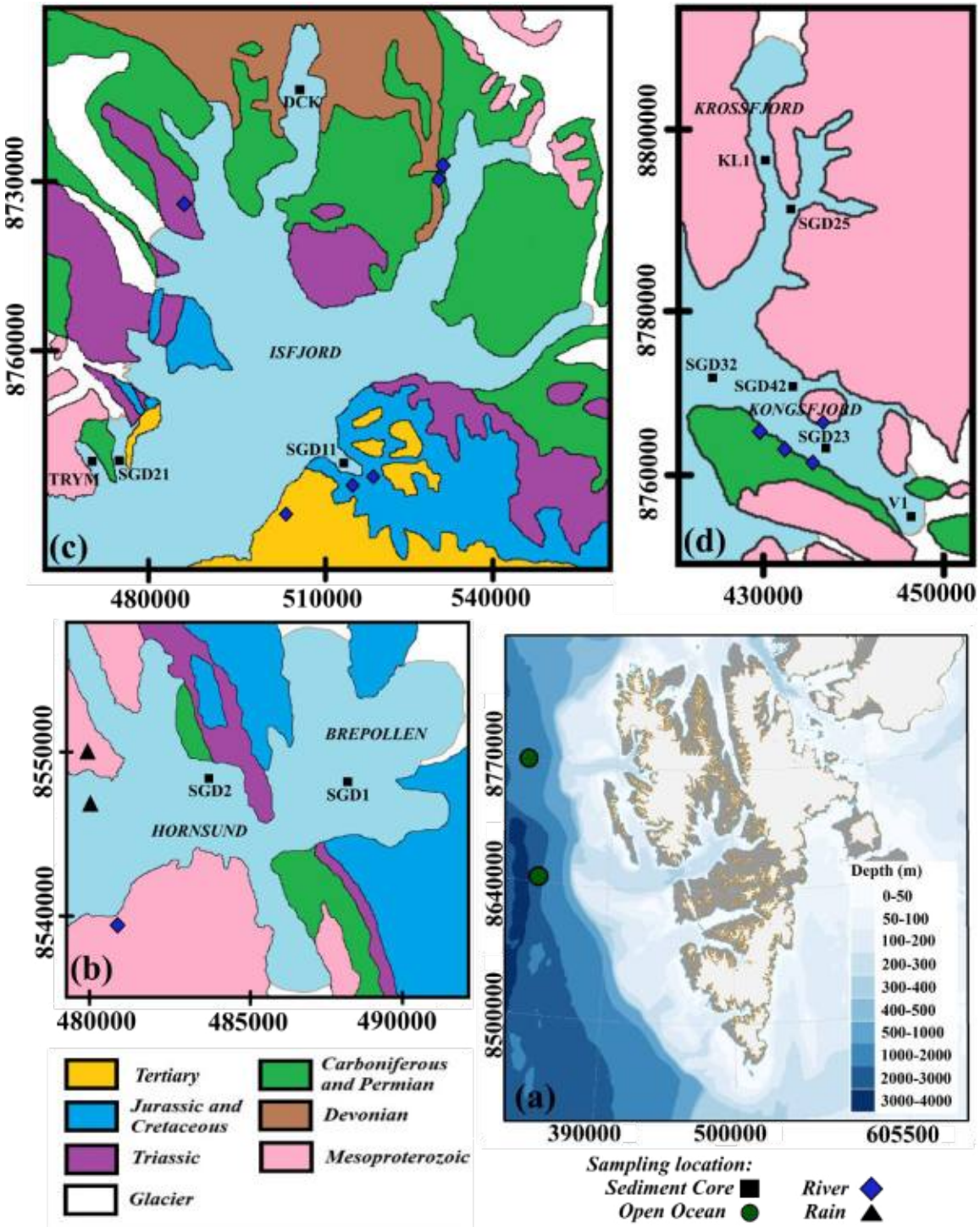

Figure 1. Map of Svalbard archipelago (a) (Vihtakari, 2022, 2020). The geological maps of Hornsund (b), Isfjord (c), and Kongsfjord-Krossfjord (d) (Dallmann, 2015; Dallmann et al., 2002; Myhre, 2023). Symbols that represent sampling locations include sediment cores (black squares), river water (blue diamonds), rainwater (black triangles), and open ocean – surface seawater (green circles). Glacier fronts are indicated by brown lines. Bottom water samples were collected at the sediment core sites.

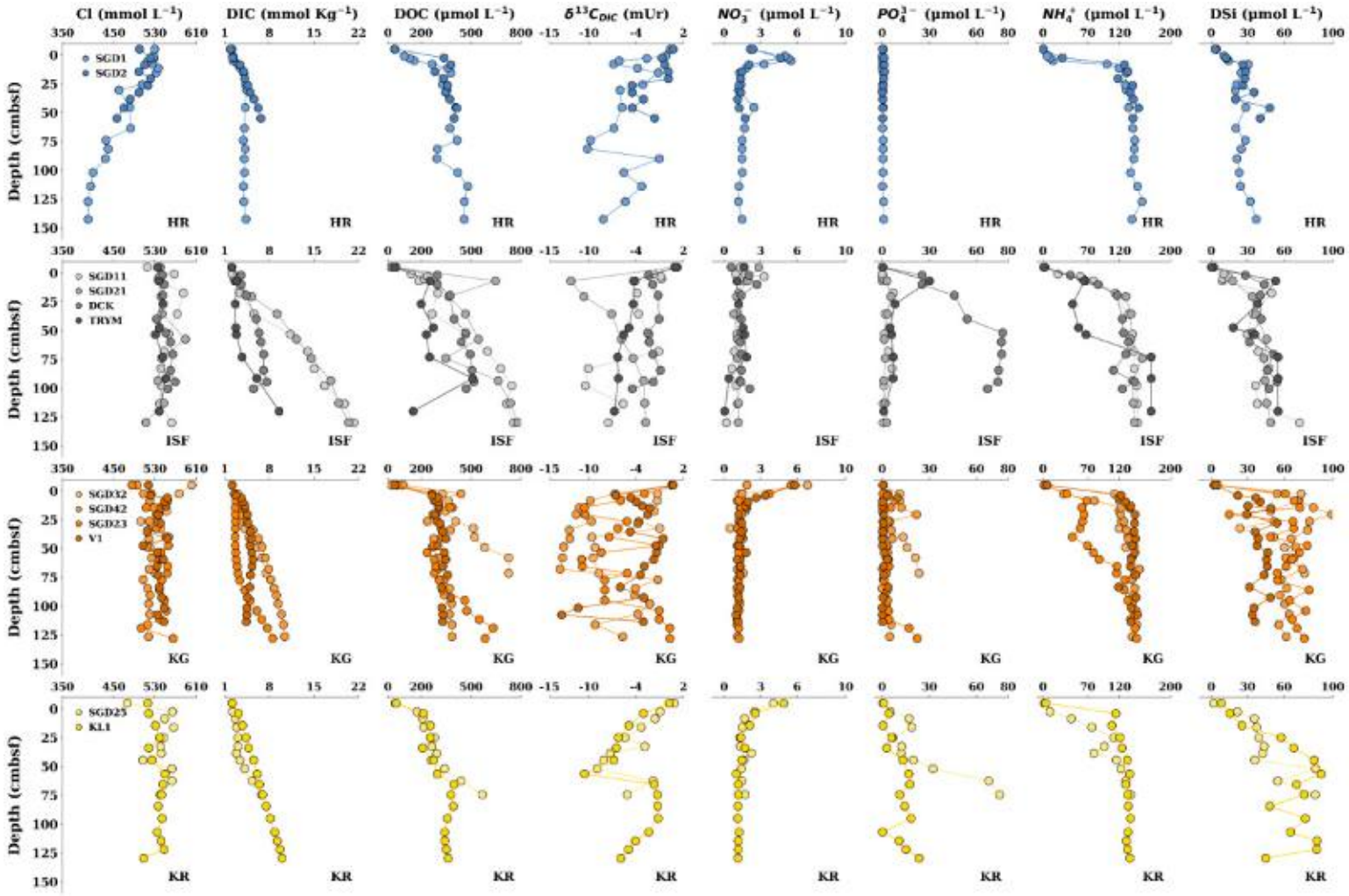

Figure 2. Depth profiles of chloride (Cl^-), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), stable carbon isotopic composition of dissolved inorganic carbon ($\delta 13C_{DIC}$), nitrate (NO_3^-), phosphate (PO_4^{3-}), ammonium (NH_4^+), and dissolved silica (DSi) in marine sediments across four Arctic fjords: Hornsund (HR), Isfjord (ISF), Kongsfjord (KG), and Krossfjord (KR). In each profile, samples are plotted along the y-axis, representing depth in centimeters below the seafloor (cmbsf). One additional sample at 5 cm represents bottom water collected just above the sediment–water interface.

