Below, we address comments from Reviewer 1 (RC1), and Reviewer 2 (RC2). We cluster each comment and separate them as “1” Reviewer comments, “2,3” are responses and revisions.

REVIEWER 1

1) The manuscript of Krause et al. presents interesting results concerning biogenic silica production and export levels as well as estimates of kinetic constants from an opportunistic sampling near the Svalbard Archipelago in the Arctic Ocean by late spring. The data presented are the first direct (silicon–32 method) measurements of biogenic silica production in the Arctic Ocean, which in themselves deserve publication. From these data, the authors then attempt to establish the potential control of diatom production by the availability of silicic acid as well as the contribution of diatoms to total primary production. However, I think the authors are pushing their limited data set much too far and that the manuscript should be shortened by getting more concise.

2,3) We thank the reviewer for the constructive criticism, these have strengthened the manuscript. Below, we address the concerns. The revisions are aimed to both address these issues and make the manuscript more concise.

1) Firstly, I find it difficult to understand why the authors focus on the so-called Egge & Aksnes 2 µM H4SiO4 threshold value, as it is clear that the data from this publication have been wrongly interpreted in several past publications (which is recognized by the authors besides).

2,3) We agree with the reviewer and the focus on this apparent threshold value is due to its wide use in the field. As of August 2018, the Egge & Aksnes (1992) manuscript has been cited over 700 times, and many explicitly regard this 2 µM threshold for diatom microplankton dominance among many systems. This type of prose has been reduced (now just in the discussion (line 480); however, given this is the threshold embraced by the community it must be acknowledged.

1) I suggest just using their kinetic values to discuss the potential limitation of diatom uptake by H4SiO4 availability, and then shortly discuss hypotheses for growth limitation, which is another point not directly assessed in this study. ON the other hand, authors might consider that the actual limitation starts under 2 times KS.

2,3) The original version discusses kinetic limitation between lines 434 to 455, followed by a section discussing the possibility that silicic acid may be low enough to limit diatom growth (line 459 – 462). If we interpret the reviewer correctly, then “under 2 times KS” (i.e. half of the half-saturation constant) is the silicic acid concentration when uptake (i.e. Vb) is 25% of maximum uptake (i.e. Vmax) which is the same metric we use to diagnose potential growth limitation (line 461). We have made this clearer (e.g. denote the equivalence of “under 2 times KS” and Vb/Vmax <0.25) in the revision (line 473-474).

1) The comparison between nitrate and silicic acid concentrations is not very clear. First, they mention a 2.5 slope (Figure 5) between nitrate and silicic acid, which means that nitrate is taken up 2.5 times faster than silicic acid, and then authors take a 1:1 ratio to discuss the potential for silicic acid limitation. I can imagine that they are trying to decipher the relative contribution of siliceous vs. non-siliceous (e.g. Phaeocystis) components of the phytoplankton community but this should be clearly indicated. On top of that, the use of a 1:1 Si:N ratio is questionable (large species–specific variations, see below for Si:C).

2,3) The approach silicic acid versus nitrate drawdown has been used elsewhere (Monterey
Bay, Brzezinski et al. 1997; Barents Sea, Rey et al. 1987; Southern Ocean diatom cultures, Takeda 1998). We agree with the reviewer that this nutrient data includes drawdown of nitrate from other organisms, likely *Phaeocystis*, hence the slope exceeds 1 (i.e. nitrate drawn down faster than silicic acid). Most polar culture work focuses on Fe-limitation (e.g. Takeda 1988, Nature) and Southern Ocean clones; however, under Fe-replete conditions Takeda (1998) reported Si:N between 0.73 (*Chaetoceros dichaeta*) and 1.2 (*Nitzschia* sp.), the average among these clones is 0.97, not unlike the 1:1 ratio from Brzezinski 1985. In the revision, we make this point with more clarity and provide the Takeda (1998) study as a literature basis for the 1:1 ratio (beyond the canonical Brzezinski stoichiometry) and also include new culture data in review (Lomas et al., which Krause is co-author on this manuscript) which examined 11 polar diatom clones (lines 416-424).

1) The contribution of diatoms to primary production is also another weak point of the ms. The calculation is based on a transformation of rSi to rC by using the average Brzezinski' ratio of 0.13. This is a very simplistic way of addressing this important question as this ratio is known to be subject to large species–specific variations (e.g. Brzezinski gives a Si:C biomass range of 0.15 ±0.04 for large diatoms, which could result in a ~2 times range for rC estimates). This is somehow risky business and should, at least, be acknowledged and discussed.

2,3) As with the previous point, we agree that there is variability within the stoichiometry. While admittedly simplistic, we also have coarse resolution (n = 6 coupled measurements), which (in our opinion) do not merit as sophisticated approach given it would not be robust; this data coupling was serendipitous (hence the low n value) but does provide a first-order estimate. We have used the Lomas et al. (in review) diatom Si:C ratios (see methods, lines 218-223), which changed the magnitude of the estimates but not the general interpretations: 1) diatoms quantitative contribution to primary production is “boom and bust” and 2) even when diatom biomass is relatively low, their contribution to production can still be quantitatively important (e.g. 25%). Additionally, the new analysis is potentially conservative (line 510) given any movement of the Si:C ratio used toward the canonical Brzezinski ration increases the proportion of production attributed to diatoms.

1) Finally, the authors present data for direct diatom cell export but the underlying issue is not clearly stated: Do they want to compare direct diatom sedimentation by mass sinking to other export vectors such as repackaging? If yes this should be clearly stressed.

2,3) The reviewer’s interpretation of our intent is correct, we suggest that the reason why cellular export is similar to previous studies, despite biogenic silica export being higher than other studies, is consistent with repackaging which we termed “food web effect.” We have revised this for clarification (paragraph starting on line 577).

1) line 28 : "diatom cellular export" – the wording is misleading (could be export from a diatom cell). I'd rather use "export of diatom cells".

2,3) Changed as suggested, here and in other places.

1) line 65 : " A more recent analysis demonstrated a decline in pre-bloom [Si(OH)4] concentrations by 1–2 µM across the north Atlantic subpolar and polar regions over the last 25 years (Hátún et al., 2017); this is consistent with the general Arctic region being a net exporter of silicic acid (Torres-Valdés et al., 2013)." – I don't see the consistence between the decrease of H4SiO4 concentrations and the net exportation of this nutrient; please rephrase.

2,3) This is rephrased, e.g. removing “this is consistent with the general Arctic region being a
net exporter of silicic acid (Torres-Valdés et al., 2013)” (now line 67).

1) line 68: "This is in stark contrast to the 10–60 µM [Si(OH)4] observed in the surface waters of the Southern Ocean and the marginal ice zone around Antarctica (Nelson and Gordon, 1982; Brzezinski et al., 2001), where [Si(OH)4] is unlikely to limit the rate of diatom production or biomass yield." – I disagree; There are ample references to state that actually the reverse is true, due to sometimes unusual high Ks (e.g. Nelson & Tréguer MEPS 1992, Nelson et al. DSR II 2001, Mosseri et al. DSR II 2008).

2,3) The reviewer is correct as kinetic limitation (i.e. ambient silicic acid limits the rate of diatom silica production) is clearly observed in the Southern Ocean. Our intent (which was not clearly conveyed) was to contrast the effects of the high silicic acid in the Southern Ocean vs. the Arctic. This is rephrased “… where [Si(OH)4] is unlikely to limit diatom growth unless iron is replete, and stimulates exceptional blooms which consume Si, or assemblages are highly inefficient for Si uptake." (line 69-71).

1) line 76: "… and a 2 µM threshold [Si(OH)4] defines where diatoms are outcompeted by flagellates (Egge and Aksnes, 1992)." – I strongly disagree with that sentence. The work of Egge and Aksnes did not evidence any real threshold (no kinetic values measured) and just merely indicated areas of realized niches for diatom vs. flagellates with regards to Si vs. P availability. Please do not cite this reference in such a way that was even not addressed by the authors of this paper. + as indicated above.

