Iron biogeochemistry in Fram Strait and on the Northeast Greenland Shelf



Dissertation

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Durch Trennung und Unterordnung der Erscheinungen, durch ahnungsvolles Eindringen in das Spiel dunkel waltender Mächte, durch eine Lebendigkeit des Ausdrucks, in dem die sinnliche Anschauung sich naturwahr spiegelt, können wir versuchen das All ($\tau \delta \pi \tilde{\alpha} v$) zu umfassen und zu beschreiben, wie es die Würde des großartigen Wortes Kosmos, als Universum, als Weltordnung, als Schmuck des Geordneten, erheischt.

Alexander v. Humboldt (1769–1859) aus Kosmos – Entwurf einer physischen Weltbeschreibung.

Abstract

Fram Strait is the major gateway for Arctic Ocean sea-ice export, and the only deep-water connection between the Arctic Ocean and high latitude North Atlantic. The region is confined by the NE Greenland Shelf to the west and Svalbard to the east; approximately half is covered by summer sea-ice. Glacial and sea-ice lead to strong year-round light limitation of phytoplankton growth across the region. Yet, rapid declines in the extent of summer sea-ice (~40%) and ice shelf coverage (~95% for the Zachariæ Isstrøm ice tongue) have been documented since the 2000s which may have increased marine primary production in Fram Strait. The bioessential micronutrient iron (Fe) limits primary production across much of the high latitude ocean, including parts of the sub-polar North Atlantic south of Fram Strait. Whilst primary production in the Arctic Ocean is generally thought to be controlled by a combination of light and fixed nitrogen availability, the potential role of trace elements as co-limiting factors for phytoplankton growth and their role in ecosystem dynamics has scarcely been investigated. What factors control the supply of Fe to the dynamic Fram Strait region and how does this affect marine primary production? To answer these questions, in late summer 2016, we performed a detailed investigation into the macronutrient and trace element micronutrient distribution across Fram Strait as part of the GEOTRACES GN05 cruise, including full Fe speciation analysis, and conducted nutrient addition bioassay experiments to assess spatial patterns in limiting nutrients.

Surface dissolved Fe (dFe), the biologically most accessible form of Fe, showed an eastto-west gradient across Fram Strait. Concentrations were elevated near the Greenlandic coast in proximity to the marine-terminating glaciers Nioghalvfjerdsbrae and Zachariæ Isstrøm, and depleted in the West Spitsbergen Current near Svalbard. Fixed nitrogen (N), the sum of nitrate, nitrite and ammonium, and dFe were deficient in seawater relative to typical phytoplankton requirements. An east-to-west trend in the relative deficiency of N and Fe was apparent, with N becoming more deficient towards Greenland and Fe more deficient towards Svalbard. This aligned with phytoplankton responses in bioassay experiments, which showed greatest chlorophyll-a increases in +N treatments near the Greenland continental margin, and +N+Fe near Svalbard. Collectively, our results suggest primary N limitation of phytoplankton growth throughout the study region, with conditions

Abstract

potentially approaching secondary Fe limitation in the eastern Fram Strait. The supply of Atlantic-derived subsurface N and Arctic-derived Fe therefore exerts a strong control on summertime primary production in the Fram Strait region. Future primary production in Fram Strait region will experience relief from light limitation yet would require additional supply of N during the post-bloom season to raise levels of phytoplankton growth. Conversely, changes in the southward flow of Arctic-derived Fe may have implications for Fe-limited productivity further south.

On the NE Greenland Shelf, surface dFe concentrations near Nioghalvfjerdsbrae and Zachariæ Isstrøm showed no connection to observed maxima in the East Greenland Current further offshore which instead appear to have arisen from Arctic sources further north. Analyses of Fe species immediately adjacent to the Nioghalvfjerdsbrae glacier terminus revealed a decoupling of dFe from labile particulate Fe inputs likely due to a prolonged residence time of meltwater beneath Greenland's largest floating ice-tongue. Subglacial removal in combination with limited stabilization from organic material (i.e. Fe-binding ligands) leads to restricted supply of 'new' Fe from meltwater. Water exchange between the subglacial cavity, formed by the 80 km long floating ice tongue, and the shelf, is driven by the cavity overturning circulation, and exerts a strong control on subglacial dFe discharge to the NE Greenland Shelf. Comparison of findings at Nioghalvfjerdsbrae to observations in Antarctica suggests a more universal role for cavity overturning circulation in determining the extent of lateral dFe fluxes to broad glaciated shelf regions. Future retreat of deep-grounded marine termini, as projected for Nioghalvfjerdsbrae, may result in increased export of glacial dFe to shelf environments and more direct connectivity between meltwater discharge and marine primary production.

Fluxes of dissolved trace elements across Fram Strait were calculated with the most recent year-round synopsis of volume transport rates available. Transport was dominated by the southward-directed East Greenland Current and the northward-directed West Spitsbergen Current, and comprised ~80% of gross dFe, dMn, dCo and dZn transport across Fram Strait. Dissolved Fe, Mn, Co and Zn fluxes on the NE Greenland Shelf were of only local importance and contributed ~10% to gross northbound and southbound transport. Greenland Ice Sheet discharge and associated near-shore sedimentary enrichment from Nioghalvfjerdsbrae were much smaller than dFe, dMn and dCo fluxes in the EGC and WSC and comprised <1% of southbound export across Fram Strait. The advection of Central

Arctic Ocean waters including the trace element-rich Transpolar Drift, feeding into the East Greenland Current, plays a fundamental role in dFe, dMn and dCo supply to surface Fram Strait. Comparison of fluxes to estimates from the Barents Sea Opening and Davis Strait stresses the importance of Fram Strait as the main gateway for Arctic-Atlantic dFe, dMn, dCo and dZn exchange, a consequence of intermediate and deep water transport between Svalbard and Greenland. Fluxes of all three gateways combined suggests the Arctic is exporting 2.7 ± 2.4 Gg·a⁻¹ dFe to the North Atlantic Ocean. Arctic export of dMn $(2.8 \pm 4.7 \text{ Gg·a}^{-1})$ and dCo $(0.3 \pm 0.3 \text{ Gg·a}^{-1})$ appears more balanced and within uncertainty. For dZn, Arctic-Atlantic exchange was balanced with an insignificant net northbound flux of 3.0 ± 7.3 Gg·a⁻¹. More observational data, particularly from non-summer months, is needed to project changes in seasonal and interannual Arctic-Atlantic micronutrient exchange and potential effects on ecosystem services sensitive to (micro)nutrient stoichiometry.

Die Framstraße ist der Hauptkorridor für den Export von Meereis aus dem Arktischen Ozean und die einzige Tiefseeverbindung zwischen dem Arktischen Ozean und dem Weltmeer. Als Teil des Nordatlantiks grenzt die Framstraße im Westen an das Kontinentalschelf vor Nordostgrönland und im Osten an die Küste Svalbards ("Spitzbergen"). Die Region ist im Sommer ungefähr zur Hälfte mit Meer- und Gletschereis bedeckt, welches den Lichteinfall reduziert und dadurch ganzjährig das Wachstum von Phytoplankton behindert. Seit den 2000er Jahren ist die Ausdehnung des Sommereises jedoch beträchtlich zurückgegangen (~40 %) und auch die schwimmenden Gletscherzungen haben sich zum Teil dramatisch zurückgezogen (z. B. Zachariæ Isstrøm: –95 %). Aufgrund erhöhten Lichteinfalls in die oberen Meeresschichten führte dies womöglich zu einer Steigerung der marinen Primärproduktion in der Framstraße.

Eisen (Fe) ist ein essentielles Spurenelement, ein Mikronährstoff, der die Primärproduktion in weiten Teilen der nördlichen Breiten begrenzt. Dies trifft auch auf den subpolaren Nordatlantik südlich der Framstraße zu. Im Gegensatz zum Nordatlantik wird das Ausmaß der Primärproduktion im Arktischen Ozean maßgeblich vom Vorhandensein von Licht und gebundenem Stickstoff (N) bestimmt, dabei ist die Rolle, die Spurenelemente als co-limitierende Faktoren spielen, bisher kaum erforscht. Welche Faktoren bestimmen den Bestand an Fe in der Framstraße und wie beeinflussen diese die marine Primärproduktion der Region? Um dieser Frage nachzugehen, untersuchten wir im Spätsommer 2016 die Verteilung von Makronährstoffen und Spurenelementen in der Framstraße. Als Teil der GEOTRACES-Expedition (GN05) analysierten wir verschiedene Fe-Spezies und führten Bioassay-Experimente durch, welche Aufschluss über die Art der Wachstumslimitierung des Phytoplanktons (Licht, Stickstoff oder Fe) geben.

Für die meisten Organismen ist gelöstes Fe die zugänglichste Form des Eisens. Konzentrationen im Oberflächenwasser der Framstraße wiesen ein West-Ost-Gefälle auf. Gelöstes Fe war nahe der grönländischen Küste in der Nähe der schwimmenden Gletscherzungen Nioghalvfjerdsbrae und Zachariæ Isstrøm erhöht und im Westspitzbergenstrom vor Svalbard erniedrigt. Das typischerweise für Phytoplankton benötigte Verhältnis von gelöstem Fe zu gebundenem N, welches Nitrat, Nitrit und

Ammonium umfasst, wies auf einen Mangel beider Stoffe im Oberflächenwasser der Framstraße hin: In westlicher Richtung wuchs der Überschuss an gelöstem Fe relativ zum Depot an gebundenem N an. Im Gegensatz dazu stieg in östlicher Richtung der Überschuss an gebundenem N relativ zum Depot an gelöstem Fe. Dieser Ost-West-Trend stimmte mit den durchgeführten Bioassay-Experimenten überein: Durch Zugabe von gebundenem N erzielte Phytoplankton nahe Grönland den größten Zuwachs an Chlorophyll-a, wohingegen Phytoplankton vor Svalbard den größten Zuwachs nach Zugabe von gebundenem N und gelöstem Fe erreichte. Diese Ergebnisse deuten darauf hin, dass das Phytoplanktonwachstum in der Framstraße maßgeblich durch einen Mangel an gebundenem N begrenzt ist. Nach N spielt im östlichen Teil der Framstraße womöglich auch ein Mangel an gelöstem Fe eine Rolle. Die Zufuhr von gebundenem N aus tiefergelegenen atlantischen Wasserschichten einerseits und Fe aus der Arktis andererseits hat daher einen maßgeblichen Einfluss auf das Ausmaß der Primärproduktion der Framstraße. Da Phytoplanktonwachstum im Spätsommer durch gebundenen N limitiert wird, ist davon auszugehen, dass der Rückzug des Meereises, und damit einhergehende verbesserte Lichtverhältnisse in oberflächennahen Schichten, womöglich nicht zu einer Steigerung der Primärproduktion in der Framstraße führen. Im Umkehrschluss könnte sich eine Veränderung der Strömungsverhältnisse in der Framstraße auf den gen Süden gerichteten Transport von Fe aus der Arktis auswirken und die dortige Fe-limitierte Primärproduktion beeinflussen.

Auf dem grönländischen Kontinentalschelf waren die erhöhten Konzentrationen an gelöstem Fe nahe der Gletscher Nioghalvfjerdsbrae und Zachariæ Isstrøm nicht mit den Konzentrationsmaxima im Ostgrönlandstrom verknüpft, welche aus der weiter nördlich gelegenen, zentralen Arktis stammen. Anhand der Analyse verschiedener Fe-Spezies konnte eine Entkopplung des Bestands an gelöstem Fe von dem Bestand an labilem, partikulär-gebundenem Fe nahe der Eiskante des Nioghalvfjerdsbrae festgestellt werden und ist womöglich auf die ausgedehnte Verweildauer des Schmelzwassers in der Kaverne, d. h. unterhalb der Gletscherzunge, zurückzuführen. Subglaziale Abscheidungsprozesse, auch aufgrund begrenzter Stabilisierungsmöglichkeit durch organisches Material (z. B. durch Fe-komplexierende Liganden), beschränken den Eintrag von "neuem", aus dem Schmelzwasser stammendem Fe innerhalb der Kaverne. Der Wasseraustausch zwischen der Kaverne und dem Schelf wird durch die Umwälzzirkulation unterhalb der 80 km langen, schwimmenden Eiszunge angetrieben und beeinflusst so maßgeblich den Export

von subglazialem Fe auf das nordostgrönländische Schelf. Der Vergleich mit antarktischen Gletschern zeigt, dass subglazialen Umwälzzirkulationen eine größere Bedeutung jenseits des Nioghalvfjerdsbrae zukommen könnte und unter Umständen auch auf globaler Ebene den Export von gelöstem Fe aus Gletscherkavernen in angrenzende Schelfregionen reguliert. Für die Zukunft ist der Rückzug tiefverankerter Gletscherzungen, wie die des Nioghalvfjerdsbrae, prognostiziert, was den Export von subglazialem, gelöstem Fe vermutlich erhöht und eine direktere Verknüpfung von Schmelzwassereintrag und mariner Primärproduktion zur Folge hat.

Für die Berechnung der Spurenelementflüsse wurde die aktuellste zur Verfügung stehende Zusammenstellung der Volumentransportraten durch die Framstraße verwendet. Der gen Süden gerichtete Ostgrönlandstrom und der gen Norden gerichtete Westspitzbergenstrom dominierten den Transport durch die Framstraße und umfassten ~80 % des Bruttotransports an gelöstem Fe, Mangan (Mn), Cobalt (Co) und Zink (Zn). Die Transportraten auf dem nordostgrönländischen Schelf waren nur lokal bedeutsam und trugen ~ 10 % zu dem nach Norden und Süden gerichteten Transport bei. Der Eintrag vom grönländischen Eisschild und küstennahen Sedimenten durch den Nioghalvfjerdsbrae war wesentlich geringer als der Transport im Ostgrönland- bzw. Westspitzbergenstrom und machte <1 % des nach Süden gerichteten Exports von gelöstem Fe, Mn und Co aus. Der Zufluss aus dem zentralen Arktischen Ozean, der in den Ostgrönlandstrom mündet, spielt eine fundamentale Rolle für den Bestand an gelöstem Fe, Mn und Co in den oberflächennahen Wassern der Framstraße. Ein Vergleich mit Abschätzungen des Transports durch die Barentssee und der Davisstraße hebt die Bedeutung der Framstraße als Hauptkorridor für den arktisch-atlantischen Austausch von gelöstem Fe, Mn, Co und Zn hervor, welches auf den Transport von Zwischen- und Tiefenwasser zwischen Svalbard und Grönland zurückzuführen ist. Die Transportraten aller Korridore zusammen deuten darauf hin, dass die Arktis $2,7 \pm 2,4$ Gg·a⁻¹ an gelöstem Fe in den Nordatlantik exportiert. Der Export von gelöstem Mn $(2,8 \pm 4,7 \text{ Gg}\cdot a^{-1})$ and gelöstem Co $(0,3 \pm 0,3 \text{ Gg}\cdot a^{-1})$ aus der Arktis ist einem Gleichgewicht näher und innerhalb der Messunsicherheit. Der arktisch-atlantische Austausch von gelöstem Zn war ausgeglichen und stellt einen insignifikant gen Norden gerichteten Transport von $3,0 \pm 7,3$ Gg·a⁻¹ aus dem Atlantik dar. Weitere Messdaten, vor allem jenseits der Sommermonate, sind erforderlich, um die saisonale und zwischenjährliche Variabilität im Austausch von Arktis und Atlantik und damit

einhergehende Auswirkungen auf das Ökosystem, welches empfindlich auf Veränderungen des (Mikro-)Nährstoffhaushalts reagiert, erfassen zu können.

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Danksagung

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1 Introduction

Life in the ocean is governed by the availability of nutrients and light (Sedwick and DiTullio, 1997; Tremblay and Gagnon, 2009; Saito *et al.*, 2014; Bristow *et al.*, 2017) and predation-mortality by higher trophic organisms (Verity *et al.*, 1993; Mojica *et al.*, 2016). Liebig's law of the minimum (Liebig, 1843), originally referring to agriculture, in a more general form is also applicable to the ocean: it is not the total amount of resources, but the availability of the scarcest factor that limits phytoplankton growth (Arrigo, 2005; Moore *et al.*, 2013). There are of course subtleties to this generalization when applied to entire ecosystems, because different primary producers may be limited by different nutrients, and the demand for nutrients may not be entirely independent of regional supply.

Oceanic primary production requires the macronutrients fixed nitrogen (N) which includes nitrate (NO₃), nitrite (NO₂) and ammonia (NH₄); phosphate (PO₄) and silicic acid (Si(OH)₄) (Zehr and Kudela, 2011; Tréguer and De La Rocha, 2013; Karl, 2014). Additionally, phytoplankton physiology relies on dissolved trace elements (i.e. micronutrients) including dissolved iron (dFe), manganese (dMn), cobalt (dCo), nickel (dNi), copper (dCu) and zinc (dZn) to maintain cell functioning. These trace elements are pivotal for metabolic activities, provide structure to proteins and form the reactive center of many enzymes that are, for example, involved in photosynthesis and respiration (Morel and Price, 2003; Twining and Baines, 2013). Micronutrients are typically present in the ocean at nano-to-pico-molar concentrations (Bruland, Middag and Lohan, 2013), and play a similarly important role to macronutrients in limiting regional surface primary production. Among the micronutrient trace elements, Fe is thought to have the most pivotal role, and is, besides Zn, the most abundant trace element in phytoplankton taxa (Twining and Baines, 2013). Approximately $\frac{2}{3}$ of the Fe requirement in oxygenic photosynthetic species is related to its use in the photosynthetic apparatus, photosystem I and II, with the rest being largely required for respiration (Morel, Milligan and Saito, 2003). Fe is also involved in various steps of the nitrogen cycle, catalyzing nitrification, denitrification and nitrogen fixation (Morel and Price, 2003; Zehr and Kudela, 2011).

Approximately one third of global ocean surface primary production is limited by the availability of dFe (Martin and Fitzwater, 1988; Boyd *et al.*, 2007; Boyd and Ellwood,

2010). Fe scarcity in surface waters, as observed in the Southern Ocean (Martin, Gordon and Fitzwater, 1990), the subpolar North Pacific (Boyd *et al.*, 2004) and North Atlantic Oceans (Ryan-Keogh *et al.*, 2013), may decrease Fe uptake and the ability of phytoplankton to harvest light that is affecting the photosynthetic production or increasing oxidative stress caused by disruption in electron transfer (Raven, Evans and Korb, 1999; Peers and Price, 2004). Fe deficiency, through its use in membrane-bound nitrate and nitrite reductases, may also limit phytoplankton growth by limiting N acquisition (Price, Ahner and Morel, 1994). Yet, in Fe-scarce environments, some phytoplankton species have developed strategies to sustain growth, for example, through the use of organic molecules with high affinity for Fe ('siderophores') and siderophore-specific uptake systems (Wilhelm, Maxwell and Trick, 1996; Hopkinson and Morel, 2009) or by substitution of Fe-bearing enzymes with non-Fe containing proteins (Peers and Price, 2006). Such competitive advantages may partly explain why cellular Fe quotas are highly variable in the ocean and generally increase with Fe availability (Twining and Baines, 2013).

Cellular Fe quotas inferred from water column geochemical data and laboratory cultures were found to be lowest in the Fe-depleted, high nutrient-low chlorophyll (HNLC) Southern Ocean, and highest in Fe-replete, non-HNLC waters (Strzepek *et al.*, 2011; Twining and Baines, 2013). Phytoplankton surrounded by elevated Fe may acquire more Fe than needed to sustain maximal growth (Sunda and Huntsman, 1995; Marchetti *et al.*, 2006). This 'luxury' uptake of Fe may extent phytoplankton community growth in an otherwise Fe-depleted environment later in the season. A particularly high Fe demand is found for diazotrophic cyanobacteria such as *Trichodesmium* which, in the absence of sufficient fixed N, are able to acquire N from dinitrogen (N₂) (Zehr *et al.*, 2001; Kustka *et al.*, 2003). Diazotrophs use Fe-bearing nitrogenase and require ~5-times more Fe when growing on N₂ instead of NH₄ (Kustka *et al.*, 2003). In the subtropical and tropical North Atlantic Ocean, this demand is met by riverine supply and atmospheric deposition of Fe and supports N₂ fixation that is off-setting the loss of fixed N caused by anaerobic ammonium oxidation, denitrification or burial (Tovar-Sanchez *et al.*, 2006; Moore *et al.*, 2009).

Critical roles determining the regional extent of phytoplankton community growth has also been suggested for dMn in the Southern Ocean (Pausch, Bischof and Trimborn, 2019; Browning *et al.*, 2021), and dCo in parts of the North and South Atlantic Oceans (Panzeca *et al.*, 2008; Browning *et al.*, 2017). Most prominently, Mn is needed for the oxidation of

water during photosynthesis (McEvoy and Brudvig, 2006), whereas Co is required for the synthesis of cobalamin (Vitamin B_{12}) that is an essential cofactor in various enzymes (Martens *et al.*, 2002; King *et al.*, 2011; Twining and Baines, 2013). Even if not limiting the extent of net primary production, micronutrient availability and changes in nutrient stoichiometry may influence phytoplankton species composition, affect biodiversity in the ocean and the biological carbon pump (DiTullio, Hutchins and Bruland, 1993; Eldridge *et al.*, 2004; Hopkinson and Barbeau, 2008; Browning *et al.*, 2019).

1.1 Trace element micronutrients

Although trace metals occur at enhanced concentrations in the earth's crust (e.g. Fe $\sim 5\%$ by mass), they occur at very low levels in seawater due to their low solubility ($\sim 10^{-9}$ for Fe) and this makes their quantification in marine waters challenging (Bruland, Middag and Lohan, 2013). Because these elements are present throughout the anthroposphere, the risk for contamination of samples is high, and particularly problematic for determination of marine dFe and dZn. For example, Fe is used for steel and Zn for galvanization, hindering ship-based investigations concerning their biogeochemistry. To account for the high risk of contamination, trace element clean sampling and laboratory instrumentation are needed to produce reliable and representative data. Before the 1980s, sporadic profiles of micronutrients were obtained, but investigations into trace element cycling on a broader scale remained impossible. Since the 2000s, developments in sampling and laboratory element analysis techniques (de Baar et al., 2008; Sohrin et al., 2008), international collaboration and implementation of uniform standards (SCOR Working Group, 2007; Cutter et al., 2017) have changed our understanding of the role that trace elements exert in marine ecosystem functioning. Yet, expeditions particularly to remote areas such as the Arctic and the Southern Oceans remain time- and money-consuming endeavors, and even after decades of marine research, our understanding of the controls on primary production across the world ocean, which underpins the well-being and livelihood of billions, is still patchy.

Micronutrient concentrations are controlled by the relative rates of input and removal. Trace elements are supplied to the ocean by benthic sediment release (Homoky *et al.*, 2013; Scholz *et al.*, 2014), riverine and submarine groundwater discharge (Hölemann, Schirmacher and Prange, 2005; Gaillardet, Viers and Dupré, 2014; Jeandel, 2016), aerosol deposition (Mahowald *et al.*, 2018; Shelley *et al.*, 2018) and hydrothermal venting (Sander

and Koschinsky, 2011; Fitzsimmons et al., 2017). Major sinks are biological uptake (Morel, Milligan and Saito, 2003; Mellett et al., 2018), passive scavenging and particle aggregation (Boyle, Edmond and Sholkovitz, 1977; Johnson, Michael Gordon and Coale, 1997; Homoky et al., 2012) that ultimately result in vertical export (Curtis, 1993; Buesseler, 1998; Lemaitre *et al.*, 2020) and the burial of trace elements in marine sediments. In between supply and burial, trace elements may undergo biogeochemical cycling for extended periods of time (Bruland, Middag and Lohan, 2013) with residence times varying from several years to hundreds of thousands of years. Biological uptake and remineralisation (Boyd and Ellwood, 2010; Tagliabue et al., 2019), scavenging-release (Homoky et al., 2012; Milne et al., 2017) and redox transformations (Sunda and Huntsman, 1988; O'Sullivan et al., 1991; Moffett and Ho, 1996) are major cycling processes and shape trace element distributions in the water column. The extent to which trace elements are involved in biogeochemical cycling is determined by biophysical properties and is controlled by a complex interplay of environmental factors, including biological demand, pH, oxygen, light levels and the presence of particles and dissolved organic matter (Morel and Price, 2003; Bruland, Middag and Lohan, 2013; Millero, 2013).

Generally, trace elements are differentiated into four groups, based on their vertical distribution and biological relevance:

- (i) Nutrient-type trace elements (e.g. Zn, Cd) show surface depletion and increasing concentrations with depth due to biological uptake in the surface ocean and remineralisation at depth of sinking phytoplankton debris, and are extensively recycled in the surface ocean before being exported to deep waters. Oceanic residence times are intermediate and range between 1000-100,000 years, thus comparable to ocean ventilation time scales (Bruland, Middag and Lohan, 2013). For Zn and Cd, deep ocean residences times of 3000-6000 years (Zn) and 22000-45000 (Cd) have been suggested (Bruland, Orians and Cowen, 1994).
- (ii) Scavenged-type trace elements (e.g. Mn, Pb) are dominated by their high affinity to particles and tend to be exported with sinking matter. Concentrations are highest near sources and decrease with distance from the source. Residence times are typically shorter than ventilation or mixing in the ocean, and may range between 50-1000 years (Bruland, Middag and Lohan, 2013). In case of Mn, the residence time in the ocean may only be 50-100 years (Bruland, Orians and Cowen, 1994), yet large regional differences (Kadko *et al.*, 2019), partially related to its redox chemistry (Sunda and Huntsman, 1988, 1994), are evident.

- (iii) Hybrid-type trace element (e.g. Fe and Co) behaviour resembles that of nutrienttype elements, that is depletion in surface water and regeneration at depth, but are also influenced by scavenging processes. In the case of Fe and Co, oceanic residence times around ~50 years for Co (Saito and Moffett, 2002) and ~200 years for Fe (Bruland, Middag and Lohan, 2013) have been suggested.
- (iv) Conservative-type trace elements (e.g. Mo) show little variation in their vertical profiles, as their distribution is primarily governed by mixing processes and hence follow similar trends to salinity. Oceanic residence times are much longer than ventilation time scales, and may be several hundred thousand years, e.g. 800000 years for Mo (Lutfi Firdaus *et al.*, 2008).

1.2 Fram Strait

1.2.1 Iron biogeochemistry in the sub-polar North Atlantic and the Arctic Ocean

Transport in the North Atlantic Ocean is dominated by the North Atlantic Current advecting warm and saline water from the Gulf of Mexico towards the Greenland Sea and Fram Strait (e.g. Rossby, 1996; Mauritzen et al., 2011). The North Atlantic Current is found at depths reaching ~600 m in the northeastern North Atlantic Ocean (Bower et al., 2002). There, depth profiles of dFe, dMn and dCo in the Iceland and Irminger Basins (Fig. 1.1) show surface depletion and subsurface maxima in July, indicative of phytoplankton drawdown and regeneration at depth (Achterberg et al., 2018, 2021). Surface dFe concentrations below 0.1 nM are observed in the season following the spring bloom. Primary production in large parts of the high latitude North Atlantic (>45°N) is seasonally limited by the availability of dFe (Nielsdóttir et al., 2009; Ryan-Keogh et al., 2013), NO₃ or both (Browning et al., 2019), and this puts an upper threshold to net phytoplankton community growth in summer. Autumn and winter minima in phytoplankton concentrations are a consequence of subdued solar irradiance and decreased water column stability (Behrenfeld and Boss, 2018). Deep winter mixing is the main driver for surface macro- and micronutrient replenishment in the high latitude North Atlantic Ocean and sets the conditions for the phytoplankton bloom next spring (Hartman et al., 2010; Achterberg et al., 2018). Sediments on the Greenland, Iceland and European Shelf are additional, yet rather localized sources of micronutrients, particularly dFe, to the North Atlantic Ocean (Birchill et al., 2017; Achterberg et al., 2018, 2021; Tonnard et al., 2020). Glacial discharge to the Greenland Shelf (Cape et al., 2019)

may also contribute to dFe maxima near the Irminger Basin margin (Achterberg *et al.*, 2018, 2021; Tonnard *et al.*, 2020).

In contrast to the high latitude North Atlantic, Arctic Ocean primary production is predominantly limited by the availability of light and fixed N (Sakshaug, 2004; Ortega-Retuerta et al., 2012; Mills et al., 2018). A much stronger seasonal cycle is evident in the Arctic compared to the high latitude North Atlantic, ranging from open water, 24 h irradiance and increased freshwater and meltwater input in summer (Pfirman et al., 1995; Bhatia et al., 2011; McClelland et al., 2012), to sea surface freeze-up and brine rejection to deep waters in winter with a complete absence of light (Midttun, 1985; McClelland et al., 2012). In sea-ice covered parts, the critical role for solar irradiation on primary production persists throughout the year. At its September 2020 minimum, 3.74 million km² of the surface Arctic Ocean was covered by sea ice (National Snow & Ice Data Center, 2020), representing ~39% of the Arctic surface area (Menard and Smith, 1966). Alleviation from light limitation through melting of sea ice increases net phytoplankton production (Carmack, Macdonald and Steve, 2004; Tremblay et al., 2008). Enhanced water column stratification through meltwater addition and solar heating assists phytoplankton growth in spring (Cherkasheva et al., 2014; Oliver et al., 2018), however it also restricts surface nutrient replenishment during the growth season (Tremblay et al., 2008; McLaughlin and Carmack, 2010; Henley et al., 2020). Macronutrient distributions (Codispoti et al., 2013; Randelhoff et al., 2020), and few bioassay incubations in prior work suggest fixed N constrains the extent of net primary production in ice-free parts of the Arctic Ocean, for example in the Chukchi Sea (Mills et al., 2018; Ko et al., 2020) and Beaufort Sea (Ortega-Retuerta et al., 2012). Following the growth season, the North Atlantic (Hartman et al., 2010; Achterberg et al., 2018) and Arctic surface ocean (Codispoti et al., 2013; Randelhoff et al., 2020) alike are critically depending upon convective supply of nutrients in winter to alleviate from post-spring bloom nutrient stress.

The widespread availability of dFe in the Central Arctic Ocean, both in absolute terms and relative to fixed N, results from advection of low salinity surface waters from Siberian riverine discharge (Klunder, Bauch, *et al.*, 2012; Charette *et al.*, 2020) amended with shelf sediment input (Rutgers van der Loeff *et al.*, 1995; Kipp *et al.*, 2018) through the Transpolar Drift towards Fram Strait (McClelland *et al.*, 2012; Rudels, 2019). Rivers such as the Lena and Ob transport large quantities of micronutrients to the Arctic Ocean shelf regions (Hölemann, Schirmacher and Prange, 2005; Escoube *et al.*, 2015; Conrad *et al.*, 2019), even

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after concentrations of some elements are reduced by estuarine removal processes (Dai and Martin, 1995). The Arctic Ocean receives additional micronutrient input from Pacific Water crossing over the Chukchi Shelf (Kondo *et al.*, 2016; Vieira *et al.*, 2019), and sea ice that may also be an important vehicle for offshore transport of trace elements (Measures, 1999; Aguilar-Islas *et al.*, 2008; Tovar-Sánchez *et al.*, 2010).

Stabilized from wind-induced turbulence through the presence of sea ice (Williams and Carmack, 2015) and aided through organic stabilization from e.g. Fe-binding ligands (Slagter et al., 2017; Laglera et al., 2019), distributions of dFe, dMn and dCo in the Central Arctic Ocean mirror the distributions in the North Atlantic Ocean (Fig. 1.1). Near the North Pole, concentrations of dFe, dMn and dCo were enriched in the surface and depleted at depth (Bundy et al., 2020; Charette et al., 2020). Effective offshore advection through the Transpolar Drift makes the Arctic Ocean different from surface micronutrient transport in the high latitude North Atlantic, where shelf sediment and riverine enrichment are more localized phenomena (Achterberg et al., 2018, 2021; Tonnard et al., 2020). However, although the central Arctic is subject to high dFe concentrations in the Transpolar Drift, dFe in the Arctic Ocean has been found to co-limit primary production in the Beaufort Sea in late summer (Taylor et al., 2013), and dFe deficiency relative to mean phytoplankton requirements was also suggested from the SE Nansen Basin (Rijkenberg et al., 2018), stressing the importance of investigations concerning dFe fluxes in the Arctic. Notably, the southern extent of trace element transport in the Transpolar Drift that is feeding into the East Greenland Current in Fram Strait (Rudels, 2019) and thus, potentially exporting dFe to the high latitude North Atlantic Ocean (Klunder, Bauch, et al., 2012; Charette et al., 2020) is currently unknown.



Figure 1.1: Comparison of dissolved Fe (dFe), Mn (dMn) and Co (dCo) depth profiles for typical stations in the Central Arctic Ocean Transpolar Drift (top row, GEOTRACES expedition PS94/GN04, station 81) (Charette *et al.*, 2020) and the North Atlantic Ocean Irminger Basin (bottom row, GEOTRACES expedition D354, station Ti-009) (Achterberg *et al.*, 2018, 2021). Map depicts the position of PS94/GN04 station 81 (red dot) and D354 station Ti-009 (brown dot) relative to the stations sampled herein during GEOTRACES expedition PS100 (GN05) in Fram Strait (blue dots). Please note the different scales on the x-axis. Figure made using OriginPro software, version 9.1.0 (OriginLab Corporation, Northampton, MA, USA), and Ocean Data View software, version 5.4.0 (Schlitzer, 2021).



Figure 1.2: Near-surface distribution of salinity (left) and temperature in the Nordic Seas including Fram Ocean. Data Strait and southern parts of the Arctic obtained from ship-based thermosalinograph measurements at 11 m depth of Polarstern expeditions to the region between 2008-2019 (top, blue lines). Isohalines (left) and isotherms (right) distinguish between the southwards-directed East Greenland Current (EGC, thin black contours, salinity <31.4, temperature <0°C), and the northward-directed West Spitsbergen Current (WSC, thick black contours, salinity >34.8, temperature >5°C). Figure made using Ocean Data View software (version 5.4.0) with DIVA gridding calculations (Schlitzer, 2021).

1.2.2 Fram Strait – Gateway of Arctic-Atlantic exchange

The Arctic is undergoing rapid change as a consequence of atmospheric and ocean warming (Meredith et al., 2019; Przybylak and Wyszyński, 2020; Tsubouchi et al., 2021), and represents the region most affected by climate change worldwide. Surface air temperatures in the Arctic are rising approximately twice as fast as the global average (Richter-Menge, Druckenmiller and Jeffries, 2019). Substantial impacts on marine ecosystems are expected from accelerating Greenland Ice Sheet loss (Straneo and Heimbach, 2013; Bevis et al., 2019), sea ice loss (Notz and SIMIP Community, 2020; Zhang et al., 2021) and increasing shelf exposure (Williams and Carmack, 2015; Kipp et al., 2018). Shifts in phytoplankton growth have been evident since the 1990s in the satellite record (Arrigo, van Dijken and Pabi, 2008; Ardyna et al., 2014) and phytoplankton ecology may overall be shifting to a more Atlantic-like community structure (Lasternas and Agustí, 2010; Nöthig et al., 2015). Increased advection of Atlantic Water to Fram Strait and the Arctic Ocean are projected for the future (Wang et al., 2020), and may contribute further to Arctic 'Atlantification'. How these changes affect micronutrient fluxes, phytoplankton abundance and phytoplankton growth in the Arctic is far from being understood. The paucity of micronutrient data is particularly problematic for Fram Strait.