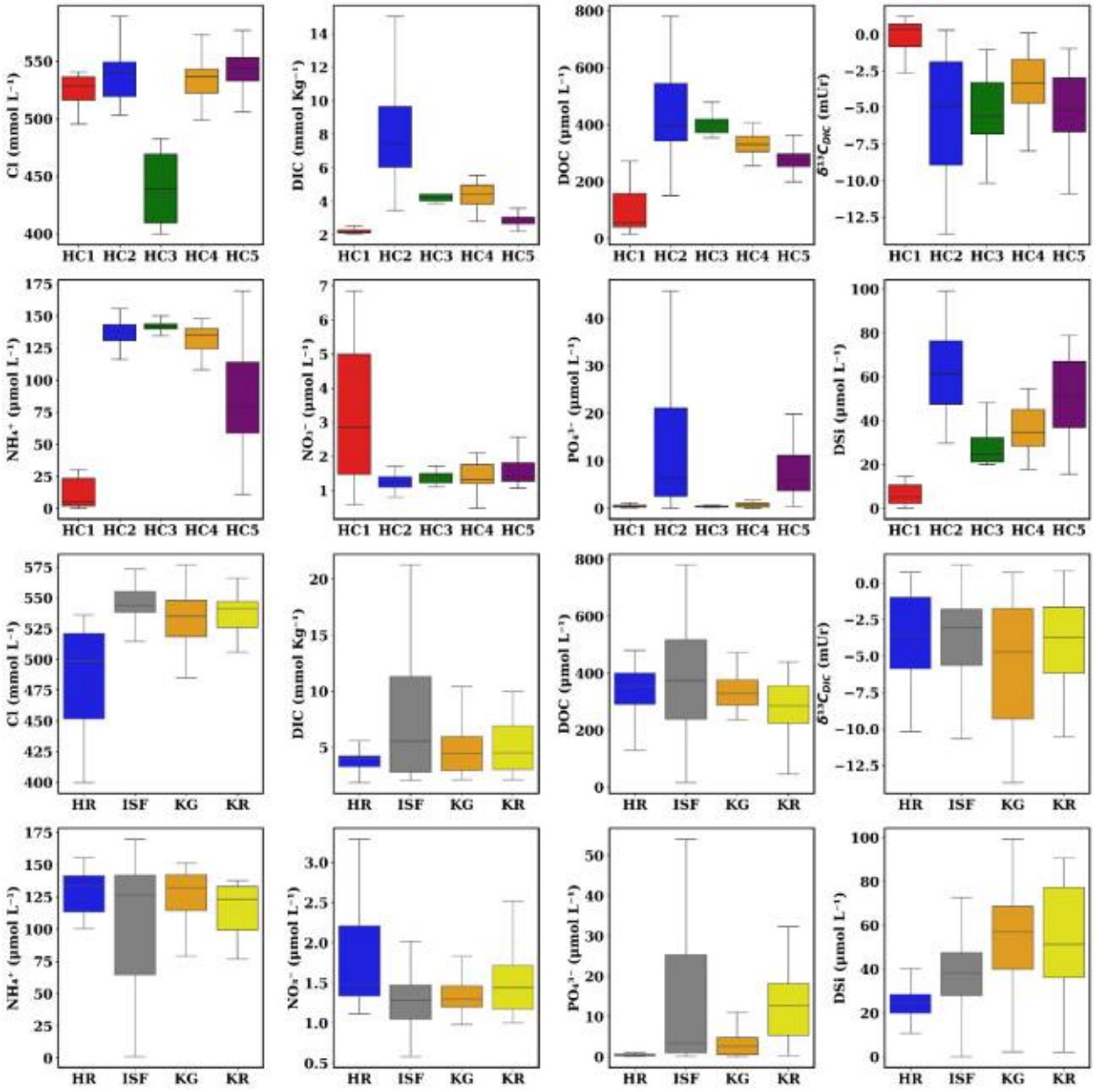

Figure 3. Box plots illustrate chloride (Cl^-), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), stable carbon isotopic composition of dissolved inorganic carbon ($\delta 13C_{DIC}$), nitrate (NO_3^-), phosphate (PO_4^{3-}), ammonium (NH_4^+), and dissolved silica (DSi) concentrations associated with clusters (HC1, HC2, HC3, HC4, HC5) and fjords: Hornsund (HR), Isfjord (ISF), Kongsfjord (KG), Krossfjord (KR).

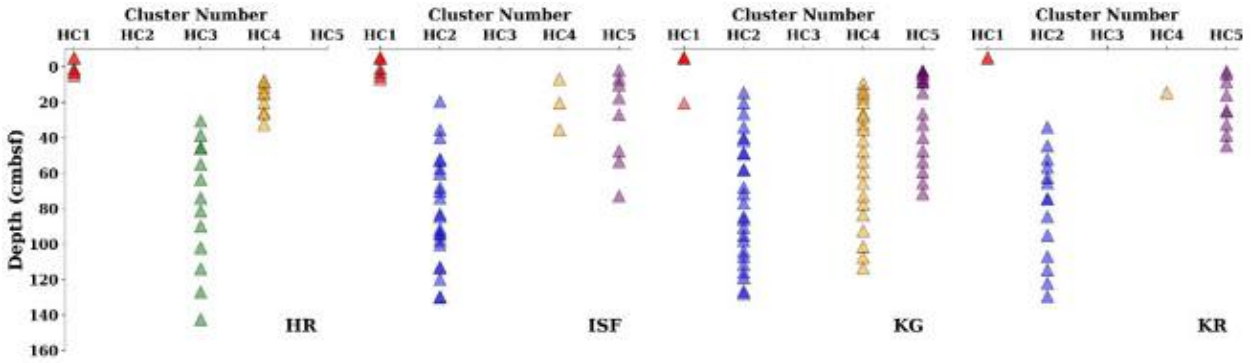

Figure 4. Distribution of hierarchical cluster analysis (HCA) results across fjords: Hornsund (HR), Isfjord (ISF), Kongsfjord (KG), Krossfjord (KR), with cluster numbers (HC1 through HC5) on the x-axis and depth (cmbsf) on the y-axis. Data points are color-coded based on cluster assignments: red (HC1), blue (HC2), green (HC3), orange (HC4), and purple (HC5).

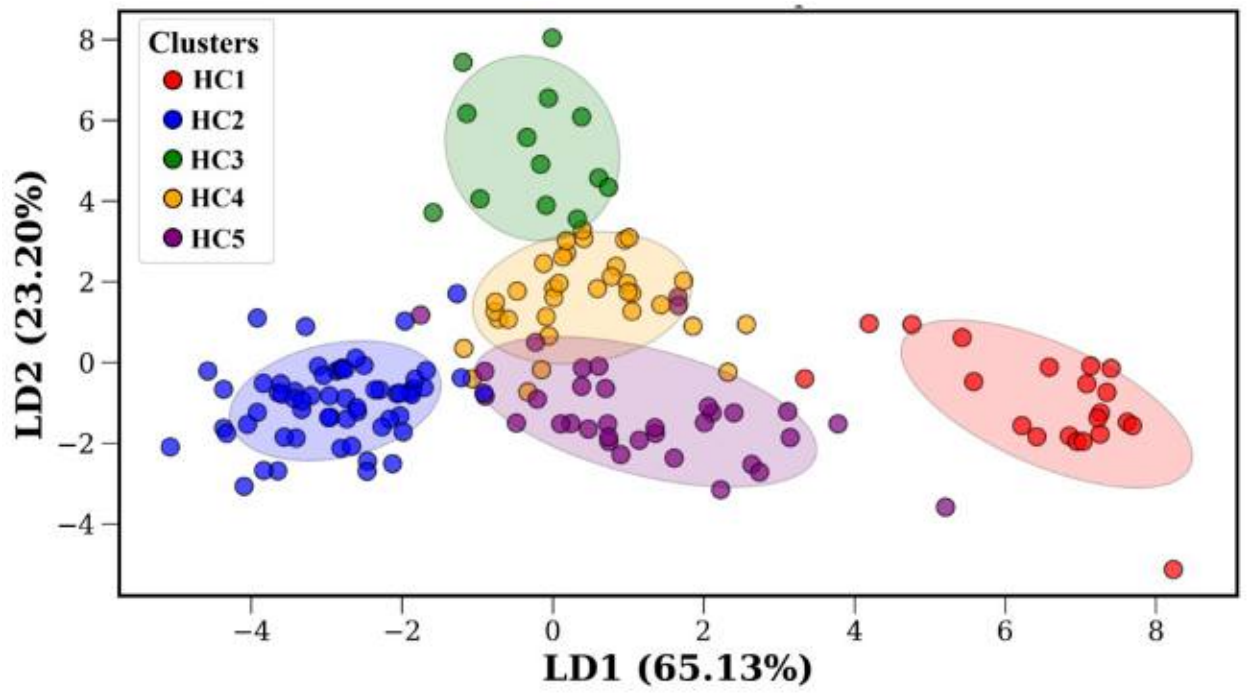

Figure 5. Linear discriminant analysis (LDA) of five clusters obtained from hierarchical cluster analysis results (HC1, HC2, HC3, HC4, HC5). Ellipses represent the distribution and separation of the clusters in the LDA space.