2,3) We agree with the reviewer, especially in the lack of physiological data used in the original study to assess a threshold silicic acid; please see reply to general comment. We have revised by using more specific language “Egge and Aksnes (1992) data set shows diatoms may be outcompeted by flagellates when [Si(OH)4] <2 µM, a value which is more reflective of an ecological niche opposed to a physiological threshold as has been purported in numerous citations of these data.” (line 480-483).

1) line 137: "… suggesting that N was likely more important than P for primary production." – As authors refer to absolute concentrations, the correct phrasing should be: "… suggesting that N was likely more important than P for potentially limiting primary production." 2,3) Changed as suggested.

1) line 138: "These phosphate data are not discussed." – Even though a range would be welcome.

2,3) Revised line 145 (e.g. “These phosphate data (0.1 – 0.6 µM in the upper 50 m) are not discussed.”)

1) line 153: "… fixed with an aldehyde mixture of hexamethylenetetramine-buffered formaldehyde and glutaraldehyde at 0.1 and 1% final concentration, respectively, as suggested by Tsuji and Yanagita (1981) …" – although this should be OK this is not the usual fixative for diatoms (acidic Lugol preferred), partly due to its toxicity for the microscopical examiner.

2,3) Agreed. Given the interdisciplinary nature of the cruise and the lack of excess operation time, this fixative was used by the Norwegian Polar Institute group to examine a wide range of protist groups from one sample; these other protist groups are beyond the scope of this communication.

1) line 164: "… neutral density screened bags …" – please mention the photometric levels used.
2,3) Added “… neutral density screened bags simulating 50%, 20% and 1% of irradiance just below the surface.” (line 171)

1) line 207: "Export rates were calculated using the standing stock measurements, length of deployment, and trap opening area." – Please give the model/type of sediment trap.
2,3) Added “KC Denmark design (outer diameter 72 mm, length 450 mm).” (line 127)

1) line 260: "… except for the Hinlopen ice algae, where the melt water …" – Is that naturally–melted ice or meltwater produced by ice melting in the lab? Please clarify.
2,3) Thank you for the question, this has been clarified, e.g. “… water, which was melted at ambient air temperature on the vessel …” (line 277).

1) Line 331: " Brown et al., 2003 " – Comment: For some strange reason L. Brown's incubations lasted for only 6 hours, which renders her production results questionable.
2,3) We agree with the reviewer; however, given the limited data from the Northeast Atlantic, we prefer to be thorough and include the Brown et al. publication here.

1) line 339: "… Varela et al. (2013) recently reported that [Si(OH)4] in surface waters (>5 µM) are unlikely to be significantly limiting to diatoms in any sector of the Bering, Chukchi or Beaufort Sea regions.” – Although for Subarctic waters Brown et al. (2003, mentioned just above) kinetic experiments show a strong limitation (non-saturating kinetics) up to 30 µM.
2,3) We agree with the reviewer; however, the goal of this sentence is to isolate the Canadian- & United-States Arctic waters with the European Arctic waters. We add the Brown et al. (2003) kinetic data in a section below (e.g. with Allen et al. 2005, Kristiansen et al. 2001 discussion in the paragraph starting at line 445).

1) line 387: " Suboptimal silicon availability affects the rate of diatom bSiO2 production and can limit their growth. A widely cited [Si(OH)4] threshold, below which diatoms will be outcompeted by other phytoplankton, is ~2.0 µM; this metric was derived from a comparison of diatom abundance (relative to total microplankton) versus [Si(OH)4] during mesocosm experiments in a Norwegian fjord system (Egge and Aksnes, 1992)." – should be removed: No need to discuss this threshold as it is mentioned that it is strongly criticized (and see my comment above).
2,3) Thank you for the perspective; this section will be removed (please see response to earlier comments on this topic).

1) line 410: " This indeed indicates that phytoplankton can deplete nitrogen to levels below detection while they appear unable to deplete Si(OH)4 pools below 0.5 µM, which would indicate 0.5 µM is the ultimate Si(OH)4 concentration required to support diatom growth." – I disagree with this interpretation. The 0.5 µM Si level just reflects the residual H4SiO4 stock after complete removal of nitrate.
line 422: "… if diatoms are limited by an absolute [Si(OH)4] (e.g. 2 µM), …" – This is speculative: By what evidence is this proposition supported?
2,3) Given the reviewer’s comments for the paragraphs starting in line 405 (i.e. line 410 comment) and line 41 (line 422 comment), these paragraphs have been revised (now line 441 – line 444).

1) line 436: "… the relationship between Vb and [Si(OH)4] also supports that Si regulates diatom productivity to some degree." – The large dispersion of data points on Figure 5
results in a very weak relationship, so that there is certainly something else explaining the low realized Vb at the 4.5 µM H4SiO4 level.

2,3) The reviewer is correct, there is variability. But please note these data are from all diatom assemblages sampled among all stations and depths; thus, the linearity of the relationship would not be expected to be high, in fact, we were surprised to see 71% of the variability explained (when Hornsunddjupet excluded) given so many assemblages. However, we feel the Fig. 5B data, which integrates all samples, is the most conservative way to estimate the aggregate Ks value for euphotic diatoms among all stations at the time of this cruise. We also note that the incorrect slope and R2 were plotted in the original version of Fig 5B (now corrected).

1) line 443: "… Allen et al. (2005) observed a linear response in Vb between ambient and 5 µM [Si(OH)4], which suggests uptake did not show any degree of saturation at this concentration." – Also in Brown et al. (2003); as mentioned above.

2,3) The Brown et al. (2003) reference has been added here, as indeed, it is the original source of the Allen et al. 2005 Si-uptake data (e.g. line 454).

1) line 517: "At van Mijenfjorden, the rate of export in the upper 40 m represented 39% of the ∫bSiO2 standing stock (23.3 mmol Si m-2) in the same vertical layer." – I don't understand as from Table 1 it seems that the standing stock is 10.8 and the export 9.03?

2,3) Thank you for the observation, this is clarified. We now reference Fig. 2C as the source of the van Mijenfjorden integral data (line 542). Table 1 integrates biogenic silica stock and production to 20 m (i.e. deepest depth among all profiles) whereas the shallowest depth for sediment traps among all deployments was from 40 m. For van Mijenfjorden, we have biogenic silica measurements down to 50 m (Fig. 2C), which allows for the comparison.

1) line 524: "The rate of bSiO2 export was also at least a factor of four higher than ∫ρ in the upper 20 m." – I was not able to find where did this come from.

2,3) Thank you for the observation, this is a general trend among stations in Table 1 (i.e. biogenic silica export was much higher than integrated biogenic silica production). This has been revised “The rate of bSiO2 export among all export- and production stations was also at least a factor of four higher than ∫ρ in the upper 20 m (Table 1)." (line 549, 550).

Below, we address comments from RC2. We cluster each comment and separate them as “1” Reviewer comments, “2,3” are responses and revisions. A pdf version (bg-2018-226-RC2-supplement_Krause_etal_response) of this response has been uploaded in the supplement.

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REVIEWER 2

1) Krause et al. investigated phytoplankton, especially diatoms, and nutrients at 9 stations in the Atlantic sector north of 76°N. They measured silicate, nitrate plus nitrite, chlorophyll a, biogenic silica, determined diatom assemblage, estimate productivity and export (based on sediment traps). The silicic acid concentration in the upper 50 m was always below 5 µmol L\(^{-1}\) and at most stations below the nitrate plus nitrite
concentration. At several stations $[\text{Si(OH)}_4]$ was below 1 or even 0.5 $\mu\text{mol L}^{-1}$ in the upper 20 m. In order to investigate Si uptake limitation, the authors performed on board growth experiments over a range of $[\text{Si(OH)}_4]$ at 4 stations. Michaelis-Menten functions for silicic acid uptake (Eq.1) were fit to the data yielding estimates for maximum uptake rates ($V_{\text{max}}$) and half- saturation constants ($K_S$). Let me suggest listing these estimates in a table. The estimates for $K_S$ are much higher than some estimates (for different diatom species) reported in the literature (for example, Paasche, 1973a,b), however, lower than the higher values given by Kristiansen et al. (2000). What might explain this large range and these differences? Could it be influenced by factors (other nutrients, grazing) differing between the various investigations/experiments?