Fram Strait, located between Svalbard ('Spitsbergen') and NE Greenland, is influenced by the Arctic Ocean and North Atlantic Ocean (Fig. 1.2). In Fram Strait, the West Spitsbergen Current transports warm and saline Atlantic Water from the North Atlantic Ocean into the Arctic Ocean (Schauer et al., 2004; Mauritzen et al., 2011). Opposed, the East Greenland Current transports cold and fresh Arctic waters to the North Atlantic Ocean (Jeansson et al., 2008; de Steur, Peralta-Ferriz and Pavlova, 2018; Richter, Von Appen and Wekerle, 2018). Fram Strait represents the only connection between the Arctic and the Atlantic Oceans exceeding 500 m depth, and thus facilitates all deep-water exchange between the two ocean basins (von Appen et al., 2015; Rudels, 2019) with far-reaching implications for the Atlantic meridional overturning circulation and Arctic heat content (Caesar et al., 2021; Tsubouchi et al., 2021). The region is highly dynamic. Fram Strait is influenced by two strong and persistent eddies that recirculate ~50% of Atlantic-derived water (Latarius and Quadfasel, 2010; de Steur et al., 2014; Hattermann et al., 2016). An anticyclonic circulation prevails on the NE Greenland Shelf via which warm Atlantic Water is advected towards the Greenlandic coast (Bourke et al., 1987; Schaffer et al., 2017), driving basal melting of the marine-terminating glaciers Nioghalvfjerdsbrae and Zachariæ Isstrøm (Mouginot et al., 2015; Schaffer et al., 2020) both of which are evidencing rapid retreat and ice shelf collapse. Approximately ~16% of the Greenland Ice Sheet is drained to the NE Greenland Shelf (Rignot and Mouginot, 2012).

Before 2016, expeditions to the Iceland and Irminger Basin (Achterberg *et al.*, 2018, 2021), near the glacial outflows of Svalbard (e.g. Wehrmann *et al.*, 2014; Zhang *et al.*, 2015) and SE-Greenland (Stevenson *et al.*, 2017; Cape *et al.*, 2019), and to the Central Arctic Ocean (Klunder, Bauch, *et al.*, 2012; Klunder, Laan, *et al.*, 2012; Charette *et al.*, 2020) were the nearest surveys from which trace element data was available, yet provided only limited coverage of the dynamic Fram Strait region, precluding insight into Arctic-Atlantic exchange of trace elements through this important gateway.

1.3 Objectives and outline of the thesis

In 2016, Polarstern expedition PS100 (GEOTRACES cruise GN05) surveyed Fram Strait and the NE Greenland Shelf, investigated on the physical oceanography of the region, and sampled for macronutrients, water mass tracers and trace elements including the micronutrients Fe, Mn, Co, Cu, Ni, Zn and Cd (18^{th} July – 6^{th} September) (Kanzow, 2017). This expedition is part of the international GEOTRACES programme that aims to 'identify
processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions' (SCOR Working Group, 2007; Anderson, 2020). The main objectives of PS100 were investigations concerning Greenland Ice Sheet-ocean interactions, Fram Strait trace element fluxes and micronutrient cycling. Bioassay experiments were conducted to assess factors constraining summertime phytoplankton growth in the region.

This thesis is an attempt to describe essentials of Fe cycling in Fram Strait, and to establish a baseline with which changes in Arctic-Atlantic dFe fluxes can be monitored in future. The key questions to this thesis are:

- Which factors control primary production in Fram Strait? Are there differences in growth restrictions and phytoplankton community structure between the Arctic- and the Atlantic-influenced parts of Fram Strait?
- Is the Arctic Ocean a source of trace element micronutrients, including dFe, to the North Atlantic Ocean? How do the West Spitsbergen Current, East Greenland Current, and Fram Strait as a whole shape Arctic-Atlantic micronutrient exchange?
- Is the NE Greenland Shelf, with its extensive glacial outflows, a substantial source of trace elements to Fram Strait? What does the future hold for elemental fluxes associated with glacial discharge from the marine-terminating Nioghalvfjerdsbrae, Greenland's largest floating ice shelf?

This work is composed of 6 chapters, including this introductory section. The second chapter outlines in more detail the methods used for trace element analyses, and provides information that is not included in the individual manuscripts. Three chapters formatted as manuscripts are presented in chapters 3, 4 and 5.

Chapter 3 investigates on factors controlling surface summer primary production in Fram Strait. The role for fixed N, dFe and light in limiting phytoplankton community growth between Svalbard and NE Greenland is discussed. This chapter addresses the importance of lateral advection of nutrients from the Atlantic and Arctic Oceans to primary production in Fram Strait. Chapter 3 has been published in *Scientific Reports* under the title '*The influence of Arctic Fe and Atlantic fixed N on summertime primary production in Fram Strait, North Greenland Sea*' (Krisch *et al.*, 2020).

The second manuscript, Chapter 4, sheds a light on the restrictions of glacial dFe supply to the NE Greenland Shelf from the cavity underneath Greenland's largest floating glacier Nioghalvfjerdsbrae. The role of subglacial processes and cavity residence time in modulating glacial dFe discharge is discussed. Chapter 4 has been published in *Nature Communications* under the title '*The* 79°*N Glacier cavity modulates subglacial iron export to the NE Greenland Shelf*' (Krisch, Hopwood, *et al.*, 2021).

Chapter 5 presents flux estimates for dFe, dMn, dCo and dZn transport between the Arctic and the Atlantic Ocean through the gateway of Fram Strait. Particular emphasis is put on the characterization of transport in the East Greenland and the West Spitsbergen Current. Fram Strait fluxes are compared to estimates of transport rates across the Barents Sea Opening and Davis Strait, and an overall budget of Arctic-Atlantic micronutrient exchange is presented. Chapter 5 is currently in preparation for submission to *Global Biogeochemical Cycles*.

Chapter 6 provides a summary of the main findings and suggests future research directions for investigating on the gaps in our current understanding of Fe biogeochemistry and micronutrient cycling in the Arctic.

2 Methods

This chapter focusses on analytical procedures that are not described fully in the following chapters. The ubiquitous presence of trace elements, particularly Fe and Zn, and the associated risk for contamination make special treatment and sample handling necessary throughout the analysis. This includes application of trace element clean sampling techniques, analyte preconcentration and quantification with high resolution mass spectrometry under clean room conditions. We refer the reader to two publications that underpin the following work; for sampling and sample handling, GEOTRACES protocols were strictly followed as described by Cutter *et al.* (2017). For the analyses of trace elements, the method described in detail by Rapp *et al.* (2017) was used. Deviations to these methods are stated in the following.

2.1 Trace elements

2.1.1 Cleaning procedure

At sea, samples were collected in low-density polyethylene (LDPE, Nalgene) bottles that have undergone a three-step cleaning procedure. Firstly, LDPE bottles soaked in 2% v/v Mucasol detergent (Sigma-Aldrich) for 24 hours before rinsing with warm tap water and de-ionized water (18.2 M Ω cm⁻¹, Milli-Q, Millipore). In a second step, LDPE bottles soaked for a duration of at least 7 days in ~3 M hydrochloric acid (Sigma-Aldrich, reagent grade), and were rinsed with de-ionized water. Lastly, LDPE bottles soaked for at least further 7 days in ~2.5 M nitric acid (Sigma-Aldrich, analytical grade), were then rinsed with de-ionized water, double-bagged and stored in the dark until usage.

For preconcentration of sub-samples, fluorinated ethylene propylene bottles (FEP, Nalgene) were used. These bottles, before their initial use, were cleaned as described above for LDPE bottles. Additionally, FEP-bottles soaked in a heated ~3 M hydrochloric acid bath (Sigma-Aldrich, analytical grade) at 50°C for 24 hours, and were then rinsed with de-ionized water. In a last step, FEP bottles were filled with ~1 M hydrochloric acid (Sigma-Aldrich, analytical grade), UV-irradiated for 4 hours in a custom-made box, and rinsed with de-ionized water. Following each use, FEP bottles were rinsed with de-ionized water and filled with 0.5 M hydrochloric acid (Ultra Purity, Romil) for the duration of at least 14 days. After final rising

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with de-ionized water, FEP bottles were ready for re-usage. LDPE and FEP bottles used to prepare standards were treated in the same manner but were not re-used.

Polypropylene (PP) vials (4 mL, scintillation vials, FisherScientific) were used for the collection of preconcentrated samples and the following ICP-MS analysis. A three-step hot acid-clean was applied. In the first step, PP vials were soaked for at least 1 day in 2% v/v Mucasol detergent (Sigma-Aldrich). After thorough rinsing with tap water and deionized water, PP vials were submerged in ~3 M hydrochloric acid (Sigma-Aldrich, analytical grade) and heated to 50°C for the duration of at least 24 h. After rising with de-ionized water, PP vials were then submerged in ~2 M nitric acid (Sigma-Aldrich, analytical grade) and heated to 50°C for at least further 24 h. After final rinsing with de-ionized water, PP vials were dried under a laminar flow laboratory bench (class 100) and double bagged till use.

2.1.2 Sample collection and speciation

Trace elements samples were taken on-board the research vessel 'Polarstern' operating in Fram Strait for GEOTRACES cruise PS100 (GN01) between 18th July and 6th September 2016. For the collection of trace element samples, clean sampling techniques were applied throughout, strictly following GEOTRACES sampling protocol (Cutter *et al.*, 2017). Briefly, trace metal samples were collected using a powder-coated aluminium GEOTRACES CTD-rosette frame (Seabird, equipped with SBE 911) equipped with 24 x 12 L GoFlo bottles (Ocean Test Equipment, OTE). The CTD unit during deployment collected vertical, full depth profiles of salinity, temperature, pressure and light attenuation (turbidity) in high-resolution (m⁻¹). The location of stations and the depths of trace elements sampling were chosen according to physical characteristics of the study region and previous deployments of an on-board CTD system (SEA-BIRD SBE 911plus).

After deployment, OTE bottles were taken from the GEOTRACES CTD-rosette and transferred into an over-pressurized clean-room (class 100) laboratory container. Samples for dissolved trace elements (<0.2 μ M) were collected at each station (S1-S26). At four station (S21, S22, S24 and S26), subsamples of dissolved trace elements were additionally passed-through a 0.02 μ m Anodisc filter (Whatman) to determine soluble trace element fractions (mainly Fe). At eight stations (S18-S25), unfiltered trace element samples were obtained to determine dissolvable trace elements after >6 months of storage. All seawater samples were immediately acidified to pH 1.9 after filtration (<4 h), shipped to GEOMAR and stored in the dark until analyses.

2.1.3 Sample analyses

The analyses for the quantification of dissolved, soluble and total dissolvable trace elements Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb followed a two-step method outlined and described in detail by (Rapp *et al.*, 2017). Firstly, seawater samples were preconcentrated using an automated SeaFAST system (SC-4 DX SeaFAST pico; Elemental Scientific Inc. (ESI)) containing a column loaded with WAKO resin (Wako Pure Chemical Industries, Japan) to retain trace elements while discarding the seawater matrix including the major ions Na⁺, K⁺, Mg⁺, Ca²⁺, Cl⁻ and SO₄²⁻. In the second step, the 10x preconcentrated samples were analyzed using high-resolution sector field inductively-coupled plasma mass spectrometry (ICP-MS, Element-XR, Thermo Fisher Scientific).

Quantification of Fe, Zn, Ni, Cu and Cd was preferentially achieved through internal calibration via isotope dilution as per Rapp *et al.* (2017). The isotope dilution spike, with artificial isotopic composition, had a concentration of 200 nM Fe (1.34% ⁵⁶Fe, 95.81% ⁵⁷Fe), 75 nM Ni (4.76% ⁶⁰Ni, 89.80% ⁶²Ni), 220 nM Cu (1.44% ⁶³Cu, 98.56% ⁶⁵Cu), 150 nM Zn (0.82% ⁶⁶Zn, 97.61% ⁶⁸Zn) and 70 nM Cd (0.35% ¹¹⁰Cd, 95.49% ¹¹¹Cd). In the seawater sample, a ratio of 1:1 between the natural (e.g. ⁵⁶Fe) and the enriched (e.g. ⁵⁷Fe) nuclide is envisaged, which ensures highest precision and smallest errors during ICP-MS analyses. The limit for quantification through isotope dilution was set to a ratio of 1:10. Within this concentration range, reference samples evidenced good agreement to consensus values (Rapp *et al.*, 2017; Rapp, 2018). 100 μ L of isotope dilution spike was added to 15 mL of seawater sample. The upper limit for quantification via isotope dilution was thus 5 nM for Ni and Cd, 10 nM for Fe and Zn, and 15 nM for Cu. For the analyses of Pb, and the monoisotopic Mn and Co, external calibration via standard addition was applied. Single element standards (Inorganic Ventures Inc.) were used to obtain a standard addition spike with 3 nM Pb, 10 nM Co and 50 nM Mn prepared in 0.3 M sub-boiled nitric acid (TraceMetal grade, FisherScientific).

However, samples in Fram Strait evidenced great variability in concentrations. With internal calibration, total dissolvable trace element samples were occasionally out of calibration range, which necessitates these samples to be re-run with increased addition of isotope dilution spike. To correct for this, the original quantification approach by Rapp *et al.* (2017) was modified and Fe (100-1000 nM), Ni (200 nM), Cu (200 nM), Zn (600 nM) and Cd (40 nM) were also added to the standard addition spike. Double quantification for Fe, Ni, Cu, Zn and Cd via internal calibration (isotope dilution) and external calibration (standard addition) has several

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advantages: (i) internal and external calibration may set a wider calibration range of up to three orders of magnitude; (ii) both calibration approaches can be monitored and checked for consistency which is particularly helpful during extended periods of analyses; (iii) internal calibration to determine procedural blanks is problematic, but through standard addition, trace element contributions from instruments and chemicals, setting the limit of quantification, can be monitored in each run alongside the analyses of seawater samples. A set of 5 external calibration samples were run every 10 samples to which isotope dilution spike was also added for consistency. Quantification via external calibration was achieved through calculations on the naturally most abundant isotope. For Fram Strait samples, both quantification approaches were tested for Fe on the in-house reference material CAB (Central Angolan Basin) and produced identical values within uncertainty (Table 2.2).

The approach of double-quantification has yet two disadvantages. Firstly, when using standard addition for quantification of samples that have received isotope dilution spike addition, contributions from the naturally most abundant isotope, also present to minor quantities in the isotope dilution spike (e.g. 1.34% ⁵⁶Fe), must be accounted for in the calculations. Secondly, by also adding Cd to the standard addition spike, isobaric interferences preclude high quality Cd data.

2.1.4 Trace element concentration calculations

Trace element concentrations via isotope dilution calibration were calculated using equation 2.1:

$$c_{Sample} = c_{Spike} \cdot \frac{R_{Sample} - R_{Spike}}{R_{Natural} - R_{Sample}} \cdot X \qquad (2.1)$$

where c_{Sample} is the concentration of the trace element in the sample, c_{Spike} is the concentrations of the trace element in the isotope dilution spike, R_{Sample} is the measured ratio of the trace element isotopes in the sample, R_{Spike} is the measured ratio of trace element isotopes in the spike solution, $R_{Natural}$ is the natural ratio of the trace element isotopes, and *X* is the natural abundance of the spike isotope.

Trace element quantification using external standard addition calibration was via equation 2.2:

$$c_{Sample} = \frac{n_{Sample}}{n_{Indium}} \cdot S^{-1} \qquad (2.2)$$

With n_{Sample} being the counts of the sample analyte, n_{Indium} being the counts of indium that has been added to the sample during SeaFAST preconcentration, and S being the slope of external calibration which is also normalized to indium counts.

Analyte concentrations in the sample require correction for background (i.e. chemical and instrumental) trace element contributions. Manifold blanks were determined by ICP-MS analyses of 1 M HNO₃ (elution acid) obtained from SeaFAST where the sample introduction step was omitted from the pre-concentration method (Rapp *et al.*, 2017). Four manifold blank measurements, two before and two after each set of 10 seawater samples, were averaged and quantified for trace elements ($c_{TE, Manifold}$) using external standard addition calibration and equation 2.2. For the buffer blank, that is the trace element contribution through the use of ammonium acetate buffer, eight samples of filtered (0.2 µm) Labrador Sea Water were diluted 1:10 with de-ionized water. A subset of four samples was acidified to pH 1.9 while the others were acidified to pH 1.6 using ultra-pure hydrochloric acid (Romil). Both set of samples were preconcentrated at pH 6.4 and analyzed in the identical way to seawater samples. The difference in trace element concentration between the subsets of pH 1.9 and pH 1.6 samples is attributable to the use of buffer (Rapp *et al.*, 2017). Buffer contribution to sample trace elements (C_{Buffer TM}) was calculated using equation 2.3:

$$c_{TE,Buffer} = \frac{V_{Buffer} \cdot c_{Buffer}}{V_{Mixture}} \qquad (2.3)$$

where V_{Buffer} is the volume of buffer added to seawater samples during preconcentration, c_{Buffer} is the concentration of the trace element in the buffer, and $V_{Mixture}$ is the volume of the seawater sample and buffer mixture.

Both, manifold blank and buffer blank, were subtracted from the trace element concentration in the sample to yield the in-situ concentration of the analyte in seawater ($c_{Seawater}$):

$$c_{Seawater} = c_{Sample} - c_{TE,Manifold} - c_{TE,Buffer}$$
 (2.4)

2.1.5 Analytical blanks and reference materials

Method accuracy was validated through the use of consensus reference materials (CRM) SAFe S and GSC (Table 2.1) obtained from Bruland Research Lab (2009). Long-term precision of SeaFAST preconcentration and ICP-MS quantification was monitored through the use of in-house reference material CAB every tenth seawater sample (Table 2.2). Manifold blanks

were monitored at least twice every 10 seawater samples, including 5 at the beginning and at the end of each the analytical sequence (Table 2.3). Procedural blanks combine SeaFAST buffer blanks, and instrumental (manifold blank) trace element contributions, and set the limit of detection (LOD, Table 2.3). The LOD is defined as three times the standard deviation of the procedural blank (σ_B) as per Rapp *et al.* (2017):

$$LOD = 3 \cdot \sigma_B$$
 (2.5)

Concentrations below LOD are indistinguishable from the background signal, and are thus excluded from further analyses.

Table 2.1: Measured concentrations (in nmol·L⁻¹, nM) and standard deviations (1 σ) of Fe, Mn, Co, Ni, Cu and Pb for reference material SAFe S, and Zn and Cd for reference material GSC. SAFe S consensus values obtained from Bruland Research Lab (2009). GSC consensus values taken from Wuttig *et al.* (2019) but refer to the labile fraction (no UV-oxidation). Conversion of consensus values adapted from nmol·kg⁻¹ to nM by density of 1.026 kg·L⁻¹. SAFe Zn and Cd measurements were below limit of dectection (<LOD). n = number of measurements.

Reference Material	Analyte	Consensus	Measured	n
	Fe	0.095 ± 0.008	0.101 ± 0.016	10
	Mn	0.81 ± 0.06	0.87 ± 0.18	10
	Co	0.0049 ± 0.0012	0.0063 ± 0.0018	10
SAE2 S (#272)	Ni	2.34 ± 0.09	2.26 ± 0.20	9
SAFE S (#215)	Cu	0.53 ± 0.05	0.52 ± 0.03	11
	Zn	0.071 ± 0.010	< LOD	
	Cd	0.0011 ± 0.0003	< LOD	
	Pb	0.0492 ± 0.0023	0.0489 ± 0.0029	11
	Fe	1.57 ± 0.12	1.89 ± 0.27	7
	Iai Analyte Consensus I Fe 0.095 ± 0.008 0 Mn 0.81 ± 0.06 0 Co 0.0049 ± 0.0012 0 Ni 2.34 ± 0.09 2 Cu 0.53 ± 0.05 0 Zn 0.071 ± 0.010 0 Cd 0.0011 ± 0.0003 0 Pb 0.0492 ± 0.0023 0 Fe 1.57 ± 0.12 1 Mn 2.21 ± 0.13 2 Co $0.086 \pm 0.004^*$ 0 Ni 4.43 ± 0.17 4 Cu $1.21 \pm 0.07^*$ 1 Zn 1.41 ± 0.10 1 Cd 0.379 ± 0.025 0	2.06 ± 0.29	5	
	Со	$0.086 \pm 0.004*$	0.143 ± 0.030	7
CSC (#21 #150)	Ni	4.43 ± 0.17	4.32 ± 0.20	7
GSC (#21, #159)	Cu	$1.21\pm0.07*$	1.35 ± 0.06	7
	Zn	1.41 ± 0.10	1.37 ± 0.14	7
	Cd	0.379 ± 0.025	0.458 ± 0.009	7
	Pb	0.040 ± 0.002	0.037 ± 0.002	7

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<u>**Table 2.2:**</u> In-house reference material CAB monitoring long-term precision of trace element analyses, and comparison between isotope dilution and standard addition calibration for Fe. Mean concentration \pm standard deviation (1 σ), n = number of measurements. All concentrations in nmol·L⁻¹ (nM). Double quantification of CAB was not tested for Mn, Co, Ni, Cu, Zn, Cd and Pb (n.d.).

Analyte	Iso. Dilution	n	Std. Addition	n
Fe	1.20 ± 0.09	69	1.03 ± 0.10	54
Zn	5.73 ± 0.48	73	n.d.	
Mn	n.d.		0.29 ± 0.02	71
Co	n.d.		$58.3 \pm 6.0 \text{ pM}$	77
Ni	5.47 ± 0.28	72	n.d.	
Cu	1.95 ± 0.28	74	n.d.	
Cd	0.517 ± 0.023	81	n.d.	
Pb	n.d.		$9.4\pm1.0\ pM$	81

<u>**Table 2.3:**</u> Manifold blanks, buffer blanks, and combined, procedural blanks of trace element quantification via SeaFAST preconcentration and inductively coupled plasma mass spectrometry. Mean concentration \pm standard deviation (1 σ). The uncertainty to the procedural blank is derived from error propagation and combines the uncertainty from manifold blank and buffer blank. The limit of detection (LOD) is defined as three standard deviations of the procedural blank (3 σ_B). All values in pmol·L⁻¹ (pM).

Analyte	Manifold blank	Buffer blank	Procedural blank	LOD
Fe	48 ± 17	17 ± 11	64 ± 20	60
Mn	12 ± 5	5 ± 2	17 ± 6	17
Co	2.0 ± 1.3	1.0 ± 0.7	3.0 ± 1.5	4.5
Ni	167 ± 75	35 ± 13	202 ± 76	229
Cu	11 ± 6	6 ± 3	17 ± 6	19
Zn	147 ± 69	23 ± 11	171 ± 70	209
Cd	5.7 ± 1.9	3.4 ± 2.2	9.1 ± 2.9	8.8
Pb	0.4 ± 0.1	0.3 ± 0.3	0.7 ± 0.3	0.9

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Abstract

Climate change has led to a ~40% reduction in summer Arctic sea-ice cover extent since the 1970s. Resultant increases in light availability may enhance phytoplankton production. Direct evidence for factors currently constraining summertime phytoplankton growth in the Arctic region is however lacking. GEOTRACES cruise GN05 conducted a Fram Strait transect from Svalbard to the NE Greenland Shelf in summer 2016, sampling for bioessential trace metals (Fe, Co, Zn, Mn) and macronutrients (N, Si, P) at ~79°N. Five bioassay experiments were conducted to establish phytoplankton responses to additions of Fe, N, Fe+N and volcanic dust. Ambient nutrient concentrations suggested N and Fe were deficient in surface seawater relative to typical phytoplankton requirements. A west-to-east trend in the relative deficiency of N and Fe was apparent, with N becoming more deficient towards Greenland and Fe more deficient towards Svalbard. This aligned with phytoplankton responses in bioassay experiments, which showed greatest chlorophyll-a increases in +N treatment near Greenland and +N+Fe near Svalbard. Collectively these results suggest primary N limitation of phytoplankton growth throughout the study region, with conditions potentially approaching secondary Fe limitation in the eastern Fram Strait. We suggest that the supply of Atlantic-derived N and Arctic-derived Fe exerts a strong control on summertime nutrient stoichiometry and resultant limitation patterns across the Fram Strait region.

3.1 Introduction

The contribution of the Arctic Ocean to global primary production is ~1% (Pabi, Van Dijken and Arrigo, 2008; Uitz *et al.*, 2010) but has increased by ~30% between 1998-2012 as a result of surface ocean warming and an associated increase in ice-free ocean surface area (Arrigo and van Dijken, 2015). Iron (Fe) and fixed nitrogen (N) are essential nutrients for phytoplankton, co-regulating growth alongside light availability throughout much of the global ocean (de Baar *et al.*, 1995; Tremblay and Gagnon, 2009; Popova *et al.*, 2012; Moore *et al.*, 2013; De Jong *et al.*, 2015). Whilst parts of the high latitude North Atlantic (>50°N) feature Fe limited phytoplankton growth in spring-summer (Nielsdóttir *et al.*, 2009; Ryan-Keogh *et al.*, 2013), summertime Arctic primary production is widely thought to be limited by fixed N availability (Taylor *et al.*, 2013; Findlay *et al.*, 2015; Hopwood *et al.*, 2018; Mills *et al.*, 2018) due to low fixed N concentrations across the Arctic basin (Codispoti *et al.*, 2013). Direct experimental assessments of (micro)nutrients limiting to phytoplankton growth in the Arctic Ocean are however sparse, despite the pronounced impacts of climate change on this region (Schauer *et al.*, 2008; Mouginot *et al.*, 2015; Smedsrud *et al.*, 2017), potentially altering nutrient fluxes and promoting Fe limitation in the Arctic Ocean (Taylor *et al.*, 2013; Rijkenberg *et al.*, 2018).

The Fram Strait region (76-82°N, 20°W-15°E) forms the northern boundary of the Greenland Sea and is the major gateway for water exchange between the Arctic and North Atlantic Oceans (Fig. 3.1) (de Steur et al., 2009; Beszczynska-Möller et al., 2011; Rudels, 2019). The region features two surface currents: (i) the West Spitsbergen Current (WSC) with warm and saline Atlantic Water (4°C, S >35.10) at its core and a less saline surface layer (<65 m) (Fig. 3.2), flowing northwards from the Greenland Sea towards the Arctic Ocean (Laukert et al., 2017; Rudels, 2019); and (ii) the southward flowing East Greenland Current (EGC), which originates in the Arctic Ocean, includes a contribution of NE Greenland Shelf waters, and constitutes lowsalinity Polar Surface Water (S < 31.40) and more-saline sub-surface waters (S < 34.80) below 50-250 m (Rudels et al., 2005; Michel et al., 2015; Laukert et al., 2017). About half of the Fram Strait region is covered by seasonal sea ice, leading to strong year-round light limitation of phytoplankton growth (Michel et al., 2015; Lalande et al., 2016; Norwegian Polar Institute, 2020). However, the extent of Arctic sea ice has diminished considerably over the past three decades (~ 40%, 1979-2018) (data from the Norwegian Polar Institute, 2020) prolonging the areal extent and duration of enhanced light availability for phytoplankton growth. At the same time, Fram Strait has experienced surface freshening that has driven enhanced water column

stratification (Marnela *et al.*, 2013; de Steur, Peralta-Ferriz and Pavlova, 2018), potentially linked to variations in the advection and recirculation of Atlantic-derived waters (Schauer *et al.*, 2008; Beszczynska-Möller *et al.*, 2012; de Steur *et al.*, 2014). It remains unclear how these on-going physical changes are affecting nutrient supply to surface waters and thereby primary production in the region.

The aim of this study was to assess the factors that currently regulate summertime phytoplankton growth in the Fram Strait region and are hence key to predicting responses of this system to future climate change. We therefore (i) performed a detailed investigation into nutrient and micronutrient concentration distributions and stoichiometry across Fram Strait as part of the GEOTRACES GN05 cruise, and (ii) conducted nutrient addition bioassay experiments as direct assessments of spatial patterns in limiting (micro-)nutrients.

3.2 Methods

3.2.1 General

Samples were collected on the RV Polarstern (PS100) as part of the GEOTRACES programme (section GN05). The cruise investigated Fram Strait (>500 m bottom depth) and the adjacent NE Greenland Shelf (<500 m, together the 'Fram Strait region') in the period 23rd July to 1st September 2016 (boreal summer), which corresponded to the peak melt season. In total, 207 stations were occupied. The water column was sampled with a stainless steel CTD-rosette frame (equipped with SEA-BIRD SBE 911plus) and a powder-coated aluminium GEOTRACES CTD-rosette frame (Seabird, equipped with SBE 911, hereafter 'ucCTD'). All stations were sampled for macronutrients silicic acid (Si(OH)₄, hereafter Si), phosphate (PO₄), ammonium (NH₄), nitrite (NO₂), and nitrate (NO₃) from the stainless steel CTD. Here we refer to the sum of NH₄, NO₂ and NO₃ as fixed N. Trace metal micronutrients manganese (Mn), Fe, cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) were sampled from the ucCTD at 26 stations (Fig. 3.1a). Near-surface temperature and salinity were recorded continuously during the cruise from the ship's thermosalinograph (11 m intake depth). The stainless steel CTD was additionally equipped with a fluorometer (WET Labs ECO AFL/FL).

Chapter 3 – The influence of Arctic Fe and Atlantic fixed N on summertime primary production in Fram Strait, North Greenland Sea



Figure 3.1: a) Bathymetry and location of ucCTD stations sampled in the Fram Strait and on the NE Greenland Shelf. Black line highlights the section from which depth profiles are obtained (**Fig. 3.3**). (b) Surface chlorophyll-a concentrations (August 2016 average) obtained from MODIS-Aqua (NASA GES DISC)(Acker and Leptoukh, 2007). Dots indicate location and outcome of nutrient addition bioassay experiments (E1-E5): Purple = N limitation; white = no response to N, Fe or dust addition. White area indicates sea-ice cover. Figure generated by Thomas J. Browning using Matlab software version 9.6.0. (R2019a, Natick, Massachusetts: The MathWorks Inc., 2019).

3.2.2 Nutrient and trace metal analyses

Unfiltered macronutrient samples (NO₂, NO₃, PO₄, Si, NH₄) from the upper 200 m were analysed on board using a QuAAtro autoanalyser as per *Grasshoff, Kremlingl and Ehrhardt* (1999), modified according to the methods provided by the manufacturer (Seal, Alliance). At all other depths filtered samples (0.2 μ m) were frozen and run at AWI following an identical procedure. Measurements were validated against the certified reference material NMIJ CRM 7602a provided by the National Metrology Institute of Japan (see data publication).

Trace metal samples were collected in 24 x 12 L GoFlo bottles (Ocean Test Equipment, OTE) following GEOTRACES sampling and sample handling protocols (Cutter *et al.*, 2014). Briefly, GoFlo bottles were transferred into an over-pressurized clean room (class 100) where water samples were filtered (Acropak 0.8/0.2 μ m pore size) into pre-cleaned 125 mL low density polyethylene (LDPE) bottles with slight overpressure provided by filtered nitrogen gas (99.999%, AlphaGaz). One additional surface (~2 m) seawater sample was collected in mid Fram Strait using a tow-fish sampling system with suction provided by a Teflon diaphragm pump (Almatec A15). Samples were acidified to pH 1.9 with 180 μ L HCl (UpA, ROMIL) and shipped to GEOMAR to determine dissolved concentrations of Mn (dMn), Fe (dFe), Co (dCo),

Ni (dNi), Cu (dCu) and Zn (dZn). Trace metal samples were measured via high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS) after pre-concentration following the method of *Rapp et al.* (2017). Briefly, 15 mL sample aliquots were pre-concentrated using an automated SeaFAST system (SC-4 DX SeaFAST pico; ESI). All reagents for SeaFAST were prepared in de-ionised water (>18.2 M Ω cm⁻¹; Milli-Q, Millipore). Single-distilled sub-boiled HNO₃ (SpA grade, Romil) was used for sample elution. Ammonium acetate buffer (pH 8.5) was prepared from glacial acetic acid and ammonium hydroxide (Optima, Fisher Scientific). The 10-fold pre-concentrated samples were analysed by HR-ICP-MS (Thermo Fisher Element XR) with quantification via isotope dilution for dFe, dNi, dCu and dZn (⁵⁷Fe-, ⁶²Ni-, ⁶⁵Cu- and ⁶⁸Zn-spike), and standard addition for dMn and dCo (every 10th sample). Measurements were checked against SAFe S reference material (Bruland Research Lab, University of California Santa Cruz) (see data publication of Krisch, Roig, *et al.*, 2021).

The deficiency of each nutrient element relative to N was calculated using assumed average phytoplankton stoichiometry $(C_{7.75}N_1Si_1P_{0.0625})_{1000}Fe_{0.469}Mn_{0.175}Ni_{0.0625}Zn_{0.05}Cu_{0.024}Co_{0.012}$ (extended Redfield ratio; Ref. 34), measured dissolved nutrient concentrations, and the following equation:

$$X_N^* = X_{\text{dis}} - R_{X:N} \cdot \mathsf{N} \qquad (3.1)$$

where X_{dis} is the concentration of dissolved nutrient X, N is the concentration of fixed N, and $R_{X:N}$ is the assumed phytoplankton requirement for nutrient X relative to N (Moore *et al.*, 2013; Moore, 2016). Positive values of X_N^* suggest nutrient X is in excess relative to fixed N, while negative X_N^* values indicate nutrient X is deficient relative to fixed N (Moore, 2016). Following Moore (2016) we then ranked the deficiencies for each nutrient at each site using:

$$X'_N = \frac{X_{\rm dis}}{N \cdot R_{X:N}} \qquad (3.2)$$

The nutrient with minimum X'_N is the most deficient.

3.2.3 Incubation experiments

Incubation experiments were conducted using seawater collected from the OTE Go Flo bottles (~10 m depth; Experiments E1, E2, E3 and E5) or the tow-fish (2 m depth; E4) following procedures described in Browning *et al.* (2017). All sampling and sample handling was carried

out on-board using trace metal clean techniques under a laminar flow hood. Eighteen trace metal clean, 1 L polycarbonate bottles (Nalgene) were filled with unfiltered seawater. Three bottles were subsampled immediately for assessment of initial conditions. Of the remaining fifteen bottles, three were spiked with fixed N (1 μ M nitrate + 1 μ M ammonium), three with Fe (2 nM FeCl₃), three with fixed N + Fe, and three with ~ 10 mg volcanic dust from the Eyjafjallajökull volcanic eruption in 2010 (same sample as described in Achterberg et al., 2013). The fixed N spike solutions were previously passed through a column of Chelex-100 to remove contaminating trace metals. Three bottles were sealed immediately with no amendment (controls). The lids were sealed with Parafilm and the bottles double-bagged before being placed in an on-deck incubator, which was filled and continuously replenished with nearsurface seawater from the ship's underway supply. The incubator was shaded with blue screening (Lee Filters 'Blue Lagoon') to yield incubator light intensities of ~35% of surface values. Samples were incubated for 72 h. Both initial (t = 0 h) and incubated (t = 72 h) samples were subsampled for chlorophyll-a via filtration of 100 mL sample onto a glass fibre filter (GFF, 0.7 µm nominal pore size, 25 mm diameter, Macherey-Nagel), extracted in the dark in 10 mL 90 % acetone at -20 °C (~12 h), then measured using a calibrated Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

At experimental start sites, samples were collected for determination of macronutrient and trace metal concentrations and phytoplankton pigment concentrations. Samples for phytoplankton pigments were collected by filtration of 2-4 L of seawater onto GFF filters and stored at -80°C. Upon return to the home laboratory, samples were analysed following van Heukelem and Thomas (2001). Pigments were extracted in 90% acetone in plastic vials using glass beads in a cell mill, centrifuged (10 min, 5200 rpm, 4 °C), and then the supernatant was filtered through PTFE filters (0.2 μ m pore size, VWR International) and analysed by reverse-phase HPLC (Dionex UltiMate 3000 LC system, Thermo Scientific). Pigment standards were acquired from Sigma-Aldrich (USA) and the International Agency for ¹⁴C Determination (Denmark). Pigment compositions were converted to the approximate contribution of different phytoplankton types to total chlorophyll-a using CHEMTAX (Mackey *et al.*, 1996) with starting pigment ratios from Coupel *et al.* (2015).