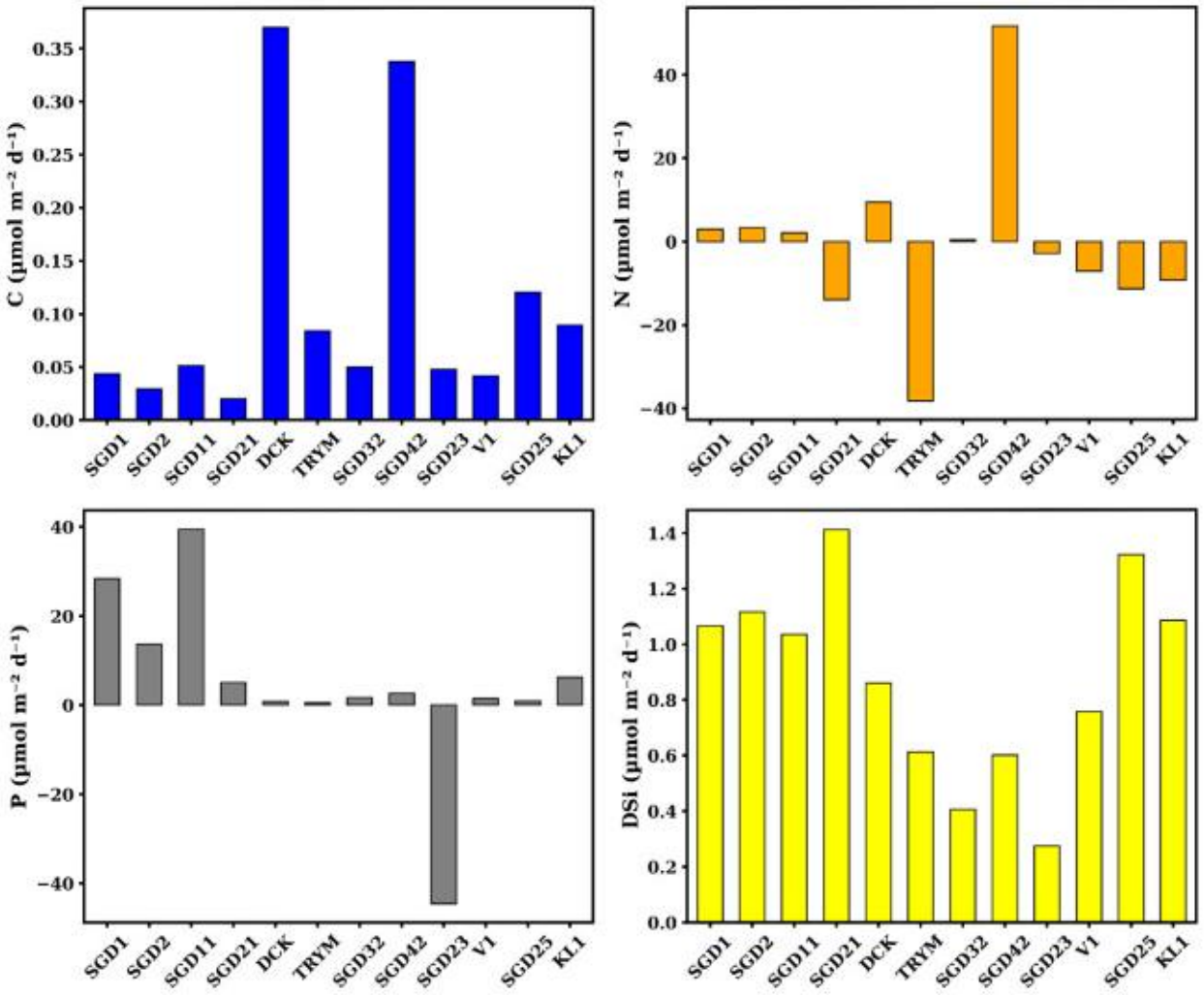

Figure 6. Benthic fluxes of carbon (C) expressed as the sum of dissolved inorganic and organic carbon, nitrogen (N) indicated as the sum of nitrate and ammonium, phosphorus (P) presented as phosphate, and silica (DSi) indicating dissolved silica.

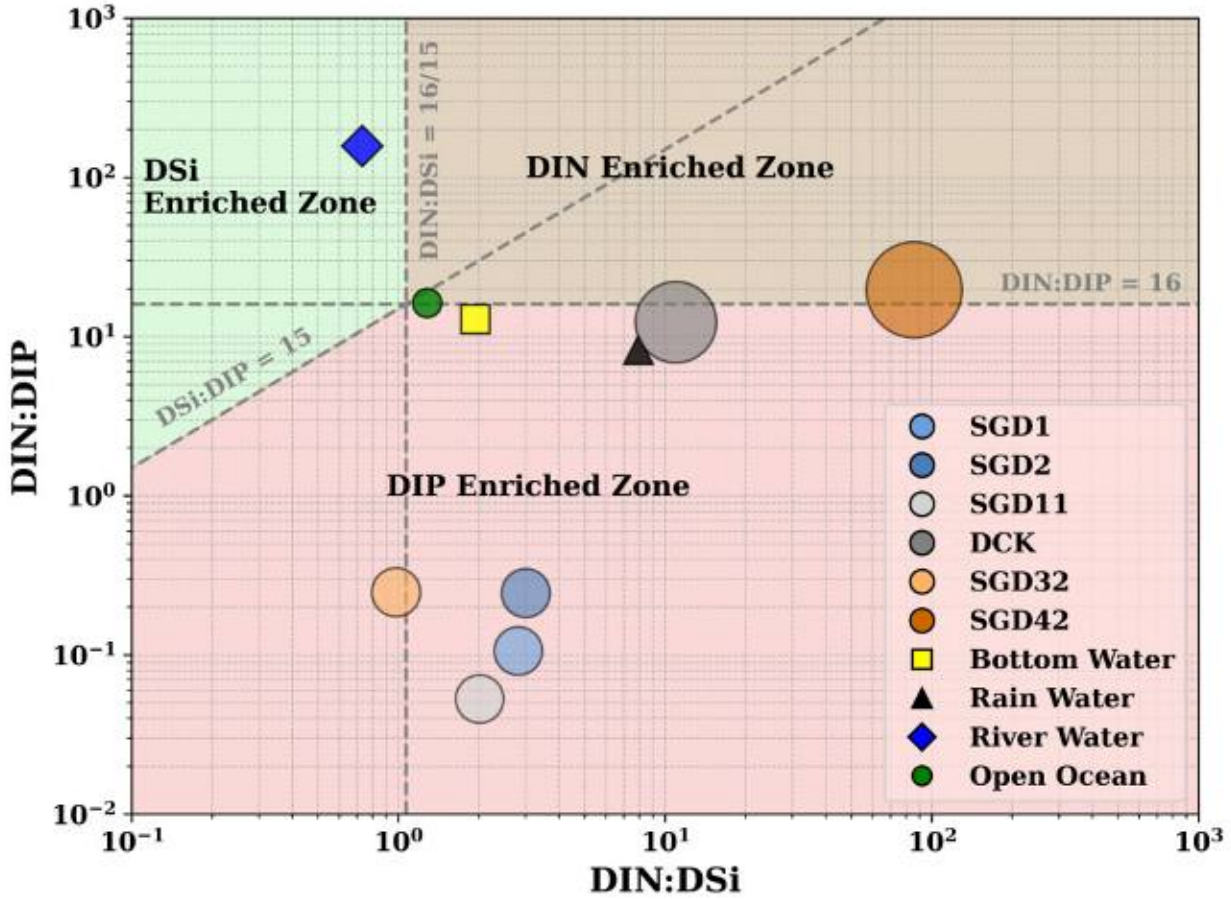

Figure 7. Nutrient ratios of calculated benthic fluxes (positive values), rain water, river water and open ocean (surface seawater) of dissolved inorganic nitrogen (DIN) represents the sum of nitrate (NO_3^-) and ammonium (NH_4^+); dissolved inorganic phosphate (DIP) reflects bioavailable phosphate (PO_4^{3-}); or dissolved silicate (DSi) includes bioavailable silica ($Si(OH)_4$) in the samples. Ratios are calculated based on the Redfield-Brzeziński ratio of N:Si:P=16:15:1. The diagram illustrates nutrient enrichment zones,

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I hereby declare that my contribution to the manuscript:

- **Saghravani, S.R.,** Böttcher, M.E., Hong, W.-L., Diak, M., Sen, A. and Szymczycha, B. 2025. Nutrients and carbon cycling in marine sediments of Arctic fjords. Submitted to *Oceanologia*

Included the conceptualization, data interpretation, methodology, data curation, visualization, investigation, and writing – original draft, reviewing, and editing.

Yours sincerely,

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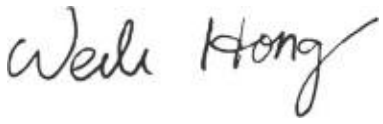

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included conceptualization, funding acquisition, methodology, supervision of data interpretation, supervision of writing the original draft, review and editing.

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RESEARCH ARTICLE 3

POLISH POLAR RESEARCH

Covariation of dissolved nutrients and carbon in seawaters and sediment porewaters of western Svalbard fjords

Współzmienność rozpuszczonych substancji biogenicznych i węgla w wodach morskich i wodach porowych osadów fiordów zachodniego Svalbardu

Seyed Reza Saghravani, Arunima Sen, Wei-Li Hong, Marc J. Silberberger

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Covariation of dissolved nutrients and carbon in seawaters and sediment porewaters of western Svalbard fjords

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Running title: Carbon–nutrient variability in Svalbard fjords

Abstract: We analyzed dissolved inorganic and organic carbon as well as dissolved inorganic nutrient concentrations in surface waters, bottom waters, water above sediments (*i.e.*, core-top water), and sediment porewaters at 19 sites in western Svalbard fjords. Multiple Factor Analysis was used to identify common patterns in the water column and sediment layers. The analysis revealed a clear separation between surface waters and all deep water and porewater layers due to the strong summer stratification. Bottom waters, water above sediments, and both upper and lower porewater layers showed strong covariation across sites, with some sites consistently exhibiting low concentrations of carbon and nutrients, and others high concentrations across these layers. In contrast, surface

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water concentrations varied more independently from the other layers. Most of the variation among deep water and porewater layers was driven by a small number of sites that showed enrichment in dissolved inorganic carbon, dissolved organic carbon, and multiple nutrients in bottom waters and porewaters. Differences among sites in fjords often exceeded those between fjord systems, suggesting that deep water and porewater biogeochemical variability is structured more strongly by local basin conditions than by fjord-wide gradients. The strong covariation between bottom water and porewater chemistry suggests that bottom water concentrations integrate sedimentary signals at sites. This fine-scale, basin-level heterogeneity implies that fjord-averaged descriptions overlook biogeochemically distinct basins and that resolving individual basins and secondary fjords is necessary to anticipate how these systems respond to ongoing Arctic change. The patterns are likely shaped by local hydrographic conditions, including winter water formation, Atlantic Water intrusion, and freshwater inputs, all of which are changing rapidly in Arctic fjords. These changes may alter the persistence of local enrichment patterns and complicate predictions of future nutrient and carbon dynamics.

Keywords: Arctic, Spitsbergen, porewater, surface water, bottom water.

Introduction

Arctic fjords are semi-enclosed transition zones where terrestrial and marine materials are transformed, retained, and redistributed under the combined influence of glacial, oceanic, and sedimentary processes (Syvitski 1989; Azetsu-Scott and Syvitski 1999). In Svalbard, fjords are density-stratified in summer, and deep water properties vary among fjords depending on sill depth and circulation. Some fjords contain Atlantic-influenced water at depth, whereas others, particularly silled inner basins, retain cold, locally formed winter-cooled water year-round (Cottier *et al.* 2005; Nilsen *et al.* 2016; Skogseth *et al.* 2020). This density stratification limits vertical exchange and influences the distribution of nutrients and carbon between surface waters dominated by photosynthetic processes and deeper waters where remineralization predominates (Sejr *et al.* 2017).

While vertical gradients in dissolved inorganic and organic carbon and nutrient concentrations in the water column are reported in some Arctic fjords (Ericson *et al.* 2019b; McGovern *et al.* 2020), recent work has quantified seawater and porewater gradients in western

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Spitsbergen fjords (Saghravani *et al.* 2024). Less is known, however, about how these layers vary spatially across sites. Sediment porewaters often have elevated nutrient and carbon concentrations that far exceed those in overlying waters, creating steep gradients at the sediment–water interface and promoting benthic–pelagic exchange (Huettel *et al.* 2014). However, it remains unclear whether nutrient and carbon concentration variability in surface waters, deep waters, and sediment porewaters responds to environmental controls, or whether distinct processes dominate different layers.