2,3) We speculate that diversity and diatom origin (e.g. more Atlantic influenced waters, perhaps residual ice diatoms) may be some of the underlying factors. However, these are (unfortunately) beyond the scope of our data. What is important, at least from a modeling perspective, is that these kinetic parameters are published and available to ground truth regional simulations.

1) The manuscript contains valuable new data, is well written, and will be of interest to many readers of Biogeosciences. I recommend publication after minor revisions.
2,3) We thank the reviewer for this assessment and reply to the revisions below.

Further remarks/suggestions:
1) L123-129 Description of trap deployment was not very detailed (‘at 3-7 depths between 20 and 150-200 m, based on bathymetry’). It would be good to add a list with depths and bottom depths (or a reference where to find this information).
2,3) This has been added to the prose (paragraph starting at line 122).

1) L132-134 Freezing sample for nutrient analysis: Procedures (thawing, measurements how long after thawing) and quality control (freeze certified reference material in parallel with samples) have been discussed in the literature (for example, Macdonald et al., 1986, Clementson & Wayte, 1992, Dore et al., 1996). Could you please give more details on the procedures and quality control?
2,3) Co-Author Kristiansen’s laboratory has extensive experience in these analyses. Pertinent details have been added (lines 132-145) beyond the reference seawater from Ocean Scientific International Ltd. (UK) and detection limits are available in the initial submission. Standard practices (slow thawing of silicic acid samples to allow depolymerization, three parallels measured, etc.), have been added (and suggested references) along with prose regarding the analytical reproducibility (median coefficient of variation was 5% for NO3+NO2 and PO4, 2% for silicic acid and 9% for NO2 $\Rightarrow$ higher coefficient of variation was observed when the absolute concentrations were low, e.g. $<0.1$ uM, hence using the median value). Because of the cruise duration and transfers, and the well-known issues of getting reliable measurements from frozen samples, no ammonium was measured (also clarified in revision).

1) L136-138 ”Phosphate was analyzed, but N:P ratios for nutrients were, on average, 8 among all stations, suggesting that N was likely more important than P for primary production.” N:P is below Redfield thus N might be limiting primary production before P. However, ’N was likely more important than P for primary production’ sounds strange. Please rewrite.
2,3) This has been modified. “Phosphate was analyzed, but N:P ratios for nutrients
were, on average, 8 among all stations; suggesting that N was likely more important than P for potentially limiting primary production. These phosphate data (0.1–0.6 µM in the upper 50 m) are not discussed.” (line 143-145)

1) L145,148,225 60°C → 60°C, -20°C → -20°C, -2-1°C → -2 to +1°C (no gaps; please check whole manuscript)
2,3) Gaps have been removed through the whole manuscript.

1) L175 please rewrite “dividing by the depth integration” → dividing by depth-integrated values
2,3) This has been modified as suggested.

1) L199 ml → mL
2,3) This has been modified.

1) L205-206 using C:Si (instead of Si:C) would avoid the exponent -1 in Eq.(2) and give values more in Redfield-style, i.e. molar Si:C = 0.13 → 7.7 C:Si (only slightly higher than the Redfield C:N). What’s the uncertainty of the Si:C estimate?
2,3) While C:Si and Si:C can both be used, we chose the Si:C based on convention established by other publications when making these types of estimates (e.g. Nelson et al. 1995, Nelson and Brzezinski 1997, Leynaert et al. 2001, Brzezinski et al. 2011, Krause et al. 2011, Krause et al. 2015). Regarding uncertainty, please see response to RC1.

1) L295-296 “The rate of diatom biogenic silica production was reduced by ambient [Si(OH)4] in 95% of the samples examined.” sounds strange. I guess you mean ‘was kinetically limited by ambient [Si(OH)4]’ based on comparison with estimated KS values or based on enhancement factors.
2,3) This has been modified.

1) L317,548 Spearman’s Rho Test: add number of data n = ...
2,3) This has been added (n = 15).

1) L380-384 What about grazing?
2,3) Grazing would affect the standing stock of diatom biomass (and thus the absolute rate of production, Rho), but not the specific rates (e.g. VAVE) which are more likely driven by growth/bottom up factors. However, in this region, grazing is likely the primary mechanism which transforms living diatom silica into detrital silica. Because the latter is a minor and speculative point given the data, we feel adding a complicated explanation about grazing here would stymie the narrative flow without adding enough clarity.

2,3) These two references were added (line 137-138); we thank the reviewer for the suggestion.
END OF RESPONSE
Biogenic silica production and diatom dynamics in the Svalbard region during spring

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Abstract.

Diatoms are generally the dominant contributors to the Arctic Ocean spring bloom, which is a key event in regional food webs in terms of capacity for secondary production and organic matter export. Dissolved silicic acid is an obligate nutrient for diatoms and has been declining in the European Arctic since the early 1990s. The lack of regional silicon cycling information precludes understanding the consequences of such changes for diatom productivity during the Arctic spring bloom. This study communicates the results from a cruise in the European Arctic around Svalbard reporting the first concurrent data on biogenic silica production and export, export of diatom cellular export, the degree of kinetic limitation by ambient silicic acid, and diatom contribution to primary production. Regional biogenic silica production rates were significantly lower than those achievable in the Southern Ocean and silicic acid concentration limited the biogenic silica production rate in 95% of samples. Compared to diatoms in the Atlantic subtropical gyre, regional diatoms are less adapted for silicic acid uptake at low substrate concentration, and at some stations during the present study, silicon kinetic limitation may have been intense enough to limit diatom growth. Thus, silicic acid can play a critical role in diatom spring bloom dynamics. The diatom contribution to primary production was variable, ranging from <10% to ~100% depending on the bloom stage and phytoplankton composition. While there was agreement with previous studies regarding the export rate of diatom cellular export, we observed significantly elevated biogenic silica export. Such a discrepancy can be resolved if a higher fraction of the diatom material exported during our study was modified by zooplankton grazers or originated from melting ice. This study provides the most-direct evidence to date suggesting the important coupling of the silicon and carbon cycles during the spring bloom in the European Arctic.
1 Introduction

Diatoms and the flagellate haptophyte Phaeocystis are the dominant contributors to the Arctic Ocean spring bloom, a cornerstone event supplying much of the annual net community production (Vaquer-Sunyer et al., 2013; Rat'kova and Wassmann, 2002; Vaquer-Sunyer et al., 2013; Wassmann et al., 1999) that fuels Arctic food webs (Degerlund and Eilertsen (2010) and references therein). Hydrographic and chemical changes in the Arctic water column are expected in the future, but whether these will alter diatoms’ contribution to spring primary production and organic matter export remains uncertain. Some studies predict lack of reduction in ice cover will enhance the spring bloom due to increased light availability (Arrigo et al., 2008), while others predict lower productivity driven by increased stratification and reduced nutrient supply (Schourup-Kristensen et al. 2018; Tremblay and Gagnon, 2009). Additionally, models predict that warming will lead to a shift from a diatom-dominated bloom to one increasingly dominated by flagellates and picoautotrophs, which has been observed in certain sectors of the Arctic (Li et al., 2009; Løseth and Agustí, 2010). Because the spring diatom bloom is arguably the single most important productivity event for the Arctic Ocean ecosystem (Degerlund and Eilertsen, 2010; Holding et al., 2015; Vaquer-Sunyer et al., 2013), understanding how diatoms’ ecological and biogeochemical importance changes in response to system-wide physical/chemical shifts is important to predict future food web alterations. Diatoms have an obligate requirement for silicon, therefore understanding of regional Si-silicon cycling can provide insights into the diatoms’ activity. However, there is a current knowledge gap of regional silicon cycling, which precludes robust assessments of the spring bloom in future scenarios, e.g. Tréguer et al. (2018).