3.3 Results and Discussion

3.3.1 Nutrient distributions

Fixed N displayed an east to west gradient in surface waters (10 m depth) (Fig. 3.2b). Maximum surface concentrations were found in the WSC $(0.7 \pm 1.0 \,\mu\text{M}, \text{mean})$ value \pm standard deviation) and at the northern-most stations in Fram Strait (1.4 \pm 1.1 μ M, 80.2-80.8°N/0-4°W). Elsewhere, relatively low fixed N concentrations were observed $(0.3 \pm 0.3 \mu M)$. Surface Si showed a north-to-south gradient within the eastern part of the EGC (Fig. 3.2c). Highest Si concentrations were found at higher latitudes $(4.2 \pm 1.6 \,\mu\text{M} \text{ at all EGC})$ stations >79°N), whereas lower Si concentrations were found at the NE Greenland Shelf break to the south $(1.2 \pm 0.5 \,\mu\text{M}$ at all EGC stations <77°N). The WSC was depleted in Si $(0.7 \pm 0.7 \,\mu\text{M})$, which contrasted to the EGC with elevated Si $(3.5 \pm 2.9 \,\mu\text{M})$ for all stations in the EGC). Surface dFe displayed maxima on the shelf at glaciated stations close to the Greenlandic coast (Fig. 3.2d; S19-S24, 1.8 ± 1.0 nM). DFe concentrations within the EGC $(1.3 \pm 0.6 \text{ nM})$ exceeded those in the WSC $(0.4 \pm 0.1 \text{ nM})$ by a factor of 3-4. In Fram Strait, dFe showed a similar trend to Si and was elevated at the two northern-most stations in its central and western parts (S8, 1.3 nM; S9, 2.5 nM), in contrast to the observed minimum dFe in the central WSC in the eastern Fram Strait (S4, 0.2 nM). Collectively, dFe and Si both showed elevated concentrations at low salinity (Fig. S3.1), which was most evident at the eastern boundary of the Polar Surface Water (0-10°W). In contrast to dFe and Si, no clear special pattern in surface fixed N concentrations relative to salinity was observed across the study region.

Concentrations of N and Si uniformly increased with depth, whereas depth profiles of dFe showed much greater spatial variability (Fig. 3.3c–e). Water column distributions of fixed N, Si and dFe in the WSC were distinctly different from the EGC. In the WSC, fixed N and Si were depleted ($< 5 \mu$ M) above ~25 m and ~450 m, respectively. In the EGC, fixed N remained depleted to greater depths nearer Greenland (21-148 m), and mean concentrations were lower (6.1 μ M ± 4.3 μ M for salinities < 34.8, corresponding to depths <20-454 m) compared to the WSC (9.4 μ M ± 3.7 μ M in the water column at salinities >35.1, corresponding to depths <71-261 m). Si on the contrary was enriched in the EGC (5.4 μ M ± 2.3 μ M) relative to the WSC (3.7 μ M ± 1.3 μ M). The distribution of Si at depth followed the spatial pattern found in surface concentrations, showing a north-to-south gradient in the water column of the EGC.

Elevated concentrations were observed at higher latitudes (all EGC stations >79°N), near the glacial termini of Zachariæ Isstrøm and Nioghalvfjerdsbrae ($6.3 \mu M \pm 3.2 \mu M$) and at the NE Greenland Shelf break ($5.8 \mu M \pm 1.3 \mu M$, EGC stations $4-8^{\circ}W$) compared to lower latitudes ($3.8 \pm 1.8 \mu M$, EGC stations $<77^{\circ}N$). Enhanced Si concentrations ($>10 \mu M$) on the inner-Greenlandic shelf at depth likely reflect elevated benthic inputs (Hong *et al.*, 2020). Mean EGC dFe concentrations ($1.1 nM \pm 0.5 nM$) were \sim 2-fold elevated over WSC values ($0.5 nM \pm 0.2 nM$). Depth profiles of dFe showed sporadic enrichment (>1 nM) that coincided with dMn (Fig. 3.3f) at multiple depths near Svalbard's continental slope, likely derived from sedimentary inputs as has been observed elsewhere in the high latitude North Atlantic (Colombo *et al.*, 2020; Tonnard *et al.*, 2020), and in central Fram Strait. Enrichment of dFe in the EGC was more sporadic than for Si, likely as a consequence of rapid scavenging of dFe sources along the Greenlandic shelf (Le Moigne *et al.*, 2014; Ardiningsih *et al.*, 2020). However, as for Si, dFe displayed maxima in the water column off Zachariæ Isstrøm and Nioghalvfjerdsbrae (S20, S22, S24, 1.5 nM \pm 0.6 nM) and near the NE Greenland shelf break (S9, S10, S12, S13, 1.2 nM \pm 0.5 nM) indicating similar shelf-associated Si and dFe sources.

A similarly extensive survey of macronutrient distributions in the Fram Strait region was previously conducted in July-August 2008. Our observations of fixed N (Jul-Aug 2016) agree well with these previous measurements, showing surface depletion ($<5 \mu$ M) increasing in depth from the WSC (16-42 m) to the EGC (12-129 m) (Beszczynska-Möller and Wisotzki, 2010; Kattner and Ludwichowski, 2014). Mean fixed N concentrations within the EGC (6.1 \pm 4.3 μ M in all EGC stations S>34.8) were comparable to observations made in 2008 ($5.3 \pm 4.1 \mu$ M), but fixed N was somewhat higher in the WSC (9.4 \pm 3.7 μ M in the water column at salinities >35.1) compared to 2008 (5.7 \pm 4.2 μ M), possibly related to increased advection and/or recirculation of Atlantic Water to the Fram Strait region in 2016 (Beszczynska-Möller et al., 2012; de Steur et al., 2014). Surface fixed N in the WSC ($0.7 \pm 1.0 \,\mu$ M) was similar to 2008 $(0.9 \pm 1.2 \,\mu\text{M})$, and falls between observations of the upstream Irminger Basin $(2.3 \pm 1.7 \,\mu\text{M})$, Jul-Aug 2010) and the downstream Arctic Ocean (Aug 2014) where complete depletion of surface Atlantic Water fixed N (<0.02 µM) is evident (Randelhoff et al., 2016; Achterberg et al., 2018). Atlantic Water is thus an essential source of fixed N to the Fram Strait region (Torres-Valdés et al., 2013). The distribution of Si showed an east-to-west gradient in 2008 similar to 2016, with elevated concentrations in the EGC at high latitudes $(5.2 \pm 2.2 \,\mu\text{M}, \text{ in all})$ EGC stations >79°N) relative to lower latitudes ($4.6 \pm 2.2 \,\mu$ M in all EGC stations at 77°N).

This north-south gradient was most pronounced for surface Si $(2.6 \pm 1.2 \,\mu\text{M}, >79^{\circ}\text{N};$ 1.4 ± 0.2 µM at 77°N), and is further evident when considering Si concentrations further north from within the Transpolar Drift (12.9 ± 0.6 µM, Sep 2015) (Ooijen *et al.*, 2016; Slagter *et al.*, 2017), and further south from the EGC bordering the Irminger Basin (1.4 ± 0.7 µM at 20 m, 58.1-60.0°N/35.0-42.7°E, Jul-Aug 2010) (Achterberg *et al.*, 2018). DFe shows the same northsouth trend, with concentrations >2-fold elevated in the surface Transpolar Drift (2.9 ± 1.3 nM) (Slagter *et al.*, 2017; Gerringa, Rijkenberg and Slagter, 2018), and an order of magnitude further depleted in the Iceland (0.1 ± 0.1 nM) and Irminger Basins (0.1 ± 0.2 nM) (Nielsdóttir *et al.*, 2009; Achterberg *et al.*, 2018). EGC dFe and Si may thus share a common regional source in the Arctic Ocean, and may themselves in turn be a source to the Greenland Sea phytoplankton communities.



Figure 3.2: Salinity and nutrient distributions at 10 to 11 m depths in the Fram Strait region. (a) Salinity, (b) fixed N, (c) Si, (d) dFe, (e) Fe(N)* nutrient deficiency, and (f) fluorescence. Primary (g) and secondary (h) nutrient deficiency after Moore (2016): Fixed N (purple), dFe (red) and Si (green). Black dots indicate the sampling locations (all 10 m depth). Black arrows indicate sites of bioassay experiments (excl. E4). The location of Nioghalvfjerdsbrae (79NG) and Zachariæ Isstrøm (ZI) are depicted in 'a'. Isohalines (contours, 11 m) distinguish the Polar Surface Water (S<31.4, bold) of the southward-directed East Greenland Current (EGC, S<34.8, <0°E) from Intermediate Water (34.8-35.1) and Atlantic Water (S>35.1, thin black) of the northward-flowing West Spitsbergen Current (WSC). Figure made using Ocean Data View software (version 5.2.1) based on DIVA gridding calculations (Schlitzer, 2021).



Figure 3.3: Fram Strait sections (79°N) of (a) salinity, (b) fluorescence (arb. units), (c) fixed N (μ M), (d) Si (μ M), (e) dFe (nM) and (f) dissolved manganese (nM), (g-h) derived primary and secondary nutrient deficiency (see equation 3.2). Fixed N (purple), dFe (red), Si (green) and dCo (orange). Black arrows (top panel) indicate the longitudinal positions of the nutrient addition bioassay experiments. The location of the presented section is shown in **Figure 3.1a.** Isohalines (contours) indicate the presence of Polar Surface Waters (S<31.4, bold) as part of the East Greenland Current (S = 34.8, bold), Intermediate Water (34.8<S<35.1) and core Atlantic Water (S>35.1). Black dots in b-f indicate the sample depths. Figure made using Ocean Data View software (version 5.2.1) based on DIVA gridding calculations (Schlitzer, 2021) and RTopo-2.0.1 bedrock topography (Schaffer *et al.*, 2016).

3.3.2 Phytoplankton abundance and community structure

Satellite-derived surface chlorophyll-a concentrations showed an east-to-west transition in phytoplankton standing stocks in August 2016, with minima in Central and Western Fram Strait, and maxima in Atlantic Waters northwest of Svalbard (Fig. 3.1b). Laboratory-determined chlorophyll-a concentrations matched the satellite-derived trend for the WSC $(0.5 \ \mu g \cdot L^{-1})$, Western and Central Fram Strait $(0.2 \ \mu g \cdot L^{-1})$, yet indicated highest phytoplankton concentrations in the EGC on the outer NE Greenland Shelf $(0.8 \ \mu g \cdot L^{-1})$ (Table 3.1). Measured pigment assemblages and associated CHEMTAX data analysis suggested an east to west transition in surface phytoplankton community composition that correlated with the region's nutrient and current regimes (Figs 3.2 and 3.4a). On the Si- and dFe-replete NE Greenland shelf, diatoms were the dominant phytoplankton group

(E1-E2, 80% of chlorophyll-a was attributable to diatoms). A similar dominance has been observed elsewhere in coastal Greenlandic waters which remain Si-replete post-spring bloom (L. Meire *et al.*, 2016; Krawczyk *et al.*, 2018). The diatom contribution decreased alongside surface Si and dFe concentrations towards western Fram Strait (E3, 27%) and central Fram Strait (E4, 25%) and was lowest in eastern Fram Strait (E5, 1%). The Eastern Fram Strait phytoplankton composition was dominated by haptophytes (E5, 68%) matching earlier observations in the Si-depleted summer WSC (Nöthig *et al.*, 2015). Haptophyte contribution declined considerably to central Fram Strait (E4, 17%) and was almost absent at western Fram Strait (E3, 2%) and on the NE Greenland Shelf (E1-E2, 0-1%). Whilst both the NE Greenland shelf and eastern Fram Strait showed dominance of either diatoms or haptophytes, stations located in western (E3) and central (E4) Fram Strait exhibited mixed assemblages of phytoplankton including enhanced contributions of cryptophytes (10% and 28% respectively), and prasinophyceae (31% and 9%).

3.3.3 Nutrient limitation

Phytoplankton responses to nutrient amendment were assessed via changes in chlorophylla concentrations, which likely reflects contributions from both bulk phytoplankton biomass changes and enhances in chlorophyll-a: carbon ratios following supply of limiting nutrient(s) (Moore et al., 2008; Browning et al., 2017). Chlorophyll-a concentrations increased significantly relative to untreated controls following addition of fixed N in Experiments 1, 2, and 5 and did not vary following supply of any nutrient combination in Experiments 3 and 4 (Fig. 3.4b-f). For Experiments 1, 2, and 5, relative chlorophyll-a increases following N supply were larger in experiments around the EGC shelf break (mean increases of +313% in E1; +628% in E2) than in the WSC in eastern Fram Strait (+241% in E5). Our observations of significant chlorophyll-a increases following N supply in these experiments suggested that fixed N was the primary summertime limiting nutrient through these parts of the Fram Strait region during our cruise occupation. These observations are consistent with prior work on the NE Greenland Shelf (Kattner and Budéus, 1997) and elsewhere in the Arctic Ocean (Maestrini et al., 1986; Smith, Gosselin and Taguchi, 1997; Ortega-Retuerta et al., 2012; Taylor et al., 2013; Mills et al., 2018). Although not statistically significant, small additional enhancements in chlorophyll-a concentrations were observed in the Experiment 5 N+Fe treatment over +N alone (+265% in comparison to +241% for N addition alone), suggesting that Fe was potentially a secondary limiting

nutrient after N in the surface WSC. The absence of any significant chlorophyll-a enhancements in response to supply of the volcanic ash dust in any of the experiments suggested that the dust was not a significant source of fixed N, as anticipated based on the results of previous bioassays and leaching experiments with this ash sample (Achterberg *et al.*, 2013).

No statistically significant responses to any of the supplied nutrient combinations relative to unamended controls were found in Experiments 3 and 4, located in the western and central Fram Straight respectively. This could either be a result of (i) limitation by an alternative resource (light or another nutrient); (ii) grazer regulation of the phytoplankton community, maintaining phytoplankton standing stocks despite enhanced specific growth rates following nutrient supply (e.g., Mann and Chisholm, 2000); or (iii) restricted net phytoplankton community growth over the experimental duration (72 hours) due to low starting biomass concentrations and/or cold temperatures (Vernet et al., 2019). Our results do not allow us to unambiguously distinguish between these; however, ancillary observations allow identification of the most probable factors. Light limitation of the ambient phytoplankton community at these sites was unlikely, as surface mixed layers were shallow (14 m at Experiment 3, Table 3.1), irradiances were elevated (E3: up to 395 W·m⁻², E4: up to 478 W·m⁻²), and day lengths long (19-24 hours). Furthermore, in-situ light limitation, if present, would likely be at least partially relieved following incubation ondeck, leading to chlorophyll-a increases in control samples (Moore et al., 2006; Browning et al., 2019), which were not observed. (Co-)limitation of phytoplankton growth by another element cannot be ruled out, however concentrations of all measured nutrients were elevated, arguing against this (Table 3.1). In addition, the absence of any response following the volcanic dust addition, which likely supplied a range of trace metal micronutrients alongside Fe (Achterberg et al., 2013), suggested that non-Fe trace elements were also not primary limiting nutrients. Slow, nutrient-replete growth, low starting phytoplankton concentrations, in combination with top-down grazer regulation therefore appears the most likely cause of the lack of net community growth response in these two experiments.

		E1	E2	E3	E4	E5
Lat	°N	80.22	76.80	79.59	79.36	78.99
Long	°E	-8.14	-8.61	-4.77	0.23	6.99
T _{pot.}	°C	-1.3	0.1	-1.6	2.7^{T}	8.8
Sal	PSU	29.97	30.62	30.03	32.67^{+}	35.07
MLD§	m	12	10	14	/	14
NO ₃		< 0.02	< 0.02	0.5	12.3	0.3
PO ₄		0.4	0.3	0.3	1.0	0.1
Si	μνι	4.4	1.1	4.4	7.4	< 0.03
NH ₄		< 0.05	< 0.05	0.5	1.6	< 0.05
dCo	pМ	202	148	164	114*	40
dFe		1.3	0.8	1.8	1.3*	0.4
dMn		5.0	4.2	5.6	2.8^{*}	1.5
dNi	nM	6.2	4.7	5.9	4.4^{*}	3.1
dCu		4.8	3.7	4.5	2.9^{*}	1.3
dZn		1.8	/	1.8	0.9*	0.8
Fe _N * initial	nM	1.3	0.8	1.3	-5.3*	0.3
Initial		0.82	0.25	0.16	0.15	0.51
Control	Chl.a in mg/m ³	0.69	0.13	0.18	0.09	0.49
+N		2.16	0.82	0.15	0.09	1.18
+Fe		0.54	0.25	0.16	0.09	0.51
+N+Fe		1.47	0.45	0.15	0.09	1.30
+Dust		0.73	0.23	0.16	0.08	0.59
N-to-initial	0/	313	628	80	58	241
(N+Fe)-to-initial	%	213	344	80	96	265

Table 3.1: Initial conditions of bioassay experiments, and chlorophyll-a biomass response to nutrient amendments.

3.3.4 Nutrient deficiency

The nutrient concentrations in seawater relative to typical phytoplankton requirements provide the capacity to predict which nutrient becomes limiting to phytoplankton growth (Moore, 2016). Either fixed N or Fe was calculated to be the most deficient nutrient in surface waters of the Fram Strait region (that is, had lowest concentrations in seawater taking into account assumed-average phytoplankton requirements; equation 3.2, Fig. 3.2). An east-to-west transition was found in the deficiency of Fe relative to N (Fe_N*). Surface waters of the EGC, where fixed N limitation was observed, showed positive Fe_N* (mean 1.1 ± 0.9 nM, range -0.3-3.2 nM), which increased towards the Greenlandic coast and the glaciated Zachariæ Isstrøm (S20, 1.7 nM) and Nioghalvfjerdsbrae Glacier (S21, 1.2 nM; S24, 3.3 nM) (Fig. 3.3d). Interestingly, the station closest to Nioghalvfjerdsbrae exhibited the EGC minimum in Fe_N* (-0.3 nM, S22), likely a result of low dFe/ low fixed N meltwater discharge in combination with dFe scavenging removal (Hopwood et al., 2018; Ardiningsih et al., 2020). The surface WSC showed lower Fe_N* $(0.1 \pm 0.4 \text{ nM}, -0.7-0.3 \text{ nM})$, with decreasing values towards the Svalbard shelf break. The

station closest to Svalbard (S1) had lowest Fe_N* (-0.7 nM) at low residual dFe (0.3 nM), suggesting phytoplankton may have may have been approaching a situation of co-limitation by Fe and N (Blain *et al.*, 2004; Ryan-Keogh *et al.*, 2013; Browning *et al.*, 2017). This is in agreement with the results of Experiment 5, where an enhanced chlorophyll-a response to Fe+N amendment over +N alone was apparent. In addition, some surface waters of the WSC also showed Si deficiency relative to fixed N, suggesting that this nutrient might be (co-)limiting for Si-requiring diatoms in this location and potentially, alongside low N and Fe levels, partly explaining their absence in these waters (Figs 3.3g and 3.4). Elsewhere, Si was generally in excess relative to N.

Subsurface (>10 m) waters were always Fe deficient relative to fixed N throughout the central Fram Strait region (Fig. 3.3g), presumably caused by remineralisation-driven increases in macronutrient concentrations, which are not reflected in dFe as a result of the high particle reactivity and scavenging removal of this element (Boyd and Ellwood, 2010; Moore, 2016). Sub-surface N-deficiency was only observed on the NE Greenland Shelf where the nitracline was deeper, suggested to be a consequence of release of low N glacial meltwater, or more generally strong stratification driven by freshwater. Making the assumption of a phytoplankton requirement for Si, this element was typically calculated as the second most deficient nutrient throughout subsurface waters (Fig. 3.3h). Repeating the analysis with Si excluded instead showed widespread secondary deficiency by dissolved Co.



Figure 3.4: Phytoplankton community composition and responses to nutrient supply at incubation sites. (a) Phytoplankton community composition at bioassay experiment water collection sites as determined by pigment analysis and CHEMTAX. (b-f) Chlorophyll-a responses to nutrient additions. Red symbols show the mean chlorophyll concentration and black symbols indicate the individual replicates. Treatments labelled with the same letter have statistically indistinguishable means (ANOVA followed by a Tukey Honest Significant Difference test, $P \le 0.05$, n = 3). Figure generated using OriginPro software, version 9.1.0 (OriginLab Corporation, Northampton, MA, USA).

3.3.5 Factors controlling nutrient limitation in Fram Strait

Like other marine regions, the drivers of phytoplankton nutrient limitation patterns strongly depend on the relative supply : demand ratio for each nutrient (Moore *et al.*, 2013). In order to categorize measured nutrient concentrations in terms of limitation potential, we assumed fixed elemental requirements for phytoplankton. The potential for high variability in elemental quotas of phytoplankton, particularly under reduced competition that exists in monoculture, has been reported (Twining and Baines, 2013). However, the success of nutrient deficiency calculations in correctly predicting the identity of the growth limiting

nutrient in the ocean (i.e., following direct experimental determination or via molecular nutrient stress signatures) argues for a relatively conserved, community-level elemental stoichiometry in natural phytoplankton communities (Moore *et al.*, 2013; Saito *et al.*, 2014; Browning *et al.*, 2017). Changes in nutrient limitation patterns, and in particular the presence of N versus Fe limitation, or the development of co-limitation, will therefore likely have a strong dependence on altered supply rates and ratios of these nutrients to the surface ocean (Ward *et al.*, 2013; Browning *et al.*, 2017).

In this respect, the southward flowing EGC and the northward flowing WSC are distinctly different in physical characteristics, nutrient content, and thereby nutrient supply to surface waters. The EGC was colder and fresher, with regionally-averaged concentrations having lower fixed N but 2-4 fold higher Si and dFe compared to the WSC (Table 3.2). Intermediate Waters, defining the boundary between these two water masses, showed values between these end members, which may have been derived from the convergence of the EGC and WSC (Rudels et al., 2005; Hattermann et al., 2016; Laukert et al., 2017). Elevated dFe and Si in the EGC was likely a result of locally-derived freshwater and southward transport in the Transpolar Drift, itself fuelled by riverine discharge to the Eurasian Arctic Shelf (Klunder, Bauch, et al., 2012; Ardiningsih et al., 2020; Charette et al., 2020). Conversely, these sources supply low amounts of fixed N (Ooijen et al., 2016; Slagter et al., 2017; Hopwood et al., 2018). In addition to the low N:P ratio of Pacific water, which is advected across the Arctic and exits via Fram Strait (Yamamoto-Kawai, Carmack and McLaughlin, 2006; Codispoti et al., 2013), this may be a contributing factor to the observed primary N limitation of the phytoplankton community in this region (Figs 3.3 and 3.4). In contrast, North Atlantic source waters supplying the WSC are depleted in Fe and Si, alongside N, which leads to conditions approaching serial N-Fe limitation (and potential co-limitation by Si for diatoms) in the eastern Fram Straight (Ryan-Keogh et al., 2013; Rijkenberg et al., 2014; Browning et al., 2019). Further north, a branch of the WSC continues to flow into the SE Nansen Basin, where - off-axis to the dFe-rich Transpolar Drift – Fe deficiency (i.e. $Fe_N^* < 0$) has also been reported (Klunder, Bauch, et al., 2012; Rijkenberg et al., 2018).

<u>**Table 3.2:**</u> Region-averaged physical characteristics and nutrient concentrations (mean value \pm standard deviation) of the East Greenland Current (EGC), West Spitsbergen Current (WSC), and Intermediate (IW) surface (10 m) waters.

		EGC	IW	WSC
T _{pot.}	°C	$\textbf{-0.5}\pm0.7$	$\textbf{-0.4} \pm 2.2$	8.3 ± 0.7
Sal	PSU	30.37 ± 0.78	32.43 ± 1.97	35.02 ± 0.06
Fixed N	μM	0.3 ± 0.5	0.6 ± 0.6	0.7 ± 1.0
dFe	nM	1.5 ± 0.8	0.8 ± 0.5	0.4 ± 0.1
Si	μM	3.5 ± 2.9	2.3 ± 1.2	0.7 ± 0.7

Prior work has shown that southward transport of N associated with the EGC $(124 \pm 22 \text{ Tg} \cdot \text{yr}^{-1})$ is almost balanced by northward transport associated with the WSC $(92 \pm 17 \text{ Tg} \cdot \text{yr}^{-1})$ (Torres-Valdés *et al.*, 2013). Surface Waters of the Fram Strait region were N depleted ($0.5 \pm 1.2 \mu$ M), but deeper waters below the mixed layer hosted enhanced fixed N concentrations (15-500 m, $8.4 \pm 4.1 \,\mu$ M) (Fig. 3.3). Summer mixed layer depths in Fram Strait are shallow (10-23 m measured on the PS100 cruise, Table 3.1) and deep-water reservoirs are thus unlikely a substantial source of fixed N to the surface ocean at this time (Randelhoff et al., 2016). Conversely, in winter, deep mixing to depths >100 m below the nutrient-depleted surface layer (10-25 m), replenishes surface waters of Fram Strait region with N (de Boyer Montégut et al., 2004; Codispoti et al., 2013). Rates of surface WSC fixed N replenishment may be an order of magnitude greater during autumn/winter than summer (Randelhoff, Sundfjord and Reigstad, 2015; Randelhoff et al., 2016), making deep winter mixing likely the dominant factor controlling the extent of annual new primary production in the Fram Strait region (Randelhoff et al., 2020). Deep-water re-supply of surface Fe is more restricted, due to deeper ferriclines that are observed to depths >150 m in the WSC of Fram Strait (Fig. S3.2). Therefore to account for near-complete drawdown of fixed N between winter and summer in the WSC, Fe must have additional supply routes (assuming that seasonally or regionally enhanced regeneration/recycling of Fe cannot fully account for such drawdown (Rafter, Sigman and Mackey, 2017)). Aside from transient, low-frequency events such as volcanic eruptions (Achterberg et al., 2013) or agricultural and forest fires (Stohl et al., 2007), atmospheric deposition of Fe across the Arctic is reportedly low (Marsay et al., 2018; Conca et al., 2019). This suggests a dominance of sediment supplied Fe from shallow bathymetry to the south (i.e. coastal Greenland and Svalbard) and supply of Arctic-derived Fe by the Transpolar Drift to the EGC waters (offshore Fram Strait region) (Charette et al., 2020). The importance of sedimentary dFe supply to Fram Strait region was also indicated from the distribution of

dissolved Mn (Fig. 3.3f), which derives primarily from sediments and shows maxima in (i) the surface EGC where the influence of the Transpolar Drift is expected (Kadko *et al.*, 2019), (ii) near the glacier termini on the NE Greenland Shelf, and (iii) on the continental slopes of Svalbard (Bucciarelli, Blain and Tréguer, 2001; Wehrmann *et al.*, 2014; Bown *et al.*, 2018).

3.3.6 Future perspectives

Our finding of widespread N deficiency in nutrient concentration fields alongside direct experimental evidence for N limitation points towards the importance of variability in N sources in regulating summertime phytoplankton productivity in Fram Strait. Consistent with prior studies, we corroborate that northward advection of Atlantic-derived fixed N is essential to sustain primary production in the N-depleted western Fram Strait and on the NE Greenland Shelf (Kattner and Budéus, 1997; Michel et al., 2015; Randelhoff, Sundfjord and Reigstad, 2015; Hopwood et al., 2018). Accordingly, we suggest that the future areal and seasonal extent of primary production in Fram Strait region might be strongly impacted by changes in the lateral advection of fixed N via the WSC, in addition to an earlier onset of phytoplankton growth resulting from reduced ice cover (Nishino et al., 2011; Randelhoff, Sundfjord and Reigstad, 2015). As an Arctic outflow region, Fram Strait is clearly strongly affected by processes occurring within the Arctic. Broad-scale changes to Arctic inflow, sea-ice cover, lateral advection via the Transpolar Drift and wind driven mixing will all have downstream effects on nutrient stoichiometry in Fram Strait (Kipp et al., 2018; Mayot et al., 2020; Randelhoff et al., 2020). How lateral and vertical nutrient supply will change in the future Arctic as a result of on-going changes to sea-ice retreat and stratification remains uncertain, as neither lateral transport of nutrients in the Transpolar Drift, or vertical turbulent supply of nutrients during summer are well quantified (Mills et al., 2018; Randelhoff et al., 2019; Charette et al., 2020).

Surface primary production in the Arctic Ocean due to increased summertime light availability has increased during the past few decades (Kahru *et al.*, 2011; Arrigo and van Dijken, 2015). Second to light limitation, Arctic Ocean net primary production seems foremost limited by the availability of fixed N (Codispoti *et al.*, 2013; Randelhoff *et al.*, 2020) and may at some point hinder future increases in productivity, although changes in nutrient supply ratios and/or phytoplankton species composition may result in other nutrients such as Si, PO₄ or dFe to become limiting factors as well (Taylor *et al.*, 2013;

Ardyna et al., 2020). In the future, the Arctic Ocean is projected to have less ice coverage and become fresher and more stratified, which would reduce winter mixing depth and the associated supply of deep water nutrients (Tremblay et al., 2008; Popova et al., 2012). Yet, conversely sea-ice loss also facilitates increased wind driven mixing, which is thought to have enhanced autumn productivity in some Arctic regions (Ardyna et al., 2014; Castro de la Guardia et al., 2019), and may also offset nutrient limitation caused by water column stratification in Fram Strait region. Additionally, some modelling suggests that decreasing sea-ice cover may lead to increased import of Atlantic Waters – and thus, fixed N – to the Fram Strait region (Wang et al., 2020). Therefore in addition to changes in the areal extent of ice-free ocean (Carmack, Macdonald and Steve, 2004; Arrigo, van Dijken and Pabi, 2008; Norwegian Polar Institute, 2020) any future projection of primary production in the Fram Strait region is also hampered by poor knowledge of changes in nutrient supply as a result of the strong seasonal and inter-annual variability in current regimes (de Steur et al., 2014; Hattermann et al., 2016), changes in phytoplankton community composition and their nutrient requirements (Lasternas and Agustí, 2010; Nöthig et al., 2015; Vernet et al., 2019). This compounds a poor mechanistic understanding of what drives elevated dFe and Si concentrations in the Transpolar Drift and how this will respond to future climate perturbations (Rijkenberg et al., 2018; Ardiningsih et al., 2020; Charette et al., 2020). In addition, the relative importance of N₂ fixation by diazotrophs in this region is poorly quantified (Zehr and Kudela, 2011; Sipler et al., 2017; Harding et al., 2018). Diazotrophs have particularly high Fe requirements, therefore the distribution of dFe, which in Fram Strait appears to be predominantly supplied by the EGC, could also be important for controlling their distribution and the rate of new fixed N introduced into this system by this process.

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Author contributions

Stephan Krisch, Thomas J. Browning and Eric P. Achterberg designed the research. Sampling and analyses were performed by **Stephan Krisch**, Martin Graeve, Kai-Uwe Ludwichowski, Pablo Lodeiro, Stéphane Roig, Jaw-Chuen Yong and Torsten Kanzow. The manuscript was written by **Stephan Krisch** and Thomas J. Browning with all authors contributing to its revision.

3.4 Supplementary Material



Figure S3.1: Fixed N, Si and dFe versus practical salinity for surface (10 m) waters in Fram Strait region.Standard error not shown for clarity but included in linear approximation through program-based directweighing:[fixed N] = -1.73 (0.90) + 0.07 (0.03) S,[Si] = 19.2 (3.8) - 0.52 (0.12) S,and[dFe] = 8.52 (1.96) - 0.23 (0.06) S. Figure plotted using OriginPro, version 9.1.0. (OriginLab Corporation,Northampton, MA, USA).



Figure S3.2: Vertical distribution (<500 m) of potential temperature (T_{pot}), fixed nitrogen (fixed-N) and dissolved Fe (dFe) of example stations in (a-c) the West Spitsbergen Current (top row, stations S1, S3 and S5), the East Greenland Current (d-f) in western Fram Strait (middle row, S14-16) and (g-i) on the outer NE Greenland Shelf (bottom row, S11-S13). Dashed line indicates mean value (± standard deviation, dotted lines) of maximum climatological winter mixed layer depths (Dec-Mar) in the West Spitsbergen Current (a-c) and the East Greenland Current (d-i) obtained from de Boyer Montégut *et al.* (2004) between 76-80°N, 20°W-15°E. Definition of West Spitsbergen Current (surface salinity >34.8) and East Greenland Current (<34.8) according to surface salinity measurements (11m) from Polarstern cruises to Fram Strait region between 2004-2019. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

4 The 79°N Glacier cavity modulates subglacial iron export to the NE Greenland Shelf

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Abstract

Approximately half of the freshwater discharged from the Greenland and Antarctic Ice Sheets enters the ocean subsurface as a result of basal ice melt, or runoff draining via the grounding line of a deep ice shelf or marine-terminating glacier. Around Antarctica and parts of northern Greenland, this freshwater then experiences prolonged residence times in large cavities beneath floating ice tongues. Due to the inaccessibility of these cavities, it is unclear how they moderate the freshwater associated supply of nutrients such as iron (Fe) to the ocean. Here we show that subglacial dissolved Fe export from Nioghalvfjerdsbrae (the '79°N Glacier') is decoupled from particulate inputs including freshwater Fe supply, likely due to the prolonged ~162 day residence time of Atlantic water beneath Greenland's largest floating ice-tongue. Our findings indicate that the overturning rate and particle-dissolved phase exchanges in ice cavities exert a dominant control on subglacial nutrient supply to shelf regions.

4.1 Introduction

Glacial weathering processes enrich meltwater in iron (Fe) and silicic acid (Si(OH)₄) relative to other nutrients such as nitrate and phosphate (L. Meire et al., 2016; Raiswell et al., 2018). The availability of Fe limits primary production across much of the high latitude oceans, including most of the Southern Ocean (de Baar et al., 1995) and parts of the sub-polar North Pacific (Boyd et al., 2005) and North Atlantic Oceans (Nielsdóttir et al., 2009). Whilst Si(OH)4 concentrations are relatively high around the coastline of Antarctica, low Si(OH)₄ availability across most of the Arctic constrains diatom growth (Krause et al., 2018, 2019) and thus Si(OH)4 availability directly influences the magnitude of the Arctic biological carbon pump (Tréguer et al., 2018). The annual supply of Fe and Si(OH)₄ from glacial meltwater, icebergs and associated particles into the high latitude oceans is presently assumed to scale with solid and liquid discharge volume (Bhatia, Kujawinski, et al., 2013; Raiswell et al., 2016; Wadham et al., 2019). With accelerating mass loss from the Greenland and Antarctic Ice Sheets, the associated nutrient supply to the ocean is therefore projected to increase in magnitude under future climate scenarios (Meredith et al., 2019; Wadham et al., 2019) with potential implications for high latitude primary production (Laufkötter et al., 2018; Krause et al., 2019; Person et al., 2019).

Dissolved Fe (dFe) and Si(OH)⁴ both exhibit non-conservative behavior across estuarine salinity gradients (Dürr *et al.*, 2011; Schroth *et al.*, 2014) which means that large differences can arise between the net and gross fluxes of these nutrients into the ocean at the glacier-ocean interface (Hopwood *et al.*, 2020). By far, the largest uncertainty in present estimates of annual dFe (e.g. Stevenson *et al.*, 2017) and Si(OH)⁴ (e.g. contrasting Meire *et al.* (2016) and Hawkings *et al.* (2017)) fluxes from Greenland to the ocean arises in how non-conservative processes are parametrized. Furthermore, there is little agreement between present model estimates concerning the magnitude of ice sheet-ocean fertilization, which partially arises because of a poor mechanistic understanding of processes occurring at the data-deficient ice-ocean interface (Person *et al.*, 2019; Straneo *et al.*, 2019). Multiple spatially overlapping factors including scavenging (Schroth *et al.*, 2014; Zhang *et al.*, 2015), particle dissolution (Hawkings *et al.*, 2017), benthic recycling of nutrients (Halbach *et al.*, 2018; Cape *et al.*, 2020), entrainment of nutrient-rich deep marine waters (Kanna *et al.*, 2018; Cape *et al.*, 2019) and biological drawdown (Meire *et al.*, 2017) affect nutrient distributions close to calving ice faces.

Subglacial discharge plumes from marine-terminating glaciers may moderate fjord-scale biogeochemistry and primary production on timescales of hours-to-weeks after freshwater discharge enters the marine environment (Meire *et al.*, 2017; Cape *et al.*, 2019). For many larger ice shelves however, freshwater first experiences prolonged residence times in subglacial cavities. For example, inflowing water masses are resident for approximately 2 years underneath the Ross Sea Ice Shelf (Reddy, Holland and Arrigo, 2010), and ~162 days underneath Nioghalvfjerdsbrae (commonly referred to as the 79° North Glacier) (Schaffer *et al.*, 2020). These dark subsurface cavities provide case studies to understand changing nutrient availability by contrasting the inflowing and outflowing properties of water masses to derive the integrated change from all glacier associated processes in the absence of confounding effects of summertime phytoplankton blooms. Given the non-conservative behavior of both Fe and Si(OH)₄ across salinity gradients, and the multiple processes affecting their exchange between the particle and dissolved phases, we hypothesize that these prolonged residence times may decouple the outflowing chemical enrichment from the ice sheet-derived inputs.