Freshwater inputs to Arctic fjords, including glacial meltwater, river discharge, and submarine groundwater discharge, deliver chemically distinct waters and organic matter to coastal environments, contributing pronounced spatial heterogeneity in nutrient and carbon concentrations (McGovern *et al.* 2020; Santos *et al.* 2021). In the Arctic, the influence of freshwater pathways is increasing as permafrost thaw and glacial retreat alter subsurface hydrology and create new routes for nutrient and carbon transport (Diak *et al.* 2023; Kleber *et al.* 2023). Where freshwater inputs interact with restricted circulation and limited deep water renewal, nutrients and both inorganic and organic carbon may accumulate in bottom waters. By contrast, nearby locations with stronger water exchange may remain comparatively low. As a result, sites of elevated nutrient and carbon concentrations may occur immediately adjacent to less enriched areas within the same fjord, suggesting that biogeochemical variability is structured by local hotspots associated with freshwater inputs, restricted deep-water renewal, and sediment organic matter supply rather than by fjord-scale gradients.

In this study, we assess whether dissolved inorganic and organic carbon, as well as nutrient concentrations, covary between surface waters, deep waters, and sediment porewaters in western Svalbard fjords or whether concentrations are controlled by layer-specific processes. We analyze concentrations of inorganic nutrients, inorganic and organic carbon in surface waters, deep waters, and sediment porewaters at multiple sites in western Svalbard fjords. To identify patterns among layers while accounting for differences in concentration magnitude, we apply multiple factor analysis (MFA) (Abdi *et al.* 2013), to the combined water column and porewater dataset. MFA is a multivariate ordination method that extends principal component analysis to datasets organized into predefined groups of variables measured on the same observations. MFA, which has recently been applied to characterize geochemical variability in Arctic marine porewater systems (Saghravani 2026), allows us to evaluate benthic–pelagic coupling and to

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determine whether spatial variability is primarily organized at the scale of individual sites or reflects broader fjord-scale gradients.

Study area

Svalbard is a High Arctic archipelago located between 74° and 81°N. The West Spitsbergen Current transports warm and saline Atlantic Water northward along the western coast, penetrating fjord systems to varying degrees depending on fjord morphology and sill depth (Cottier *et al.* 2005). Three fjord systems along western Spitsbergen, the largest island in the archipelago, were selected for this study: Hornsund in the south, Isfjorden in central Spitsbergen, and the connected Kongsfjorden-Krossfjorden system in the north (Fig. 1).

Hornsund is a relatively small fjord (~30 km long, 2–5 km wide) with more than ten marine-terminating glaciers that deliver large sediment loads via glacial discharge to the fjord (Smith *et al.* 2015; Pawłowska *et al.* 2016). The fjord consists of an outer basin (~180 m deep) and an inner basin (Brepollen) separated by a sill at approximately 50 m water depth. This sill limits exchange between the basins, and bottom waters are typically cold throughout the fjord (−1.2 to 1.6°C) (Promińska *et al.* 2018). Bedrock in the Hornsund catchment is dominated by Precambrian granitic and metamorphic rocks (Görlich 1986).

Isfjorden is the largest fjord system in Svalbard and includes several secondary fjords with contrasting hydrographic settings. Inner secondary fjords such as Billefjorden and Tempelfjorden are characterized by shallow sills that restrict deep-water exchange, whereas outer secondary fjords (*e.g.,* Adventfjorden) are more open to the influence of shelf waters (Szczuciński *et al.* 2009). Although Atlantic Water influences Isfjorden overall, its penetration varies among fjord basins: inner silled fjords such as Billefjorden retain cold winter water, whereas outer areas experience warmer conditions due to greater Atlantic Water intrusion (Saghravani *et al.* 2024). The Isfjorden catchment is underlain by complex Paleozoic and Mesozoic sedimentary sequences, including hydrocarbon-bearing strata (Roy *et al.* 2015) that influence organic carbon cycling in the fjord's sediments (Szymczycha *et al.* 2025).

Kongsfjorden and Krossfjorden are connected fjords in northwestern Spitsbergen with open connections to the continental shelf, allowing frequent intrusions of Atlantic Water, similar to the outer parts of Isfjorden (Hop *et al.* 2002; Piwosz *et al.* 2009). As a result, bottom waters are generally warmer (1.9–2.9°C) than in Hornsund and the inner, silled secondary fjords of

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Isfjorden (such as Billefjorden). Kongsfjorden and Krossfjorden receive freshwater and sediment inputs from marine-terminating and land-terminating glaciers. The surrounding bedrock consists of mixed sedimentary and metamorphic sequences, including marble and carbonate-bearing units (Svendsen *et al.* 2002).

Methods

Sampling design and water layers

Sampling was conducted aboard the R/V *Oceania* between July and September in 2021 and 2022 as part of the Arctic Expedition (AREX), the long-term multidisciplinary Arctic monitoring program of the Institute of Oceanology, Polish Academy of Sciences. A total of 19 sites were sampled in the three western Svalbard fjord systems, as illustrated in Fig. 1. Water column depths at the sampling sites ranged from 33 to 374 m (Table 1).

At each site, a single sample was collected from each of five layers: (*i*) surface water (0-2 m depth), (*ii*) bottom water (2–3 m above the seafloor), (*iii*) water directly overlying the sediment (*i.e.* water contained within the sediment core liner above the sediment-water interface; water above sediment), (*iv*) upper sediment porewater (1–7 cm sediment depth), and (*v*) lower porewater (21.5–280 cm sediment depth, representing the deepest porewater interval recovered at each site, depending on core penetration). The upper porewater interval represents near-surface sediments influenced by benthic exchange, bioturbation, and bioirrigation, whereas the deeper porewater interval reflects more isolated geochemical conditions below the main zone of macrofaunal influence.

Surface and bottom waters were collected using a Sea-Bird Scientific SBE 911 Plus conductivity–temperature–depth (CTD) rosette profiler equipped with 10-L Niskin bottles and an SBE 43 oxygen module (calibrated prior to the cruise). Sediment cores were collected with a gravity corer. Sediment porewaters were extracted through pre-drilled holes in the core liners using Rhizon® samplers (Rhizosphere, 2.5 mm diameter, mean pore size 0.15 µm). In addition, either a GEMAX or a Niemistö corer were deployed at the same locations to collect water directly overlying the sediment (Saghravani *et al.* 2024). Water overlying the sediment surface in the core liner was collected immediately after core retrieval using a syringe carefully inserted into the overlying water column within the core liner, avoiding disturbance of the sediment-water interface.

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Sample handling and preservation

Upon collection, each water sample was sub-sampled into several aliquots for different analyses. For inorganic nutrient analyses (ammonium – NH_4^+, nitrate – NO_3^-, phosphate – PO_4^{3-}, dissolved silica – DSi), up to 5 mL of porewater was transferred into pre-cleaned (rinsed with Milli-Q water) high-density polyethylene (HDPE) bottles, and 10 mL of seawater was filtered through 0.45 µm cellulose acetate filters into pre-cleaned (rinsed with Milli-Q water) HDPE bottles. All sub-samples were then stored frozen at −20°C until analysis. Sub-samples for dissolved inorganic carbon (DIC) were collected in gas-tight glass bottles (250 mL for seawater, 12 mL for porewater), poisoned with a saturated $HgCl_2$ solution (25 µL for porewater, 100 µL for seawater), and stored without headspace to prevent biological activity and gas exchange. For dissolved organic carbon (DOC) analysis, 20 mL and 12 mL of seawater and porewater, respectively, were filtered through 0.45 µm MN GF-5, acidified with HCl to pH ~2, and stored at 4°C until analysis. Approximately 2 mL of sample for chloride (Cl^-) analysis was transferred to PET vials, which were stored at 4°C. Approximately 10 mL of porewater samples for major cation analysis were acidified with ultrapure HNO_3 to a pH < 2 and stored at 4°C until measurement.

Laboratory analysis

Nutrient concentrations were determined using a SEAL AA500 AutoAnalyzer (Seal Analytical) with standard photometric methods (Grasshoff *et al.* 1999). Quality control included repeated measurements of two Certified Reference Materials (QC3179 from Sigma Aldrich, and HAMIL from Environment Canada). The accuracy of NO_3^-, NH_4^+, PO_4^{3-}, and DSi measurements was 98.8%, 98.8%, 99.0%, and 100.1%, respectively. The precision was 0.01 µmol L^{-1}, 0.02 µmol L^{-1}, 0.01 µmol L^{-1}, and 0.03 µmol L^{-1}, respectively (the reported NO_3^- values are nitrate only and do not include nitrite). Cl^- concentrations were determined by potentiometric titration to a precision of 0.1 mmol L^{-1} (Kłostowska *et al.* 2020). DIC analyses were conducted with Apollo SciTech's AS-C6L DIC Analyzer, which features a laser-based CO_2 detector (LI-7815, Li-Cor, USA). Measurement accuracy was ensured by analyzing certified reference materials (CRMs, batches #190 and #195) from A.G. Dickson (Scripps Institution of Oceanography, USA). Precision was assessed from triplicate measurements of individual samples and was no worse than ±3 µmol L^{-1}, with an average recovery of 99.0%. DOC analyses were conducted on a TOC-

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L analyzer (Shimadzu) using a high-temperature (680°C) oxidation method with a Pt catalyst. The precision of DOC measurements was ±4 µmol L^{-1}. Accuracy was determined by repeated measurements of certified reference materials (CRMs) provided by the D. Hansell Laboratory (University of Miami, USA), with a recovery of 99%. Major cations were measured using a flame atomic absorption spectrometer (AAS; Shimadzu AA-6800 Series). Samples were diluted 10-to 100-fold with ultrapure water before AAS analysis to bring concentrations within the instrument's optimal range. Analytical precision was < 2% relative standard deviation for all cations, with detection limits of 0.4 µmol L^{-1} (0.01 mg L^{-1}) for sodium (Na^+), 0.26 µmol L^{-1} (0.01 mg L^{-1}) for potassium (K^+), 0.12 µmol L^{-1} (0.005 mg L^{-1}) for calcium (Ca^{2+}), and 0.21 µmol L^{-1} (0.005 mg L^{-1}) for magnesium (Mg^{2+}). Accuracy was verified using a certified reference material (CASS-6 seawater standard), yielding recoveries of 95-105% for all elements. Cation concentrations were converted to mmol L^{-1} for all subsequent analyses.