Diatom production is dependent on the availability of dissolved silicic acid ([Si(OH)₄]), which they use to build their shells of biogenic silica (bSiO₂). [Si(OH)₄] has been observed to be low (<5 μM) in the Norwegian Seas and declining over time (Rey, 2012). A more recent analysis demonstrated a decline in pre-bloom [Si(OH)₄] concentrations by 1–2 μM across the north Atlantic subpolar and polar regions over the last 25 years (Hátún et al., 2017); this is consistent with the general Arctic region being a net exporter of silicic acid (Torres‐Valdés et al., 2013). This is in stark contrast to the 10–60 μM [Si(OH)₄] observed in the surface waters of the Southern Ocean and the marginal ice zone around Antarctica (Nelson and Gordon, 1982; Brzezinski et al., 2001), where [Si(OH)₄] is unlikely to limit diatom growth unless iron is replete, and stimulates exceptional blooms which consume Si, or assemblages are highly inefficient for Si uptake (citations). Where [Si(OH)₄] is unlikely to limit the rate of diatom production or biomass yield, additionally, the stoichiometry of Si(OH)₄ availability relative to nitrate (Si:N <1) in the source waters, which fuel the spring bloom in most of the north Atlantic and European polar seas, suggests that during a bloom cycle diatoms may experience Si limitation prior to N limitation, especially if diatoms consumed Si and N in near equal quantities as in other diatom bloom regions (Brzezinski et al., 1997; Brzezinski, 1985; Dugdale et al., 1995). And a 2 μM threshold [Si(OH)₄] defines where diatoms are outcompeted by flagellates (Egge and Aksnes, 1992).

Compared to the Southern Ocean, there is a paucity of field Si-cycling studies in the European Arctic. Reports of diatom silica production are only available from the subarctic northeast Atlantic near ~60°-øN, e.g. between Iceland and Scotland (Allen et al., 2005; Brown et al., 2003), Oslofjorden (Kristiansen et al., 2000), and limited data from Baffin Bay (Hoppe et al., 2018; Tremblay et al., 2002); these previous studies are in zones with higher Si(OH)₄ availability than in the European Arctic. Other studies have reported standing stocks of bSiO₂ and export in Oslofjorden or the European Arctic, e.g. Svalbard vicinity, Laptev Sea (Hodal et al., 2012; Heiskanen and Keck, 1996; Paasche and Ostergren, 1980; Lalande et al., 2016; Lalande et al.,...
2013), but none have concurrent measurements of bSiO$_2$ production. Indeed, in the last major review of the global marine silicon cycle, Tréguer and De La Rocha (2013) reported no studies with published bSiO$_2$ production data derived from field measurements from the Arctic. Currently, we lack a baseline understanding about diatom Si-cycling in the European Arctic and broader high-latitude north Atlantic region. And while models in the Barents Sea use Si as a possible limiting nutrient (Wassmann et al., 2006; Slagstad and Støle-Hansen, 1991), there are no field data to ground truth the modeled parameters governing diatom Si uptake. Thus, there is no contextual understanding to determine the consequences of the observed changes in regional [Si(OH)$_4$] since the 1990s and if these affect spring bloom dynamics. This study communicates the results from a cruise in the European Arctic around Svalbard reporting the first concurrent datasets on regional bSiO$_2$ production and export, the export of diatom cellular export, and the degree of kinetic limitation by ambient [Si(OH)$_4$]. Additionally, coupling bSiO$_2$ production rates with contemporaneous primary production measurements provides an independent assessment for the diatom contribution to system primary production.

2 Methods

2.1 Region and Sampling

This study was conducted aboard the RV *Helmer Hanssen* between May 17–29, 2016 as part of the broader project, ARCEx–The Research Centre for ARCTic Petroleum Exploration ([http://www.arcex.no](http://www.arcex.no)). The main goal of this cruise was to study the pelagic and benthic ecosystem during the Arctic spring bloom around Svalbard and in the northern Barents Sea at stations influenced by various water masses. The cruise started in the southwestern fjords influenced by relatively warm Atlantic water, then transited east of Svalbard toward more Arctic-influenced water (Fig. 1 blue arrow) before turning south towards stations near the Polar Front and south of the Polar Front in more Atlantic-water-influenced water (Fig. 1 red arrows) located to the south of the Polar Front.

Vertical profiles with a CTD were conducted at all stations. Hydrocasts were conducted using a Seabird Electronics 911 plus CTD with an oxygen sensor, fluorometer, turbidity meter and PAR sensor (Biospherical/LI-COR, SN 1060). The CTD was surrounded by a rosette with 12 five-liter Niskin bottles. At two stations, Edgeøya, and Hinlopen, only surface samples were collected (no vertical profiles with ancillary measurements, Fig. 1). Water was sampled from the rosette at depths within the upper 40 m (i.e. the extent of the photic layer); for any incubation described below, the approximate irradiance at the sample depth during collection was mimicked by placing incubation bottles into a bag made of neutral density screen. Incubation bags were placed in a deck board acrylic incubator cooled with continuously flowing surface seawater. At Hinlopen, a block of ice was collected by hand within ~10 m of the vessel and allowed to thaw in a shaded container for 24 hours at ambient air temperature. After thawing, the melted solution was homogenized and treated like a water sample for measurement of biomass and rates.

Four sediment trap arrays were deployed between 19 and 23 hours. Arrays in van Mijenfjorden and Hornsund were anchored to the bottom (60 and 130 m, respectively), whereas the other two arrays (Erik Eriksenstretet, 260 m bottom depth; Polar Front, 290 m bottom depth) were quasi-Lagrangian and drifted between 14–16 km during the deployment. During the Erik Eriksenstretet deployment, the array was anchored to an ice floe. Arrays included sediment trap cylinders (72 mm internal diameter x 450 mm length ~1.8 L volume; KC Denmark) at 3 (van Mijenfjorden) –to 7
Atlantic Station) depths between 20 and 150–200 m, based on bathymetry. After recovery, trap
contents were pooled and subsampled for bSiO$_2$ and phytoplankton taxonomy.

2.2 Standing stock measurements

A suite of macronutrients were analyzed at all stations except Hinlopen (just Si(OH)$_4$).

Water was sampled directly from the rosette, filtered (0.7 µm pore size) and immediately frozen.
In the laboratory, nutrients were analyzed using a Flow Solution IV analyzer (O.I. Analytical,
USA) and calibrated with reference seawater (Ocean Scientific International Ltd. UK). Detection
limits for [NO$_3$ + NO$_2$] and [Si(OH)$_4$] were 0.02 and 0.07 (µM), respectively. No ammonium was
measured. To avoid artefacts with prolonged freezing (Clementson and Wayte, 1992; Macdonald
et al. 1986), samples were analyzed within 4 months of collection and standard practices were used
(e.g. prolonged thawing of Si(OH)$_4$ samples to allow depolymerization, three parallels measured).

The median coefficient of variation among parallels was 5% for [NO$_3$ + NO$_2$] and [PO$_4$], 2% for
[Si(OH)$_4$] and 9% for [NO$_2$] —higher coefficient of variation was observed when the absolute
concentrations were low, e.g. <0.1 µM. Reproducibility was sufficient, and no parallels were
excluded. Phosphate was analyzed, but N:P ratios for nutrients were, on average, 8 among all
stations, suggesting that N was likely more important than P for potentially limiting primary production. These phosphate data (0.1–0.6 µM in the upper 50 m) are not discussed.