Here we investigate constraints on lateral Fe and macronutrient supply into the Atlantic from the large cavity underneath the floating ice tongue of the Nioghalvfjerdsbrae glacier (hereafter the 79NG). During GEOTRACES cruise GN05, a comprehensive survey of Fe fractions (Table 1) alongside other trace elements and macronutrients was conducted up- and downstream of the 79NG following the main pathways of Atlantic water inflow and glacial meltwater outflow close to the peak of the melting season (August 2016). Due to favorable weather and ice conditions, oceanographic sampling was conducted immediately adjacent to the ice tongue, providing, to our knowledge, a unique dataset to investigate nutrient fluxes exiting a subglacial cavity where the water residence time is well constrained from prior surveys (Wilson and Straneo, 2015) as well as 5 moorings on the shelf which were deployed for the same year where we present nutrient distributions, 2016-2017 (Schaffer *et al.*, 2020). Please note that for the sake of clarity, station numbering in this chapter, accepted for publication in *Nature communication*, differs from the original data publication, and the labelling sequence in Chapters 3 (Krisch *et al.*, 2020) and 5.

$< 0.02 \mu m$	E'llere (c	
. 0.2		
< 0.2 µm	rnirale	e.g. Fitzsimmons <i>et al.</i> (2015)
0.02- 0.2 μm	Determined as difference between dFe and sFe (cFe = dFe $-$ sFe)	
< 0.2 µm	Dissolved Fe bound to organic molecules (samples for iron ligands are filtered; dFeL is part of the dFe pool)	e.g. Ardiningsih <i>et al.</i> (2020)
> 0.2 µm	Reactive particulate fraction, including nanoparticulate ferrihydrite physically immobilized on particles and cellular Fe.	e.g. Berger <i>et al.</i> (2008)
Unfiltered Segurator	Dissolved and particulate Fe released	e.g. Edwards and Sedwick (2001)
0 0 < > U S	$0.02 - 0.2 \ \mu m$ $0.02 - 0.2 \ \mu m$ $0.02 \ \mu m$ $0.02 \ \mu m$ $0.02 \ \mu m$ Unfiltered deawater	0.02- 0.02-Determined as difference between dFe and sFe (cFe = dFe - sFe)0.02- 0.2 μ mDissolved Fe bound to organic molecules (samples for iron ligands are filtered; dFeL is part of the dFe pool)0.2 μ mReactive particulate fraction, including nanoparticulate ferrihydrite physically immobilized on particles and cellular Fe.0.1 μ mDissolved and particulate Fe released after storage at pH 1.9

Table 4.1: Definition of Fe fractions in seawater.

4.2 Methods

4.2.1 Sampling and nutrient analyses

Vertical, full depth profiles of salinity, temperature, pressure and light attenuation (turbidity) were conducted at high-resolution (m⁻¹) using a SEA-BIRD SBE 911 ultraclean CTD rosette (ucCTD) at all stations where trace elements were collected. For water column physical properties (salinity, temperature, pressure, turbidity, UV-light fluorescence) and macronutrient distributions (NO₂, NO₃, PO₄, and Si(OH)₄), the dataset from the ucCTD was combined with the largeCTD data (SEA-BIRD SBE 911plus) from the same campaign.

Trace metal samples were collected using the ucCTD rosette, equipped with 24 x 12 L GoFlo bottles following GEOTRACES sampling protocols (Cutter *et al.*, 2017). LDPE bottles were pre-cleaned with sequential leaches in 2% detergent (mucasol), 1.2 M HCl and 1.2 M HNO₃ with ultra-pure water rinses (>18.2 M Ω cm; Milli-Q, Millipore) between each stage. On deck, GoFlo bottles were then transferred into an overpressured clean room where water samples were filtered (Acropak 0.8/0.2 µm) into pre-cleaned LDPE (low density polyethylene) 125 mL bottles and acidified to pH 1.9 with 180 µL HCl (UpA, ROMIL) to determine dissolved trace metals. A further filtered (0.8/0.2 µm) sample was retained, passed through a 0.02 µm Anodisc peristaltic filtration unit within 4 hours of sample collection, and then acidified to determine the sFe fraction (<0.02 µm). An unfiltered water sample was retained and acidified as above to determine total dissolvable trace metals after analysis >6 months later.

Particulate trace metal samples were collected onto pre-acid leached Polyethersulfone (PES) Membrane Filters ($0.2 \mu m$, Sartorius) through pressurization (0.2 atm) from each GoFlo bottle

with filtered Nitrogen gas. 1.2-4.1 liters of seawater were passed through individual sample filters which were then sealed in clean petri-dishes, stored in a deep freezer immediately after collection at -20 °C and kept frozen until analysis. The determination of the labile particulate trace metals (i.e. LpFe) was conducted by applying a weak acid leach (25% acetic acid, Optima grade, Fisher Scientific) with a mild reducing agent (0.02 M hydroxylamine hydrochloride, Sigma TM grade) and a short heating step (10 min, 90-95 °C) with a total leach time of 2 h (Berger *et al.*, 2008).

Seawater for macronutrient analyses of NO₂, NO₃, PO₄ and Si(OH)₄ was also retained from each GoFlo rosette bottle. Note that while refer to Si(OH)₄ and PO₄, as is conventional, it may also incorporate other species of dissolved silicon and phosphorus. Unfiltered surface macronutrient samples (upper 200 m) were stored at 5 °C and run within 18 h using the QUAATRO autoanalyzer (Grasshoff, Kremlingl and Ehrhardt, 1999) modified according to the methods provided by the manufacturer (Seal, Alliance). At all other depths, filtered samples (0.2 µm) were frozen and run at AWI using the same procedure.

Trace metal concentrations (i.e. dFe, sFe and TdFe) were measured via ICP-MS after preconcentration exactly as per Rapp *et al.* (2017). Briefly, 15 mL sample aliquots were preconcentrated using an automated SeaFAST system (SC-4 DX SeaFAST pico; ESI). All reagents for SeaFAST were prepared in MQ-Water (>18.2 M Ω cm⁻¹; Milli-Q, Millipore). Single-distilled sub-boiled HNO₃ (SpA grade, Romil) was used for sample elution. Ammonium acetate buffer (pH 8.5) was prepared from glacial acetic acid and ammonium hydroxide (both Optima, Fisher Scientific). The 10-fold pre-concentrated samples were analyzed by highresolution inductively coupled plasma-mass spectrometry (HR-ICP-MS; Thermo Fisher Element XR). Calibration was via isotope dilution for Fe, and standard addition for Mn and Co. For labile particulate analyses, samples were measured via ICP-MS without preconcentration and were quantified using external calibration prepared in the same sample matrix using multi-element standards (Inorganic Ventures). For details of quality control, see supplementary material or method section 2.1.5.

4.2.2 Stable Fe isotopic composition (δ^{56} Fe)

Stable Fe isotopic composition (δ^{56} Fe) was measured in seawater samples at the University of South Florida (USF) following a modification of Conway *et al.* (2013). Filtered trace metal samples were combined from several depths (see Supplementary Table 9) to provide sufficient

dFe for isotope analysis (10-20 ng). Fe was extracted from acidified seawater samples using a two-stage resin extraction method (Nobias PA-1 at pH 2, and AGMP-1), followed by analysis by Thermo Neptune Plus multi-collector ICP-MS with introduction via an ESI Apex Ω desolvator (with Ar but not N₂ added gas), Pt Jet and Al 'x-type' sample cones. The procedural blank using this method at USF has been established at 0.24 ± 0.04 ng Fe (1SD, n = 10), similar to previous studies (Conway *et al.*, 2013). Instrumental mass bias was accounted for using an ⁵⁷Fe-⁵⁸Fe double spike, with δ^{56} Fe expressed in standard delta notation relative to the IRMM-014 standard. For this method we assess long-term instrumental precision using repeat analyses of the NIST-3126 Fe standard, for which we obtain a δ^{56} Fe value of +0.36 ± 0.04‰ (2SD, n = 351 during 24 sessions over 3 years). We apply this value as an estimate of 2 σ uncertainty on δ^{56} Fe for all samples, except for samples where the larger 2 standard internal error is a more conservative estimate of uncertainty, as applies to samples in this study.

4.2.3 Stable oxygen isotopes (δ^{18} O)

Stable oxygen isotopes (δ^{18} O) were analyzed following the procedure described in Meyer *et al.* (2000). In short, seawater samples collected with the largeCTD were equilibrated for 6.5 hours using carbon dioxide gas of known isotopic composition and platinum as catalyst. The equilibrated CO₂ gas was transferred into a Finnigan MAT Delta-S mass spectrometer equipped with two equilibration units, where the oxygen isotopic composition was analyzed a total of eight times. The oxygen isotopic composition is reported relative to a V-SMOW standard.

4.2.4 Natural radium isotopes (²²⁶Ra, ²²⁸Ra)

Natural radium isotopes (²²⁶Ra, ²²⁸Ra) were measured via gamma spectrometry (Moore, 1984) following the procedure of Rutgers van der Loeff *et al.* (2018). Briefly, water column profiles were obtained using in-situ pumps including 0.8 μ m Supor filtration and Ra adsorption in MnO₂-coated cartridges. At 10, 50, and 350 m depth, two cartridges were used in series, allowing the calculation of Ra absorption efficiency. At the other depths only one cartridge was mounted, assuming the mean collection efficiency of all cartridge pairs (93 ± 8%). The cartridges were leached by Soxhlet extraction with 6 N HCl refluxing over 10 hours, followed by Ra-coprecipitation with BaSO₄ as described in Cutter *et al.* (2017).

4.3 **Results and Discussion**

4.3.1 Study region

Hydrographic and trace metal clean chemical profiles were conducted at 11 stations upstream and downstream of the 79NG (S1-11, Fig. 4.1). Three major water masses are present on the NE Greenland Shelf: Polar Surface Water (PSW, $\sigma_{\Theta} < 26.1 \text{ kg/m}^3$), Atlantic Intermediate Water (AIW, $\sigma_{\Theta} > 27.73 \text{ kg/m}^3$), and Atlantic Intermediate Water modified by mixing with glacial meltwaters (mAIW, $\sigma_{\Theta} = 27.00-27.73 \text{ kg/m}^3$) (Schaffer *et al.*, 2020). The ocean circulation on the continental shelf is steered by the underlying shelf bathymetry. The East Greenland Current follows the shelf break forming the eastern limb of the anti-cyclonic shelf circulation (Budéus, Schneider and Kattner, 1997; Jeansson *et al.*, 2008). On the continental shelf, AIW follows a C-shaped trench system (passing stations S8-S10; Fig. 4.1) towards the vicinity of the 79NG (Schaffer *et al.*, 2017).

Warm (0.6-1.3°C) and saline (S = 34.58-34.80) AIW found at depths >268 m (Fig. S4.1a/b) induces basal melting along the floating 79NG ice-tongue that covers the entire length of Nioghalvfjerdsfjorden (Wilson and Straneo, 2015; Mayer et al., 2018). This inflow of heat presently occurs throughout the year and thus, as the basal melt of the ice tongue accounts for ~89% of freshwater exiting the cavity (Schaffer et al., 2020), there is less pronounced seasonality in mAIW outflow than would be expected in a system dominated by subglacial discharge which largely occurs over a narrow time period in summer (Mankoff et al., 2020). Basal melt and subglacial discharge at 79NG combined result in a total cavity freshwater flux of 0.63 ± 0.21 mSv (19.9 ± 6.6 km³·yr⁻¹) (Schaffer *et al.*, 2020), which is roughly equivalent to 2% of annual runoff from the Greenland Ice Sheet (2016 values) (Bamber et al., 2018). Mixing between inflowing AIW, subglacial discharge, and basal ice melt dictates the properties of mAIW which exits the 79NG cavity as a subsurface flow (Fig. 4.2). The mean residence time of water in the cavity for 2016-2017 was ~162 days (Schaffer et al., 2020). The mAIW is observed exiting the cavity between 96-268 m depth at the glacial front (S1) (Fig. 4.3a). Oxygen stable isotope measurements (δ^{18} O) and calculated meteoric freshwater fractions (Fig. 3b-c) corroborate the lateral transport calculations as per Schaffer et al. (2020), demonstrating that mAIW is subsequently carried with the anti-cyclonic shelf-circulation away from the fjord mouth following the Westwind Trough (via S3 and S5) towards the shelf break (S6) in a northeasterly direction (Budéus, Schneider and Kattner, 1997; Wilson and Straneo, 2015).



Figure 4.1: Topography and location of sampling stations on the NE Greenland Shelf. Norske Trough (S8-10), the 79NG front (S1) and Dijmphna Sund side-exit (S4, a sill station), Nioghalvfjerdsfjorden Bay (S2), Westwind Trough (S3, S5), the shelf break (S6) and a station in Fram Strait (S7). One station (S11) was sampled in proximity to Zachariæ Isstrøm (ZI). Two further stations were sampled in the center (S12) and outer (S13) NE Greenland Shelf. Other stations from the same cruise, not discussed herein, are marked for completion (see Krisch *et al.* (2020) - Chapter 3 for an overview). The black thin line from S1 to S7 highlights the section from which depth profiles are discussed in **Figs. 4.3-4.5**. The predominant circulation of Atlantic Intermediate Water (AIW), modified AIW (mAIW) and the East Greenland Current (EGC) is shown. Figure generated by Janin Schaffer using MATLAB version 9.6.0 (R2019a, Natick, Massachusetts: The MathWorks Inc., 2019).



Figure 4.2: Concept figure illustrating the subglacial cavity underneath the Nioghalvfjerdsbrae (79NG) floating ice tongue and illustrated with key aspects of the Fe cycle. The majority of glacial freshwater is released as basal melt into Atlantic Intermediate Water (AIW) forming modified AIW (mAIW). A further portion of glacial freshwater is discharged into Polar Surface Water (PSW). Only a fraction of subglacial freshwater dissolved Fe (dFe_{FW}) is stabilized through the aid of ligands (dFeL) derived from dissolved organic matter (DOM). The majority of freshwater-derived dFe, not stabilized ('excess dFe', dFe_{xs}.) aggregates and forms (labile) particulate Fe (LpFe, pFe).

From the shelf-break proceeding towards the 79NG terminus, hydrographical measurements show freshening of surface waters (Fig. 4.3), a deepening of the AIW core, and thickening of the mAIW and PSW layers driven by freshwater release from the 79NG and its neighboring glacier, Zachariæ Isstrøm. A comparison of mean water properties entering (S = 34.81 for AIW) and exiting the 79NG subglacial cavity (S = 34.41 for mAIW) suggests a meltwater to AIW ratio of 1:84 indicative of strong dilution of glacial freshwater close to source. This physical framework provides an interesting case study to quantify the net effects of subglacial processes on Atlantic water properties. During GN05 it was possible to sample AIW and mAIW immediately adjacent (<1 km distance) to the glacier terminus i.e. prior to any subsequent modification from dilution or uptake due to summertime primary production (Fig. 4.1), representing the only site where AIW inflow and mAIW outflow was simultaneously observed.



Figure 4.3: Freshwater distribution following the main Nioghalvfjerdsbrae (79NG) discharge into Nioghalvfjerdsfjorden Bay. (a) Salinity. Dots (black) indicate the locations of discrete macronutrient measurements, vertical lines (bold black) indicate locations of trace metal profiles as per **Fig. 4.1**. (b) δ^{18} O. Dots (black) indicate the locations of discrete oxygen isotope measurements; negative values suggest release of meteoric freshwater. (c) Meteoric water fractions calculated from $\delta^{18}O$ and a freshwater reference $\delta^{18}O$ value of -20‰ (Azetsu-Scott and Tan, 1997). Isopycnal surfaces (white contours) distinguish between Polar Surface Water $(\sigma_{\Theta} < 26.1 \text{ kg/m}^3)$, Atlantic Intermediate Water (AIW, $\sigma_{\Theta} > 27.73 \text{ kg/m}^3$), and modified AIW (mAIW, $\sigma_{\Theta} = 27.00-27.73 \text{ kg/m}^3$). Two thirds of subglacial cavity outflow is observed between $\sigma_{\Theta} = 27.5 \cdot 27.73 \text{ kg/m}^3$ corresponding to depths of 125-268 m at S1 (Schaffer et al., 2020). The 19°W Bank between S1 and S2 is bypassed both to its north (main AIW gateway) and south and thus does not impede the flow of AIW. Additional mAIW via Dijmphna Sund outflows between S3 and S5. Figure made using Ocean Data View (Schlitzer, 2021).

4.3.2 Geographical nutrient distributions

Note that due to the deployment of two sampling rosette systems (ultraclean CTD for contamination prone trace metal sampling and large CTD for general sampling), the dataset for macronutrients is larger than for trace metals. For consistency and to facilitate a single statistical analysis, we primarily discuss the distribution of all components at ultraclean CTD stations S1-11 (Fig. 4.1), but also include additional analysis (see Supplement) demonstrating that there are no significant changes to our interpretation when the two data sets are considered separately or in combination.

Similar to summertime macronutrient distributions elsewhere in Greenland's glacier fjords, concentrations of nitrate (NO₃, Fig. 4.4a) and phosphate (PO₄, Fig. 4.4b) in the 79NG coastal region were depleted in surface waters (~0.1 μ M NO₃, ~0.3 μ M PO₄) and increased with depth (up to 12 μ M NO₃ and 0.9 μ M PO₄) (Rysgaard, Nielsen and Hansen, 1999; Meire *et al.*, 2017; Kanna *et al.*, 2018). In contrast to the relatively homogenous distribution of NO₃ within mAIW and AIW, Si(OH)₄ concentrations were enriched sporadically at multiple depths close to the glacier front across all 3 water masses (range 2.3-41.3 μ M for all stations >19°W), indicating a glacier-associated Si(OH)₄ source (Fig. 4.4c). Distinct maxima in Si(OH)₄ enrichment were observed in PSW (30.4 and 36.3 μ M, <20 m at large CTD station 228), and once in mAIW (41.3 μ M at 100 m at large CTD station 229). Elevated Si(OH)₄ concentrations (> 8 μ M) were however absent throughout the inner-shelf area (S2-S5, Fig. 4.4c).

Positive Fe anomalies were observed across the region (Fig. 4.5). A pronounced maximum in labile particulate Fe (LpFe) was found within mAIW (~100 nM, Fig. 4.4d) coinciding with maximum light attenuation indicative of a particle-rich layer exiting the cavity (Figs. 4.4e and S4.2). Concentrations of LpFe in mAIW and AIW greatly exceeded dFe in the vicinity of the glacier; dFe was equivalent to $7.6 \pm 5.5\%$ (mean \pm standard deviation) of LpFe concentrations at S1 and S2. Yet similar to the localized nature of the Si(OH)₄ anomalies at the ice front, a clear LpFe maximum was no longer evident 20 km away from the glacier terminus at any depth (at S2). This sharp decline may have occurred through either a loss of particles from the water column (i.e. sedimentation) or from a decrease in the lability of particulate Fe following particle aging (Chen and Wang, 2001; Schlosser *et al.*, 2018). Across all stations LpFe constituted $9.8 \pm 2.7\%$ to TdFe indicating that the variability in particle Fe lability along the fjord $(9.0 \pm 2.4\%$ at station S1 and S2) was not pronounced. Combined with the strong gradient in

turbidity between S1 and S2, this suggests sedimentation, rather than particle aging, was the dominant loss process for LpFe from the water column. More modest peaks in LpFe and light attenuation were evident at the sediment-bottom water interface near the glacier terminus (~40 nM at S1 and S2, Fig. 4.4d) possibly indicating re-suspension of labile particles. Elsewhere across the NE Greenland Shelf, LpFe generally exhibited low nanomolar concentrations 3.6 ± 2.8 nM (Fig. S4.3).



Figure 4.4: Macronutrient, labile particulate Fe (LpFe) and radium (Ra) distributions in Nioghalvfjerdsfjorden. (a) Nitrate (NO₃), (b) phosphate (PO₄), (c) silicic acid (Si(OH)₄) and (d) LpFe at the inner-most stations close to the Nioghalvfjerdsbrae (79NG) terminus (S1-S3 as per **Fig. 4.1**). Sample depths used for interpolation are shown as black dots. Additional macronutrient stations from large CTD measurements (stations 213, 229, 231-233, 252, 254, section 'Data availability') are shown alongside S1-S3. Isohalines (white contours) distinguish between water masses: Polar Surface Water (<70 m), Atlantic Intermediate Water (AIW, >270 m) and modified AIW (100-270 m). Station bottom depth is applied to define a basic bathymetry for clarity. (e) Depth profile of light attenuation (S1 in red, S2 in blue, S3 in black) evidences greatest turbidity between 190-250 m depth at S1 corresponding to the main subglacial cavity outflow. (f) Depth profile of ²²⁶Ra near the calving front (S1). Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).

In contrast to LpFe, the distribution of dFe across the shelf was not dominated by mAIW (Fig. 4.5). Dissolved Fe peaks were generally observed near the surface (Fig. 4.5b) and coincided with strong negative isotopic shifts in δ^{18} O indicative of meteoric freshwater

supply (Azetsu-Scott and Tan, 1997; Bauch *et al.*, 2011) (Fig. 4.3b-c). Modest dFe maxima were observed near the 79NG glacial terminus (S1, 2.3 nM at 25 m depth and 2.1 nM at 50 m depth), but also in the surface waters of Fram Strait (S7, 2.5 nM at 10 m depth) (Fig. 4.5a). In mAIW, mean dFe concentrations steadily decreased away from 1.3 nM at the glacier terminus (S1) to 0.6 nM beyond the shelf break (S7). Within AIW, dFe was rather uniformly distributed with a concentration of 0.72 ± 0.21 nM (mean for S1, S2 and S8-10). The shelf break station (S6) showed bottom water dFe enrichment, but no similar enrichment was observed throughout the inner shelf region (S1-S5, Fig. 4.5). Among other environmental factors, this may result from higher turbulence at the shelf break (de Steur *et al.*, 2014).

Surface dFe concentrations close to the 79NG (1.5 nM at 5 m, S1) and neighboring glacier termini (2.5 nM at 10 m, S11) were comparable to, or lower than, concentrations downstream of other Arctic glacier catchments at similar salinities (e.g. 4-7 nM, Kongsfjorden (Svalbard) (Zhang *et al.*, 2015); <3-6 nM, Godthåbsfjord (Hopwood *et al.*, 2016); ~4 nM, Copper River estuary (Crusius *et al.*, 2017); ~4 nM, Inglefield Bredning (Kanna *et al.*, 2020)). Whilst a pronounced peak in surface dFe was observed beyond the NE Greenland shelf break in Fram Strait (S7, Fig. 4.5a), the discontinuity with other surface samples suggest that this peak did not arise from local freshwater sources. Note that whilst this only appears as a single elevated surface dFe datapoint in the plotted section (Fig. 4.5a), elevated dFe concentrations were consistently found in East Greenland Current surface waters across the broader region surveyed by the GN05 cruise (1.1 nM ± 0.7 nM, 0-10°W, n=10) (Krisch *et al.*, 2020 - Chapter 3).

Long-lived radium isotopes (²²⁸Ra $t_{1/2}$ 5.75 years and ²²⁶Ra $t_{1/2}$ 1600 years), which are produced continuously from decay of Th in sediment (Annett *et al.*, 2013), are useful tracers of subglacial influence. Similarly, noble gases provide two further chemical tracers of subglacial influence, due to enhanced Ne and He concentrations in subglacial discharge (Beaird, Straneo and Jenkins, 2018; Rhein *et al.*, 2018). He and Ne data from the same expedition demonstrate a relatively uniform subglacial content throughout mAIW and show no He/Ne at any site beyond the Greenland shelf break (Huhn *et al.*, personal communication), which further corroborates the lateral transport calculations based on water mass analysis (Schaffer *et al.*, 2020) and highlights the disparity between peaks in dFe close to the glacier termini and over the shelf.

²²⁸Ra distributions in surface waters across the region largely reflect an Arctic derived signal from further north (Kipp *et al.*, 2018; Rutgers van der Loeff *et al.*, 2018), but the Ra depth

profiles obtained at S1 are insightful (Fig. 4.4f-g). ²²⁶Ra and ²²⁸Ra both show high activities in PSW (97 \pm 8 dpm·m⁻³ ²²⁶Ra and 60 \pm 15 dpm·m⁻³ ²²⁸Ra). In the AIW (300-450m depth), ²²⁶Ra and ²²⁸Ra vary around 80 and 17 dpm·m⁻³, respectively, as in other stations sampled over the shelf. At 150-250 m in the mAIW, ²²⁶Ra is unchanged while ²²⁸Ra is slightly enriched compared to shelf stations at the same depth. At 125 m, we observe a signal of highly elevated ²²⁶Ra (111 dpm·m⁻³) and ²²⁸Ra (48 dpm·m⁻³), indicative of a sedimentary input to cavity mAIW (with a ²²⁸Ra/²²⁶Ra ratio of 0.9). Subglacial runoff is estimated to be 0.07 mSv (2.2 km³·yr⁻¹) or only 0.15% of the cavity overturning rate (calculated from Schaffer *et al.*, 2020). With the discharge-averaged concentrations found in subglacial runoff of the Leverett Glacier in western Greenland (Linhoff, Charette and Wadham, 2020) this would, after mixing in the cavity, cause increases of only 0.03 dpm·m⁻³ ²²⁶Ra and 0.35 dpm·m⁻³ ²²⁸Ra in the cavity outflow, negligible compared to the observed signals at 125 m. We conclude that the radium is sedimentary in origin, either emerging from the seafloor or from sediments entrained within the ice-tongue and released into the water column by basal melting.



Figure 4.5: Dissolved Fe (dFe) concentrations in Nioghalvfjerdsfjorden and Westwind Trough. (a) Cross-section of the main flow path of modified Atlantic Intermediate Water ($\sigma_{\Theta} = 27.00-27.73 \text{ kg/m}^3$) from Nioghalvfjerdsbrae (79NG, S1) to Fram Strait (S7) following Westwind Trough. The location of the presented section is shown in **Fig. 4.1**. Sample depths used for interpolation are shown as black dots. Isohalines (white contours) distinguish between water masses (as per Fig. 3). (b) Depth profiles for dFe (left) and labile particulate Fe (LpFe, right) at the 79NG terminus (S1, red), Nioghalvfjerdsfjorden Bay (S2, blue), Dijmphna Sund (S4, green) and Zachariæ Isstrøm (S11, black). Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).

4.3.3 Statistical data treatment

A linear, positive correlation between salinity and macronutrient concentrations for all 3 macronutrients (R^2 : 0.75 NO₃, 0.56 PO₄, 0.50 Si, Fig. S4.4), indicates relatively conservative behaviour and the dominance of AIW as a nutrient source to the region (Tables S4.4 and S4.5).

Whilst the intercepts for all macronutrients are negative, a linear regression between salinity and dFe for all samples collected on the shelf has a zero salinity intercept of 7.34 ± 0.70 nM (Fig. S4.6).

We conducted a redundancy analysis (RDA) that considers chemical, physical and geographical factors that may explain the distribution of nutrients downstream of 79NG, with two additional factors added to the nutrient and oceanographic data for every sampling depth. Firstly, a lateral distance was calculated between each station and the glacier terminus along sections connecting adjacent stations (Fig. 4.1) e.g. 0.1 km at S1 to 260 km at S6. Secondly, a vertical distance from seafloor to the sampling depth at each station was computed. Additionally, we consider the distribution of other trace elements (Co and Mn) alongside dFe and LpFe to assist our interpretation. Like Fe, Co and Mn are both scavenged type elements; but with subtle differences in their oceanographic distributions. Dissolved Co (dCo) is less prone to scavenging than Fe, and dissolved Mn (dMn) generally shows increased dissolved concentrations in near-surface waters due to a more pronounced positive effect of photochemical cycling on its stability (e.g. Noble *et al.* (2017) and Colombo *et al.* (2020).

The RDA explains 61% of the variance (p <0.001) shown by all trace elements and macronutrients using four explanatory variables (Fig. 4.6). There are strong similarities in the factors that explain the distribution of Si(OH)₄, PO₄ and NO₃ with all macronutrients closely associated with increasing salinity and proximity to the seafloor (i.e. AIW inflow and remineralization processes). Dissolved trace elements (dFe, dCo and dMn) cluster with decreasing salinity and increasing proximity to surface waters. Labile particulate trace elements (LpFe, LpCo and LpMn) on the other hand are mainly explained by proximity to the terminus and high turbidity.

Through the use of General Additive Models (GAMs) on water mass properties downstream of 79NG, it is possible to investigate nutrient-distance relationships that are not necessarily linear (Hastie and Tibshirani, 1986). GAMs for all nutrients produced good fits to equation 1, where [x] is the concentration of a nutrient, and *c* is an intercept and *s*(*Distance to terminus | Salinity*) represents a term composed of the interaction between salinity and the distance from glacier terminus (R^2 : 0.773 dFe, 0.878 Si(OH)₄, 0.965 NO₃ and 0.944 PO₄, respectively, with p<0.001 in all cases) (Table S4.6). As per RDA (Fig. 4.6), the three macronutrients are clearly similar in their behavior whereas dFe displays a distinct

distribution which is roughly inverted compared to the macronutrients (Fig. 4.7). As per linear regression, the output of GAMs at glacier terminus and zero salinity for all macronutrients was negative (Table S4.6), whereas predicted dFe concentration was 3.13 ± 0.96 nM (SE).

Equation 1:
$$[x] = c + s(Distance to terminus | Salinity)$$

Having considered the oceanographic context of inflowing AIW and outflowing mAIW (Figs. 4.1 and 4.2), one further statistical test is to determine whether or not significant changes occur in the concentrations between these two water masses (Table S4.7). Irrespective of where mAIW and AIW are defined, there is always an enrichment in dFe contrasting mAIW with AIW ranging from 0.46 ± 0.27 to 0.67 ± 0.23 nM depending on the stations used to define each water mass (Table S4.7). Conversely, there is no significant (p < 0.05) change in Si(OH)₄ concentrations contrasting the two water masses (maximum calculated change $0.38 \pm 3.6 \,\mu$ M), suggesting that any Si(OH)₄ inputs from ice melt, subglacial discharge and the subsequent reworking of sediments are too small to be detected as a regionally significant nutrient flux. For NO₃, there is a slight decline in concentration from AIW to mAIW of up to $-1.0 \pm 1.4 \mu$ M, however its significance depends on the exact distance from the terminus where mAIW is defined. This suggests increasing NO₃ drawdown with time, and distance, from the termini. For PO₄, there is a significant (p<0.05) decline of as much as $-0.17 \pm 0.12 \,\mu\text{M}$ contrasting mAIW with AIW which is evident irrespective of the stations considered. Importantly, this trend is already evident at S1 (0.1 km from the terminus) and thus must partially reflect a net PO₄ loss in the subglacial cavity or close to the glacier termini as has been reported in limited examples elsewhere (Cape et al., 2019; Cantoni et al., 2020).

The distribution of nutrients downstream of 79NG suggests that the only nutrient enriched significantly by glacier-associated processes is dFe. The negative zero salinity intercepts for $Si(OH)_4$, NO₃ and PO₄ calculated by GAMs and linear regressions alike must reflect a change of gradient in the macronutrient-salinity relationship at salinities <24 (i.e. in the subglacial cavity). This is not unexpected given that similar shifts occur at low salinities in other large glacier fjords with similar two-dimensional inflow and outflow dynamics (e.g. Kanna *et al.* (2018) and Cape *et al.* (2019)).



Figure 4.7: Predicted concentration of all nutrients for stations S1 to S11 using a General Additive Model (GAM) generated by the interaction between salinity and distance to the glacier terminus. (A) Nitrate (NO₃), (B) phosphate (PO₄), (C) silicic acid (Si(OH)₄) and (D) dissolved Fe (dFe). Each contour plot shows the predicted nutrient concentration while the dots represents the conditions (salinity, distance to glacier terminus and depth) of the data used to generate the GAM. Station numbers are shown above each panel. Concentrations for NO₃, PO₄ and Si(OH)₄ are in μ M, whereas dFe concentrations are in nM. Figure plotted by Juan Höfer using package *ggplot2* for R (Wickham, H. 2009. Elegant Graphics for Data Analysis. Springer, New York).

4.3.4 Insights into lateral dFe export

A GAM fit and a linear regression produced comparable dFe concentrations at zero salinity of 3.13 ± 0.96 and 7.34 ± 0.70 nM, respectively. The difference likely arises because the GAM fit considers the relationship between distance from the terminus and salinity, while the linear regression solely considered salinity. These values represent the dFe concentration remaining after significant loss of dFe has occurred across the salinity gradient. This is useful in a model context because estuarine losses are challenging to constrain and occur on a scale which is subgrid even in high resolution models. Alternatively, when a removal factor is multiplied by freshwater concentration to estimate lateral fluxes, small changes in the estuarine removal factor, for example contrasting rough lower and upper estimates for estuarine dFe loss of 90% and 99%, produce very large differences in the net dFe flux (Stevenson *et al.*, 2017). A further implication of the difference between a GAM fit based on salinity and distance, and a regression for salinity alone, is that dFe loss is continuing downstream of the 79NG terminus in mAIW. This is also evident when considering the station-by-station dFe concentration from S1 to S7 (Fig. 4.8).



Figure 4.8: Dissolved Fe (dFe) concentrations modified Atlantic Intermediate Water in (mAIW) downstream of the Nioghalvfjerdsbrae (79NG) terminus. Stations S1 to S6 follow the main outflow path via Nioghalvfjerdsfjorden Bay (S2) towards Fram Strait (S7). Whiskers show the standard deviation to the mean mAIW dFe concentration. **Ouasi-exponentially** decreasing dFe concentrations (red curve) with distance from the 79NG terminus were observed. Station S2 functions as reference station for the dFe concentration of AIW prior to entering beneath the ice-tongue (red closed circle). Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, USA).

Further insight into the nature of dFe sources close to 79NG can be gained from stable dFe isotopic composition (δ^{56} Fe, Table S4.1). Isotopically light δ^{56} Fe values were observed for the local dFe maxima in PSW at the Nioghalvfjerdsbrae glacial front (-0.12 ± 0.09‰ at 25 m, S1) and likewise near Zachariæ Isstrøm (-0.60 ± 0.09‰ at 10-19 m, and -0.89 ± 0.09‰ at 39 m, S11). These light δ^{56} Fe values likely reflect recent meltwater discharge as dFe in glacial

meltwater around Greenland is typically enriched with light isotopes potentially due to reductive dissolution and dissolved Fe²⁺ in subglacial environments (Stevenson *et al.*, 2017). Observed freshwater dFe δ^{56} Fe values in Arctic glacier outflows include Russell Glacier (West Greenland, range -0.64 to -2.12‰), Glacier 'G' (East Greenland, range -0.19 to -0.92‰), Kongsfjorden (Svalbard, range -0.11 to +0.09‰) and the Copper River (Alaska, -0.81‰) (Escoube *et al.*, 2015; Zhang *et al.*, 2015; Stevenson *et al.*, 2017).

In contrast to the isotopically light dFe signal in surface water near the Nioghalvfjerdsbrae glacial front, mAIW from 125-200 m at the same station (+0.07 \pm 0.09‰, S1) had heavier, near-crustal δ^{56} Fe values (~+0.1‰) (Poitrasson, 2006), equivalent to the isotopic composition of the West Spitsbergen Current (+0.15 \pm 0.09‰). It is clear that mAIW is enriched in dFe compared to AIW and that this enrichment occurs either at the glacier terminus or underneath it (Fig. 4.8). We therefore suggest that any primary isotopically-light δ^{56} Fe signature originating from dissolved Fe²⁺ in subglacial discharge and basal meltwater is lost during extensive reworking and differential loss of dissolved, ligand-bound, particulate and sedimentary phases within the subglacial cavity, as well as exchange between the different phases (Homoky *et al.*, 2013; Conway and John, 2014; Fitzsimmons *et al.*, 2017). Cavity reworking is consistent with Ra data showing a sedimentary rather than direct subglacial signal emerging from the cavity (Fig. 4.4).