Data organization and multiple factor analysis

MFA was used to investigate spatial covariation among nutrient and carbon concentrations measured in the water column and sediments. In simple terms, MFA was used to assess whether dissolved nutrient and inorganic and organic carbon concentrations showed similar spatial patterns in the water column and sediment layers among sampling sites.

Variables were grouped by sampling layer. Accordingly, five groups of active variables were defined: surface water, bottom water, water above sediment, upper sediment porewater, and lower sediment porewater. Each group contained the same six chemical variables: DIC, DOC, NH_4^+, NO_3^-, PO_4^{3-}, and DSi. This resulted in a dataset comprising 30 active chemical variables (6 variables × 5 distinct layers) across 19 sampling sites.

Environmental variables describing hydrographic and site characteristics were included as supplementary variables to aid interpretation of ordination patterns. These included water depth, sediment core length, bottom water temperature, distance from land, distance from glaciers, distance from rivers, Cl^- concentrations in surface water and lower porewater, and major cation concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}) measured in water overlying the sediment and in porewaters. Supplementary variables were projected onto the MFA ordination space after analysis and therefore did not influence the calculation of the MFA dimensions.

Prior to analysis, all active variables were standardized to unit variance to account for differences in concentration ranges across the five sampled layers. Following standard MFA

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procedures, each layer, treated as a separate group of variables, was weighted by its internal variance structure to ensure equal contribution to the overall analysis. Although each layer contained the same set of chemical variables, this weighting accounts for differences in the correlation structure within each layer, preventing any single layer from exerting a disproportionate influence on the results. Consequently, the analysis extracts a set of new axes, referred to as dimensions, that represent the main patterns of variation shared across the water column and porewater layers. Each dimension summarizes a set of chemical variables that vary together in samples. The position of a layer relative to a dimension, referred to as its group loading, indicates how strongly that layer reflects the shared pattern, whereas the position of an individual variable indicates the direction and strength of its association with that pattern with values near 1 indicating close alignment and values near 0 indicating little association.

Results

Vertical distribution of chemical concentrations

Clear vertical gradients were observed for most dissolved carbon and nutrient species in the five layers (Fig. 2). DIC, DOC, NH_4^+, PO_4^{3-}, and DSi showed low concentrations in surface and bottom waters, modest increases in water above sediment, and higher concentrations in sediment porewaters. For example, DIC rose from ~1900–2110 µmol L^{-1} in surface waters to 2650–21260 µmol L^{-1} in lower porewaters; NH_4^+ from < 0.3–2.4 to 87–773 µmol L^{-1}; DOC from 19–85 to 230–2690 µmol L^{-1}; PO_4^{3-} from 0.1–0.4 to up to ~75 µmol L^{-1}; and DSi from 0.7–2.8 to up to ~290 µmol L^{-1}. In particular, DIC and NH_4^+ concentrations increased sharply from the water column to the porewaters. NO_3^- showed a different pattern: concentrations were low in surface waters (0.3–3.7 µmol L^{-1}), higher in bottom waters and water above sediment (up to ~13–14 µmol L^{-1}), and declined in both upper and lower porewaters.

Cl^- and major cations measured in water above sediment and in porewaters showed variable distributions without a consistent monotonic vertical pattern. As expected in these marine systems, Na^+ tracked Cl^- conservatively; Ca^{2+}, K^+, and Mg^{2+}, in contrast, showed site-specific variability, particularly in the lower porewaters.

Across-fjord variability

Nutrient and dissolved (in)organic carbon concentrations in surface water, bottom water, water above sediment, and porewaters were broadly similar across the fjord systems (Fig. 3). For most

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variables, interquartile ranges and medians overlapped among the three fjord systems. NO_3^-, NH_4^+, DSi, and PO_4^{3-} concentrations varied considerably among fjords, particularly in Isfjorden, but no differences among fjord systems were evident. DOC concentrations showed greater variability in Hornsund and Isfjorden than in Kongsfjorden and Krossfjorden, although the concentration ranges overlapped. Similarly, DIC and Cl^- concentrations showed no clear separation among fjords. Major cation concentrations (Na^+, Ca^{2+}, K^+, Mg^{2+}) varied across sites but did not differ by fjord. Overall, variability among sites within fjords was comparable to, or even greater than, that between fjord systems.

Multiple factor analysis

The first three MFA dimensions (composite axes representing the main patterns of chemical variation across sites) accounted for 57.4% of the total variance (29.9%, 14.4%, and 13.2% for dimensions 1 to 3, respectively). Together, the first five dimensions explained 73.5% of the total variance (Table 2).

Dimension 1 was strongly represented by bottom water, water above sediment, and upper and lower porewater layers (group loadings 0.65-0.72, *i.e.*, these layers align closely with this axis), whereas surface water showed a weak association with this dimension. Site contributions to Dimension 1 were uneven, with SGD9 accounting for 40.8% of the variance, followed by SGD4 (18.0%) and SGD3 (14.6%). Dimension 2 is represented mainly by surface water (loading 0.56) and upper porewater (loading 0.40). Sites SGD27 and SGD5 contributed 23.9% and 11.0%, respectively, to the variance explained by this dimension. Dimension 3 was represented primarily by surface water (loading 0.50), whereas bottom water showed a weaker association (0.32). SGD5 contributed 39.2% to the variance in Dimension 3, followed by SGD25 (13.0%). Taken together, the first three dimensions indicate that surface water chemistry varied largely independently of the deep water and porewater layers.

At the variable level, Dimension 1 was characterized by high positive coordinates (0.70–0.90) for DOC, DSi, and PO_4^{3-} in the bottom water and porewater groups, indicating that these variables increase together across sites. By contrast, surface water variables had near-zero coordinates on Dimension 1, indicating that they were largely unrelated to deep water and porewater patterns. Dimension 2 was associated with surface water NO_3^-, PO_4^{3-}, and NH_4^+, along with selected porewater variables. Dimension 3 was driven mainly by surface water DIC, NO_3^-, and PO_4^{3-} concentrations. The MFA biplots visualize relationships among variables, layers, and

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sites along the main dimensions of variation (Fig. 4). In the Dimension 1–Dimension 2 projection, bottom water, water above sediment, and porewater variables cluster along the positive side of Dimension 1, indicating that they increase together across sites, whereas surface water variables align along Dimension 2, reflecting a distinct pattern of variation. In the Dimension 1–Dimension 3 projection, surface-water variables are separated primarily along Dimension 3. Sites contributing most strongly to Dimension 1, particularly SGD9, are located at the positive end of this axis.

Discussion

Deep water and porewater coupling and surface water decoupling

Across most sites in all three fjord systems, concentrations of carbon and nutrients in bottom water, water above sediment, and both porewater layers showed coordinated variation, whereas concentrations in surface waters varied independently. This coupling is the dominant pattern captured by the MFA: the four deep water and porewater layers load strongly on Dimension 1 (0.65–0.72), meaning their variables align closely with this axis, whereas surface water does not. Dimension 1 separates sites with relatively low versus high concentrations of nutrients and carbon in deep waters and porewaters, explaining 29.9% of the total variance (Fig. 4). Variables including NO_3^-, PO_4^{3-}, DSi, DOC, and DIC from several layers are similarly distributed along this dimension, indicating that enrichment occurs simultaneously across multiple constituents rather than in isolated variables.

The similarity between bottom water and water above sediment on Dimension 1 indicates strong covariation between near-bottom water and sediment porewater chemistry. Sites with high porewater concentrations of nutrients and carbon showed elevated bottom water concentrations, supporting the interpretation that bottom water chemistry reflects integrated sedimentary biogeochemical conditions at the site scale (Kostka *et al.* 1999). This interpretation is supported by the concentration profiles (Fig. 2), which show coordinated increases in carbon and nutrient concentrations from bottom water through water above sediment into the porewaters. It is further supported by their relationships with Cl^- (Fig. 5), where porewater DIC, DOC, NH_4^+, PO_4^{3-}, and DSi concentrations lie well above the conservative seawater–freshwater mixing line, indicating that the enrichment reflects in-situ remineralization rather than physical mixing. Importantly, the sites contributing most strongly to this pattern are characterized by concurrent enrichment in DIC,

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DOC, NH_4^+, PO_4^{3-}, and DSi rather than by elevated concentrations of any single variable. This coordinated enrichment across multiple carbon and nutrient species indicates that organic-matter remineralization in the sediments is the common driver of these chemical patterns, with its products accumulating in the porewaters and the overlying bottom water.

Sites with deeper water columns often showed elevated concentrations in bottom water, water above sediment, and porewaters. The weak relationship ($r = 0.42$) reflects variation in basin ventilation: deep basins behind shallow sills often accumulate remineralization products due to limited exchange and long residence times, whereas similarly deep but more open basins are better ventilated (Skogseth *et al.* 2005; Inall and Gillibrand 2010).

Conversely, surface water had little impact on Dimension 1 but was the primary driver of Dimensions 2 and 3. The orientation of surface nutrient variables along these secondary dimensions indicates that surface water variability is organized separately from the main deep water and porewater pattern. This separation aligns with the strong summer stratification observed in Arctic fjords, which restricts vertical mixing and allows surface processes, such as biological uptake, atmospheric exchange, and freshwater input, to proceed independently of deep water and sediment activities (Cottier *et al.* 2005; Stigebrandt 2012; McGovern *et al.* 2020; Meyer *et al.* 2020).