Samples for biogenic particulates and phytoplankton community composition were taken
directly from the rosette and sediment traps. For bSiO$_2$ samples, 600 mL of seawater was collected
from the rosette, filtered through a 1.2 µm polycarbonate filter (Millipore); for sediment trap
material, less volume was necessary (e.g. 50–100 mL). Most bSiO$_2$ protocols use a 0.6 µm filter
cutoff, e.g. Lalande et al. (2016), however, given the magnitude bSiO$_2$ quantified and the size
range for regional diatoms we are confident that there was no meaningful systematic
underestimate. After filtration, all samples were dried at 60°C and stored until laboratory analysis
using an alkaline digestion in Teflon tubes (Krause et al., 2009). For Chl $a$, water-column and
sediment samples were collected similarly, filtered on Whatman GF/F (0.7 µm pore size) and
immediately frozen (-20 °C). In the laboratory, Chl $a$ was extracted in 5 mL methanol in the dark
at room temperature for 12 h. The solution was quantified using a Turner Design 10-AU
fluorometer, calibrated with Chl $a$ standard (Sigma C6144), before and after adding two drops of
5% HCl (Holm-Hansen and Riemann, 1978). Phytoplankton taxonomy and abundance samples
were collected in 200 mL brown glass bottles from both the water column and sediment traps,
immediately fixed with an aldehyde mixture of hexamethylenetetramine-buffered formaldehyde
and glutaraldehyde at 0.1 and 1% final concentration, respectively, as suggested by Tsuji and
Yanagita (1981) and stored cool (5°C) and dark. Samples were analyzed with an inverted
epifluorescence microscope (Nikon TE300 and Ti-S, Japan), using the Utermöhl (1958) method,
in a service laboratory for diatom taxonomy (>90 individual genera/species categories were
identified) and abundance at the Institute of Oceanology Polish Academy of Science.

2.3 Rate measurements

Biogenic silica production was measured using the radioisotope tracer $^{32}$Si. Approximately
150 or 300 mL samples, depending on the station biomass, were incubated with 260 Bq of high
specific activity $^{32}$Si(OH)$_4$ (>20 kBq µmol Si$^{-1}$). After addition, samples were transported to the
deck-board incubator and placed in neutral density screened bags, simulating 50%, 20% and 1%
of irradiance just below the surface, neutral density screened bags for 24 hours. After incubation,
samples were processed immediately by filtering bottle contents through a 25 mm, 1.2 µm polycarbonate filter (Millipore) —matching bSiO₂ filtrations. Each filter was then placed on a nylon planchette, covered with Mylar when completely dry, and secured using a nylon ring.

Samples were aged into secular equilibrium between ³²Si and its daughter isotope, ³²P (~120 days).

³²Si activity was quantified on a GM Multicounter (Risø National Laboratory, Technical University of Denmark) as described in Krause et al. (2011). A biomass-specific rate (i.e. V_b) was determined by normalizing the gross rate (ρ) to the corresponding [bSiO₂] at the same depth of collection using a logistic-growth approach (Kristiansen et al., 2000; Krause et al., 2011). For bSiO₂ and ρ, values within a profile were integrated throughout the euphotic zone (i.e. surface to 1% I_0) using a trapezoidal scheme. A depth-weighted V_b was calculated within the euphotic zone by integrating V_b and dividing by the depth-integrated values (Krause et al., 2013).

Two methods were used to assess whether ambient silicic acid (Si(OH)₄) limited diatom Si uptake. The ³²Si activity additions, incubation conditions, and sample processing are as described above. At four stations (Edgeøya, Polar Front, Hinlopen and Atlantic), eight 300-mL samples collected at a single depth within the euphotic zone and were manipulated to make an eight-point concentration gradient between ambient and +18.0 µM [Si(OH)₄]; the maximum concentration was assumed to saturate Si uptake. Si uptake has been shown to conform to a rectangular hyperbola described by the Michaelis-Menten equation:

\[ V_b = \frac{V_{max}[\text{Si(OH)}_4]}{K_S + [\text{Si(OH)}_4]} \]  

where V_{max} is the maximum specific uptake rate and K_S is half-saturation constant, i.e. concentration where V_b = \frac{1}{2} V_{max}. Data were fit to the Eq. 1 using a non-linear curve fit algorithm (SigmaPlot 12.3). The second type of experiment used only two points: ambient and +18.0 µM [Si(OH)₄]; four-depth profiles were done at three stations (Bellsund Hula, Hornsunddjupet, Erik Eriksenstretet). The ratio of Si uptake at +18.0 µM [Si(OH)₄] to Si uptake at ambient [Si(OH)₄] defines an enhancement (i.e. Enh) statistic. This two-point approach was conducted at all depths in the euphotic zone; Enh ratios >1.08 imply kinetic limitation beyond analytical error given the methodology (Krause et al., 2012).

Net primary productivity (PP) was quantified concurrently with biogenic silica production at six stations at the depth of approximately 50% of surface irradiance (Table 1). Carbon uptake rates were measured using a modification of the ¹⁴C uptake method (Steemann Nielsen, 1952). Water samples were spiked with 0.2 µCi mL⁻¹ of ¹⁴C labelled sodium bicarbonate (Perkin Elmer, USA) and distributed in three clear and one dark plastic bottles and one dark (40 mL each). Subsequently, they were incubated for 24 h in the deck incubator with a 50% light reduction mesh. After incubation, samples were filtered onto 0.2 µm nitrocellulose filters. The filters were stored frozen (-20°C) in scintillation vials with 10 mL EcoLume scintillation liquid (MP Biomedicals LLC, USA) until further processing. Once on land, the particulate ¹⁴C was determined using a scintillation counter (TriCarb 2900 TR, Perkin Elmer, USA). The carbon uptake values in the dark were subtracted from the mean of the triplicate carbon uptake values measured in the light incubations. Using contemporaneous ρ measurements and PP measurements, the diatom contribution to PP is estimated as:

\[ \text{Diatom }%PP = 100 \times \frac{\rho \times (\text{Si:C})^{-1}}{\text{PP}} \]  

where the Si:C ratio for diatoms can be used from culture values. The most widely-used Si:C ratio is e.g. 0.13 (Brzezinski, 1985); however, this study lacked polar diatom strains. Takeda (1998) grew two polar diatoms at 2°C and in iron-replete media and reported Si:C from 0.10–0.18; however, this was extrapolated based on direct measurement of cellular N and converting using
the Redfield-Ketchum-Richards C:N ratio of 6.6. A more recent study, Lomas et al. (in review), reported data on 11 polar diatom species grown at 2°C with direct measurement of biogenic silica and particulate organic carbon and nitrogen. For larger diatom species (>1000 µm⁢³ biovolume) these authors observed the average Si:C was 0.25 ±0.04 (SE), with a higher ratio for smaller species (<1000 µm⁢³) 0.32 ±0.04 (SE). Most of the diatom assemblage during ARCEx was composed of larger cells, thus, we use Si:C of 0.25.

Export rates were calculated using the standing stock measurements, length of deployment, and trap opening area (0.004 m²). These approaches are common and detailed elsewhere (Wiedmann et al., 2014; Krause et al., 2009).

3 Results
3.1 Hydrography and Spatial patterns

The regional ecosystem around Svalbard is driven by ice dynamics (Sakshaug, 2004). One week prior to the cruise, a majority of the southern Svalbard archipelago had open water, which was anomalous compared to similar dates in previous years (e.g. 2014, 2015, ice data archived at http://polarview.met.no/). By the end of the cruise, Svalbard could have been entirely circled by the vessel, with only open drift ice in the northeastern region. While 2016 was among the lowest years for total Arctic sea ice, the ice extent in Svalbard and the Barents Sea is highly dynamic. Ice edges may be pushed southward into the Barents Sea proper by wind while areas to the north remain ice free, e.g. Wassmann et al. (1999) and references therein.

Spatial patterns in hydrography and nutrients were highly variable. In the southwestern stations (e.g. fjords and Atlantic-influenced water), the surface temperature ranged between 1–4 °C; similar temperature was observed in the Atlantic station south of the Polar Front (Fig. 1E). Northeastern domain stations were more influenced by Arctic water and the surface temperatures ranged between -2 and -1 °C (Fig. 1E). Surface nutrient concentrations, particularly [NO₃+NO₂] and [Si(OH)₄], showed a broad range. The highest surface [NO₃+NO₂] was observed in the southwestern fjords, between 2 and >8 µM, and the Atlantic station (~3 µM, Fig. 1A). The surface concentrations at the remaining stations were <0.5 µM or near detection limits (Fig. 1A). [Si(OH)₄] was lower than [NO₃+NO₂] (i.e. Si:N <1) among stations where [NO₃+NO₂] was > 0.1 µM. At high [NO₃+NO₂] stations, the [Si(OH)₄] ranged from 1.1–4.5 µM (Fig. 1B) but the range was lower among other stations (0.4–1.1 µM, Fig. 1B). bSiO₂ (proxy for diatom biomass, Fig. 1C) was typically similar to, or lower than, surface [Si(OH)₄]. The highest surface [bSiO₂] was observed in the southern stations (Atlantic-influenced waters), ~ 2–3 µmol Si L⁻¹ (Fig. 1C). At most other stations the [bSiO₂] was <1 µmol Si L⁻¹. Among all stations/depths bSiO₂ varied by a factor of ~40 (does not include Hinlopen ice algae).