Further evidence for notable transformations in the fractionation of Fe between glacial and saline environments can be found when specifically considering the colloidal fraction. Dissolved Fe concentrations herein are inclusive of colloidal Fe (Table 4.1) which is thought to be released from the surface of glacier-derived particles (Hawkings *et al.*, 2014) and to constitute the majority (98-99%) of the dFe input from glaciers into the ocean (Raiswell and Canfield, 2012). Yet due to a paucity of cFe data in marine environments, it has not been possible previously to assess the cFe contribution to lateral export. The 79NG terminus (S1) exhibited cFe concentrations, calculated as the difference between measurements of sFe and dFe, of ~0.1 nM in the top 100 m excluding one outlier of 0.6 nM at 50 m which could be attributed to recent glacial freshwater input (Fig. S4.6). Colloidal Fe concentrations of ~0.7 nM were observed at 100-400 m and an anomalously low concentration (< 0.1 nM) near the bottom (460 m depth), possibly because of enhanced scavenging.

Within the inner-shelf region (S1, S2, S4) cFe constituted 3-54% (mean 27%) of dFe (Fig. 4.9). The sFe and cFe fractions are therefore of roughly comparable importance for Fe availability downstream of 79NG. This contrasts with freshwater Fe fractionation in glaciated catchments where cFe is 20-60 times greater than sFe concentration (Raiswell *et al.*, 2018). Our findings are consistent with evidence from glacial meltwater input to Kongsfjorden (Svalbard) where colloidal/nanoparticulate Fe (0.02-0.4 μ m) appears to preferentially precipitate during estuarine mixing (Zhang *et al.*, 2015). The δ^{56} Fe composition of mAIW and high fraction of sFe:cFe in mAIW compared to that expected in fresh glacial meltwater therefore all indicate pronounced re-working of Fe fractions within the ice cavity. By contrast, in surface waters near glacier termini, the concentration of cFe was higher and dFe was isotopically lighter.



Figure 4.9: Correlation of soluble Fe (sFe) and colloidal Fe (cFe) concentrations for three stations close to the Nioghalvfjerdsbrae (79NG): S1 (red dots), S2 (blue), and S4 (black). Standard error (whiskers) of cFe obtained from error propagation and corresponds to the square root of the sum of squares. Linear fit (red line) combines S1, S2 and S4, and is calculated with direct weighting of standard errors. Dashed line depicts 1:1 ratio of sFe and cFe. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

4.3.5 What controls dFe export?

Having quantified the enrichment of dFe in mAIW and attributed the increase to sedimentary processes occurring beneath the floating 79NG ice tongue, a critical question is how this dFe enrichment scales with environmental change. Would lateral dFe export be expected to increase with increasing discharge, turbidity or glacier terminus retreat – changes which are all anticipated as the ice tongue continues to disintegrate and regional warming continues?

As widely observed in both meltwater (Hawkings *et al.*, 2014) and near-shore waters in glaciated regions (Lippiatt, Lohan and Bruland, 2010; Crusius *et al.*, 2017; Merwe *et al.*, 2019), LpFe concentrations close to the 79NG terminus vastly exceeded dFe concentrations. Our hypothesis of substantial reworking of Fe phases in the glacier cavity supports the notion that

LpFe is an important pool of labile Fe subject to dynamic exchange with dFe. Yet, LpFe and dFe were not closely correlated; increased dFe was notably not observed either at locations with high LpFe at the sediment-bottom water interface or in the mAIW outflow close to the 79NG terminus (Fig. 4.4d). The divergent behavior of LpFe and dFe is also evident from RDA (Fig. 4.6).

Considering the whole dataset, there was no clear correlation between dFe and either TdFe or LpFe (Fig. 4.6, Fig. S4.7). For surface waters, this could simply reflect fast drawdown of dFe by biota while LpFe and TdFe remain in suspension. For example, downstream of the Pine Island Glacier (Antarctica) a faster decline in dFe than TdFe concentrations is attributed mainly to rapid biological uptake of dFe (Gerringa et al., 2012). However, the absence of a correlation between dFe and either LpFe or TdFe in the 79NG dataset remains even if surface water masses are excluded. Dissolved Fe and total dissolvable Fe data from other, smaller Arctic glacier catchments including Godthåbsfjord (Hopwood et al., 2016), Kongsfjorden (Svalbard) (Zhang et al., 2015), Bowdoin Fjord (Kanna et al., 2020) and the Gulf of Alaska (Lippiatt, Lohan and Bruland, 2010; Schroth et al., 2014) corroborate our observations near the 79NG of intense localized particulate Fe enrichment and decoupling of dFe and LpFe concentrations. This suggests that the distribution of dFe downstream of the 79NG is not unusual compared to other Arctic glacier fjords despite the presence of an ice tongue. The independence of dFe and particulate Fe distributions supports the hypothesis that factors other than particulate Fe availability control dFe distribution across the region. Across the NE Greenland shelf, dFe concentration was relatively constant (1.14 \pm 0.48 nM, range 0.36-3.4 nM across S1-13) despite strong spatial gradients in LpFe (range 0.1-95 nM) and TdFe (range 2-1020 nM). Although there are inevitably biases in sampling of particles from water collectors depending on the apparatus used (McDonnell et al., 2015), the observed relationship between dissolved and particulate fractions of Fe is fundamentally different to other metals. For example, an increase in dMn at enhanced particle concentrations is evident at the 79NG marine terminus (Fig. S4.7).

The role of particle-bound LpFe as a large pool of labile Fe should also be considered alongside the role of ligands, small organic molecules that bind Fe, as critical agents for maintaining dFe in solution (Ardiningsih *et al.*, 2020). Organic ligands are able to maintain dFe concentrations in seawater >1 nM (Gledhill and Buck, 2012), an order of magnitude greater than inorganic dFe solubility under oxic conditions (Liu and Millero, 2002). The ability of ligands to maintain

dFe in solution depends on a combination of their concentration and binding strength, with the binding strength depending on many factors including pH, salinity, temperature and the nature of organic material present (Gledhill *et al.*, 2015; Lodeiro *et al.*, 2020). Particle surfaces also compete with ligands to bind dFe and thus at high particle loadings, increasing LpFe can coincide with decreasing dFe concentrations. This phenomenon is not unique to glacier-derived particles and has been observed following sediment resuspension and dust deposition in other marine environments (e.g. Homoky *et al.* (2012), Wuttig *et al.* (2013) and Rogan *et al.* (2016)). In this context, LpFe may be better described as a buffer of dFe rather than a dFe source.

Analysis of dFe-binding ligands from the GN05 cruise suggests bacterial remineralisation and organic degradation have transformed the pool of ligands close to the 79NG terminus, resulting in elevated ligand concentrations but overall weaker ligands that are in total less efficient in stabilizing dFe (Ardiningsih et al., 2020). The absence of ligand production in the euphotic zone in combination with degradation of organic material (Gledhill and Buck, 2012) underneath 79NG may explain why dFe-binding ligands, generally undersaturated on the shelf $(45 \pm 17\% \text{ at } S2, S8-10)$, were approaching saturation at the terminus $(63 \pm 13\% \text{ at } S1)$ with a ligand concentration of 2.3 ± 0.2 nM eq. Fe and a corresponding dFe concentration of 1.5 ± 0.3 nM (Ardiningsih *et al.*, 2020). It is well established that ligand properties and ligand concentration are a limiting factor for what fraction of glacier derived LpFe is dispersed as dFe (Lippiatt, Lohan and Bruland, 2010; Thuróczy et al., 2012) and so the concentration of ligands, which ranged up to 2.6 nM eq. Fe, places a cap on the dFe concentration that can be laterally exported. Yet the outcompeting of ligands by scavenging at the 79NG terminus implies further subtleties to how ligands moderate downstream dFe supply (Ardiningsih et al., 2020). The optimum conditions for achieving ligand saturation and thus maximizing lateral transfer of ligand-bound dFe may be intermediate, rather than high turbidity and LpFe.

4.3.6 Implications for lateral dFe transport

Observations herein could be used to estimate the dFe flux out of the 79NG cavity in several ways. The 7.34 ± 0.70 or 3.13 ± 0.96 nM extrapolated freshwater concentrations from linear regression (Table S4.4) and GAM (Table S4.6) can be combined with the total cavity freshwater flux of 0.63 ± 0.21 mSv (19.9 ± 6.6 km³·yr⁻¹) (Schaffer *et al.*, 2020) to estimate net dFe outflow to the NE Greenland Shelf for comparison with existing literature. This approach produces dFe fluxes of 3.5 ± 2.2 (GAM) or 8.1 ± 3.5 Mg·yr⁻¹ (linear regression), and is

inclusive of dFe loses occurring prior to S1, and so is therefore more useful in an oceanographic context than fluxes derived from surface runoff, i.e. prior to estuarine loss. However, this approach also assumes that the lateral dFe flux scales with freshwater discharge. The distribution and role of Fe ligands (Ardiningsih *et al.*, 2020), the δ^{56} Fe and Ra signatures of mAIW, and the relative concentrations of sFe and cFe downstream of 79NG are all more consistent with cavity overturning dictating the lateral dFe flux. Inflowing AIW provides the heat responsible for basal ice melt of the floating ice tongue and the ligands required to maintain dFe in solution. The rate of AIW inflow also controls flushing of the subglacial cavity. Given the very limited contribution of freshwater input to cavity overturning (~1.4%) (Schaffer et al., 2020), lateral chemical fluxes scaled to freshwater discharge are likely very different from those scaled to overturning. To estimate fluxes from overturning, the dFe concentration in mAIW can be contrasted with the dFe concentration in AIW at any specific flux gate (Fig. 4.8) and combined with the cavity overturning flux of 46 ± 11 mSv. The largest (smallest) change in dFe concentration between mAIW and AIW attributable to processes occurring within the cavity is 0.67 ± 0.26 nM (0.46 ± 0.25 nM), corresponding to overturning driven lateral dFe flux estimates 54.3 ± 24.5 (37.3 ± 21.8) Mg yr⁻¹.

Neither of these approaches is free from caveats. The extrapolation of regional data to calculate an integrated dFe zero salinity endmember assumes that dFe distribution is largely driven by one dominant freshwater source which is clearly incorrect as evidenced by high shelf concentrations in the ECG likely originating from the Transpolar Drift (Charette *et al.*, 2020) (Fig. 4.5). The scaling of lateral flux to overturning volume assumes ligand properties in inflowing AIW are constant. The variation in ligand concentration across the region was modest (mean 2.1 ± 0.4 nM eq. Fe, range: 1.0-3.6 nM eq. Fe) (Ardiningsih *et al.*, 2020). Yet given that the concentration and binding strength of ligands along the AIW inflow from S8-10 during August 2016 appeared to be distinct from those in Fram Strait, and were likely affected by an earlier phytoplankton bloom on the shelf (Ardiningsih *et al.*, 2020), there may be seasonal variation in ligand concentrations. Further refinement of these fluxes is not possible without better constraints on seasonality in the cycling of Fe and ligands. To the best of our knowledge, no such data is available from any geographical location close to ice shelves. Whilst logistically challenging, spring and summertime data from ice stations coupling trace metal, ligand and inert tracer (for example, Noble gases or ²²⁸Ra/²²⁶Ra) would facilitate increased knowledge on

the processes controlling lateral Fe transport with reduced uncertainties (Loose and Jenkins, 2014; Charette *et al.*, 2016).

Whilst we cannot further reduce the uncertainty on lateral dFe transport at present, a comparison to findings from other ice shelf regions suggests that the overturning-driven flux, between 37.3 ± 21.8 and 54.3 ± 24.5 Mg·yr⁻¹ dFe, is more realistic than a flux derived from freshwater endmembers. It is also considerably larger than fluxes derived from freshwater discharge, inclusive of estuarine losses (3.5 ± 2.2 or 8.1 ± 3.5 Mg·yr⁻¹, see above). Surveys near the Dotson Ice Shelf and the Pine Island Glacier similarly suggested benthic shelf derived dFe, rather than direct glacial meltwater input was the dominant source of dFe input into outflowing glacially modified waters (Gerringa *et al.*, 2012; Sherrell *et al.*, 2015). This is corroborated by the most recent model studies of the Antarctic continental shelf suggesting that only 2-23% of dFe in glacially modified surface water originates directly from ice shelf meltwater (Dinniman *et al.*, 2020) with the majority sourced from sediments and delivered to the upper water column via cavity overturning (St-Laurent *et al.*, 2017). The rate of overturning is therefore likely the major factor controlling lateral fluxes.

Present estimates of Greenland Ice Sheet-to-ocean Fe fluxes are universally derived from measured freshwater concentrations and discharge volumes. A variety of approximations have been made to account for loss of dFe across the salinity gradient downstream of glacier outflows. If these are standardized at 10% of the freshwater concentration, flux estimates for the Greenland Ice Sheet to date range from 0.07-4.91 Gg·yr⁻¹ (Statham, Skidmore and Tranter, 2008; Bhatia, Kujawinski, et al., 2013; Hawkings et al., 2014; Stevenson et al., 2017). The literature dFe concentrations for comparison to the GAM $(3.13 \pm 0.96 \text{ nM})$ and regression derived values $(7.34 \pm 0.70 \text{ nM})$ herein would range from 5 to 370 nM. It should be noted however that the extent to which dFe concentrations change along freshwater water courses and during mixing with saline waters is poorly constrained. The extent of dFe removal on timescales of hours to days may vary both between catchments and temporally with estimates ranging from 76% to 99% dFe loss (Schroth et al., 2014; Zhang et al., 2015; Kanna et al., 2020). Fluxes derived only from measured freshwater concentrations are thereby subject to uncertainty of at least an order of magnitude. Glacial dFe endmembers designed to be conservative in recent model studies for example range from 90 to 3000 nM (Laufkötter et al., 2018; Person et al., 2019), compared to 3-7 nM deduced herein at the point of outflow from an ice shelf cavity (Tables S4.4-S4.6) and do not directly reflect the notion supported by recent

observations that most of the outflow from ice shelves is derived from sediment interaction rather than from freshwater outflow (Sherrell *et al.*, 2015; St-Laurent *et al.*, 2017).

Whilst cavities created by floating ice tongues or shelves can only be found in northern Greenland and Antarctica, the basic two-dimensional description of glacier fjords as consisting of a deep saline inflow and a glacially modified near surface outflow is common to most large Greenland systems (Straneo and Cenedese, 2015). An open research question is therefore whether or not lateral export of trace metals such as dFe can be estimated from freshwater concentrations and discharge volume in these systems. For large marine-terminating glaciers where ice melt provides the largest fraction of freshwater to the cavity (~89% for 79NG) (Schaffer et al., 2020), estimates on freshwater nutrient inputs derived from surface runoff endmembers (e.g. Bhatia, Kujawinski, et al., 2013; Hawkings et al., 2014, 2020) are likely overestimating glacial dFe shelf supply, also because ice melt contains comparatively sparse amounts of dFe, with concentrations presumably more akin to iceberg values (Hopwood et al., 2017). An alternative hypothesis, which is supported by work in a range of catchments beyond 79NG, is that ligand dynamics and overturning - which are interrelated - constrain lateral export (Lippiatt, Lohan and Bruland, 2010; Thuróczy et al., 2012; Ardiningsih et al., 2020). In systems like 79NG, where shelf forcing rather than freshwater discharge controls the residence time of water masses within the glacier fjord (von Albedyll, 2018; Schaffer et al., 2020), lateral dFe flux may be completely insensitive to short-term changes in freshwater and sedimentary dFe or LpFe supply (although is still ultimately dependent on a supply of labile Fe to maintain a large LpFe pool within the subglacial cavity) and far more sensitive to changes in ligand properties of AIW and cavity inflow rate.

4.3.7 How representative is one process study at the 79NG to constrain nutrient export?

Freshwater discharge at glacier calving fronts is highly variable on both sub-daily and seasonal timescales (Straneo and Cenedese, 2015; Sundfjord *et al.*, 2017; Slater *et al.*, 2018). Whilst herein we characterize mAIW and AIW water mass properties well enough to discuss the net changes induced by the 79NG system, only one ultraclean station was sampled at the 79NG glacier terminus (S1). This station (S1) was, however, located at the center of the sole cavity inflow depression (~480 m deep and ~2 km wide) (Schaffer *et al.*, 2017, 2020) and thus represents the only pathway via which AIW interacts with the 79NG (Wilson and Straneo,

2015; Schaffer *et al.*, 2020). Furthermore, the seasonal variability in freshwater export from 79NG is less pronounced than for most of Greenland as the main fraction is derived from basal melt rather than subglacial runoff (Schaffer *et al.*, 2020). The highly dynamic nature of meltwater discharge and sediment re-suspension nevertheless imply that it is highly unlikely nutrient concentrations determined at S1 represent either mean or peak summertime values. Small changes in the location of this station in time or space along the ice front would likely have revealed high heterogeneity in turbidity and nutrient concentrations as was observed vertically at S1 and S2 (Figs. 4.3 and 4.5) for LpFe, dFe and Si(OH₄). However, the prolonged residence time of AIW within the 79NG ice cavity combined with the absence of phytoplankton blooms in this water mass as it exits the cavity in summer is advantageous for deriving the integrated modification of AIW as a result of all glacier-associated processes. Furthermore, the chemical signatures in mAIW denote a strong control of sedimentary processes in modulating cavity-exiting waters, suggesting limited influence of seasonal shifts in meltwater properties.

Whilst few dFe concentrations are available in similar localities worldwide, dFe concentrations reported herein are similar to those observed in outflow from the Dotson, Crosson and Getz Ice Shelf cavities (~0.7 nM) (Gerringa *et al.*, 2012; Sherrell *et al.*, 2015) and in the outflow from beneath the Pine Island Glacier (0.2-1.4 nM) (Gerringa *et al.*, 2012). Interestingly, dFe enrichment in subglacial discharge downstream to the Ross Ice Shelf was within uncertainty relative to shelf stations not affected by ice sheet discharge (Marsay *et al.*, 2017). A comparison with the Pine Island Glacier system is particularly insightful as there, similarly to 79NG, ligand dynamics were also found to constrain lateral dFe transfer (Thuróczy *et al.*, 2012). This is despite lower dFe concentrations in the corresponding shelf stations (<0.6 nM) and less pronounced changes in salinity (range 33.1-34.8 along a comparable 250 km long transect) (Gerringa *et al.*, 2012).

We suggest a key reason for similarities in dFe concentrations between these diverse field sites is the prolonged residence time of water in ice cavities that allows thermodynamic equilibrium to be approached between dFe, LpFe and ligand concentrations. Higher dFe concentrations on the order of 10-100 nM are invariably associated with runoff corresponding to much more recent time periods since freshwater entered the marine environment (Bhatia, Kujawinski, *et al.*, 2013; Zhang *et al.*, 2015; Kanna *et al.*, 2020) and thus could be described as under kinetic control. In a few case studies the timeframe of lateral dFe export has been quantified. Surface glacially modified water transports dFe from Heard Island (Southern Ocean) to 100 km

offshore over a timescale of 1 month, with much of the ~80% decline in dFe over this spatiotemporal attributed to biological uptake (Holmes *et al.*, 2019; Merwe *et al.*, 2019). In contrast, AIW/mAIW enriched in dFe would still be present underneath the floating ice-tongue on this timescale (Wilson and Straneo, 2015; Schaffer *et al.*, 2020) with the removal of dFe independent of near-surface primary production.

4.3.8 Future perspectives

It is not yet clear how shrinking ice-tongues will affect shelf biogeochemistry, neither specifically for the 79NG nor more generally from ice-shelves elsewhere. Past observations (Mouginot *et al.*, 2015; Mayer *et al.*, 2018; Schaffer *et al.*, 2020) and models concerning the future of the 79NG (Choi *et al.*, 2017) both project thinning of the ice-tongue in coming decades in response to increased ocean heat supply. Indeed, the ice tongue is significantly smaller at the time of writing than it was in August 2016 following the breakup of Spalte Glacier in July 2020 (which previously branched off from the 79NG). For systems such as the 79NG where the vast majority of nutrient export does not presently reach the euphotic zone, a disintegrating ice-tongue could create a more direct connection between overturning driven nutrient fluxes and primary production.

Based on our observations, we expect long-term disintegration of the ice tongue and shrinking of the association subglacial cavity to lead to higher dFe concentrations at stations close to the glacier terminus, potentially with a lighter δ^{56} Fe signal and a higher ²²⁸Ra:²²⁶Ra ratio. Similarly, disintegration may result in the more rapid downstream transport of (sub-)glacial modified waters, but will also likely affect interannual sea-ice dynamics (Syring *et al.*, 2020) and thus the anticipated change to regional primary production and nutrient dynamics is more challenging to predict. Given that the 79NG ice tongue appears to be primed for further ice thinning and retreat, it however remains an interesting case study to investigate the marine biogeochemical responses to prolonged glacier retreat in coming decades.

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Author contributions

Stephan Krisch and Mark J. Hopwood conceived the study. Sampling was conducted by **Stephan Krisch**, Janin Schaffer, Michiel M. Rutgers van der Loeff and Pablo Lodeiro. Trace metals were analysed by **Stephan Krisch**, Ali Al-Hashem and Tim Steffens. Raisotope analyses were performed by Michiel M. Rutgers van der Loeff. Fe-isotopes analyses were conducted by Tim M. Conway and Brent A. Summers. Fe-ligands were analysed by Indah Ardiningsih. Statistical analysis was conducted by Juan Höfer and **Stephan Krisch**. The manuscript was written by **Stephan Krisch** and Mark J. Hopwood with all authors contributing to its revision.



4.4 Supplementary Material

Figure S4.1: NE Greenland Shelf section of (a) potential temperature, (b) salinity, (c) light attenuation (turbidity), and (d) UV-light fluorescence. Section is following the main Atlantic Intermediate Water (AIW) inflow from Norske Trough (S8-S10) towards the Nioghalvfjerdsbrae (79NG) terminus (S1), and glacial modified AIW (mAIW) outflow from Nioghalvfjerdsfjorden Bay (S1, S2), Westwind Trough (S3, S5) towards the shelf break (S6) and Fram Strait (S7). The isobar (white contours, in kg/m³) $\sigma_{\Theta} = 27.73$ distinguishes between AIW and mAIW. Approximately two thirds of the subglacial cavity outflow is contained between $\sigma_{\Theta} = 27.5-27.73$ kg/m³ corresponding to depths of ~120-270 m at S1. Polar Surface Water (including glacial runoff and sea-ice melt) is present at $\sigma_{\Theta} < 26.1$ kg/m³. Black dots indicate location of discrete large-CTD measurements; vertical lines (bold black) indicate data obtained from ultraclean CTD measurements. Ultraclean CTD station numbers are indicated in 'a'. Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).



Figure S4.2: Depth profiles of Fe at the Nioghalvfjerdsbrae (79NG) terminus (S1). Labile particulate Fe (LpFe, black stars), total dissolvable Fe (TdFe, black triangles) and light attenuation (i.e. turbidity, blue dots). A correlation between LpFe, TdFe and turbidity is evident, particularly at the mAIW outflow (~120-270 m depth). Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).



Figure S4.3: NE Greenland Shelf section for Fe passing the Nioghalvfjerdsbrae (79NG) glacier terminus (S1). Isobars (white contours) as per Supplementary **Fig. S4.1**. Black dots indicate location of ultraclean CTD sampling. Ultraclean CTD station numbers are indicated in 'a'. (a) Dissolved Fe (dFe), (b) total dissolvable Fe (TdFe), and (c) labile particulate Fe (LpFe) following the main Atlantic Intermediate Water (AIW) inflow towards the glacier terminus (S1) and the main modified AIW outflow towards Fram Strait. Station bottom depth is applied to define a basic bathymetry for clarity. Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).



Figure S4.4: Linear regressions for macronutrients across the NE Greenland shelf (S1-6, S8-13). Nitrate (NO₃, black squares), silicic acid (Si(OH)₄, blue triangles) and phosphate (PO₄, red dots) concentrations all show a positive relationship with salinity. Error bars not shown for clarity. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).



Figure S4.5: Practical salinity versus dissolved Fe (dFe) for all stations on the NE Greenland Shelf: Norske Trough (S8-S10), Nioghalvfjerdsfjorden Bay (S1, S2) including one station near Zachariæ Isstrøm (S11), Dijmphna Sund (S4), Westwind Trough (S3, S5), the shelf break (S6), and two stations on the Central (S12) and outer NE Greenland Shelf (S13). Standard error (blue bars) was included in the linear approximation through program-based direct weighting. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

<u>**Table S4.1**</u>: Stable Fe isotope composition (δ^{56} Fe) in dissolved Fe (dFe) samples of the NE Greenland Shelf, and the West Spitsbergen Current (WSC), expressed relative to IRMM-014. Samples were pooled according to water mass properties. Measurement uncertainties for δ^{56} Fe are reported as two standard error of the mean of analysis (2SE, 2 σ ; see Methods).

Station	Latitude	Longitude	Depth	dFe	δ ⁵⁶ Fe	2SE	
Station	[°N]	[°E]	[m]	[nM]	[‰]	[‰]	
C 1	S1 70.5699 10.5190	25	2.3	-0.12	0.09	79NG surface discharge (PSW)	
51	79.3088	-19.3180	125-200	1.3-1.5	+0.07	0.09	79NG cavity discharge (mAIW)
C 11	70 2972	19 0079	10-19	1.4-2.5	-0.89	0.09	Zachariæ Isstrøm
511	19.2875	-18.0978	39	2.6	-0.60	0.09	surface discharge
	79.0003	7.4983	85-125	0507	0.15	0.00	WSC Atlantic Water
	78.9860	6.9943	101-176	0.3-0.7	+0.15	0.09	wSC Atlantic water



Figure S4.6: Depth profiles of Fe at stations S1, S2 and S4. Soluble Fe (sFe, red triangles), dissolved Fe (dFe, blue dots) and labile particulate Fe (LpFe, black squares) for the (a) Nioghalvfjerdsbrae (79NG) terminus (S1), (b) Nioghalvfjerdsfjorden Bay (S2) and (c) the 79NG side-exit Dijmphna Sund (S4, sill station). Error bars not shown for clarity. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).



Figure S4.7: A comparison of dissolved versus particulate fractions of Fe and Mn. (a) Dissolved Fe (dFe) and labile particulate Fe (LpFe, black stars), (b) dFe and total dissolvable Fe (TdFe, blue stars), (c) dissolved Mn (dMn) and labile particulate Mn (LpMn, black dots), and (d) dMn and total dissolvable Mn (TdMn, blue dots) for stations S1 and S2 downstream to the Nioghalvfjerdsbrae (79NG) glacier terminus. Standard errors are depicted as whiskers and included in the calculation of linear fits (red line) by direct weighting. Figure plotted with OriginPro, version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

4.4.1 Quality assurance

Validation of method accuracy for seawater analyses was achieved through the reference material 7602a (National Metrology Institute of Japan) for macronutrients (given in the datasheet), and SAFe S for soluble, dissolved and total dissolvable trace metals (Table S4.2) (Bruland Research Lab, 2009). Method sensitivity for seawater trace metals was monitored through SeaFAST-ICP-MS system ('manifold') blanks (Table S4.3). Labile particulate analyses were validated against BCR-414 reference and indicative values (Joint Research Centre, 2017), and monitored against process blanks (filter digest).

<u>**Table S4.2:**</u> Analyzed reference materials SAFe S (entire PS100/GN05 dataset), and BCR-414 (stations S1-S6, S10) for Fe analyses, n = number of measurements. ^A Conversion from nmol·kg⁻¹ using density of 1.026 kg·L⁻¹

Reference Material	Consensus value	Reported value
SAFe S (#273)	$0.095 \pm 0.008 \ nM^{\rm A}$	$0.101 \pm 0.016 \text{ nM} (n = 10)$
BCR-414	$1.85 \pm 0.19 \text{ mg} \cdot \text{g}^{-1}$	$2.06 \pm 0.10 \text{ mg} \cdot \text{g}^{-1} (n = 6)$

<u>**Table S4.3:**</u> Method sensitivity determined as system ('manifold') blank for sFe, dFe, and TdFe analyses (entire PS100/GN05 dataset), and digestion process blanks for particulate Fe fractions (stations S1-S6, S10), n = number of measurements.

SeaFAST-ICP-MS Procedural blank	$48 \pm 17 \text{ pM} (n = 465)$
Digestion Process Blank	$23 \pm 3 \text{ pM} (n = 7)$

4.4.2 Supplementary Notes

4.4.2.1 Nutrient fluxes, dilution and sinks across salinity gradients

From a freshwater perspective, a glacier outflow will always result in a positive flux of any chemical component into the marine environment (Wadham *et al.*, 2019). Yet this can still result in a negative change in the availability of a nutrient in the ocean either by dilution (L. Meire *et al.*, 2016; Höfer *et al.*, 2019), as a result of prolific non-conservative removal in estuaries (L. Meire *et al.*, 2016), or because the stratification driven by freshwater discharge decreases vertical mixing and thereby suppresses marine primary production (Holding *et al.*, 2019). This results in inconsistent terminology between research fields because what always constitutes a nutrient flux at 0 salinity can also be a nutrient sink when considering a flux gate after the major non-conservative mixing processes have occurred or using a box model. Similarly, what always constitutes a nutrient source into the ocean as a whole (especially when considering geological timescales), can still reduce nutrient availability on annual timescales.

This is exemplified by the behavior of phosphate (PO₄). Freshwater PO₄ concentrations are generally low across the cryosphere relative to saline waters (L. Meire *et al.*, 2016; Wadham *et al.*, 2019). Furthermore, PO₄ seems to be subject to a degree of non-conservative removal downstream of glaciers related to high turbidity (Cape *et al.*, 2019; Cantoni *et al.*, 2020). This results in negative PO₄ anomalies (e.g. Fig. 4.4), i.e. the concentration of PO₄ is lower than can be explained by mixing processes. Glacier outflows can therefore both dilute marine PO₄ concentrations (L. Meire *et al.*, 2016) and result in local net PO₄ removal (Cape *et al.*, 2019) despite constituting a measurable PO₄ flux based on freshwater measurements (Wadham *et al.*, 2019).

4.4.2.2 Estuarine removal

The change in salinity, and other properties such as temperature and turbidity across the salinity gradient, affect chemical components to varying degrees. Conservative components are those that scale linearly with salinity during mixing whereas non-conservative components show pronounced positive or negative deviations from the expected conservative mixing line. Dissolved Fe invariably shows a classic non-conservative estuarine mixing behavior with dFe concentrations always lower than expected from conservative mixing due to prolific removal of dFe onto particles (Boyle, Edmond and Sholkovitz, 1977).

Whilst most literature concerning estuarine mixing of (micro)nutrients concerns temperate river estuaries, non-conservative losses of dFe are also well documented downstream of glacier outflows (Schroth *et al.*, 2014; Zhang *et al.*, 2015; Hopwood *et al.*, 2016; Kanna *et al.*, 2020) with 76-99% removed at intermediate salinities. Dissolved silicic acid (Si(OH)₄) behavior is more variable; some glacier catchments show close to conservative mixing over the observed salinity gradient (Brown, Lippiatt and Bruland, 2010), and others indicate non-conservative addition at salinities lower than ~10 (Hawkings *et al.*, 2017; Kanna *et al.*, 2018). Deriving the net fluxes of dFe and Si(OH)₄ arising from glacier outflows is challenging, particularly for large marine-terminating systems, because of the general paucity of data close to glaciers where subglacial discharge first enters the marine environment and the few case studies where extensive data is available spanning the salinity gradient (Hopwood *et al.*, 2020). As elsewhere, in glacier fjords nutrient distributions are also affected by uptake by biota and benthic processes that act to add/remove nutrients from solution over the same spatial/temporal scale where inorganic processes arising from the change in salinity, turbidity, temperature and pH occur.

The non-conservative aspects of dFe and Si(OH)₄ across the salinity gradient account for practically all of the order-of-magnitude variation in flux estimates from Greenland into the ocean, depending on what flux gate window is defined (Hopwood *et al.*, 2020). But variation also arises from a process perspective in how fluxes are scaled. For Si(OH)₄, a ten-fold difference in the two available flux estimates from the Greenland Ice Sheet occurs despite using similar freshwater and intermediate salinity Si(OH)₄ concentrations (L. Meire *et al.*, 2016; Hawkings *et al.*, 2017).

4.4.2.3 Applying linear regression to 79NG

A linear regression of any concentration against salinity should derive the approximate freshwater concentration inclusive of non-conservative effects. However, even in the absence of non-conservative chemical effects, Arctic glacier fjords can exhibit v-shaped nutrient distributions across the salinity gradient because of the multi-dimensional nature of saline water inflow at depth and modified water outflow closer to the surface. In the immediate vicinity of a glacier outflow, a transient increase in all macronutrient concentrations with salinity can therefore be observed followed by a steady decline in surface waters due to biological drawdown. The 0-salinity intercept of a linear regression is therefore sensitive to the range of salinity data selected.

Component	Gradient \pm SE (R ²)	Intercept (± SE)
NO ₃	$2.357 \pm 0.098 \ (0.75)$	-71.3 ± 3.26
PO ₄	$0.080 \pm 0.005 \; (0.56)$	-1.94 ± 0.17
Si(OH) ₄	$0.666 \pm 0.0483 \ (0.50)$	-16.4 ± 1.60
dFe	$-0.183 \pm 0.021 \ (0.27)$	7.34 ± 0.70

Table S4.4: Linear regression for all nutrient data at trace metal clean stations S1-13 (Figs. S4.4 and S4.5).

Table S4.5: Linear regression for all nutrient data at trace metal clean stations downstream of 79NG across the section from S1 to S6.

Component	Gradient ± SE (R ²)	Intercept (± SE)
NO ₃	2.11 ± 0.125 (0.759)	-62.4 ± 4.12
PO ₄	$0.0769 \pm 0.0053 \ (0.70)$	-1.88 ± 0.175
Si(OH) ₄	$0.636 \pm 0.047 \; (0.674)$	-15.2 ± 1.54
dFe	$-0.113 \pm 0.024 \ (0.198)$	4.96 ± 0.789

The 0 salinity intercepts for all macronutrients downstream of 79NG are negative. Whilst this suggests a minor role for freshwater outflow on the scale of the region sampled, it is not particularly informative concerning the freshwater concentration as it mainly reflects the v-shaped macronutrient distribution seen in other Greenland fjord systems when considering data across a salinity gradient from ~10-35 (Hopwood *et al.*, 2020). For dFe, conversely, the intercept is positive (7.3 ± 0.7 nM for the region, or 5.0 ± 0.8 nM for stations S1-6) suggesting a freshwater concentration of ~5-7 nM. This is derived from saline data with S > 24, so the intercept is informative concerning the dFe remaining after non-conservative loss and not the freshwater concentration before this loss (which would invariably be much higher) (Schroth *et al.*, 2014; Zhang *et al.*, 2015; Kanna *et al.*, 2020).

4.4.2.4 General Additive Model (GAM)

GAMs are more useful than linear regressions because they are able to optimize a non-linear fit to multiple parameters simultaneously. Some nutrients clearly display similar spatial trends that can be explained by the same key factors. A Redundancy Analysis clearly shows that nitrate (NO₃), PO₄ and Si(OH)₄ cluster together, as do the dissolved metals Fe, Co and Mn (Fig. 4.6). This suggests that similar factors explain their distributions. Relatively good (R^2 >0.75) fits were obtained for all nutrients with a GAM generated by the interaction between salinity and the distance to glacier terminus demonstrating that these variables were able to explain most of the variance in nutrient datasets and these fits were used to obtain estimated 0 salinity concentrations at the glacier terminus (Fig. 4.7).

	GAM fit R ² (p-value)	Estimate 0 salinity
dFe	0.753 (<0.001)	$3.13\pm0.96~nM$
Si(OH) ₄	0.878 (<0.001)	$-12.8\pm1.96\mu M$
NO ₃	0.965 (<0.001)	$-35.5\pm3.55\mu M$
PO ₄	0.944 (<0.001)	$-1.44\pm0.150~\mu M$

Table S4.6: GAM-modelled estimates of freshwater concentrations at 0 salinity.

In all cases, a GAM fit was very good and the predicted intercepts were very similar to that predicted from linear regression. In the case of dFe, a positive intercept $(3.13 \pm 0.96 \text{ nM})$ is consistent with the dFe enrichment expected from fresh water and is, as per linear regression, a value derived after the majority of non-conservative loses have occurred. The negative predictions for macronutrients again verify that there must be a change in gradient for all macronutrients within the subglacial cavity. The differences between linear regression and GAMs in terms of the predicted intercept can be explained by considering that the GAM fit includes variables other than salinity (i.e. distance to glacier terminus), although salinity remains a major factor in explaining the variance in all nutrient datasets (as is shown by RDA).