Biogeochemical hotspots and basin morphology

A small number of sites account for a disproportionate share of the coordinated deep water and porewater enrichment. Three sites (SGD9 in Billefjorden, Isfjorden; SGD3 and SGD4 in the main basin of Hornsund), representing 16% of sampled sites, explained 73.4% of the variance in Dimension 1. These sites are located in basins with limited deep-water exchange, where water depth exceeds the sill depth, promoting prolonged isolation of dense bottom waters (Inall and Gillibrand 2010). The site in silled Billefjorden recorded the coldest bottom water temperature during the study period (−1.7°C), consistent with locally formed winter water and limited renewal (Cottier *et al.* 2005). SGD3 and SGD4 lie in the main basin of Hornsund, where water depth (181 and 240 m) exceeds the ~150 m depth at the fjord entrance, favoring isolation of dense bottom water. In this case, bottom water is warmer than in Billefjorden (> 1°C) but is overlain and isolated by Atlantic Water (Swerpel 1985). In contrast, sites in well-ventilated settings, including SGD32 at the mouth of Kongsfjorden, showed little deep water and porewater enrichment despite

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reaching depths of 374 m. Frequent Atlantic Water intrusions at this location probably hinder the continual accumulation of remineralization products (Tverberg *et al.* 2019).

Basin isolation alone, however, does not fully explain enrichment patterns. For example, SGD1 in Brepollen, the inner deep basin of Hornsund, lies behind a shallow sill, has cold bottom water, yet shows slight enrichment in deep water and porewater. One possible explanation is that increased exchange is linked to submarine groundwater discharge, indicated by Cl^- depletion in lower porewaters (Table 1) and by previous reports of hydrological connectivity in Arctic fjords (Taniguchi *et al.* 2019; McGovern *et al.* 2020). Although the co-occurrence of Cl^- depletion and nutrient/carbon enrichment at SGD3 and SGD4 is consistent with a groundwater contribution, submarine groundwater discharge is characteristically low in DIC and nutrients and cannot, by itself, account for the magnitude of enrichment observed; in-situ remineralization is therefore required, with groundwater discharge potentially modulating the physical environment. Alternatively, the inner part of Hornsund may experience a reduced influence from Atlantic Water relative to SGD3 and SGD4, potentially limiting the supply of labile marine organic matter to sediments and thereby constraining remineralization rates despite physical isolation. Although these mechanisms cannot be determined from the present dataset, contrasting behavior among morphologically similar basins suggests that basin restriction and organic matter supply influence hotspot formation.

Secondary dimensions revealed distinct surface-dominated patterns. SGD5 in inner Hornsund accounted for 39.2% of the variance in Dimension 3 due to elevated surface DIC and nutrient concentrations, whereas SGD27 in Nordfjorden (Isfjorden) drove Dimension 2. These two sites stood out for surface-layer enrichment rather than subsurface coupling: SGD5 in inner Hornsund, with markedly elevated surface DIC and nutrient concentrations, and SGD27 in Nordfjorden (Isfjorden). These surface signals defined the secondary MFA dimensions (Dimensions 3 and 2, respectively), confirming that surface-water variability is organized independently of the subsurface pattern.

Mosaic structure of biogeochemistry in western Svalbard fjords

Our data showed that deep water and porewater enrichment varied markedly among the inner sub-fjords of the Isfjorden system. Billefjorden and Dicksonfjorden are shallow-silled inner basins with less influence from Atlantic Water than the outer Isfjorden. Yet, they exhibit markedly different enrichment patterns, indicating that local basin morphology and circulation exert a

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stronger influence on deep water and porewater biogeochemistry than the broader fjord-scale setting.

The fine-scale heterogeneity aligns with previous observations that Arctic fjords exhibit strong spatial variability driven by local hydrographic and geomorphological factors (Cottier *et al.* 2005; McGovern *et al.* 2020). Western Svalbard fjords display a mosaic spatial structure, a patchwork in which adjacent basins within the same fjord system have distinct biogeochemical conditions rather than a smooth fjord-wide gradient. This pattern is consistent with the established understanding of systems such as Isfjorden, where secondary fjords differ markedly in temperature, circulation, and biogeochemistry depending on sill depth, access to Atlantic Water, and proximity to land- and marine-terminating glaciers (Skogseth *et al.* 2020). In the same western Spitsbergen fjords, the distribution of inorganic carbon and the carbonate system is governed by the relative contributions of Atlantic Water, colder coastal-current water, and glacial freshwater (Fransson *et al.* 2015, 2016), consistent with the water-mass and freshwater controls on deep water and porewater biogeochemistry inferred here. Deep water and porewater enrichment develop where physical isolation and biogeochemical production coincide, whereas nearby sites in the same fjord can carry different chemical signatures even at similar depths or comparable proximity to land-based inputs. The role of proximity to freshwater sources such as river mouths and glacier fronts remains unclear in this dataset, since distance alone does not capture differences in discharge or freshwater composition among sources. Overall, however, the results indicate that deep water and porewater enrichment is more strongly controlled by restricted deep-water renewal than by proximity to land.

Because sampling was distributed across two summers (2021 and 2022), with each site visited only once, spatial and inter-annual variation cannot be fully separated in this dataset, and the pattern reported here should be interpreted in light of the inter-annual variability documented for these fjords. In Kongsfjorden, Fransson *et al.* (2016) found that a shift in the balance between Atlantic Water and the colder, CO_2-rich coastal current between 2013 and 2014 lowered summer pH and aragonite saturation in the year with weaker Atlantic inflow, and that the biological imprint on the carbonate system varied more between years than the freshwater imprint. In Tempelfjorden, Fransson *et al.* (2015) showed that an anomalously mild winter with delayed sea-ice formation during 2012 produced the highest freshwater fractions and the lowest saturation states in their record. Sea ice contributes directly: brine rejected during ice formation generates

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dense, DIC-enriched water that can sink into the deeper basins, while the coastal current carries CO_2-rich, sea-ice-influenced water of Storfjorden origin into the western fjords. These processes act mainly on the surface and bottom waters and on the external source waters, rather than on the porewater enrichment described above, which is set by in-situ remineralization; they nonetheless imply that absolute concentrations, though not necessarily the layer-to-layer covariation structure, would differ in a year with contrasting ice cover or Atlantic inflow.

Implications for fjords under changing Arctic conditions

Projected changes in winter water formation, Atlantic Water intrusion, and freshwater inputs may alter the persistence of isolated bottom waters and the associated enrichment patterns. Reduced winter renewal, already observed in parts of the Svalbard fjords (Cottier *et al.* 2005), may prolong isolation in silled basins, whereas increased Atlantic inflow could enhance ventilation and disrupt locally accumulated deep water and porewater signals (Tverberg *et al.* 2019). Concurrent changes in primary production and terrestrial inputs due to glacial retreat and permafrost thaw (McGovern *et al.* 2020; Diak *et al.* 2023) may further influence whether fjord basins with restricted water renewal develop coordinated deep water and porewater enrichment.

The pronounced site-scale heterogeneity documented in this study suggests that responses to climate forcing will vary locally, complicating fjord-scale predictions of future nutrient and carbon dynamics (Fransson *et al.* 2015, 2016; Ericson *et al.* 2019a). The spatial organization revealed here indicates that predictive models of Arctic fjord biogeochemistry need to account for basin-scale heterogeneity and variations among secondary fjords and inner basins within larger systems, rather than relying solely on fjord-wide averages.

Conclusion

MFA of dissolved carbon and nutrient concentrations across five water column and sediment layers in western Svalbard fjords revealed strong covariation among bottom water, water above sediment, and porewaters, decoupled from the overlying surface water, which is set apart by summer stratification. Bottom water chemistry closely tracked porewater chemistry at the site scale, indicating that near-bottom waters integrate the sedimentary biogeochemical signal. Most deep water and porewater variability was driven by a few sites in restricted, poorly ventilated basins, where enrichment in DIC, DOC, NH_4^+, PO_4^{3-}, and DSi, as confirmed by concentration profiles and their relationships with Cl^-, reflected in situ remineralization rather than physical

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mixing, producing local biogeochemical hotspots. Differences among sites within fjords were as great as, or even greater than, differences between fjord systems, pointing to a mosaic structure governed by local basin morphology and circulation rather than fjord-wide gradients. As winter water formation, Atlantic Water intrusion, and freshwater inputs shift under continued Arctic warming, this fine-scale heterogeneity implies that fjord-averaged predictions will miss biogeochemically important basins, and that resolving individual basins and secondary fjords will be essential for anticipating future carbon and nutrient dynamics.

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Table 1. Selected environmental characteristics of sampling sites in four Svalbard fjords

Site	Fjord[a]	Date	Water Depth	Core penetration depth	Bottom water Temp	Distance from Glacier	Distance from Land	SW Cl^-	LP Cl^-
			(m)	(cm)	(°C)	(km)	(km)	(mmol L^{-1})	(mmol L^{-1})
SGD1	HR	2022	124	142.5	-1.2	5.0	2.2	490.5	399.9
SGD2	HR	2021	83	55	1.1	13.0	2.5	456.1	456.0
SGD3	HR	2021	240	280	1.6	6.7	2.7	502.7	505.9
SGD4	HR	2021	181	268.5	1.4	5.3	3.5	468.3	320.5
SGD5	HR	2021	53	90	1.5	3.7	1.7	477.7	335.4
JMW25	ISF	2021	33	85	3.1	2.5	1.1	486.0	455.6
IT3	ISF	2021	39.4	41.5	1.8	1.9	1.0	470.2	502.5
JMW4	ISF	2021	72	180	1.5	15.2	0.9	500.9	364.3
Yol2	ISF	2021	71	21.5	1.5	11.8	4.8	469.5	549.1
SGD9	ISF	2021	146	234	-1.7	13.1	1.9	528.8	525.8
SGD11	ISF	2022	65	130	2.4	1.7	1.7	503.4	562.5
DCK	ISF	2022	17	100.5	5.0	7.0	2.5	414.0	555.1
SGD21	ISF	2022	100	129.7	0.8	2.2	2.2	482.8	512.2
SGD27	ISF	2022	35	146	3.0	28.8	1.7	425.8	488.6
SGD23	KG	2022	153	128	2.5	3.4	2.2	468.5	565.2
SGD32	KG	2022	374	71.5	1.3	5.2	12.0	492.3	530.6
V1	KG	2022	98.4	113.5	2.9	2.2	1.8	490.5	547.2
SGD25	KR	2022	146	74.5	2.9	6.0	1.5	457.3	539.8
KL1	KR	2022	287	129.5	1.9	11.1	1.2	446.2	508.3

[a] HR - Hornsund; ISF - Isfjord; KG - Kongsfjord; KR - Krossfjord. SW - surface water; LP - lower porewater.