Primary productivity, measured at six stations at 5 m (approximately 50% of surface irradiance), varied over two orders of magnitude. The lowest rates were observed at the four stations having lowest surface [NO₃+NO₂] and ranged from 2–13 µg C L⁻¹ d⁻¹; at these stations [Chl a] ranged from 2.0–4.8 µg L⁻¹ (Table 1, Fig. 1D). The highest rates were measured at van Mijenfjorden and Bredjupet, 100 ±65 µg C L⁻¹ d⁻¹ and 27 ±1 µg C L⁻¹ d⁻¹, respectively, and corresponded to high [NO₃+NO₂] and low [Chl a] 1.8 and 0.7 µg L⁻¹, respectively (Table 1, Fig. 1D).

3.2 Vertical profiles
As expected, most stations showed strong vertical gradients in nutrient concentrations. Profiles in the southwestern region of Svalbard (van Mijenfjorden, Bredjupet) had elevated [Si(OH)₄], with little vertical structure. Vertical [Si(OH)₄] profiles among other stations showed typical nutrient drawdown between the surface and ~20 m. At these stations, surface [Si(OH)₄] concentrations were typically <1.5 µM and subsurface values (to 20 m) ranged from 0.5–3.0 µM (Fig. 2A). [NO₃+NO₂] exceeded [Si(OH)₄] among all depths at five stations (van Mijenfjorden, Bredjupet, Hornsund, Atlantic; Fig. 2B), whereas in the remaining stations [NO₃+NO₂] exceeded [Si(OH)₄] (i.e. Si:N <1) at depths >5 m (Bellsund Hula), >20 m (Erik Eriksenstretet), and >27 m (Polar Front). For the latter three stations, [NO₃+NO₂] had a significant drawdown in surface waters, but then increased with depth without a similar degree of vertical enhancement in [Si(OH)₄] (Fig. 2).

[bSiO₂] was typically highest at or near the surface, with a maximum of ~2 µmol Si L⁻¹ (Fig. 2C). At the Bellsund Hula and Erik Eriksenstretet stations, subsurface [bSiO₂] maxima were present (Fig. 2C; note–no surface data are available for van Mijenfjorden). Among non-profile stations, [bSiO₂] was within the range observed among vertical profiles except for the Hinlopen ice algae, where the melt water had exceptionally high [bSiO₂] (Fig. 2C). The surface-to-20-m integrated bSiO₂ ([bSiO₂]) spanned over an order of magnitude, with a low at Bredjupet (1.9 mmol Si m⁻²) and a high at Hornsund (42.4 mmol Si m⁻², Table 1) despite their proximity (~50 km).

Diatom abundance and taxonomy data were sampled at fewer stations, but the vertical and spatial variability generally mirrored trends in [bSiO₂]. In the surface waters of van Mijenfjorden and Hornsund, diatom abundances ranged between 5x10⁴–5x10⁵ cells L⁻¹ in the upper 50 m (Fig. 3A). However, within the same vertical layer at the Erik Eriksenstretet stations, diatom abundances were enhanced by up to two orders of magnitude (4x10⁶–4x10⁷ cells L⁻¹, Fig. 3A). When integrated to 40-m depth (∫Diatom), matching the shallowest sediment-trap depth among the three stations reported (Fig. 3E–H), diatom inventories also showed a two-order of magnitude variability as observed in ∫bSiO₂. ∫Diatom was lowest at van Mijenfjorden (7.67x10⁹ cells m⁻²) and highest at Polar Front station (527 x10⁹ cells m⁻², Table 1).

Among the stations which had corresponding sediment trap deployments (van Mijenfjorden, Hornsund, Erik Eriksenstretet), the diatom-assemblage composition was similar despite differences in abundance. The van Mijenfjorden station was dominated by Thalassiosira (e.g. T. antarctica var. borealis, T. gravida, T. hyalina, T. nordenskioeldii), Fragilariopsis cylindrus, and Chaetoceros furcellatus (Fig. 3B). Chaetoceros spp. was nearly absent from Erik Eriksenstretet (Fig. 3D) and of little importance at Hornsund (Fig. 3C). Thalassiosira species (same as van Mijenfjorden) cells also dominated Hornsund and Erik Eriksenstretet among most depths (Fig. 3C, D). However, at Hornsund, deeper depths were dominated by diatom groups less frequently observed (“Other diatom” category, Fig. 3), and with small contributions from Fragilariopsis cylindrus and Navicula vanhoeffeni.

Diatom bSiO₂ productivity, ρ, mirrored trends in biomass. Among the profiles, rates generally varied from ρ <0.01 to 0.11 µmol Si L⁻¹ d⁻¹ (Fig. 2D). ρ was highest in the Atlantic station (Fig. 2D), which was expected given the higher bSiO₂ (Fig. 2C). However, the rates in the Hinlopen ice algae were like those quantified at Hornsund, ~ 0.1 µmol Si L⁻¹ d⁻¹, despite the ice algae station having an order of magnitude more biomass. This suggests the Hinlopen ice algae were senescent or stressed and a sizable portion of the measured bSiO₂ was non-active or detrital.
When integrated in the upper 20 m, $\int \rho$ ranged from 0.27–1.46 mmol Si m$^{-2}$ d$^{-1}$ (Table 1), which is a smaller proportional range than observed in $\int$Diatoms and $\int$bSiO$_2$. Overall, bSiO$_2$-normalized rates ($V_b$) were low among all stations and depths (<0.01 to 0.13 d$^{-1}$). The depth-weighted $V_b$, i.e. $V_{AVE}$, had a narrower range between 0.03–0.13 d$^{-1}$. Thus, doubling times for bSiO$_2$ in the upper 20 m ranged between 5–23 days.

The rate of diatom biogenic silica production was kinetically limited reduced by ambient [Si(OH)$_4$] in 95% of the samples examined. Full kinetic experiments verified that Si uptake conformed to Michaelis-Menten kinetics (Fig. 4A; adjusted $R^2$ ranged 0.64–0.92 among experiments). The highest $V_{max}$ was observed in the Atlantic station (0.36±0.02 d$^{-1}$), which also had the highest ambient [Si(OH)$_4$] among the full kinetic experiments (1.4 µM). $V_{max}$ observed at Edgeoya and the Polar Front were nearly identical (0.05±0.01 d$^{-1}$ for both) and lowest in the Hinlopen ice diatoms (0.02±0.01 d$^{-1}$). $K_s$ constants had a narrower range, with a low of 0.8±0.3 µM at the Polar Front and between 2.1–2.5 µM among the other three stations. Among these full-kinetic experiments, the Enh ratio ranged from 1.8–7.7 with the most intense [Si(OH)$_4$] limitation of uptake observed in the Hinlopen ice diatoms. For profiles where two-point kinetic experiments were conducted, the same trends were observed (Fig. 4B). The Enh ratio was similar among depths at Bellundula Hula (1.5–2.2), Hornsund jupet and Bredjupet (3.4–5.4 for latter two stations, Fig. 4B). At Erik Erikssenstretet, Enh ratios were more variable, ranging from 2.8–7.3 in the upper 10 m with no Enh effect (i.e. <1.08) observed at 20 m —this was the only sample and depth which showed no resolvable degree of kinetic limitation for Si uptake.