4.4.2.5 Contrasting concentrations of macronutrients in mAIW and AIW

To add robustness to our discussion we test how changes in the collection of stations used to assess Atlantic Intermediate Water (AIW) and modified AIW (mAIW) properties would affect our interpretation. For trace metal data, all stations on the shelf are included within the main text. For macronutrients, there is additional data from the large volume CTD that expands the data available. Here we define mAIW (27.00-27.73 kg/m³) and AIW (>27.73 kg/m³) using the
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same density definition throughout to different subsets of all the large CTD cruise data. The standard deviation of measurements is generally lower using the more extensive combined datasets, although the means remain similar.

<u>**Table S4.7:**</u> Concentrations of NO₃, PO₄, Si(OH)₄ and dFe in mAIW and AIW following different boundary conditions. *One outlier in the silicic acid dataset has a large effect on the mean with (*), or without, its inclusion. For further data analysis the outlier was not excluded. ** This refers to only two measurements of PO₄ and is thus not considered further.

	Boundaries	NO ₃ [µM]	PO ₄ [μM]	Si(OH) ₄ [µM]	dFe (refers
	(clean stations				to S stations
	in zone)				only) [nM]
mAIW	(i) Inner-fjord				
	79.399-79.724°	11.45 ± 1.41	0.706 ± 0.110	$7.57 \pm 3.20*$	1.18 ± 0.24
	N, 16.150° W	11.43 ± 1.41	0.790 ± 0.119	7.29 ± 0.83	1.10 ± 0.24
	(S1,2,3 and 4)				
mAIW	(ii) Inner-fjord				
	79.399-79.724°	11.55 ± 1.34	0.702 ± 0.123	$7.63 \pm 3.56*$	1.28 ± 0.22
	N, 18.680° W,	11.55 ± 1.54	0.792 ± 0.123	7.30 ± 0.852	1.20 ± 0.22
	(S1, 2 and 4)				
AIW	(a) S10 and				
	associated cross-	12.46 ± 0.31	0.964 ± 0.013	7.25 ± 0.18	0.61 ± 0.09
	section				
AIW	(b) S2 and				
	associated cross-	12.44 ± 0.30	$0.935 \pm 0.007 **$	7.47 ± 0.087	0.72 ± 0.11
	section				
AIW	(c) AIW				
	(combined S10	12.45 ± 0.30	0.960 ± 0.016	7.38 ± 0.17	0.67 ± 0.11
	and S2 sections)				

From an oceanographic perspective concerning the detection of any changes attributable to local input from the 79NG, the most meaningful definitions of mAIW are those determined immediately adjacent to the ice-tongue as this determines the properties of outflow before any extensive nutrient drawdown, or dilution of mAIW can occur. The most meaningful definition of AIW is that determined at the deepest stations outside the fjord and upstream of the glacier outflow as this precludes any local processes in addition to those occurring underneath the 79NG ice-tongue (e.g. benthic inputs across the shelf) (Hong *et al.*, 2020) which could affect the properties of AIW as it flows along the fjord prior to entering underneath the subglacial cavity.

Comparing the mAIW and AIW concentrations of macronutrients suggests that there is possibly a decline in NO_3 concentration between AIW and mAIW within Nioghalvfjerdsfjorden, but whether or not this is the case is sensitive to the definition of mAIW

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and only significant (p < 0.05) when using the broader definition of mAIW. This suggests that NO₃ loss is not specifically related to processes occurring within the cavity and likely reflects biological drawdown of NO₃ beyond the ice-tongue at stations downstream of S1 (Fig. S4.1d). For PO₄, the changes between mAIW and AIW are more evident than for NO₃ as a statistically significant loss (p < 0.05) of PO₄ is determined when comparing AIW with mAIW outflow by any definition. This may therefore partially reflect a process occurring under the ice cavity as the difference is already evident at the ice-tongue. Some low PO₄ concentrations are evident at S1 when considering the section S1 to S3 and this is similar to observations in Sermilik Fjord (East Greenland) (Cape *et al.*, 2019). For Si(OH)₄, there is no significant difference between any of the defined water masses (ANOVA, p > 0.9).

<u>Table S4.8</u>: Level of significance (p-value) in glacial NO₃ decline following transformation of AIW to mAIW tested by a set of different boundary conditions (Table S4.7).

NO ₃	mAIW (i)	mAIW (ii)
AIW (a)	0.039	Not significant
AIW (b)	0.010	Not significant
AIW (c)	< 0.001	Not significant

<u>Table S4.9</u>: Level of significance (p-value) for glacial PO₄ decline following transformation of AIW to mAIW tested by a set of different boundary conditions (Table S4.7).

PO ₄	mAIW (i)	mAIW (ii)
AIW (a)	< 0.001	< 0.001
AIW (b)	Not tested**	Not tested**
AIW (c)	< 0.001	< 0.001

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Abstract

The Arctic Ocean is considered a source of micronutrient trace elements to the high latitude North Atlantic through the gateway of Fram Strait. However, trace element data from across the Arctic Ocean gateways are lacking, and so it remains unclear how the Arctic and the North Atlantic Oceans shape trace element exchange and micronutrient availability in the two ocean basins. In 2015 and 2016, two GEOTRACES cruises were conducted to sample the Barents Sea Opening (GN04, 2015) and Fram Strait (GN05, 2016) for dissolved iron (dFe), manganese (dMn), cobalt (dCo) and zinc (dZn). Together with the most recent synopsis of Arctic-Atlantic volume fluxes, observed trace element distributions suggest that Fram Strait is the most important gateway for Arctic-Atlantic trace element exchange, as a consequence of Intermediate and Deep Water transport. Arctic dFe, dMn and dCo export is predominantly governed by a southward advection of Arctic Ocean waters, including the trace element-rich Transpolar Drift which feeds into the East Greenland Current. The Atlantic-sourced West Spitsbergen Current is the dominant component in Arctic dZn import. Combining trace element fluxes from Fram Strait and the Barents Sea Opening with estimates for Davis Strait (GN02, 2015) suggests a net Arctic export of -2.7 ± 2.4 Gg·a⁻¹ dFe to the North Atlantic Ocean. Arctic export of dMn $(-2.8 \pm 4.7 \text{ Gg} \cdot a^{-1})$ and dCo $(-0.3 \pm 0.3 \text{ Gg} \cdot a^{-1})$ were within uncertainty. For dZn, Arctic-Atlantic exchange was balanced with a net flux of 3.0 ± 7.3 Gg·a⁻¹ dZn from the Atlantic to the Arctic Ocean. Our results suggest that ongoing changes to shelf inputs and sea ice dynamics in the Arctic may affect trace element availability, especially dFe, in the downstream East Greenland Current and the high latitude North Atlantic.

5.1 Introduction

Fram Strait is situated between Svalbard and NE Greenland, and functions as a major gateway for water exchange between the Arctic and North Atlantic Oceans (Tsubouchi et al., 2018; Rudels, 2019). The North Atlantic Ocean plays a central role in the meridional overturning circulation (Thornalley et al., 2018; Fu et al., 2020), and its intermediate and deep waters that ultimately reach the Arctic Ocean are young with lower concentrations of nutrients and many trace elements compared to e.g. deep North Pacific waters (Ezoe et al., 2004; Achterberg et al., 2021). The Arctic Ocean comprises only 3% of the global ocean by area (Menard and Smith, 1966), but receives a disproportionally large fraction of global riverine discharge (~11%, Aagaard and Carmack, 1989) with ~50% of its surface area being shelf seas (Jakobsson, 2002). Large rivers such as the Lena, Ob and Yenisei transport large quantities of organic material (Amon et al., 2012) and micronutrient trace elements including iron (Fe), manganese (Mn), cobalt (Co) and zinc (Zn) to the Arctic Ocean shelf regions (Dai and Martin, 1995; Guieu et al., 1996). Even after substantial flocculation and loses of some dissolved trace elements in estuaries (e.g. >90% for dissolved Fe (dFe) in the Lena River) (Conrad et al., 2019), a substantial flux of dFe, dissolved Mn (dMn), dissolved Co (dCo) and dissolved Zn (dZn) enters the Arctic coastal waters annually from rivers, shelf sediments and coastal erosion. A plume of elevated concentrations of shelf derived radium and metals including dFe and dCo, effectively stabilized by organic complexation, is subsequently advected offshore across the Arctic Ocean within the Transpolar Drift (Slagter et al., 2017; Bundy et al., 2020). This results in pronounced near-surface concentration maxima in the Central Arctic Ocean (Klunder, Bauch, et al., 2012; Kadko et al., 2019; Charette et al., 2020) and an unusual depth distribution of these elements compared to the Atlantic (Rijkenberg et al., 2014; Achterberg et al., 2018, 2021). The southward extent of these elevated surface concentrations has to be determined, yet recent repeat sections of radium in the central Arctic indicate that the cross-Arctic transfer of shelf derived elements increased from 2007 to 2015 (Kipp et al., 2018).

Volume exchange between the Arctic and the high latitude North Atlantic Oceans (>65°N) is controlled by three gateways: (i) Fram Strait (net southward flux, 1.1 ± 1.2 Sv), (ii) Barents Sea Opening, located between Svalbard and coastal Norway (net northward flux, 2.3 ± 1.2 Sv), and (iii) Davis Strait, separating the Labrador Sea to the south from Baffin Bay and the Canadian Arctic Archipelago (net southward flux, 2.1 ± 0.7 Sv) (Tsubouchi *et*

al., 2018). Fram Strait is the only deep water connection with depths exceeding 500 m (Jakobsson *et al.*, 2012) and thus facilitates all intermediate and deep water exchange (Mauritzen, Rudels and Toole, 2013; von Appen *et al.*, 2015). Approximately $\frac{2}{3}$ of northward flowing warm and saline Atlantic Water (2.4-5.4 Sv) enters the Arctic Ocean through Fram Strait as part of the West Spitsbergen Current (WSC, 6.6 ± 0.4 Sv) formed by contributions from the North Atlantic Current and the coastal Norwegian Atlantic Current (Fig. 5.1) (Beszczynska-Möller *et al.*, 2012; Rudels, 2019). The remaining fraction (1.5-2 Sv) enters the Arctic Ocean via the Barents Sea Opening ('Barents Sea Branch') and is mostly derived from the Norwegian Atlantic Current (Rudels, 2019). In Fram Strait, low-salinity Polar Surface Water, cooled and freshened Arctic Atlantic Water together, with locally recirculating Atlantic Water, forms the East Greenland Current (EGC, 5.8 ± 1.8 Sv at 79°N, de Steur *et al.*, 2005; de Steur *et al.*, 2014; Richter, Von Appen and Wekerle, 2018). Approximately 30-50 % of the total annual net Arctic Ocean outflow thus occurs through Fram Strait (Rudels, 2019).

The composition of North Atlantic waters reaching the Arctic Ocean can be assumed to be rather stable over the coming decades, with perhaps minor changes related to anthropogenic perturbation including climate change. In contrast, the Arctic is currently undergoing rapid change as a consequence of atmospheric and oceanic warming (IPCC 2019). Increasing riverine discharge (Rawlins et al., 2010), and increasing supply of organic matter (Feng et al., 2013) containing trace element-binding ligands (Gledhill and Buck, 2012), may result in enhanced trace element concentrations in Polar Surface Water and increase lateral dFe, dMn, dCo and dZn transport towards Fram Strait (Kipp et al., 2018; Charette et al., 2020). Conversely, decreasing sea ice cover may facilitate enhanced primary production and trace metal drawdown within the Arctic. Sea ice further functions as a vehicle for lateral shelfsediment transport (Dethleff and Kuhlmann, 2010) and may release substantial quantities of dissolved and particulate trace elements to the surface ocean during the melt season (Tovar-Sánchez et al., 2010; Wang et al., 2014). Fram Strait presently accounts for >90% of all Arctic Ocean sea ice export (Kwok, 2009), an aerial extent that has been increasing since 1979 (+6% per decade, Smedsrud et al., 2017) although export of sea ice formed in shallow areas of the Arctic Ocean is declining (-17% per decade since 1998, Krumpen et al., 2019). The interactive effects of sea ice loss on trace metal supply and demand are therefore challenging to predict. Future projections suggest the loss of sea ice cover may

also result in increased advection of Atlantic Water into the Arctic Ocean (Wang *et al.*, 2020) driving 'Atlantification'. How these changes will affect dFe, dMn, dCo and dZn exchange remains unknown due to a lack of trace element data across Fram Strait.

The present study forms part of the international GEOTRACES programme, and focuses on the distribution and advection of dFe, dMn, dCo and dZn in water masses of the Fram Strait (cruise GN05) and Barents Sea Opening (cruise GN04). Among the trace element micronutrients, Fe is of particular interest as its availability limits primary production in large parts of the North Atlantic Ocean (Nielsdóttir et al., 2009; Ryan-Keogh et al., 2013; Browning et al., 2019), and also parts of the Arctic Ocean are deficient in dFe relative to typical phytoplankton requirements (Rijkenberg et al., 2018) or displays Fe co-limitation (Taylor et al., 2013). A similar role in (co-)limiting phytoplankton community growth may be expected for dMn (Wu et al., 2019; Browning et al., 2021), dCo (Panzeca et al., 2008; Browning et al., 2017) and dZn (Crawford et al., 2003), raising questions about how broadscale changes as a result of Arctic amplification and Arctic 'Atlantification' will affect the supply of trace metal micronutrients in the high latitude ocean. Combined with the most recent year-round synopsis of Arctic-North Atlantic volume transport fluxes, we calculate the associated dFe, dMn, dCo and dZn fluxes for the Fram Strait and Barents Sea Opening gateways. For comparison, we estimated net fluxes for Davis Strait using the limited available GEOTRACES data (GN02, 2015) from stations within the Baffin Current. The aim of this study is to establish a baseline against future changes in trace element fluxes between the Arctic and Atlantic Oceans. To our best knowledge, this is the first attempt to quantify micronutrient trace element exchanges between the Arctic and North Atlantic Oceans.

5.2 Methods

5.2.1 Sampling

Samples were collected during two GEOTRACES expeditions in 2015 (section GN04, 17 Aug – 15 Oct), and 2016 (GN05, 21 Jul – 6 Sep) on-board the research vessel Polarstern (Fig. 5.1). On cruise GN05 a transect was conducted from the West Svalbard shelf towards coastal NE Greenland covering Fram Strait at 79°N and the NE Greenland Shelf (e.g. Ardiningsih *et al.*, 2020; Krisch *et al.*, 2020 - Chapter 3). Four stations were located within the WSC (>5°E), nine stations within the EGC ($6.5^{\circ}W-2^{\circ}E$), with one station in

between ('Middle', 2-5°E), and twelve stations on the NE Greenland Shelf (> $6.5^{\circ}W$) (Tsubouchi *et al.*, 2018). GN04 investigated the Barents Sea Opening through a transect of six stations near the continental shelf break between coastal Norway and Hopen Island (Svalbard) (Slagter *et al.*, 2017). Four additional stations were occupied during cruise GN04 in the central Arctic Ocean Transpolar Drift around 90°N (81, 91, 96 and 99 as per Slagter *et al.*, 2017).

On GN05, sampling was conducted using a powder-coated aluminium GEOTRACES frame (Seabird, equipped with a SBE 911 CTD) with 24 x 12 L GoFlo bottles (Cutter *et al.*, 2017). Sampling on GN04 used the titanium NIOZ frame (equipped with a Seabird SBE 911) and 24 x 24 L polyvinylidene fluoride samplers (Rijkenberg *et al.*, 2015). Vertical, full depth profiles of salinity, temperature, pressure and light attenuation (turbidity) were conducted at high-resolution on both expeditions. Following GEOTRACES sampling protocols (Cutter *et al.*, 2017), both expeditions sampled the water column to full depth and utilized an over-pressured class 100 ultraclean laboratory container for subsampling immediately after deployment. Samples were filtered (Acropak 0.8/0.2 μ m pore size) into pre-cleaned LDPE (low density polyethylene) 125 mL bottles and acidified to pH 1.9 (GN05) or pH 1.8 (GN04) with ultrapure HCl (GN05: ROMIL, GN04: Seastar Chemicals Inc.) for subsequent dissolved trace element analysis.



Figure 5.1: Schematic of current flow paths and locations sampled during GEOTRACES expeditions GN05 (2016) in Fram Strait (black circles), and GN04 (2015) in the Barents Sea Opening (green circles). Thin arrows (black, green) highlight the sections which are shown in **Figs. 5.2-5.3**. Warm, saline (cold, fresher) Atlantic-derived (Arctic-derived) currents are depicted in bold-red (bold-blue): North Atlantic Current (NAC), Norwegian Atlantic Current (NAC), Barents Sea Branch (BSB), West Spitsbergen Current (WSC), Recirculating Atlantic Water (RAW), Polar Surface Water (PSW), East Greenland Current (EGC).

5.2.2 Trace element analyses

Dissolved trace element concentrations in samples collected during cruise GN05 were analysed via high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS) following solid-phase pre-concentration, exactly as per *Rapp et al.* (2017). Briefly, 10 mL sample aliquots were pre-concentrated using an automated SeaFAST system (SC4 DX SeaFAST pico; ESI). All reagents for SeaFAST were prepared in deionised water (>18.2 M Ω cm⁻¹; Milli-Q, Millipore). Single-distilled sub-boiled HNO₃ (SpA grade, Romil) was used for sample elution. Ammonium acetate buffer (pH 8.5) was prepared from glacial acetic acid and ammonium hydroxide (Optima grade, Fisher Scientific). The 10fold preconcentrated samples were analysed by HR-ICP-MS (Thermo Fisher Element XR). Calibration was via isotope dilution for Fe and Zn, and standard addition for Mn and Co (Inorganic Ventures standard solutions).

Samples from GN04 were analysed via HR-ICP-MS (Thermo Finnigan Element 2) following the procedure of Biller and Bruland (2012) with the addition of indium, lutetium and rhodium as internal standards (Middag *et al.*, 2015). Reagents were prepared in de-ionised water (>18.2 M Ω cm⁻¹; Milli-Q, Millipore) from double-distilled sub-boiled HNO₃ and glacial acetic acid, and ammonium hydroxide (Suprapur grade, Merck). Seawater samples were pre-concentrated 37-fold into acid-cleaned Cryo polypropylene vials (Fisher Scientific) using an automated SeaFAST (SC-4 DX SeaFAST pico; ESI). Calibration for Fe, Mn, Co and Zn was via standard addition from a mixed standard, made form single spike standards (TraceCERT, Sigma-Aldrich).

Validation of method accuracy for dFe, dMn, dCo and dZn analyses was through GEOTRACES SAFe D1 (GN04), SAFe S and GSC (GN05) reference materials (Bruland Research Lab, 2009) (Table 5.1). In-house reference seawater CAB (GN05) and NADW (GN04) were used to monitor long-term precision (Table S5.1). Procedural blank contribution was determined by ICP-MS analyses of 1M HNO₃ (elution acid) obtained from SeaFAST where the sample introduction step was omitted from the pre-concentration method and includes contribution from the SeaFAST buffer (GN05), or from acidified de-ionised water (pH 1.8) treated as a 'regular' sample to SeaFAST pre-concentration (GN04) (Table S5.2). Limits of detection were defined as three times the standard deviation of the blank.

Reference Material	Analyte	Consensus ^A	Measured
CIN64	dFe	0.69 ± 0.04	0.82 ± 0.04
GN04 SAE2 D1 (#500)	dMn^B	0.43 ± 0.02	0.41 ± 0.002
SAFE DI (#399)	dCo	$46.6\pm4.8\ pM$	$43.2\pm1.9\ pM$
$\Pi = 0$	dZn	7.59 ± 0.36	7.53 ± 0.05
GN05	dFe	0.095 ± 0.008	0.101 ± 0.016
SAFe S (#273)	dMn	0.81 ± 0.06	0.87 ± 0.18
n = 10	dCo	$4.9\pm1.2\;pM$	$6.3\pm1.8\ pM$
GSC (#21, #159) n = 7	dZn ^B	1.41 ± 0.10	1.37 ± 0.14

<u>**Table 5.1**</u>: Measured concentrations (in nmol·L⁻¹, nM) and standard deviations ($\pm 1\sigma$) of dissolved Fe, Mn, Co and Zn for reference materials SAFe D1 (GN04), SAFe S and GSC (GN05); n = number of measurements.

^A Conversion from nmol·kg⁻¹ by density of 1.026 kg·L⁻¹.

^B Value obtained from Wuttig *et al.* (2019).

5.2.3 Flux calculations

Calculations of dFe, dCo, dMn and dZn fluxes through the Fram Strait, Barents Sea Opening, and Davis Strait are based on monthly mean volume transport estimated from mooring observations for the period September 2005 – August 2006 (Tsubouchi *et al.*, 2018) and concentrations observed along the cruise sections GN04 and GN05. Water masses of Fram Strait, i.e. WSC (>5°E), Middle section (25°E), EGC (2°E – 6.5°W), and the NE Greenland Shelf (>6.5°W) are differentiated into layers of Surface Water ($\sigma_0 < 27.1 \text{ kg/m}^3$), Upper Atlantic Water (27.10 σ_0 - 27.50 σ_0 kg/m³), Atlantic Water (27.50 σ_0 - 30.28 $\sigma_{0.5}$ kg/m³), Intermediate Water (30.28 $\sigma_{0.5}$ - 32.75 $\sigma_{1.0}$ kg/m³), and Deep Water ($\sigma_0 > 32.75 \text{ kg/m}^3$) by definition of isopycnal surfaces and potential density relative to 0 dbar (σ_0), 500 dbar ($\sigma_{0.5}$) and 1000 dbar ($\sigma_{1.0}$) following Tsubouchi *et al.* (2018) (Fig. 5.2a). The water column of the Barents Sea Opening is analogously distinguished into layers (Fig. 5.3a), but treated as one water mass in accordance with *Petrova et al.* (2020).

Trace element fluxes were calculated using mean volume transport flows, and mean concentrations of dFe, dMn, dCo and dZn for each individual water mass within every layer ('component'). Uncertainties in component trace element transport are derived from error propagation and include the standard deviation of volume transport (i.e. seasonal variation) and standard deviation (1σ) of observed dFe, dMn, dCo and dZn concentrations from section cruises (i.e. without seasonal variation). To establish annual net dFe, dMn, dCo and dZn fluxes, we average over monthly mean net trace element fluxes (Sep-Aug) and report uncertainty as one standard deviation (1σ) of monthly variations following *Petrova et*

al. (2020). Because the Arctic Ocean is a closed system where volume fluxes are not independent variables, classical error propagation cannot be used to estimate uncertainty in annual trace element fluxes as this would lead to an over-estimation in net Arctic-Atlantic trace element exchange. We explore the potential implications of seasonal variations for annual fluxes based on the multi-seasonal trace metal data available for the high latitude North Atlantic (Achterberg *et al.*, 2018, 2021).

5.3 **Results and Discussion**

5.3.1 Distributions of dFe, dMn, dCo and dZn

In Fram Strait, Surface Water was absent in the WSC and increased in thickness from western Fram Strait towards Greenland (Fig. 5.2a). Upper Atlantic Water formed the surface layer in the WSC and also increased in thickness towards the Greenlandic coast. Atlantic Water was present across the section and increased in thickness towards eastern Fram Strait and the Atlantic-sourced WSC. Intermediate Waters were observed across Fram Strait and deeper parts (i.e. troughs) of the NE Greenland Shelf. The layer of Intermediate Water was thickest in the EGC. Deep Water layer thickness varied little in the deeper parts of Fram Strait (>630 m), and Deep Water was absent elsewhere.

The distribution of dFe in Fram Strait (Fig. 5.2a, Table S5.3) showed an unusual gradient of decreasing concentrations with depth in the EGC (range: 0.2-3.0 nM) and on the NE Greenland Shelf (0.5-3.4 nM), in agreement with observations in the Central Arctic Ocean (Klunder, Bauch, *et al.*, 2012; Rijkenberg *et al.*, 2018). Both water masses contrast starkly with the increase in concentrations with depth observed elsewhere across the Atlantic, Pacific and Southern Oceans (Rijkenberg *et al.*, 2014; Schlitzer *et al.*, 2018). Conversely, in the WSC (0.2-1.9 nM) concentrations increased with depth, which is more typical for Atlantic waters due to biological drawdown in surface waters and remineralisation at depth (Rijkenberg *et al.*, 2014; Tonnard *et al.*, 2020). An east-to-west gradient in Surface Water dFe was consequently evident. Maxima were observed in the Surface Waters of the EGC (1.0 ± 0.6 nM, mean concentration \pm standard deviation (1σ)) near the Greenland continental slope (stations S9-S10, S12-S13, S25; 1.3 ± 0.3 nM) and on the NE Greenland Shelf proximal to the Nioghalvfjerdsbrae and Zachariæ Isstrøm glacier outflows (stations S20, S22, S24, 1.7 ± 0.6 nM). Further east, Upper Atlantic Water exhibited a pronounced dFe minimum in the WSC (S4, 0.22 ± 0.01 nM), potentially as a consequence of primary

production in eastern Fram Strait (Krisch *et al.*, 2020 - Chapter 3). Dissolved Fe within Atlantic Water and Intermediate Water was more uniformly distributed and showed comparatively little variation between the WSC $(0.7 \pm 0.3 \text{ nM}, 0.6 \pm 0.1 \text{ nM}, \text{respectively})$ and the NE Greenland Shelf $(0.9 \pm 0.3 \text{ nM}, 0.9 \pm 0.6 \text{ nM}, \text{respectively})$. Dissolved Fe maxima in Atlantic Water and Intermediate Water were evident above the Svalbard (S1, 500 m, 1.6 nM) and Greenland shelf break (S9, 250 m, 3.0 nM; S25, 225 m, 2.6 nM), near the glacier termini of Nioghalvfjerdsbrae (S22, 100-150 m, 1.5 nM) and Zachariæ Isstrøm (S20, 355 m, 2.4 nM), and in the northern parts of the NE Greenland Shelf (S10, 200 m, 1.7 nM). These maxima indicate localized sedimentary inputs across the region, as have been observed in other Arctic shelf environments (Kondo *et al.*, 2016; Vieira *et al.*, 2019). Deep Water contrasted with Intermediate Water and showed increasing dFe concentrations with depth across Fram Strait. The distribution of dFe in Deep Water did not vary between the EGC ($0.9 \pm 0.4 \text{ nM}$) and the WSC ($0.9 \pm 0.2 \text{ nM}$). Overall, average concentrations indicated that the WSC was depleted in dFe ($0.7 \pm 0.3 \text{ nM}$) relative to the EGC ($0.9 \pm 0.6 \text{ nM}$) and waters on the NE Greenland Shelf ($1.1 \pm 0.5 \text{ nM}$ dFe).

The vertical and horizontal distribution of dMn showed similar trends to dCo (Fig. 5.2bc, Table S5.3) in Fram Strait. As was the case for dFe, an east-to-west gradient was apparent with increasing concentrations towards the Greenlandic coast. Maximum concentrations were observed in Surface Water on the NE Greenland Shelf $(3.1 \pm 2.2 \text{ nM dMn},$ 204 ± 49 pM dCo), and were most pronounced near the glacier termini of Nioghalvfjerdsbrae and Zachariæ Isstrøm (S20, S22, S24, 4.2 ± 2.7 nM dMn, 237 ± 45 pM dCo). Both trace elements showed surface maxima and decreasing concentrations with depth. Surface layers were enriched by 170-1240% (dMn) and 120-300% (dCo) compared to mean bottom layer concentrations, likely reflecting photochemical stabilisation of dMn (Sunda and Huntsman, 1988) and organic stabilisation of dCo (Bundy et al., 2020) in surface waters. Dissolved Co, but not dMn, showed surface layer minima in the WSC and in western Fram Strait (60 ± 10 pM in the WSC; 47 ± 12 pM at S6, S15 and S16), and subsurface layer maxima (86 ± 13 pM in the WSC, 93 ± 9 pM at S6, S15 and S16) likely as a consequence of drawdown by primary production (Krisch et al., 2020 - Chapter 3). Average concentrations of dMn and dCo indicated that the WSC was depleted $(0.9 \pm 0.4 \text{ nM dMn}, 81 \pm 15 \text{ pM dCo})$ similar to the EGC $(0.8 \pm 0.8 \text{ nM dMn}, 81 \pm 25 \text{ pM})$ dCo), and contrasted to waters on the NE Greenland Shelf $(2.1 \pm 2.0 \text{ nM} \text{ dMn})$, $157 \pm 64 \text{ pM dCo}$).





Figure 5.2: Dissolved distribution of (a) Fe, (b) Co, (c) Mn and (d) Zn in Fram Strait at 79°N (GN05). Section plotted as indicated in **Fig. 5.1** ('Section GN05'). Sample depths used for interpolation are shown as black dots. Station numbers indicated in top panel. Isopycnals (blank contours) distinguish between water masses: Surface Water (SURF, $\sigma_0 < 27.1 \text{ kg/m}^3$), Upper Atlantic Water (UAW, 27.10-27.50 kg/m³), Atlantic Water (AW, 27.50- 30.28 kg/m³), Intermediate Water (IW, 30.28-32.75 kg/m³) and Deep Water (DW > 32.75 kg/m³). Vertical red lines delineate the West Spitsbergen Current (WSC, >5°E), the Middle (2-5°E), the East Greenland Current (EGC, 6.5°W-2°E) and the NE Greenland Shelf (>6.5°W) following the definitions of Tsubouchi *et al.* (2018). Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).

Dissolved Zn mirrored the general distribution of dFe, dMn and dCo across Fram Strait (Fig. 5.2d). Minima were observed in the surface layer and increased with depth, and in an easterly direction towards Svalbard. Depleted dZn in EGC Surface Water $(1.2 \pm 0.6 \text{ nM})$ and Upper Atlantic Water $(1.0 \pm 0.5 \text{ nM})$ contrasted with the WSC where surface (Upper Atlantic Water and Atlantic Water) dZn was ~2-fold elevated (Table S5.3). Mean dZn concentrations in the EGC $(2.2 \pm 1.1 \text{ nM} \text{ for all stations between } 2^{\circ}\text{E}, 6.5^{\circ}\text{W})$ were similar to observations in the WSC $(2.5 \pm 1.3 \text{ nM} \text{ for all stations } >5^{\circ}\text{E})$. This was a clear contrast with the water column on the NE Greenland Shelf where dZn was most elevated $(3.1 \pm 1.4 \text{ nM} \text{ for all stations } >6.5^{\circ}\text{W})$ indicative of a shelf sediment source (Vieira *et al.*, 2019). Dissolved Zn maxima were observed in the bottom water of the non-glaciated inner-

shelf region (5.2 ± 0.3 nM in Atlantic Water of station 11) and close to the seafloor near the Greenland continental margin (5.4 ± 1.7 nM in waters >150 m at stations 12 and 13).

In the shallow Barents Sea Opening, Atlantic Water was the dominant water mass and deepened closer to Svalbard (station 149), where it occupied the full water column (Fig. 5.3). Surface Water was only observed near coastal Norway (station 173) making saline Upper Atlantic Water the main surface layer in the Barents Sea Opening. Intermediate and Deep Waters were not observed. Dissolved Fe concentrations across the Barents Sea Opening (Fig. 5.3a) exhibited surface minima (~0.2 nM) and increased at depth (~1.0 nM) matching observations of the WSC in Fram Strait (Table S5.3). The distribution of dZn (Fig. 5.3d) showed similar trends to dFe with surface layer minima (~0.4 nM) and bottom depth maxima (~1.1 nM). Both dFe and dZn evidenced local maxima in the water column of coastal Norway (station 173, 0.8 ± 0.2 nM dFe, 1.2 ± 0.1 nM dZn) and in the central deep (stations 153, 157) above the seafloor (~1.6 nM dFe, ~1.1 nM dZn). Yet, dZn was depleted ~3-fold in the Barents Sea Opening compared to values in Fram Strait; a discrepancy that increased between the surface and bottom layers. Dissolved Mn and Co mirrored the distributions of dFe and dZn between coastal Norway and the central deep (station 161-173, Fig. 3b-c). There, surface maxima and a gradient to lower concentrations at depth (range: 0.6-2.8 nM dMn, 64-143 pM dCo) were observed. All other stations showed increasing dCo concentrations with depth. Local maxima of all dissolved trace elements near coastal Norway and just above the seafloor in the central deep suggests shelf sediments were net sources of dFe, dMn dCo and dZn to the water column of the Barents Sea Opening.



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Figure 5.3: Dissolved distribution of (a) Fe, (b) Co, (c) Mn and (d) Zn in the Barents Sea Opening between Norway and Svalbard (GN04). Section plotted as indicated in **Fig. 5.1** ('Section GN04'). Sample depths used for interpolation are shown as black dots. Station numbers indicated in top panel. Isopycnals (blank contours) as per **Fig. 5.2**. Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).



Figure 5.4: Principal Component Analysis (PCA) loading plots illustrating trends in the distribution of dissolved trace elements (dFe, dMn, dCo and dZn) and macronutrients (nitrate, silicic acid, phosphate) relative to salinity (Sal) in the water column of Fram Strait (GN05, left) and the Barents Sea Opening (GN04, right). Figure made using Minitab statistical software version 19.2020.1 (Minitab Inc., State College, PA, USA).

Principal Component Analysis was conducted to investigate regional relationships between micronutrient trace elements (dFe, dMn, dCo and dZn), macronutrient (nitrate, phosphate, silicic acid) and salinity observations (Fig. 5.4). The two principal components PC1 and PC2 reflect 72.1% of variance in parameters (52.0% for PC1 and 20.1% for PC2) observed across Fram Strait. In Fram Strait, dFe, dMn and dCo were grouped in opposition to salinity, suggesting the distribution of these trace elements is influenced by a common, low salinity source. Dissolved Fe, Mn and Co did not show a strong relationship with depth suggesting a minor significance of remineralisation on the general distribution in Fram Strait. Dissolved Zn was more positively correlated with salinity, depth, phosphate and nitrate, and showed a close relationship with silicic acid. This is consistent with phytoplankton uptake of dZn followed by remineralisation of dZn alongside silicic acid (Vance *et al.*, 2017; Middag, de Baar and Bruland, 2019) with less influence from low salinity sources.

In the Barents Sea Opening, dissolved inorganic carbon measurements were also available. For a similar analysis of macronutrients, trace elements, salinity and depth, PC1 and PC2 represent 62.7% (PC1) and 24.1% (PC2) of variance. As was the case for Fram Strait, dMn and dCo in the Barents Sea Opening were grouped in opposition to salinity suggesting the distribution of dMn and dCo is strongly influenced by sources associated with low salinity waters. Macronutrients across the Barents Sea Opening aligned much more closely with salinity and depth and dissolved inorganic carbon, suggesting remineralisation as the main driver controlling their distributions. In between these two groupings, dFe and dZn across the Barents Sea Opening were aligned suggesting that their distributions are similarly influenced by a mixture of factors including biological activity and the associated remineralisation, and low salinity waters.

5.3.2 Trace element sources to Fram Strait

Macronutrient and trace element distributions in Fram Strait are strongly influenced by North Atlantic and Arctic waters (Torres-Valdés *et al.*, 2013; Krisch *et al.*, 2020 -Chapter 3). Atlantic Water that forms the core of the WSC (Beszczynska-Möller *et al.*, 2012; Rudels, 2019) showed 0.7 ± 0.3 nM dFe, 1.1 ± 0.3 nM dMn and 86 ± 13 pM dCo in Fram Strait, matching observations of Atlantic Water in the Barents Sea Opening (Table S5.3). Dissolved Zn was ~3-fold elevated in Atlantic Water of the WSC (2.1 ± 1.1 nM) compared to concentrations in the Barents Sea Opening (0.7 ± 0.2 nM), but

showed only a slight increase relative to measurements of Atlantic Water in the upstream Iceland and Irminger Basins $(1.5 \pm 0.5 \text{ nM} \text{ at } 80\text{-}3100 \text{ m} \text{ for all stations } 20\text{-}35^{\circ}\text{W}$, Achterberg *et al.*, 2020). Atlantic Water in the Barents Sea Opening is primarily derived from the Norwegian Atlantic Current, whilst the WSC of Fram Strait also comprises Atlantic Water from the North Atlantic Current flowing through the central Greenland Sea (Mauritzen *et al.*, 2011) (Fig. 5.1). Water column dZn enrichment in the WSC but not the Barents Sea Opening, may thus arise from differences in primary production (Kohly, 1998; Vernet *et al.*, 2019) and water mass mixing (Roshan and Wu, 2015; Middag, de Baar and Bruland, 2019) between these two Atlantic Water source regions.