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Table 2. Summary of MFA results for the first five retained dimensions. Eigenvalues and percentages of explained variance are shown for each dimension. "Main Contributing Groups" identify layers with group loadings > 0.40, indicating strong association with the corresponding dimension. "Key Site Contributors" represent sampling sites with the largest percentage contributions to each dimension's variance.

Dimension	Eigenvalue	Variance (%)	Cumulative (%)	Main Contributing Groups (Loading > 0.40)	Key Site Contributors
1	2.92	29.9	29.9	Bottom water (0.70) Water above sediment (0.72) Upper porewater (0.65) Lower porewater (0.72)	SGD9 (40.8%) SGD4 (18.0%) SGD3 (14.6%)
2	1.41	14.4	44.3	Surface water (0.56) Upper porewater (0.40)	SGD27 (23.9%) SGD5 (11.0%)
3	1.29	13.2	57.4	Surface water (0.50)	SGD5 (39.2%) SGD25 (13.0%)
4	0.89	9.1	66.5	None > 0.40	DCK (34.0%)
5	0.69	7.0	73.5	None > 0.40	SGD11 (21.4%)

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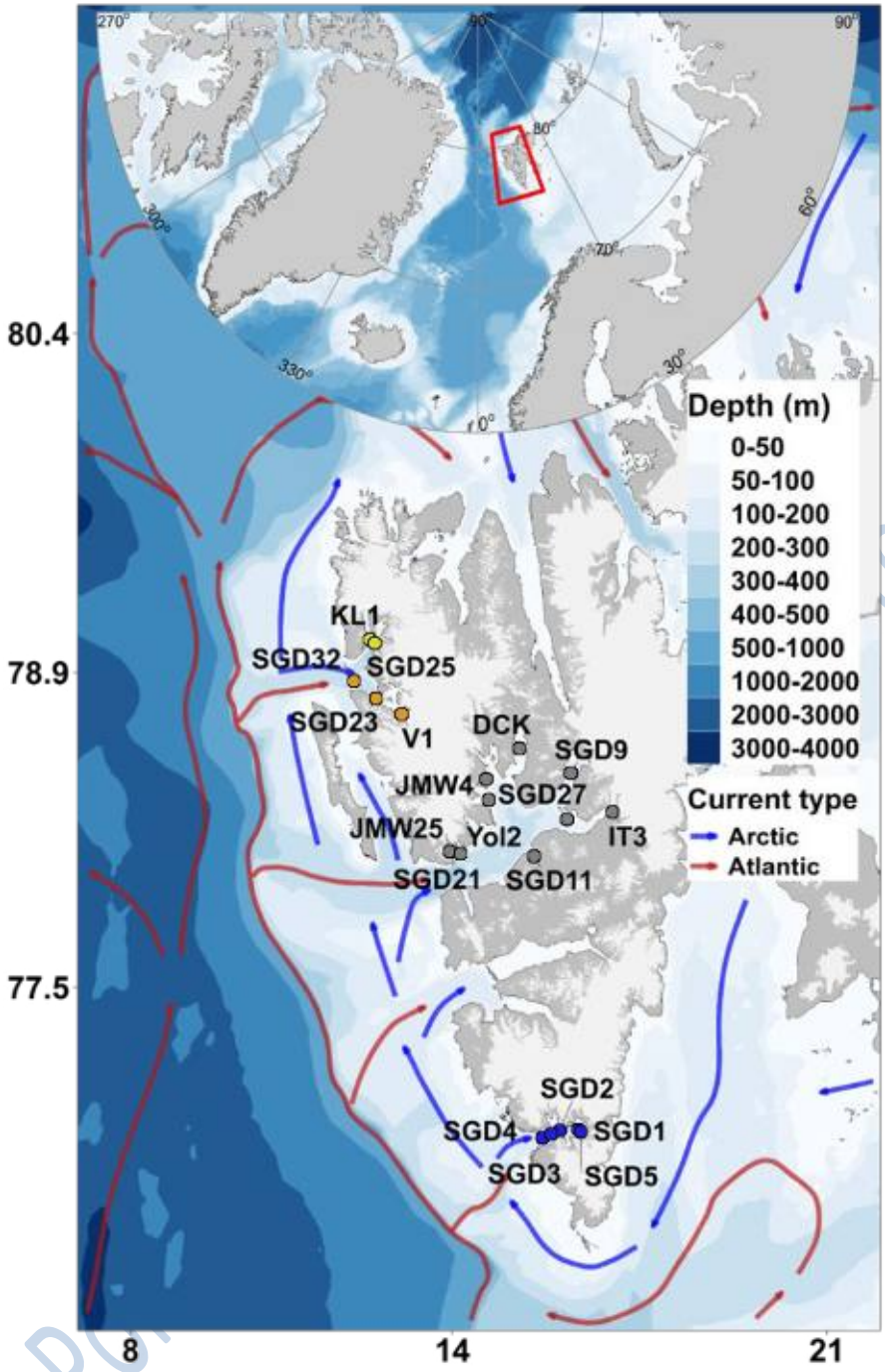

Fig. 1. Bathymetry of western Svalbard showing Atlantic (red) and Arctic (blue) current pathways and sampling sites in Krossfjord (yellow), Kongsfjorden (orange), Isfjorden (grey), and Hornsund (blue). Basemap data from GEBCO (Jakobsson *et al.* 2024), IBACO (Jakobsson *et al.* 2012), and PlotSvalbard (Vihtakari 2020).

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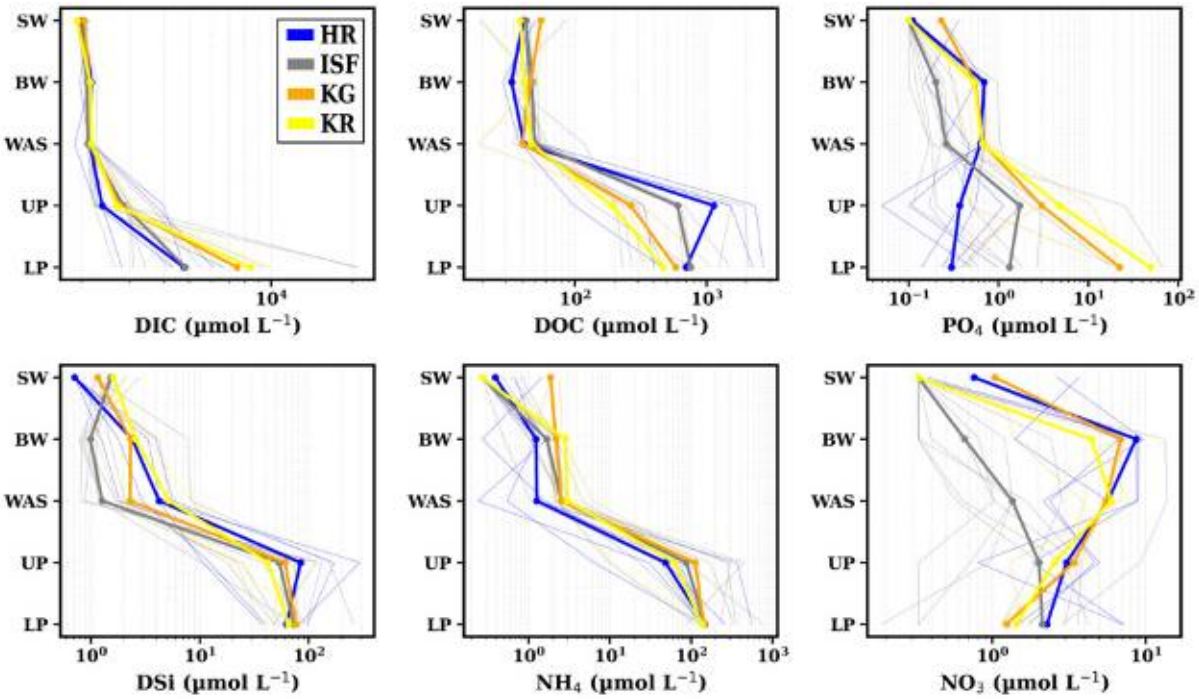

Fig. 2. Vertical concentration profiles of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), PO_4^{3-}, DSi, NH_4^+ and NO_3^- in the five sampled layers from surface downward: SW - surface water, BW - bottom water, WAS - water above sediment, UP - upper porewater, and LP - lower porewater. Thin lines are individual stations and bold lines are the median profile for each fjord; colors denote the fjords: HR - Hornsund (blue), ISF - Isfjorden (grey), KG - Kongsfjorden (orange), and KR - Krossfjorden (yellow).