Rates of bSiO$_2$- and diatom export were variable. Among the three sediment trap regions, bSiO$_2$ export rates ranged from ~4–10 mmol Si m$^{-2}$ d$^{-1}$ (Fig. 2E). These rates are significant and represent up to 50% of the bSiO$_2$ in upper 20 m at van Mijenfjorden (Table 1). For diatom cells, a similar degree of variability was observed. Export at van Mijenfjorden ranged from 390–1500 x10$^6$ cells m$^{-2}$ d$^{-1}$, similar ranges to Hornsund (520–2800 x10$^6$ cells m$^{-2}$ d$^{-1}$) and Erik Erikssenstretet (510–860 x10$^6$ cells m$^{-2}$ d$^{-1}$, Fig. 3E). The Atlantic station had significantly higher diatom export (800–2300 x10$^6$ cells m$^{-2}$ d$^{-1}$) among all depths in the upper 120 m (Fig. 3E). The bSiO$_2$ and the export of diatom cellular export were highly correlated ($r = 0.67$, $p<0.01$, $n = 15$; Spearman’s Rho Test). Among all stations, Fragilariopsis cylindrus had the highest contribution to diatom export, and Thalassiosira species (e.g. T. antarctica, T. gravida, T. hyalina, T. nordenskioeldii) were also important (Fig. 3F–H). In Hornsund, Navicula (N. vanhaeovenii, N. sp.) was an important genus for export (Fig. 3G) but this was not observed elsewhere. Similarly, “Other diatom” groups were proportionally important at Erik Erikssenstretet (Fig. 3H), as were Thalassiosira resting spores at the Atlantic station (data not shown). Among all diatoms, the only groups which were numerically important in both the water column and the sediment traps were Fragilariopsis cylindrus and Thalassiosira species (Fig. 3B–D, F–H).

4 Discussion

4.1 Diatom Si cycling relative to other systems

To our knowledge, this is the first report of bSiO$_2$ production data of the natural diatom community in this sector of the Arctic. Other studies have reported $\rho$ data in the subarctic Atlantic Ocean (Brown et al., 2003; Kristiansen et al., 2000; Allen et al., 2005) ~10–20° latitude south of our study region or in Baffin Bay (Hoppe et al., 2018; Tremblay et al., 2002). However, the Hoppe et al. (2018) study only includes $\rho$ measured after a 24-hour manipulation experiment and only at one site and depth near the Clyde River just east of Nunavat (Canada), no data are reported for the
ambient conditions, and the measurements from Tremblay et al. (2002) are based on net changes in standing stocks instead of gross bSiO$_2$ production. Banahan and Goering (1986) report the only ρ to date in the southeastern Bering Sea; however, Varela et al. (2013) recently reported that [Si(OH)$_4$] in surface waters (>5 µM) are unlikely to be significantly limiting to diatoms in any sector of the Bering, Chukchi or Beaufort Sea regions. Around Svalbard, some previous studies have examined other Si-cycling components including variability in bSiO$_2$ in the water column (Hodal et al., 2012) and sediments (Hulth et al., 1996), bSiO$_2$ and diatom export (Lalande et al., 2016; Lalande et al., 2013), or trends in [Si(OH)$_4$] (Anderson and Dryssen, 1981). The ρ measurements presented here have no straight forward study for comparison; therefore, we compare these to the previous high-latitude Atlantic data and to well-studied sectors of the Southern Ocean.

During our study, ∫ρ in the Svalbard vicinity was low. Working in the NE Atlantic between Iceland and Scotland, Brown et al. (2003) the reported ∫ρ ranged between 6–166 mmol Si m$^{-2}$ d$^{-1}$ (Brown et al. 2003; Allen et al. 2005). In the same region, under post-bloom conditions, Allen et al. (2005) reported 7 mmol Si m$^{-2}$ d$^{-1}$ for one profile. These rates are significantly higher than at our four profile stations (Table 1), and the degree of difference does not appear to be driven by differences in integration depth (compared to our study, Table 1). Given the higher [Si(OH)$_4$] in the southern region of the Atlantic subpolar gyre (Hátún et al., 2017), the maximum achievable ∫ρ may vary with latitude. While our profile sampling was opportunistic, it appears we sampled some stations with significant diatom biomass (high ∫bSiO$_2$), but the corresponding production rates (∫ρ) were low, with estimated doubling times on the order of 11–23 days. This suggests these high-biomass stations may have been near, or past, peak bloom conditions (Fig. 2A, B) and the seasonal timing is consistent with regional field and modeling studies inferring diatom bloom dynamics from Chl a trends (Wassmann et al., 2010; Oziel et al., 2017). Kristiansen et al. (2000) reported ρ in Oslofjorden during the late winter (February–March), ranging from 0.03–2.0 µmol Si L$^{-1}$ over nine sampling periods with corresponding Vb between <0.01–0.28 d$^{-1}$. However, this system has a higher Si(OH)$_4$ supply and surface concentrations at the start of the bloom period (>6 µM), approximately 50% higher than the highest surface concentrations observed during our study (Fig. 2A). Nearly all the initial Si(OH)$_4$ was eventually converted to bSiO$_2$ during the bloom (Kristiansen et al., 2001; Kristiansen et al., 2000). The specific rates observed in our study fall within the lower values reported by Kristiansen et al. (2000), which may be explained by the reduced uptake from lower [Si(OH)$_4$] (e.g. Fig. 4).

The Southern Ocean is one of the most globally significant regions for production of bSiO$_2$. The surface [Si(OH)$_4$] and [NO$_3$+NO$_2$] are among the highest in the ocean and the source waters usually have >50% excess Si(OH)$_4$ relative to nitrate (Brzezinski et al., 2002). Thus, exceptional Si(OH)$_4$ drawdown relative to nitrate is required for diatom biomass yield to be limited by Si in this region. The mean ∫ρ in sectors of the Southern Ocean are variable. In the Weddell Sea, winter rates range between 2.0–3.2 mmol Si m$^{-2}$ d$^{-1}$ in the seasonal ice zone (Leynaert et al., 1993). Within the sub-Antarctic zone, rates averaged 1.1 and 4.8 mmol Si m$^{-2}$ d$^{-1}$ in the summer and spring, respectively (Fripiat et al., 2011). At the terminus of diatom blooms in the sub-Antarctic and polar frontal zone, rates can be lower, e.g. 0.1–0.3 mmol Si m$^{-2}$ d$^{-1}$ (Fripiat et al., 2011); such values are similar to the range observed during our study, especially since these Southern Ocean studies integrated ∫ρ deeper than 40 m (e.g. 50–100 m). Brzezinski et al. (2001) reported average ∫ρ~25 mmol Si m$^{-2}$ d$^{-1}$ (integrated from surface to 80–120 m) during intense blooms in the seasonal ice zone which propagated south of the Antarctic polar front. But despite the massive diatom bSiO$_2$ accumulating in these blooms, V$_{AVE}$ generally ranged between 0.05–0.15 d$^{-1}$ (Brzezinski et al.,
Given the order-of-magnitude difference in $[\text{Si(OH)}_4]$ and $\dot{\rho}$ between the Arctic and Southern Ocean, the similar $V_{\text{AVE}}$ in both regions may be more reflective of thermal effects on diatom growth rate, since Si uptake and diatom growth rates are tightly coupled, or a significant accumulation of detrital bSiO$_2$ (i.e. diatom fragments) in the Southern Ocean, where low temperatures reduce bSiO$_2$ remineralization rates (Bidle et al., 2002).