Dissolved Fe in Atlantic Waters of the Fram Strait (0.8 ± 0.4 nM for all stations) and Barents Sea Opening (0.6 ± 0.3 nM) showed typical concentrations for the North Atlantic and was comparable to observations from Atlantic Water in both, the upstream Iceland and Irminger Basins (0.7 ± 0.4 nM, Achterberg *et al.*, 2018), and the downstream SE Nansen Basin (0.7 ± 0.2 nM at stations 239-260 as per Klunder, Laan, *et al.*, 2012). Similarly, dCo in Atlantic Water from Fram Strait (91 ± 17 pM) and the Barents Sea Opening (73 ± 8 pM) matched observations in the Iceland and Irminger Basins (90 ± 24 pM, Achterberg *et al.*, 2020). Dissolved Mn on the other hand was ~2-fold elevated in Atlantic Water from Fram Strait (1.0 ± 0.3 nM) relative to observations from Atlantic Water in the Iceland and Irminger Basins (0.5 ± 0.4 nM, Achterberg *et al.*, 2020). This suggests that during northward transport in the high latitude North Atlantic sources and sinks of dFe and dCo are roughly balanced, whereas other trace elements such as dMn and dZn are subject to ongoing net inputs before entering the Arctic Ocean.

Trace element concentrations in the EGC were higher than any other water mass and showed greater spatial variability. While dMn and dCo showed similar concentrations in the EGC in Fram Strait (0.8 ± 0.8 nM dMn, 81 ± 25 pM dCo) to those observed in the EGC off Southeast Greenland (0.8 ± 0.4 nM dMn and 94 ± 34 pM dCo at 60° N, $41-43^{\circ}$ W, Achterberg *et al.*, 2020), dFe and dZn were ~50% elevated in the EGC in Fram Strait (0.8 ± 0.5 nM dFe, 2.2 ± 1.1 nM dZn) compared to concentrations in the EGC further south (0.5 ± 0.3 nM dFe, 1.5 ± 1.5 nM dZn, Achterberg *et al.*, 2020). The apparent loss of dFe and dZn in the EGC between Fram Strait and Southeast Greenland may be linked to phytoplankton uptake (Morel, Milligan and Saito, 2003), and incorporation of ambient low dFe and low dZn waters (Achterberg *et al.*, 2018, 2021). This north-south gradient in

summertime (July-August), whilst from different years (2010 and 2016), extends further north when considering prior observations in the Central Arctic Ocean. Near the North Pole, concentrations of dFe (2.3 ± 1.0 nM), dMn (3.7 ± 1.4 nM) and dCo (145 ± 31 pM) are even more elevated in the Transpolar Drift. The Transpolar Drift holds a fraction of up to 25% meteoric freshwater and is rich in shelf derived material (Kipp *et al.*, 2018; Rutgers van der Loeff *et al.*, 2018; Charette *et al.*, 2020), including ligands that stabilize concentrations of trace elements such as dFe several factors beyond the capacity of ambient seawater (2.5-4.4 nM dFe inside the Transpolar Drift compared to ~0.6 nM outside the Transpolar Drift) (Klunder, Bauch, *et al.*, 2012; Slagter *et al.*, 2017; Rijkenberg *et al.*, 2018). Ligand stabilization may similarly cause elevated concentrations of other organically complexed elements including dCo within the Transpolar Drift (Bundy *et al.*, 2020; Charette *et al.*, 2020). The Transpolar Drift is advected towards Fram Strait (Mysak, 2001; Krumpen *et al.*, 2019), and so Arctic Ocean surface waters contribute to the EGC (Richter, Von Appen and Wekerle, 2018; Rudels, 2019) and appear to function as a source of elevated trace element concentrations to the North Atlantic.

The water column of stations in the EGC and the Transpolar Drift revealed similar trends in the distribution of dFe, dMn and dCo; only deeper waters (>1500 m) differed between the sites (Fig. S5.1, Table S5.3). Concentrations of dFe, dMn and dCo measured in Surface Water of the EGC were at the lower end of observations in the Transpolar Drift suggesting progressive dilution/loss of dissolved trace elements as the current progresses southwards across the Arctic (Aagaard and Carmack, 1989; Smedsrud et al., 2017; Charette et al., 2020). Additionally, there may have been mixing with trace element depleted Polar Surface Water and Recirculating Atlantic Water to the north of Fram Strait (Rudels et al., 2005; de Steur et al., 2014; Richter, Von Appen and Wekerle, 2018). Dissolved Zn showed a contrasting behaviour and was neither enriched in the Transpolar Drift (1.6 ± 0.8 nM) nor in EGC Surface Water (1.2 ± 0.6 nM). Other trace elements from the same expeditions such as mercury ('total Hg', tHg, Charette et al., 2020; Petrova et al., 2020) corroborate our conclusion: The WSC $(0.80 \pm 0.26 \text{ pM})$ and the water column in the downstream SE Nansen Basin (0.78 ± 0.24 pM at stations 32, 40 and 50 as per Charette *et al.*, 2020) were depleted in tHg, compared to elevated concentrations in the EGC (1.29 ± 0.43 pM) and the Transpolar Drift (1.35 \pm 0.34 pM). This north-south gradient in Arctic-Atlantic tHg extends to observations in the EGC off Southeast Greenland (0.43 ± 0.06 pM, station 53, Cossa et al., 2018), similar to dFe, dMn and dCo.

5.3.3 Siberian shelf sources

If the Transpolar Drift acts as a source of Arctic Ocean shelf-derived trace elements to the North Atlantic, dFe, dMn and dCo enrichment in surface Fram Strait should show a correlation with meteoric freshwater and ligand content similar to observations in the Central Arctic Ocean. For the calculation of meteoric freshwater contents, we use oxygen isotope measurements (δ^{18} O) from GN05 (Meyer *et al.*, 2021) with a freshwater reference δ^{18} O value of -20‰ which is an average for riverine discharge to the Arctic Ocean shelves (Bauch *et al.*, 2011; Dubinina *et al.*, 2017). The δ^{18} O measurements reveal an east-to-west gradient of meteoric freshwater contents in surface waters of Fram Strait (Fig. S5.2) following the trend that is observed for dFe, dMn and dCo (Fig. 5.2). Minima were calculated for the surface WSC (~0% at <50 m between 7.0-8.6°E) which is consistent with prior surface δ^{18} O measurements (+0.2 ± 0.1‰ at <50 m) and corresponding meteoric freshwater contents (~0%) in the upstream Norwegian and Greenland Sea (65-75°N, 10°E-10°W; Schmidt, Bigg and Rohling, 1999). The surface EGC showed pronounced maxima in meteoric freshwater ($14 \pm 3\%$ in the water column <50 m at 80°N, 4.0-8.2°W) comparable to the lower end of observations in the Central Arctic Ocean near the North Pole ($20 \pm 4\%$ at >88°N; Pasqualini *et al.*, 2017). As was the case in the Transpolar Drift, these low salinity waters in Fram Strait were enriched in dFe-binding ligands $(1.9 \pm 0.6 \text{ nM eq.} \text{dFe in the EGC} < 75 \text{ m})$ relative to ligand concentrations in saline Atlantic and Upper Atlantic Water of the WSC $(1.2 \pm 0.2 \text{ nM eq. Fe})$ (Slagter *et al.*, 2017; Ardiningsih et al., 2020).

The flow path of trace element transport from the Siberian shelf via the Transpolar Drift to Fram Strait can also be traced through the use of radium (Ra). Ra is released from shelf sediments through continuous decay of thorium (²³⁰Th and ²³²Th) (Rutgers van der Loeff *et al.*, 1995; Kipp *et al.*, 2018). While thorium is particle-reactive and largely immobilized on lithogenic material (Trimble, Baskaran and Porcelli, 2004; Santschi *et al.*, 2006), ²²⁸Ra (half-life of 5.75 years) and ²²⁶Ra (half-life of 1600 years) are soluble in seawater and, after release, advected with the prevailing currents across the Arctic Ocean (Kipp *et al.*, 2018, 2019; Rutgers van der Loeff *et al.*, 2018). In 2015, activity ratios of ²²⁸Ra(1.0 ± 0.7 at >85°N) showed a close relationship with meteoric freshwater content (0.077 S, 0.91 R², Fig. S5.3) in the upper 500 m of the Central Arctic Ocean (Charette *et al.*, 2020), pointing towards riverine discharge and shelf sediments as strong sources of ²²⁸Ra to the region near

the North Pole (Kipp et al., 2018; Rutgers van der Loeff et al., 2018). The water column of Fram Strait as of 2016 showed a similar relationship between ²²⁸Ra/²²⁶Ra and meteoric freshwater content, although with a smaller slope (0.029 S, 0.81 R², Fig. S5.3), implying that compared to observations in the Central Arctic Ocean, ²²⁸Ra in Fram Strait was ~2-fold depleted relative to ²²⁶Ra. On the Northeast Greenland Shelf both the meteoric freshwater content and the ²²⁸Ra activity are enhanced by local sources (Krisch, Hopwood, et al., 2021 - Chapter 4) but for the EGC beyond the shelf break such a local source is unlikely to be a major influence (Laukert *et al.*, 2017). We explain the reduction in ²²⁸Ra/²²⁶Ra as the result of radioactive decay of ²²⁸Ra during transit from the Siberian shelves to Fram Strait, which can in part occur during the residence of surface waters in the Canada Basin (Kipp et al., 2019). Using Ra as tracer, the timescale of Polar Surface Water advection from the Laptev Sea to the Central Arctic Ocean has been estimated to range between 0.5-3 years (Rutgers Van Der Loeff et al., 2012; Kipp et al., 2018). From ¹²⁹I and ²³⁶U measurements (Casacuberta et al., 2018; Wefing et al., 2019) we may infer a further 2-2.5 years for surface waters of the Central Arctic Ocean to reach Fram Strait. This suggests trace elements supplied from the Siberian Shelf may reach the ~3000 km-distant North Atlantic Ocean within 3-5 years. A total transit time in the order of the ²²⁸Ra half-life (5.75 years) is also roughly consistent with the observed decrease in activity.

5.3.4 Fram Strait flux estimates

In the following, we will discuss dFe, dMn, dCo and dZn transport rates ('fluxes') across Fram Strait for August 2016. By the definition applied herein, negative values indicate Arctic transport to the North Atlantic Ocean, while positive values indicate transport from the North Atlantic to the Arctic Ocean.

Observations of volume fluxes in August 2006 across Fram Strait suggest transport of North Atlantic-derived trace elements to the Arctic as part of the WSC and waters on the NE Greenland Shelf (Tsubouchi *et al.*, 2018). The volume fluxes suggest transport of Arctic Ocean-derived trace elements to the North Atlantic as part of the EGC, and waters of the Middle section in the deeper parts of Fram Strait (between 2-5°E). The northbound WSC and southbound EGC are the dominant water masses by both volume and trace element transport. Together, the WSC and EGC constitute ~80% of gross northbound and southbound dissolved trace element fluxes across Fram Strait (Table 5.2). Atlantic Water advected from the Greenland and the Norwegian Sea is the dominant component in the

WSC's transport for dFe (30-55%), dMn (62-74%) and dCo (48-58%) as a consequence of the large volume transport (~3.4 Sv) in this layer (Table S5.4). Deep Water forms the most dZn enriched water mass and constitutes the largest fraction of WSC dZn transport (33-55%). Dissolved trace element transport in the EGC are different. The gross of dFe, dCo and dZn transport in the EGC occurs via Intermediate and Deep Water originating from the Arctic Ocean (Meincke, Rudels and Friedrich, 1997; Laukert *et al.*, 2017). Intermediate Water dominates southbound trace element transport and comprises 16-46% of gross dFe, 21-43% of gross dCo, and 31-57% of gross dZn fluxes across Fram Strait. Major transport of EGC dMn occurs in the Surface Water layer (14-52%).

<u>**Table 5.2**</u>: August 2016 fluxes of dFe, dMn, dCo and dZn in the (a) West Spitsbergen Current, (b) 'Middle' section, (c) East Greenland Current, and (d) on the NE Greenland Shelf. Dissolved trace element fluxes were calculated from mean volume fluxes through Fram Strait as of August 2006 (Tsubouchi et al., 2018), and mean concentrations of dFe, dMn, dCo and dZn in the corresponding components sampled between 22 Jul – 1 Sep 2016 (Table S3). Negative (positive) values indicate Arctic export to (import from) North Atlantic Ocean. Uncertainties reflect temporal variability in volume transport and include uncertainty in trace element concentration (error propagation). Cut out of **Table S5.4**.

	Volume	dFe	dMn	dCo	dZn
Component	[Sv]	[Gg•a ⁻¹]	[Gg·a ⁻¹]	[Mg·a ⁻¹]	[Gg·a ⁻¹]
West Spitsbergen Current	6.86 ± 0.96	8.8 ± 2.4	9.4 ± 1.8	1006 ± 147	37.7 ± 10.9
Middle	-2.64 ± 2.52	-3.1 ± 2.7	-2.6 ± 3.4	-342 ± 267	-10.0 ± 12.2
East Greenland Current	-5.26 ± 0.98	-7.2 ± 2.1	-8.3 ± 2.6	-813 ± 169	-22.4 ± 5.8
NE Greenland Shelf	0.73 ± 1.10	1.4 ± 1.4	2.5 ± 2.6	205 ± 192	5.2 ± 5.4

The NE Greenland Shelf, is an additional, yet minor source of dFe, dMn, dCo and dZn to Fram Strait and contributed ~10% to gross northbound and southbound fluxes across Fram Strait (Table 5.2). Dissolved Fe, Mn and Co fluxes on the shelf are comparable in magnitude to Arctic export in the EGC Surface Water (Table S5.4). Fluxes of dZn on the shelf were factor 3 elevated relative to transport rates in the EGC Surface Water, likely in consequence to pronounced sedimentary release of dZn as observed, for example, in the Chukchi Shelf Sea (Jensen *et al.*, 2019). Fluxes of dFe, dMn, dCo and dZn on the NE Greenland Shelf were factor 3-5 smaller with respect to EGC as a whole. The shelf region and EGC are both influenced by sources in the Arctic Ocean (Michel *et al.*, 2015; Laukert *et al.*, 2017; Krisch *et al.*, 2020 - Chapter 3). Shelf processes that affect these fluxes include Greenland Ice Sheet discharge (Chapter 4, Ardiningsih *et al.*, 2020). We estimated the glacial trace element supply from Nioghalvfjerdsbrae to the Fram Strait (Table S5.5) following the approach outlined in Section 4.3.6, using the mean cavity volume overturning rate ($46 \pm 11 \text{ mSv}$, Schaffer *et al.*, 2020) and the difference in dissolved trace element load

between station S19 (cavity-entering Atlantic Intermediate Water) and station S22 (cavityexiting, glacially modified Atlantic Intermediate Water). We assume, surface runoff is neglectable compared to subglacial discharge, which in case of Nioghalvfjerdsbrae is likely correct as subglacial melting accounts for >80% of the annual non-calving mass loss (Wilson, Straneo and Heimbach, 2017). This suggest glacial discharge from Nioghalvfjerdsbrae to the NE Greenland Shelf of $56 \pm 37 \text{ Mg} \cdot a^{-1} \text{ dFe}$, $70 \pm 85 \text{ Mg} \cdot a^{-1} \text{ dMn}$ and $4.9 \pm 4.7 \text{ Mg} \cdot a^{-1} \text{ dCo}$. Glacial dZn enrichment in waters downstream to the marine terminus was not observed. Nioghavfjerdsbrae, as the largest contributor of freshwater onto the shelf accounting for ~6% of Greenland Ice Sheet discharge (Rignot and Mouginot, 2012), contributes <1% to southbound micronutrient transport across the strait, and suggests a comparatively minor role for glacial discharge to Arctic export in general.

5.3.5 Annual trace element fluxes and Arctic-Atlantic exchange

The WSC and EGC remain the dominant water masses for dFe, dMn, dCo and dZn transport across Fram Strait between September 2005 and August 2006 (Fig. 5.5, Table S5.6). Our data suggests, Atlantic-derived dFe, dMn and dCo transport to the Arctic Ocean as part of the WSC is approximately counter-balanced by Arctic transport to the high latitude North Atlantic in the EGC between May and February. A balancing of WSC and EGC macronutrient fluxes has previously been reported for fixed nitrogen, phosphate, and silicic acid (Torres-Valdés et al., 2013). With contributions from the Middle section and the NE Greenland Shelf, there is a net southward transport through Fram Strait of Arctic dFe $(-2.3 \pm 1.7 \text{ Gg} \cdot a^{-1})$ and possibly dMn $(-1.7 \pm 2.0 \text{ Gg} \cdot a^{-1})$ and dCo $(-0.2 \pm 0.2 \text{ Gg} \cdot a^{-1})$ to the North Atlantic Ocean (Table 5.3). Net exchange rates across Fram Strait show a seasonal trend with maxima in Arctic export in late summer (September) and winter (January-March). Contrarily, net northbound transport of dFe, dMn and dCo to the Arctic Ocean was calculated for May and August, possibly related to the seasonal variability in recirculation and southbound freshwater transport across Fram Strait (de Steur et al., 2009, 2014; Hattermann et al., 2016). As a consequence of the dominance of dZn fluxes in the WSC over the EGC, a net northward flux, but within uncertainty, of 4.9 ± 6.2 Gg·a⁻¹ dZn to the Arctic Ocean has been calculated. Net fluxes suggest maxima in dZn transport to the Arctic Ocean in spring (April-May), late summer (August) and winter (December), and contrast to observations in September where a pronounced maximum of transport to the North Atlantic Ocean is suggested.

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Figure 5.5: Monthly mean estimates of dFe (top left), dMn (top right), dCo (bottom left) and dZn (bottom right) fluxes as part of the (a) West Spitsbergen Current (WSC), (b) East Greenland Current (EGC), (c) 'Middle' section, and the (d) NE Greenland Shelf of Fram Strait (FS), and the Barents Sea Opening (BSO). Negative (positive) values indicate Arctic export to (import from) the high latitude North Atlantic Ocean. Visualized from **Table S5.6**. Figure plotted using OriginPro version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

Analogous to Fram Strait, we have calculated trace element fluxes through the Barents Sea Opening (Table S5.6). A detailed report concerning trace element cycling in the Barents Sea Opening will follow elsewhere (Middag *et al.*, in preparation). Our data indicate a net transport of trace elements from the Atlantic to the Arctic Ocean through the Barents Sea Opening throughout the year (Fig. 5.5). Annual net fluxes are 2.2 ± 1.1 Gg·a⁻¹ dFe, 5.9 ± 2.7 Gg·a⁻¹ dMn, 0.4 ± 0.2 Gg·a⁻¹ dCo and 3.8 ± 1.8 Gg·a⁻¹ dZn. Atlantic Water was the dominant component of this net flux for dFe (6-70%) and dZn (13-62%) transport, whereas Surface and Upper Atlantic Water were the main components for dMn (46-75%) and dCo (40-68%). As observed for Fram Strait, a seasonal trend in trace element transport across the Barents Sea Opening based on volume transport rates is evident. Transport to the Arctic Ocean peaked from late summer to winter, followed by steady decreasing dFe, dMn, dCo and dZn fluxes in late winter and spring. Interestingly, trace element fluxes through the Barents Sea Opening mirrored net transport rates of Fram Strait. This was most evident

in May, when the balancing of trace element fluxes across the Barents Sea Opening coincided with stagnating Arctic export through the Fram Strait 'Middle' section $(2-5^{\circ}E)$ and decreased dFe, dMn, dCo and dZn transport in the WSC.

Contributions to Arctic Ocean - North Atlantic trace element transport were also calculated for Davis Strait for comparison. Because monthly mean volume fluxes and trace element data are not available, calculations for Davis Strait differ from the micronutrient flux calculations of the Fram Strait and Barents Sea Opening. A detailed investigation concerning trace element cycling and fluxes across Davis Strait will be published elsewhere (Colombo, Cullen et al., in preparation). We apply annual mean net volume fluxes in components of Davis Strait (Tsubouchi et al., 2018) to trace element data from two stations sampled in Baffin Bay (part of GEOTRACES expedition GN02, August 2015) (Tables S5.3 and S5.7). These stations (BB1, BB3) have been analysed for dFe, dMn, dZn, and the labile fraction of dCo referring to weakly complexed and inorganic dCo (e.g. Saito and Moffett, 2001). Stations BB1 and BB3 are affected by the southbound Baffin Current and are representative for Arctic trace element export across Davis Strait (Colombo et al., 2020). Our calculations suggest Davis Strait is an additional gateway for transport of dFe (net $-2.6 \pm 1.3 \text{ Gg} \cdot a^{-1}$), dMn (net $-7.0 \pm 3.3 \text{ Gg} \cdot a^{-1}$), labile dCo (net $-0.5 \pm 0.1 \text{ Gg} \cdot a^{-1}$) and dZn (net -5.7 ± 3.5 Gg·a⁻¹) from the Arctic to the North Atlantic Ocean (Table 5.3). Surface Water was the dominant component in the water column and comprised 71-85% of dFe, 89-96% of dMn, 83-89% of dCo, 60-80% of dZn fluxes across Davis Strait. Atlantic Water constituted <5% to observed fluxes, making trace element fluxes across Davis Strait fundamentally different to those across Fram Strait and the Barents Sea Opening. Unfortunately, with missing data on monthly changes in volume fluxes and trace element concentrations, we cannot explore seasonal trends in Davis Strait trace element fluxes. A strong gradient in trace element concentrations between regions influenced by the North Atlantic inflow (along the West Greenland coastline) and Arctic Ocean outflow (coastal Canada) is generally expected (Colombo et al., 2019, 2020). Based on the limited available data from GEOTRACES cruises GA01 and GN02, trace element concentrations in North Atlantic inflow (Tonnard *et al.*, 2020) are most likely lower than concentrations in Arctic outflow (Colombo et al., 2020). Using only dFe, dMn, labile dCo and dZn concentrations of the Baffin Current herein likely overestimates contributions to Arctic outflow across Davis Strait. However, it is clear from the limited available data that net southbound

transport through David Strait may be in the same range as net northbound transport of dFe, dMn, dCo and dZn through the Barents Sea Opening (Fig. 5.6).

Trace element fluxes from all three gateways combined suggest that there is a net flux of -2.7 ± 2.4 Gg·a⁻¹ dFe, -2.8 ± 4.7 Gg·a⁻¹ dMn and -0.3 ± 0.3 Gg·a⁻¹ dCo from the Arctic to the North Atlantic Ocean – although the dMn and dCo fluxes calculated remain within uncertainty (Table 5.3). Northward and southward dZn transport was balanced with net exchange rates of 3.0 ± 7.3 Gg·a⁻¹ dZn from the Atlantic to the Arctic Ocean. Our data suggests Fram Strait is the most important gateway for Arctic – North Atlantic trace element transport. This arises due to gross dFe, dMn, dCo and dZn transport in individual water masses (EGC, WSC) rather than from net exchange rates (Table S5.6).

<u>**Table 5.3**</u>: Annual net Arctic-North Atlantic trace element fluxes across Fram Strait, the Barents Sea Opening, and Davis Strait. Negative (positive) values indicate Arctic export to (import from) the North Atlantic Ocean. Mean value of monthly net trace element fluxes \pm standard deviation (1 σ) of monthly variations (Sep 2005 - Aug 2006).

	dFe	dMn	dCo	dZn
Gateway	[Gg·a ⁻¹]	[Gg·a ⁻¹]	[Mg·a ⁻¹]	[Gg·a ⁻¹]
Fram Strait	-2.3 ± 1.7	-1.7 ± 2.0	-186 ± 202	4.9 ± 6.2
Barents Sea Opening	2.2 ± 1.1	5.9 ± 2.7	374 ± 177	3.8 ± 1.8
Davis Strait ^A	-2.6 ± 1.3	-7.0 ± 3.3	-461 ± 147	-5.7 ± 3.5
Net Flux	-2.7 ± 2.4	-2.8 ± 4.7	-273 ± 306	$\textbf{3.0} \pm \textbf{7.3}$

5.3.6 Seasonality

Estimates of annual trace element fluxes across the Arctic Ocean boundaries based on trace element data from August 2015 (Davis Strait, GN02), October 2015 (Barents Sea Opening, GN05) and July-August 2016 (Fram Strait, GN05) are subject to uncertainty concerning seasonal variations in trace metal concentrations. Unfortunately, data on seasonal trace element concentrations in the Arctic Ocean boundary regions considered herein are lacking. Two sampling campaigns in spring and summer 2010 to the Irminger and Iceland Basins are the only available datasets, showing seasonal cycling of dFe, dMn, dCo and dZn in the high latitude North Atlantic to date (Achterberg *et al.*, 2018, 2021). In the Irminger Basin, dissolved Fe, Mn, Co and Zn in surface waters are progressively depleted and exported to depth because of primary production in spring and summer, followed by deep winter mixing which resupplies trace elements to surface waters. Trace element concentrations in deeper waters (>500 m) remained fairly constant (Fig. S5.4), a consequence of an established equilibrium between dissolution and scavenging (Achterberg *et al.*, 2018,

2021). For Fram Strait, the same is to be expected, yet superimposed on these processes is the overwhelming influence of southward transport of dFe, dMn and dCo from the Central Arctic. Arctic Ocean shelf supply is seasonally variable (Hölemann, Schirmacher and Prange, 2005; Holmes *et al.*, 2012; Kipp *et al.*, 2018), and seasonal variability is also seen in the formation of the EGC in Fram Strait (de Steur *et al.*, 2014; de Steur, Peralta-Ferriz and Pavlova, 2018; Tsubouchi *et al.*, 2018). Likewise, seasonal variability in sea ice dynamics, glacial discharge (Mortensen *et al.*, 2013), shelf benthic processing, upwelling or downwelling (Schulze and Pickart, 2012; Williams and Carmack, 2015), and the general circulation pattern on the NE Greenland shelf (Michel *et al.*, 2015) may result in pulses of dissolved trace element mobilisation in Fram Strait which are unconstrained to date.

Changing seasonal sea ice dynamics may be particularly important for future Arctic-Atlantic exchange via Fram Strait because of the multiple trace metal sources and sinks affected by shifts in sea ice seasonality. The loss of sea ice may further increase export of redox-sensitive trace element such as dMn and dCo in response to enhanced photodissolution and solubilisation processes in the surface ocean (Sunda and Huntsman, 1994; Moffett and Ho, 1996). Although, conversely, rapid increases in Arctic primary production in response to reductions in summertime sea ice cover may increase demand for micronutrient trace elements within the Arctic, making it challenging to predict net changes in lateral transfer across the Arctic basin and into the EGC. Because of data scarcity, it is therefore challenging to predict when seasonal maxima and minima of trace element transport occur, especially in the surface water masses of western Fram Strait.

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Figure 5.6: Schematic of annual dFe, dMn, dCo and dZn fluxes (in $Gg \cdot a^{-1}$) in major water masses of Arctic Ocean-high latitude North Atlantic micronutrient transport: the West Spitsbergen Current (WSC), the Barents Sea Branch (BSB), the East Greenland Current (EGC) and the Baffin Current (BC). Positive fluxes (in black) suggest net import of Atlantic micronutrients to the Arctic Ocean. Negative fluxes (in white) suggest net export of Arctic micronutrients to the high latitude North Atlantic. Red arrows (blue arrows) indicate flow path of warm and saline (cold and fresh) Atlantic waters (Arctic waters). Location of stations depicted as red dots (GN05, Fram Strait), green diamonds (GN04, Barents Sea Opening) and blue squares (GN02, Baffin Bay). For WSC, EGC and BSB: mean value of monthly net trace element fluxes \pm standard deviation (1 σ) of monthly variations (Sep 2005 - Aug 2006, **Table S5.6**). Calculation for DS conducted from the annual mean net volume flux, and uncertainty derived from error propagation including the standard deviation in annual volume flux and the standard deviation of observed dFe, dMn, dCo and dZn concentrations (error propagation). Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).

5.4 Conclusion

This study represents the first attempt to quantify fluxes of micronutrient trace elements between the Arctic and Atlantic Oceans across the gateways of the Fram Strait, Barents Sea Opening and Davis Strait. Among the Arctic-Atlantic gateways, Fram Strait is most important for dissolved micronutrient exchange which is a consequence of deep water mass movement (>500 m) across the strait. However, large uncertainties in seasonal changes remain, especially in the western part influenced by the EGC, where dFe, dMn and dCo show unusual maxima in surface waters due to pronounced Arctic export. Data deficiency is presently most problematic in determining fluxes across Davis Strait, which may be comparable in magnitude to those across the Barents Sea Opening. We show that the Transpolar Drift is the most important contributor to transport maxima in surface Fram

Strait (<500 m) including waters on the NE Greenland Shelf. This trace element-rich source water has a profound impact on the net flux of Arctic dFe, dMn and dCo to the North Atlantic. Recent investigations concerning the future of the Transpolar Drift project increasing transport of shelf-derived material (Kipp *et al.*, 2018), including trace elements towards Fram Strait (Kadko *et al.*, 2019; Charette *et al.*, 2020) suggesting a potential for increasing Arctic export of these elements in the future due to a combination of inter-linked effects associated with increased sea ice loss and shelf interaction.

Contributions from the NE Greenland Shelf to Fram Strait budgets are currently minor. Fluxes to the Arctic Ocean are dominated by advection of the Atlantic WSC. Recirculation of Atlantic waters (de Steur *et al.*, 2014; Hattermann *et al.*, 2016) may thus, exert a strong control on the amount of trace element import to the Arctic Ocean. Seasonal, interannual and decadal variability in Atlantic Water transport have been observed (Hattermann *et al.*, 2016; Tsubouchi *et al.*, 2021). The associated biogeochemical effects, particularly of long-term alteration in current regimes, remain challenging to constrain (De Jong *et al.*, 2012; Tsubouchi *et al.*, 2021). Yet, projections concerning the future of the WSC suggests an intensification of Atlantic Water supply to the Arctic Ocean (Wang *et al.*, 2020), or 'Atlantification', which may result in increased transport of dFe, dMn, dCo and dZn to the Arctic Ocean. Long-term observations at the Arctic Ocean boundaries are needed to gain a better understanding on the variability in trace element exchange between the Arctic and Atlantic Ocean, and potential impacts on phytoplankton communities and primary production.

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Author contributions

Stephan Krisch, Mariia V. Petrova, Lars-Eric Heimbürger-Boavida and Eric P. Achterberg designed the research. Sampling and analyses were performed by **Stephan Krisch**, Stephané Roig, Loes J.A. Gerringa, Rob Middag, Michiel M. Rutgers van der Loeff, Pablo Lodeiro, Manuel Colombo, Jay T. Cullen and Sarah L. Jackson. All authors contributed to the interpretation of results. The manuscript was written by **Stephan Krisch** with the help of Mark J. Hopwood and Eric P. Achterberg.

5.5 Supplementary Material

5.5.1 Quality assurance

<u>Table S5.1:</u> In-house reference materials NADW (GN04) and CAB (GN05) monitoring long-term precision of dFe, dMn, dCo and dZn analyses. Mean concentration \pm standard deviation (1 σ), n = number of measurements.

<u>Table S5.2</u>: Procedural blanks (mean concentration \pm standard deviation (1 σ)) and limits of detection (LOD) for GN04 and GN05 datasets. LOD is defined as three times the standard deviation of the procedural blank (3 σ). All values in pM.

Dataset	Analyte	Reported [nM]	-	Dataset	Analyte	Blank	LOD
	dFe	$0.55 \pm 0.03 \ (n = 87)$			dFe	22 ± 8	24
GN04 Nadw	dMn	$0.43 \pm 0.01 \ (n = 90)$	GN04		dMn	2 ± 2	7
	dCo	$0.054 \pm 0.005 \ (n = 90)$			dCo	2 ± 1	3
	dZn	$3.07 \pm 0.27 \ (n = 87)$			dZn	25 ± 18	55
	dFe	$1.20 \pm 0.09 \ (n = 69)$			dFe	64 ± 20	60
GN05	dMn	$0.29 \pm 0.02 \ (n = 71)$		C N05	dMn	17 ± 6	17
CAB	dCo	$0.058 \pm 0.006 \; (n=77)$	GINU5	dCo	3.0 ± 1.5	4.5	
	dZn	$5.73 \pm 0.48 \ (n = 73)$			dZn	171 ± 70	209

5.5.2 Trace element profiles in the East Greenland Current and the Transpolar Drift



Figure S5.1: Vertical distribution of dFe (in black), dMn (orange) and dCo (blue) in the East Greenland Current (EGC; stations 8, 9 and 25; squares) and the Central Arctic Ocean influenced by the Transpolar Drift (TPD; stations 81, 91 and 96; stars). Inlay details upper 500 m of the water column. Figure generated using OriginPro software version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

5.5.3 Dissolved Fe, Mn, Co and Zn in water mass components

<u>Table S5.3</u>: Average concentrations (in nmol·L⁻¹, nM) of dissolved Fe (dFe), Mn (dMn), Co (dCo) and Zn (dZn) in Surface Water (SURF), Upper Atlantic Water (UAW), Atlantic Water (AW), Intermediate Water (IW) and Deep Water (DW) of the (a) West Spitsbergen Current, (b) 'Middle' section, (c) East Greenland Current, (d) NE Greenland Shelf, (e) Barents Sea Opening, and (f) Baffin Current in Baffin Bay. Water mass definition as per Tsubouchi *et al.* (2018). Mean value \pm standard deviation.

Compor	nent	dFe [nM]	dMn [nM]	dCo [pM]	dZn [nM]			
	SURF	absent						
West	UAW	0.32 ± 0.03	1.79 ± 0.38	60 ± 10	1.47 ± 0.29			
Spitsbergen	AW	0.67 ± 0.32	1.11 ± 0.26	86 ± 13	2.06 ± 1.10			
Current	IW	0.64 ± 0.06	0.44 ± 0.09	79 ± 4	2.88 ± 0.86			
	DW	0.88 ± 0.19	0.37 ± 0.11	70 ± 10	3.56 ± 1.15			
	SURF		abs	ent				
	UAW		abs	ent				
Middle	AW	0.67 ± 0.21	$1.01\pm0.32^{\rm A}$	60 ± 3	2.96 ± 0.79			
	IW	$0.69\pm0.31^{\rm A}$	$0.39\pm0.11^{\rm A}$	$75 \pm 21^{\text{A}}$	$2.65\pm0.86^{\rm A}$			
	DW	0.66 ± 0.29	$0.37\pm0.15^{\rm A}$	74 ± 19	0.99 ± 0.98			
	SURF	1.02 ± 0.62	2.38 ± 1.55	112 ± 48	1.21 ± 0.56			
East	UAW	0.61 ± 0.13	1.50 ± 0.50	89 ± 23	1.02 ± 0.51			
Greenland	AW	0.84 ± 0.47	0.92 ± 0.34	90 ± 14	1.85 ± 1.18			
Current	IW	0.71 ± 0.35	0.38 ± 0.11	73 ± 24	2.57 ± 0.83			
	DW	0.94 ± 0.43	0.37 ± 0.16	66 ± 10	2.74 ± 0.83			
	SURF	1.35 ± 0.46	3.15 ± 2.23	204 ± 49	2.55 ± 1.25			
NE	UAW	1.01 ± 0.30	1.45 ± 0.64	126 ± 29	3.81 ± 1.59			
Greenland	AW	0.89 ± 0.26	0.84 ± 0.29	100 ± 18	4.22 ± 1.05			
Shelf	IW	0.85 ± 0.56	0.68 ± 0.21	76 ± 4	3.98 ± 1.39			
	DW		abs	ent				
	SURF	0.65 ± 0.16	2.17 ± 0.43	128 ± 11	1.11 ± 0.12			
Demonstra Cara	UAW	0.37 ± 0.29	1.80 ± 0.44	82 ± 9	0.64 ± 0.37			
Barents Sea	AW	0.59 ± 0.33	1.01 ± 0.64	73 ± 8	0.74 ± 0.23			
Opening	IW	absent						
	DW	absent						
	SURF	0.69 ± 0.21	2.26 ± 0.94	127 ± 9	1.19 ± 0.47			
Deffin	UAW	0.77 ± 0.13	0.63 ± 0.12	94 ± 11	1.85 ± 0.33			
Barrin	AW	1.13 ± 0.29	0.91 ± 1.00	76 ± 16	2.81 ± 0.61			
Current	IW	absent						
	DW	absent						

^A Mean of West Spitsbergen Current and East Greenland Current concentrations (same layer).