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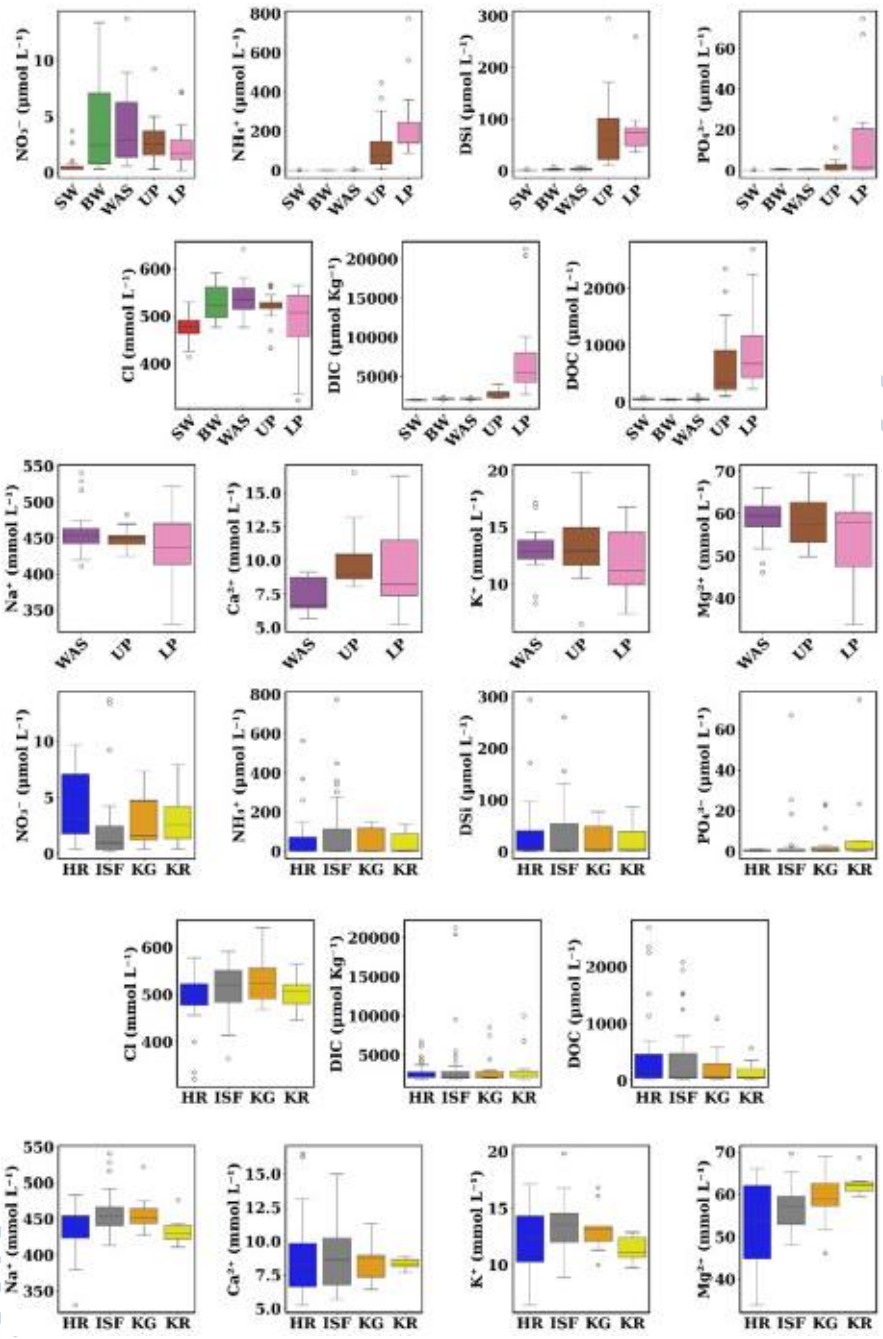

Fig. 3. Distributions of dissolved nutrients and carbon in water types and fjords. Box plots show NO_3^-, NH_4^+, DSi, PO_4^{3-}, Cl^-, DIC, DOC, and the major cations including Na^+, Ca^{2+}, K^+, and Mg^{2+}. The upper three rows group samples by water type, SW (surface water), BW (bottom water), WAS (water above sediment), UP (upper porewater) and LP (lower porewater), and the lower three rows group the same data by fjord: HR (Hornsund), ISF (Isfjorden), KG (Kongsfjorden) and KR (Krossfjorden). Cations are shown only for the WAS, UP and LP layers. Boxes span the interquartile range (IQR) with the median marked, whiskers extend to 1.5 × IQR, and points beyond the whiskers are plotted as outliers.

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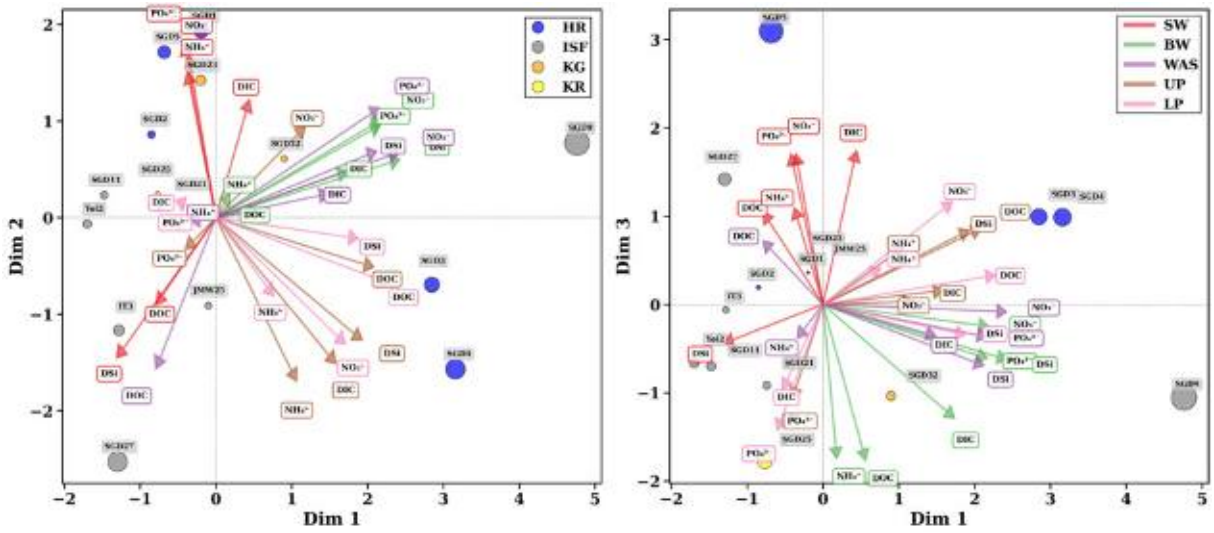

Fig. 4. Multiple factor analysis biplots in left panel: Dimension 1 (Dim 1) versus Dimension 2 (Dim 2); in right panel: Dimension 1 versus Dimension 3 (Dim 3) illustrating relationships among sampling sites and chemical variables in the first three ordination dimensions. Sampling sites are shown as colored points according to fjord system, with point size proportional to their cumulative contribution to the displayed dimensions. Larger points indicate sites with higher contributions to the variance of the corresponding dimensions. Site labels are shown in gray boxes. Variables are represented as arrows originating from the origin, with arrow direction indicating the gradient of increasing values and arrow length reflecting the strength of association with the ordination axes. Variables are color-coded by layer: SW - surface water (blue), BW - bottom water (green), WAS - water above sediment (purple), UP - upper porewater (brown), and LP - lower porewater (pink).

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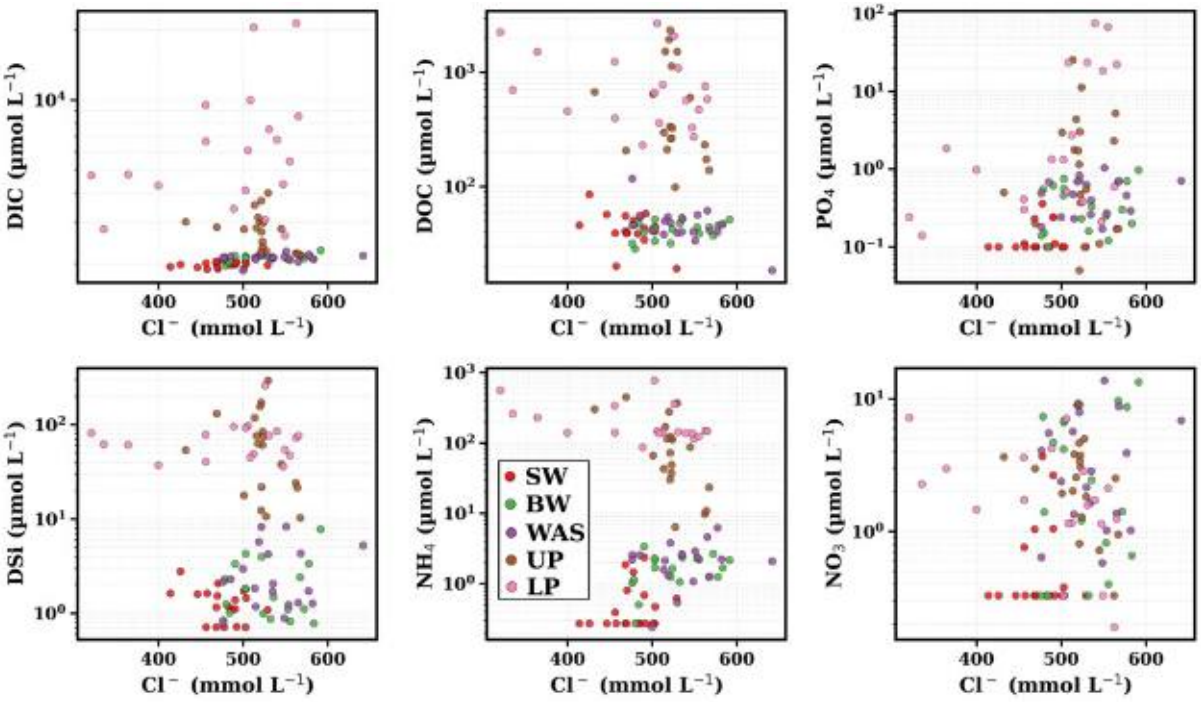

Fig. 5. Variables–chloride mixing diagrams for DIC, DOC, PO_4^{3-}, DSi, NH_4^+, and NO_3^-. Each point is a sample plotted against its Cl^-, used here as a conservative tracer of seawater–freshwater mixing; colors denote the water type including SW - surface water (blue), BW - bottom water (green), WAS - water above sediment (purple), UP - upper porewater (brown), and LP - lower porewater (pink).

Polish Polar Research

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AUTHOR CONTRIBUTION STATEMENT

I hereby declare that my contribution to the manuscript:

- **Saghravani, S.R.,** Sen, A., Hong, W.-L., and Silberberger, M.J. 2026. Covariation of Dissolved Nutrients and Carbon in Seawaters and Sediment Porewaters of Western Svalbard Fjords. *Polish Polar Research*, doi:10.24425/ppr.2026.3128.

included the conception and design of the study, data collection, curation, and analysis, interpretation of results, preparation of figures, and writing and revision of the manuscript.

Yours sincerely,

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included the reviewing and editing.

Yours sincerely,



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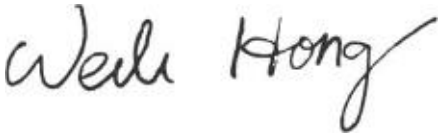
included the reviewing and editing.

Yours sincerely,

Wei-Li Hong



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included the included conceptualization, methodology, supervision of data interpretation, review and editing.

Yours sincerely,



Marc J Silberberger

Date and Place 27.08.2026, Gdynia