^B Concentrations obtained from two stations in Baffin Bay (BB1, BB3) sampled in Aug 2015 during GEOTRACES expedition GN02 (Colombo *et al.*, 2020). Dissolved Co (labile fraction) and Zn data unpublished (Cullen *et al.*).



5.5.4 Stable oxygen isotopic composition and radium isotopes

Figure S5.2: Distribution of oxygen isotopic composition (δ^{18} O, top left), meteoric freshwater content (top right), and activity ratios of ²²⁸Ra/²²⁶Ra (bottom left) at 10 m depth in surface Fram Strait. Meteoric freshwater contents were calculated from oxygen isotopic composition (δ^{18} O) (Meyer *et al.*, 2021), and freshwater reference δ^{18} O value of -20‰ (Bauch *et al.*, 2011; Dubinina *et al.*, 2017). Figure made using Ocean Data View, version 5.4.0 (Schlitzer, 2021).



Figure S5.3: Activity ratios of ²²⁸Ra/²²⁶Ra (RaAR) in the Central Arctic Ocean (left, in black, >85°N, top 500 m, Charette *et al.*, 2020) and Fram Strait (right, in blue, 76-81°N, entire water column) versus meteoric freshwater content calculated from oxygen isotopic composition (δ^{18} O) (Pasqualini *et al.*, 2017; Meyer *et al.*, 2021) and freshwater reference δ^{18} O value of -20‰ (Bauch *et al.*, 2011; Dubinina *et al.*, 2017). Standard errors (bars) were included in the linear approximation (red line) through program-based direct weighing. Figure generated using OriginPro software version 9.1.0. (OriginLab Corporation, Northampton, MA, USA).

5.5.5 Dissolved Fe, Mn, Co and Zn fluxes through Fram Strait (August data)

Table S5.4: August transport of dFe, dMn, dCo and dZn in the (a) West Spitsbergen Current, (b) 'Middle' section, (c) East Greenland Current, and (d) on the NE Greenland Shelf. Dissolved trace element fluxes were calculated from mean volume fluxes (V) through Fram Strait as of August 2006 (Tsubouchi *et al.*, 2018), and mean concentrations of dFe, dMn, dCo and dZn in the corresponding components sampled between 22^{nd} Jul – 1st Sep 2016 (**Table S5.3**). Negative (positive) values indicate Arctic export to (import from) the high latitude North Atlantic Ocean. Uncertainties reflect temporal variability in volume transport and include uncertainty in trace element concentration (error propagation).

Component		V	dFe	dMn	dCo	dZn		
Component		[Sv]	[Gg∙a⁻¹]	[Gg·a ⁻¹]	[Mg•a ⁻¹]	[Gg·a ⁻¹]		
	SURF	absent						
West	UAW ^A	0.22 ± 0.03	0.1 ± 0.0	0.7 ± 0.2	24 ± 5	0.7 ± 0.2		
West	AW	3.37 ± 0.41	4.0 ± 2.0	6.5 ± 1.7	541 ± 107	14.3 ± 7.9		
Spitsbergen	IW	0.95 ± 0.29	1.1 ± 0.3	0.7 ± 0.3	141 ± 43	5.7 ± 2.4		
Current	DW	2.32 ± 0.61	3.6 ± 1.2	1.5 ± 0.6	300 ± 90	17.0 ± 7.1		
	Total	6.86 ± 0.96	8.8 ± 2.4	9.4 ± 1.8	1006 ± 147	37.7 ± 10.9		
	SURF			absent				
	UAW	absent						
Middle	AW	-0.83 ± 1.86	-1.0 ± 2.2	-1.5 ± 3.3	-93 ± 208	-5.1 ± 11.4		
Middle	IW	-0.36 ± 0.45	-0.4 ± 0.6	-0.2 ± 0.3	-50 ± 63	-2.0 ± 2.5		
	DW	-1.45 ± 1.06	-1.7 ± 1.4	-0.9 ± 0.8	-199 ± 155	-3.0 ± 3.6		
	Total	-2.64 ± 2.52	-3.1 ± 2.7	-2.6 ± 3.4	-342 ± 267	$\textbf{-10.0} \pm \textbf{12.2}$		
	SURF	-0.77 ± 0.26	-1.4 ± 1.0	-3.2 ± 2.3	-161 ± 88	-1.9 ± 1.1		
East	UAW	-0.70 ± 0.15	-0.7 ± 0.2	-1.8 ± 0.7	-115 ± 38	-1.5 ± 0.8		
East	AW	-0.84 ± 0.23	-1.2 ± 0.8	-1.3 ± 0.6	-140 ± 45	-3.2 ± 2.2		
Greemand	IW	-2.51 ± 0.49	-3.1 ± 1.6	-1.7 ± 0.6	-343 ± 129	-13.3 ± 5.0		
Current	DW	-0.44 ± 0.21	-0.7 ± 0.5	-0.3 ± 0.2	-54 ± 27	-2.5 ± 1.4		
	Total	-5.26 ± 0.98	-7.2 ± 2.1	-8.3 ± 2.6	-813 ± 169	-22.4 ± 5.8		
	SURF	0.29 ± 0.31	0.7 ± 0.8	1.6 ± 2.0	111 ± 120	1.5 ± 1.8		
NE	UAW	0.26 ± 0.64	0.5 ± 1.1	0.6 ± 1.6	60 ± 150	2.0 ± 5.1		
Greenland	AW	0.19 ± 0.08	0.3 ± 0.2	0.3 ± 0.2	36 ± 17	1.7 ± 0.8		
Shelf	IW	-0.01 ± 0.01	0.0 ± 0.0	0.0 ± 0.0	-1 ± 1	0.0 ± 0.1		
	Total	0.73 ± 1.10	1.4 ± 1.4	2.5 ± 2.6	205 ± 192	5.2 ± 5.4		

^AWest Spitsbergen Current Upper Atlantic Water was absent during 2005-2006 observation (Tsubouchi *et al.*, 2018). Estimation based on assuming proportionality between layer thickness and volume transport from the West Spitsbergen Current Atlantic Water layer (in *italic*).

^B Flux calculated from mean concentration in West Spitsbergen Current and East Greenland Current (same layer) due to data scarcity.

5.5.6 Glacial dissolved Fe, Mn and Co supply

Table S5.5: Estimates of subglacial dFe, dMn and dCo discharge from Nioghalvfjerdsbrae. Calculation based on mean cavity-overturning volume rate ($46 \pm 11 \text{ mSv}$, Schaffer *et al.*, 2020), and dFe, dMn and dCo concentrations in cavity-exiting modified Atlantic Intermediate Water (mAIW, station 22) relative to cavity-entering AIW (average from station 19). Standard deviation determined by error propagation, considering variability in glacial freshwater release and dFe, dMn and dCo concentration determination. For more details, please see Section 4.3.6.

	dFe	dMn	dCo
AIW [nM]	0.61 ± 0.08	0.64 ± 0.12	0.084 ± 0.008
Modified AIW [nM]	1.31 ± 0.21	1.52 ± 0.73	0.140 ± 0.034
Flux [Mg·a ⁻¹]	56 ± 37	70 ± 85	4.9 ± 4.7

5.5.7 Trace element distribution in the North Atlantic Irminger Basin and eastern Fram Strait (West Spitsbergen Current)



Figure S5.4: Vertical distribution of dFe, dMn, dCo and dZn in the high latitude North Atlantic Irminger Basin (grey-boxed) and the West Spitsbergen Current (WSC) in Fram Strait (left and right column). Sampling conducted in Spring and Summer 2010 (stations 3-5 of expedition D350, and stations 9, 15-22 of expedition D354 in the Irminger Basin, Achterberg *et al.*, 2018, 2020), and summer 2016 (stations 1-4 of expedition GN05 in Fram Strait). Summer concentrations in Surface Water (SURF, light blue), Upper Atlantic Water (UAW, in blue), Atlantic Water (AW, dark blue), Intermediate Water (IW, brown) and Deep Water (DW, black) depicted as stars. Spring concentrations in Upper Atlantic Water (UAW, orange) and Atlantic Water (AW, red) depicted as diamonds. Water mass definition as per Tsubouchi *et al.* (2018). Figure generated using OriginPro software, version 9.1.0 (OriginLab Corporation, Northampton, MA, USA).
Chapter 5 – Arctic-Atlantic exchange of Iron, Manganese, Cobalt and Zinc with a focus on Fram Strait

5.5.8 Annual trace element fluxes through Fram Strait, the Barents Sea Opening and Davis Strait

Table S5.6: Monthly mean estimates of dissolved Fe, Mn, Co and Zn fluxes through Fram Strait (FS), and the Barents Sea Opening (BSO), with particular focus on the Fram Strait West Spitsbergen Current (WSC), East Greenland Current (EGC), Middle section (M) and NE Greenland Shelf (NEGS). Fluxes calculated from monthly mean volume transport (Tsubouchi *et al.*, 2018), and mean concentrations of dFe, dMn, dCo and dZn in the corresponding components (**Table S5.3**). Contribution of West Spitsbergen Current Upper Atlantic Water, absent during the 2005-2006 observation of volume fluxes, was estimated from assuming proportionality between layer thickness and volume transport from the West Spitsbergen Current Atlantic Water layer. Annual mean net trace element fluxes (AVG) calculated as average of monthly fluxes; the corresponding uncertainty (STD) is reported as standard deviation (1σ) to monthly variations. Negative (positive) values indicate Arctic export to (import from) the high latitude North Atlantic Ocean.

	Dissolved Fe						Dissolved Mn					Dissolved Co					Dissolved Zn							
Month	WSC	EGC	Μ	NEGS	FS	BSO	WSC	EGC	Μ	NEGS	FS	BSO	WSC	EGC	Μ	NEGS	FS	BSO	wsc	EGC	Μ	NEGS	FS	BSO
Sep 05	8.0	-9.7	-2.6	-1.2	-5.5	4.0	8.7	-8.1	-2.6	-2.1	-4.1	10.3	929	-980	-279	-167	-497	667	34	-32	-10	-4	-11.9	6.8
Oct 05	9.7	-10.0	-1.8	-0.2	-2.3	2.0	11.0	-9.0	-1.8	-0.6	-0.4	6.6	1139	-995	-190	-34	-80	386	41	-31	-6	0	3.5	3.7
Nov 05	9.1	-10.9	-0.6	0.0	-2.5	2.9	10.7	-10.1	-0.1	-0.6	-0.1	8.4	1076	-1079	-78	-21	-102	505	38	-34	-1	1	4.6	5.0
Dec 05	10.5	-10.3	-1.5	-0.1	-1.4	1.8	11.1	-9.8	-1.1	-0.8	-0.5	6.0	1217	-1059	-165	-36	-42	347	45	-33	-4	1	9.6	3.3
Jan 06	11.3	-10.0	-3.4	-2.5	-4.6	4.0	12.5	-9.0	-1.8	-5.3	-3.7	9.3	1312	-1026	-397	-383	494	623	48	-32	-7	-6	2.0	6.5
Feb 06	8.8	-10.5	1.1	-2.3	-3.0	1.8	9.7	-9.8	1.4	-5.5	-4.1	4.7	1034	-1103	106	-377	-341	306	38	-34	6	-5	4.2	3.1
Mar 06	10.3	-6.2	-5.3	-2.0	-3.1	1.4	10.9	-6.7	-3.7	-4.8	-4.2	3.2	1229	-719	-596	-322	-408	216	45	-20	-17	-4	4.3	2.2
Apr 06	13.0	-5.4	-6.9	-1.2	-0.5	1.3	12.3	-5.4	-6.2	-2.2	-1.4	3.2	1436	-574	-747	-175	-60	211	57	-17	-25	-4	11.1	2.2
May 06	9.1	-7.9	-0.2	-0.8	0.3	-0.3	10.4	-7.2	0.5	-1.7	2.0	0.3	1095	-803	-32	-122	138	-11	39	-26	1	-2	12.3	-0.3
Jun 06	9.1	-9.0	-1.2	-0.6	-1.6	2.7	9.0	-8.5	-0.7	-1.7	-2.0	6.2	1029	-944	-134	-103	-152	415	40	-29	-4	0	6.7	4.4
Jul 06	8.1	-8.6	-1.5	-1.0	-2.9	2.5	9.4	-8.3	-0.8	-2.6	-2.3	6.4	974	-882	-175	-165	-247	413	35	-27	-4	-1	1.5	4.2
Aug 06	8.8	-8.6	-3.1	1.4	-0.1	2.2	9.4	-8.3	-2.6	2.5	1.0	6.6	1006	-882	-175	-165	57	411	38	-22	-10	5	10.4	4.0
AVG	9.7	-8.9	-2.2	-0.9	-2.3	2.2	10.4	-8.3	-1.6	-2.1	-1.7	5.9	1123	-920	-238	-172	-186	374	41	-28	-6.7	-1.7	4.9	3.8
STD	1.4	1.7	2.1	1.1	1.7	1.1	1.2	1.3	1.9	2.2	2.0	2.7	144	152	229	122	202	177	6	6	7.8	3.1	6.2	1.8

5.5.9 Annual transport of dFe, dMn, dCo and dZn across Davis Strait

Table S5.7: Annual transport of dFe, dMn, dCo and dZn in components of Davis Strait. Dissolved trace element fluxes were calculated from mean annual volume fluxes (V) across Davis Strait of Sep 2005 to Aug 2006 (Tsubouchi *et al.*, 2018), and mean concentrations of dFe, dMn, dZn, and the labile fraction of dCo in the corresponding components of the Baffin Current in Baffin Bay (station BB1 and BB3, Colombo *et al.*, 2020) (**Table S5.3**). Negative (positive) values indicate Arctic export to (import from) the high latitude North Atlantic Ocean. Uncertainties reflect temporal variability in volume transport during the 2005-2006 observation of components and include the uncertainty in measured trace element concentrations (error propagation).

Component		V [Sv]	dFe [Gg·a ⁻¹]	dMn [Gg∙a⁻¹]	dCo [Mg∙a ⁻¹]	dZn [Gg∙a⁻¹]
	SURF	-1.69 ± 0.40	-2.1 ± 0.8	-6.6 ± 3.2	-398 ± 99	-4.2 ± 1.9
Davis Strait	UAW	-0.33 ± 0.55	-0.4 ± 0.7	-0.4 ± 0.6	-58 ± 96	-1.3 ± 2.1
(Baffin Current)	AW	-0.04 ± 0.35	-0.1 ± 0.7	$\textbf{-0.1}\pm0.6$	-6 ± 50	-0.2 ± 2.0
	Total	$\textbf{-2.06} \pm \textbf{0.66}$	-2.6 ± 1.3	-7.0 ± 3.3	-461 ± 147	-5.7 ± 3.5

6 Conclusions and future perspectives

PS100 provides a unique data set for investigating Fe, Mn, Co and Zn cycling at the interface between the Arctic and Atlantic Ocean. The dissolved and total dissolvable trace element data is provided as part of my PhD study and has been published in the Pangaea depository (Krisch, Roig, *et al.*, 2021) or can be found in the Source Data File in the online version of Chapter 4 (Krisch, Hopwood, *et al.*, 2021). Major aims of this project were to unravel key aspects of trace metal cycles in Fram Strait, and to establish a baseline for future investigations concerning changes in trace metal biogeochemistry as consequence of Arctic warming. Particular emphasis is put on the role of Fe and fixed N in limiting primary production in the region, factors controlling glacial Fe supply to the NE Greenland Shelf, and quantification of micronutrient trace element fluxes (dFe, dMn, dCo and dZn) between the Arctic and the high latitude North Atlantic Ocean.

Surface primary production in Fram Strait is governed by two contrasting nutrient regimes (Chapter 3). The North Atlantic supplies fixed N-rich and dFe-depleted Atlantic Water to the eastern part of Fram Strait, and the Arctic Ocean supplies dFe-rich and fixed N-depleted Polar Surface Water to the western part of Fram Strait. This results in a pronounced eastto-west gradient in between Svalbard and coastal Greenland. Late summer surface phytoplankton community growth was predominantly limited by the availability of fixed N, suggesting that the areal and seasonal extent of primary production in the region is not prolonged by an earlier onset of phytoplankton growth, but determined by advection and incorporation of WSC and subsurface-derived fixed N. Atlantic Water volume transport to the Arctic has remained rather stable for the past ~30 years (Tsubouchi et al., 2021), suggesting that fixed N supply to Fram Strait has not increased while sea ice loss has continued (-40% between 1980 and 2018, Norwegian Polar Institute, 2020). Further increases in regional net surface primary production and carbon sequestration are therefore unlikely, perhaps decoupling Fram Strait, as of today, from the general trend of increasing net primary production across the Arctic (Renaut, Devred and Babin, 2018; Lewis, Van Dijken and Arrigo, 2020).

The critical role for additional supply of fixed N to increases in net primary production has previously been suggested for surface waters on the NE Greenland Shelf (Lara *et al.*, 1994)

and the shelf slope to the north of Svalbard (Randelhoff, Sundfjord and Reigstad, 2015). Yet, this is the first time that factors constraining net primary production in Fram Strait have been investigated 'in-situ' on the basis of phytoplankton responses to macro- and micronutrient additions, contributing to the limited pool of observations investigating nutrient limitation in the Arctic (Ortega-Retuerta *et al.*, 2012; Taylor *et al.*, 2013; Mills *et al.*, 2018). The wide-spread availability of dFe in surface Fram Strait is a consequence of efficient supply from the Arctic Ocean. Only the very eastern part evidenced surface Fe deficiency relative to typical phytoplankton requirements. This, together with the greatest observed chlorophyll-a increases in N+Fe addition experiments, suggests that phytoplankton communities may experience dFe stress later in the season, especially if dFe supply were to be reduced relative to fixed N supply, for example as a result of progressing Atlantification.

In future, short- and long-term trends in Atlantic Water advection and its effects on primary production in Fram Strait may, to some extent, be monitored through the use of satellites. Satellite remote sensing of sea surface salinity and sea surface temperature show a warm and saline West Spitsbergen Current (WSC) that is distinctly different to its counterpart, the cold and fresh East Greenland Current (EGC) (Acker and Leptoukh, 2007). The satellite-determined flow-field of the WSC matches satellite observations of summer surface chlorophyll-a (Fig. 3.1b) that functions as an indicator for phytoplankton biomass, and contributes further evidence that surface primary production across the region relies largely on the advection of fixed N with saline Atlantic waters in summer. Monitoring of sea surface salinity, temperature and chlorophyll-a combined may thus help to unravel short- and long-term effects of changes in Atlantic Water and Polar Surface Water advection, its correlation to sea ice retreat and effects on surface primary production in the region.

Sensors operating on autonomous underwater vehicles provide 'in-situ' macronutrient data in much higher resolution (Johnson and Needoba, 2008) and may extent fixed N monitoring into ice-covered areas of Fram Strait that are 'invisible' to satellite observations. While sensor trace element analysis of seawater has yet not produced reliable data at low ambient concentrations (e.g. Milani *et al.*, 2015; Geißler *et al.*, 2017), preliminary results of nitrate and silicic acid-detection with AUVs operating in Fram Strait highlight the dynamic nature of nutrient regimes in Fram Strait and the need for higher resolution data beyond the snapshot-like sampling conducted by shipboard expeditions if the seasonal cycle and feedbacks of Atlantification on species composition and the carbon pump is to be understood (Wietz *et al.*, 2021). Until robust sensor analysis of dFe and other micronutrients in open-ocean waters is possible, the correlation between silicic acid and Fe in surface Fram Strait (Fig. 3.2) suggests that Si could be used as a proxy for surface dFe supply to Fram Strait, which requires further examination but has great potential to monitor Arctic Ocean dFe export to the North Greenland Sea in high resolution through AUVs.

Because primary production in Fram Strait is, as of today, limited by the availability of fixed N, future research should include phytoplankton species analyses to investigate the contributions of diazotrophs to nitrogen fixation and oceanic N inventories in the region. This can be done, for example, through sequencing of phytoplankton taxa for the nitrogenase (nif) genes that are expressed in diazotrophs growing on N₂ (Zehr, Mellon and Zani, 1998; Blais et al., 2012). In the Arctic Ocean Chukchi Shelf Sea, nitrogen fixation may offset 40% of the nitrogen loss caused by denitrification (Sipler *et al.*, 2017), and may thus play an important role for non-diazotrophic primary producers in seasonally fixed Nlimited surface waters of the region (Ortega-Retuerta et al., 2012; Mills et al., 2018). There, diazotrophic growth occurs under low ambient fixed N (<2 µM) concentrations (Sipler et al., 2017) and, in consequence to the high Fe requirement in nitrogenase (Kustka et al., 2003), is likely promoted by high dFe availability in surface waters (Kondo *et al.*, 2016; Vieira et al., 2019). Similar conditions are found in the surface EGC and surface waters on the NEGS (Fig. 3.2). Whether diazotrophs contribute to fixed N supply in Fram Strait, and if this N-fixation is depending on Arctic Ocean dFe supply, warrants further investigation. With Fe being involved in many enzymic reactions, it seems plausible that the southward advection of trace element replete surface waters from the Arctic Ocean is not only influencing phytoplankton species composition (Fig 3.4) (Twining and Baines, 2013), but may also shape carbon and nitrogen cycling (Morel and Price, 2003; Morel, Milligan and Saito, 2003) in the North Greenland Sea.

On the NE Greenland Shelf, Fe enrichment from glacial discharge and sediment sources was evident downstream from Nioghalvfjerdsbrae and Zachariæ Isstrøm (Chapter 3, 4). Nioghalvfjerdsbrae drains ~6% of the Greenland Ice Sheet (Rignot and Mouginot, 2012) and is the single most important source of freshwater onto the shelf; approximately 80% of Nioghalvfjerdsbrae non-calving mass loss is through subglacial freshwater discharge and melting of the marine terminus (Wilson, Straneo and Heimbach, 2017; Schaffer *et al.*, 2020). Subglacial discharge from the cavity underneath Nioghalvfjerdsbrae floating ice

tongue accounts for <1% to southbound dFe fluxes across Fram Strait (Chapter 5). In the light of previous Greenlandic studies (e.g. Bhatia, Kujawinski, *et al.*, 2013; Hawkings *et al.*, 2014), Nioghalvfjerdsbrae discharge might have been hypothesized to produce a significantly, perhaps orders of magnitude, greater dFe flux associated with low salinity runoff (Chapter 4). However, downstream of Nioghalvfjerdsbrae, Greenland's largest floating ice-tongue, subglacial Fe supply to the shelf is limited by the lack of efficient stabilization of dFe in cavity-exiting waters, likely due to low organic carbon (i.e. ligand) content of meltwater (Hood *et al.*, 2009; Bhatia, Das, *et al.*, 2013; Paulsen *et al.*, 2017). A combination of the restricted ligand supply in cavity-entering waters (Ardiningsih *et al.*, 2020), and the prolonged residence of waters beneath the Nioghalvfjerdsbrae floating ice tongue drives efficient removal of the non-stabilized dFe fraction during estuarine mixing. This has a subtle, but significant implication for how lateral dFe fluxes are scaled.

By combining cross-shelf metal distributions and radium (226 Ra, 228 Ra) and iron (δ^{56} Fe) isotope measurements at the glacier calving front with the well characterized physical oceanography in the region, this study is the first to explicitly show that cavity overturning circulation must be the dominant factor controlling subglacial dFe export from Nioghalvfjerdsbrae. As the rate of cavity overturning is almost completely independent of freshwater discharge rate, our findings challenge the perception that glacial dFe shelf supply scales with glacial freshwater release. Prior work has, to our knowledge, universally scaled fluxes with freshwater discharge rate (Bhatia, Kujawinski, et al., 2013; Hawkings et al., 2014; Stevenson et al., 2017), yet, we present multiple lines of evidence that such scaling is not appropriate at Nioghalvfjerdsbrae. Cavity overturning at Nioghalvfjerdsbrae, driven by subglacial melting of the floating ice-tongue (Wilson and Straneo, 2015; Schaffer et al., 2020), produces a flux 10-times larger than expected based on freshwater discharge rate alone. Similar conditions may be found in northern Greenland (Wilson, Straneo and Heimbach, 2017; Washam et al., 2019) and Antarctica (Shepherd, Wingham and Rignot, 2004; Stevens et al., 2020), as also there, subglacial melting comprises the majority of glacial freshwater discharge to the shelf. If the constraints found at Nioghalvfjerdsbrae may apply to subglacial dFe export from glaciers on a broader scale in fjords without similar extensive ice cavities, remains an open research question.

The two-dimensional inflow-outflow concept that is described for Nioghalvfjerdsbrae, consisting of a warm and saline shelf bottom water inflow, upwelling near the glacial source, formation of glacially modified water and offshore transport at intermediate depths,

is observed around Greenland and Antarctica, for example, in Sermilik (SE-Greenland, Cape *et al.*, 2019), Nuup Kangerlua (SW-Greenland, Meire *et al.*, 2016), Bowdoin Fjord (NW-Greenland, Kanna *et al.*, 2020) or Pine Island Glacier (Amundsen Sea, Antarctica, Gerringa *et al.*, 2012). Contrasting fjord-inbound to fjord-outbound waters using the rate of overturning circulation at a given flux gate window, is likely a better representation of glacial nutrient supply to downstream environments, because this concept accounts for all combined estuarine processes, including estuarine loss or gain and also biological uptake or sedimentary release. The difference between this approach and earlier work scaling to freshwater discharge may also result in profound differences for species other than Fe. For example, we find limited evidence of a significant glacier-associated silicic acid source at Nioghalvfjerdsbrae, perhaps questioning the interpretation of silicate data downstream of Greenlandic glaciers elsewhere (Hawkings *et al.*, 2017).

In Svalbard, microbial transformations of glacier-derived sediments have shown to increase Fe lability and resulted in a sedimentary flux of dFe into fjord bottom waters (Laufer-Meiser *et al.*, 2021). Glacial upwelling of fjord bottom waters (Meslard *et al.*, 2018) may thus supply benthic Fe to near-surface waters. In the light of our findings at Nioghalvfjerdsbrae where sediment-sourced dFe is evident in cavity-exiting waters and ligands and extended subglacial residence time limit dFe export (Chapter 4), deep water that is advected over broad shelf regions may approach Fe-saturation before being in contact with glacial freshwater dFe. In extreme cases, this may result in the lack of freshwater dFe addition to glacially modified waters at the point of subglacial discharge onto the shelf. While this may explain statistically insignificant dFe enrichment in subglacial discharge relative to non-glaciated stations downstream to the Ross Ice Shelf (Antarctica, Marsay *et al.*, 2017), the global importance of 'ligand-limitation' restricting glacial dFe export remains a matter of future investigation.

Presently, subglacial dFe discharged from Nioghalvfjerdsbrae does not reach the euphotic zone, and is thus largely unavailable to phytoplankton communities on the shelf. However, continuous thinning and retreat of the marine terminus, as projected in coming decades (Choi *et al.*, 2017; Mayer *et al.*, 2018), may increase glacial dFe export to shelf surface waters (Carroll *et al.*, 2015). With the ultimate retreat of glaciers onto land, surface runoff supplies dFe primarily into fjord surface waters. Because of wide-spread N-limitation (Chapter 3), changing dFe fluxes alone is unlikely to increase net primary production on the NE Greenland Shelf, yet as a case study in ice shelf retreat, research concerning the

future of Nioghalvfjerdsbrae may be valuable to project future shifts in Antarctic glacial micronutrient supply and consequences to primary production in environments where Fe is a limiting nutrient for primary production (e.g. Alderkamp et al., 2012; Herraiz-Borreguero et al., 2016; Merwe et al., 2019). Research concerning Antarctic glacial dFe discharge is hampered by poor mechanistic understanding of Fe biogeochemistry inside subglacial cavities, lack of knowledge concerning physical constraints of meltwater discharge, and general inaccessibility of glacial sites. This leads to poor representations of the Fe cycle in models which may be a cause of uncertainty in future trends of Southern Ocean productivity (Person et al., 2019). Nioghalvfjerdsbrae, on the other hand, is one of the best studied marine-terminating glacial systems worldwide. Its geometry and susceptibility to physical forcing are well constrained, and moorings on the shelf continuously monitor cavity-shelf exchange (Wilson and Straneo, 2015; Schaffer et al., 2017, 2020). Furthermore, Nioghalvfjerdsbrae shows severe signs of destabilisation. The break-off of Spalte Glacier in July 2020 has likely altered dFe discharge and potentially increased dFe supply to surface waters in consequence to decreased cavity residence time and a more direct connection between freshwater and the shelf ocean. Coupling physical observations to trace element data from Nioghalvfjerdsbrae in future is therefore likely to be highly insightful, especially if the existing sensor arrays can be expanded to include fixed N, silicic acid or dFe measurements.

The WSC and EGC are the dominant drivers of Arctic-Atlantic trace element exchange in Fram Strait (Chapter 5). Both currents contribute ~80% to observed dFe, dMn, dCo and dZn fluxes across Fram Strait. The NE Greenland shelf is of only minor importance and comprises ~10% of gross micronutrient transport rates, making the shelf an equally important source of dFe to transport in the EGC Surface Water. An array of trace elements shows surface dFe, dMn and dCo maxima in the EGC are not locally sourced but arise from southward advection of trace elements from the Central Arctic Ocean within the Transpolar Drift. Fram Strait, thus receives trace element input from sediments and riverine discharge on the Siberian Shelf. It may seem counterintuitive that Fram Strait region is perhaps equally influenced by trace element sources on the NE Greenland Shelf, and sediment and freshwater sources from 3000 km-distant shelf areas. However, dFe transport across the Arctic Ocean is assisted through efficient stabilization with dissolved organic material in low salinity surface waters (Slagter *et al.*, 2017; Charette *et al.*, 2020), while waters in Fram Strait are generally depleted in ligand material (Ardiningsih *et al.*, 2020) and regional restrictions such as to subglacial dFe discharge apply (Chapter 4). Furthermore, the longrange advection of the Transpolar Drift surface plume towards Fram Strait benefits from the presence of sea ice that protects from wind-induced mixing and also restricts biological drawdown.

Together with the most recent synopsis of volume fluxes across Fram Strait (Tsubouchi *et al.*, 2018), southbound transport of dFe from the Arctic Ocean to the North Atlantic, including the NE Greenland Shelf, is estimated to 11.9 ± 1.9 Gg·a⁻¹. This transport is counter-balanced by a northbound dFe flux of 9.7 ± 1.4 Gg·a⁻¹ from the Atlantic to the Arctic Ocean. Combined, Fram Strait exports net 2.3 ± 1.7 Gg·a⁻¹ dFe to the high latitude North Atlantic. Transport in Atlantic waters across the Barents Sea Opening towards the Arctic Ocean contributes further 2.2 ± 1.1 Gg·a⁻¹ to Arctic-Atlantic dFe exchange, and is approximately balanced by Arctic export of 2.6 ± 1.3 Gg·a⁻¹ dFe to the North Atlantic Ocean through Davis Strait. The data from Fram Strait, the Barents Sea Opening and Davis Strait combined suggests that the Arctic Ocean is a net source of 2.7 ± 2.4 Gg·a⁻¹ dFe to the North Atlantic To the North Atlantic Ocean. Among the Arctic-Atlantic gateways, Fram Strait is the most important for dFe exchange between the ocean basins which is a consequence of deep water transport across the strait. This study is the first to quantify trace element fluxes between the Arctic Ocean and the high latitude north Atlantic.

Arctic Ocean dFe export is perhaps not only important to surface primary production in Fram Strait (Chapter 3) but may be essential to phytoplankton communities further downstream the East Greenland Current. Phytoplankton in large parts of the high latitude North Atlantic displays growth limitation caused by dFe stress (Nielsdóttir *et al.*, 2009; Ryan-Keogh *et al.*, 2013; Browning *et al.*, 2019). If this is the case for the Greenland Sea, or if the EGC contributes to surface dFe availability there, remains a matter of future investigation. The importance of Arctic Ocean trace element supply to primary production in the Greenland Sea should be investigated by trace element sampling and a series of bioassay experiments covering the east-to-west gradient in nutrient regimes that is suggested from our data in Fram Strait. Incubation experiments should, besides fixed N and Fe, also include Co and vitamin B12 additions, as Surface Waters in the WSC evidenced pronounced dCo depletion that may be colimiting the seasonal extent of phytoplankton community growth.

Preliminary results from expedition MSM85 to the western boundary of the Greenland Sea (unpublished), suggests that Arctic Ocean dFe may be exported much further south than

Fram Strait, potentially contributing to observed dFe maxima in the EGC off South Greenland (Achterberg *et al.*, 2018; Tonnard *et al.*, 2020). In the light of restricted subglacial dFe export to the NE Greenland Shelf (Chapter 4), glacial dFe supply to coastal SE Greenland (Cape *et al.*, 2019) may be less significant than currently perceived (Hendry *et al.*, 2019; Wadham *et al.*, 2019), with the dominant component originating from the Arctic Ocean instead. Future research, e.g. through the use of Ra isotopes (Fig. S5.3), might establish how far south the influence of the Transpolar Drift can be traced (Rutgers van der Loeff *et al.*, 1995, 2018; Kipp *et al.*, 2018). Understanding the relative importance of dFe sources in the EGC downstream to Fram Strait is crucial to project effects of climate change on dFe availability in the high latitude North Atlantic. Ultimately, biogeochemical models concerning the future of North Atlantic productivity should incorporate Arctic Ocean-derived micronutrient sources and aim to represent the unusually elevated micronutrient concentrations advected across the Arctic in the Transpolar Drift.

As for the future of Arctic-Atlantic micronutrient exchange, increased advection of shelf material to the Central Arctic Ocean and towards Fram Strait (Kipp et al., 2018; Charette et al., 2020) may increase Arctic Ocean micronutrient export. On the other hand, retreat of sea ice decreases water column stability and enhances phytoplankton drawdown (Arrigo and van Dijken, 2015; Falk-Petersen et al., 2015; Henley et al., 2020), and may thwart increases in Arctic Ocean micronutrient export. Paucity in water mass movement and trace element data, between the Central Arctic Ocean and Fram Strait in particular, make it currently impossible to draw conclusions on the future of Arctic Ocean micronutrient export. Conversely, Atlantic Water volume transport to the Arctic Ocean has remained rather stable for the past 30 years (Tsubouchi et al., 2021), suggesting that WSC dFe transport to the Arctic Ocean has not substantially changed. Yet, as the Atlantic Meridional Overturning Circulation is weakening (Caesar et al., 2021) and Arctic Ocean sea ice declining (Boé, Hall and Qu, 2009; Notz and SIMIP Community, 2020), this may in future affect Atlantic Water volume transport across Fram Strait (Wang et al., 2020; Tsubouchi et al., 2021), with potential consequences for fixed N and dFe availability in downstream waters. A series of surveys capturing trace element biogeochemistry in, upstream and downstream of Fram Strait are suggested to project the future of Arctic-Atlantic micronutrient exchange and potential perturbation in Arctic Ocean and high latitude North Atlantic primary production.

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8 Statement of declaration

I, Stephan Krisch, born on 13th March 1988 in Fulda, hereby declare that I have written this Ph.D. thesis independently, under compliance of the rules for good scientific practice of the German Research Foundation. I declare that I used only the sources, the data and the support that I have clearly mentioned. Moreover, I assure that this Ph.D. thesis has not been submitted for the conferral of a degree elsewhere, neither in part or as a whole, and that none of my academic degrees has ever been withdrawn. Published manuscripts are identified at the relevant places.

Stephan Clush

(Stephan Krisch)

Kiel, 03.06.2021

Wer nicht von dreitausend Jahren Sich weiß Rechenschaft zu geben, Bleibt im Dunkeln unerfahren, Mag von Tag zu Tage leben.

Johann Wolfgang v. Goethe (1749–1832).