### 4.2 Potential for Silicon limitation of diatom productivity

Suboptimal silicon availability affects the rate of diatom bSiO$_2$ production and can limit their growth. A widely-cited $[\text{Si(OH)}_4]$ threshold, below which diatoms will be outcompeted by other phytoplankton, is ~2.0 µM; this metric was derived from a comparison of diatom abundance (relative to total microplankton) versus $[\text{Si(OH)}_4]$ during mesocosm experiments in a Norwegian fjord system (Egge and Aksnes, 1992). Applying this metric globally has been criticized due to observation of diatom dominance among microplankton when $[\text{Si(OH)}_4]$ < 1 µM in systems ranging from fjords to the open-ocean (Krause et al., 2013; Hodal et al., 2012; Kristiansen et al., 2001) and also culture studies showing some diatom species can maintain high growth rates when $[\text{Si(OH)}_4]$ <0.5 µM (reviewed by Kristiansen and Hoell (2002)). Stoichiometry of silicon availability relative to nitrate also help diagnose Si limitation; the most widely accepted diatom Si:N ratio is ~1 based on temperate and low-latitude clones (Brzezinski, 1985). There is a paucity of diatom culture studies examining stoichiometry in polar diatoms, but Si:N during spring blooms in Oslofjorden are close to Brzezinski’s Si:N ratio (Kristiansen et al., 2001). For diatoms in Svalbard and the broader region of the subpolar and polar European Atlantic, both $[\text{Si(OH)}_4]$ and its availability relative to N appear to be suboptimal for creating intense diatom blooms, such as those occurring in the Southern Ocean. Yet, the Arctic spring bloom is consistently dominated by diatoms or Phaeocystis (Degerlund and Eilertsen, 2010), which suggests some level of adaptation for diatoms to the low $[\text{Si(OH)}_4]$ environment of the region. Stoichiometry of silicon availability relative to nitrate can help diagnose Si limitation; the most widely accepted diatom Si:N ratio is ~1 based on temperate and low-latitude clones (Brzezinski, 1985). The average Si:N ratio for two polar diatom clones (silicic acid and iron replete) reported in Takeda (1998) was 0.96±0.24 (SE). A more recent culture study by Lomas et al. (in review), reported Si:N for 11 polar diatom clones grown at 2°C among exponential/stationary growth phases, and replete/N-limiting nutrient conditions; these authors observed Si:N among all clones, treatments, and nutrient conditions (>150 data points) was 1.7±0.10 (SE).

Nutrient relationships support the potential for silicon to be a controlling factor of regional diatom productivity. When plotting $[\text{NO}_3+\text{NO}_2]$ as a function of $[\text{Si(OH)}_4]$ (Fig. 5A) a few trends emerge: 1) The slope of the linear regression relationship (2.5 ± 0.1 mol N (mol Si)$^{-1}$) denotes that NO$_3$+NO$_2$ is consumed at over twice the rate per unit $[\text{Si(OH)}_4]$—2) Given that the source water $[\text{NO}_3+\text{NO}_2]$ concentration is only ~twice that of $[\text{Si(OH)}_4]$, a 2.5 drawdown ratio would predict NO$_3$+NO$_2$ to be depleted before Si(OH)$_4$. This indicates that phytoplankton can deplete nitrogen to levels below detection while they appear unable to deplete Si(OH)$_4$ pools below 0.5 µM, which would indicate 0.5 µM is the ultimate Si(OH)$_4$ concentration required to support diatom growth. Nitrate and silicic acid drawdown within the upper 50 m during the spring season (1980–1984) was discussed by Rey et al. (1987) who suggested apparent nitrate limitation (1980, 1981) and silicic acid limitation (1983, 1984) are annually variable. The Reigstad et al. (2002) analysis of nitrate and silicic acid drawdown in the central Barents Sea shows similarities in that the diatom assemblage could only drawdown $[\text{Si(OH)}_4]$ to ~1 µM (May 1998) and ~0.5 µM (July 1999). These authors suggest that physical effects on phytoplankton explain the interannual
variability in the maximum \([\text{Si(OH)}_4]\) drawdown, where diatoms dominate in shallow, mixed waters opposed to \textit{Phaeocystis pouchetii} dominating in deeper mixed waters. Clearly, interannual and local differences in mixing, which may favor \textit{Phaeocystis pouchetii} over diatoms (Reigstad et al., 2002), can affect the assemblage and nutrient drawdown trajectory (e.g. see points with high \([\text{Si(OH)}_4]\) and little measurable \([\text{NO}_3+\text{NO}_2]\), Fig. 5A); therefore, diagnosing whether Si could limit diatom growth requires additional analyses.

The silicon kinetic data provide clarity for interpreting Si and N nutrient drawdown. None of these nitrate and silicic acid relationships capture the progressive dynamics of an active diatom bloom. Using the ARCEx data (Fig. 5A), if diatoms are limited by an absolute \([\text{Si(OH)}_4]\) (e.g. 2 µM), then at this concentration there is still ample residual \([\text{NO}_3+\text{NO}_2]\) (3.8 µM) which could be used by other phytoplankton that do not consume Si (Fig. 5A). Even if the diatom \([\text{Si(OH)}_4]\) threshold is closer to 1 µM, this observation of excess \([\text{NO}_3+\text{NO}_2]\) (1.4 µM) still holds.

Diatoms have an \(r\)-selected ecological strategy and are typically the first phytoplankton group to bloom in this region under stratified shallow-mixed conditions (Reigstad et al., 2002). The 1.7 Si:N from Lomas et al. (in review) for nutrient-replete polar diatoms suggests they consume 70% more Si relative to N. However, under kinetic limitation diatoms have long been inferred to reduce Si per cell in culture to avoid growth limitation (Paasche 1973) —this was recently observed directly in the field for the first time (McNair et al., in press). Given the clear kinetic limitation observed during ARCEx (Fig. 4), this likely reduced the diatom Si:N ratio closer to the canonical 1:1 ratio. Thus, the kinetic limitation in this region may result if they are consumed in near equal amounts (i.e. Si:N ~1) without significant competition for N by other major phytoplankton groups, it is highly probable that Si would limit them first during a bloom and previous inferences of diatom processes based on 1:1 Si:N drawdown appear valid.

Nutrient relationships support the potential for silicon to be a controlling factor of regional diatom productivity. When plotting \([\text{NO}_3+\text{NO}_2]\) as a function of \([\text{Si(OH)}_4]\) (Fig. 5A) a few trends emerge: 1) The slope of the linear regression relationship (2.5 ± 0.1 mol N (mol Si)) denotes that NO\(_3+\text{NO}_2\) is consumed at over twice the rate per unit \([\text{Si(OH)}_4]\). 2) Given that the source water \([\text{NO}_3+\text{NO}_2]\) concentration is only ~twice that of \([\text{Si(OH)}_4]\), a 2.5 drawdown ratio would predict \([\text{NO}_3+\text{NO}_2]\) to be depleted before \([\text{Si(OH)}_4]\). The latter observation suggests that \([\text{Si(OH)}_4]\) could be the yield limiting nutrient for diatoms during a spring bloom period only if they dominate the phytoplankton assemblage and consume Si:N in ratios >1, e.g. 1.7 as reported by Lomas et al. (in review). Field data demonstrate interannual variability. Nitrate and silicic acid drawdown within the upper 50 m during the spring season (1980–1984) was discussed by Rey et al. (1987) who suggested apparent nitrate limitation (1980, 1981) and silicic acid limitation (1983, 1984). The Reigstad et al. (2002) analysis of nitrate and silicic acid drawdown in the central Barents Sea shows similarities to ARCEx in that the diatom assemblage could only drawdown \([\text{Si(OH)}_4]\) to ~1 µM (May 1998) and ~0.5 µM (July 1999). These authors suggest that physical effects on phytoplankton explain the variability, where diatoms dominate in shallow mixed waters opposed to \textit{Phaeocystis pouchetii} dominating in deeper mixed waters. Clearly, interannual and local differences in mixing, which may favor \textit{Phaeocystis pouchetii} over diatoms (Reigstad et al., 2002), can affect the assemblage and nutrient drawdown trajectory (e.g. see points with high \([\text{Si(OH)}_4]\)).
and little measurable \([\text{NO}_3^- + \text{NO}_2^-]\) close to detection limit, Fig. 5A); therefore, diagnosing whether Si could limit diatom production should be accompanied by additional analyses.

When considering the European sector of the Arctic/sub-Arctic between 60°–80° N, there is compelling evidence that ambient \([\text{Si(OH)}_4^-]\) limits the rate of diatom bSiO\(_2\) production. During ARCEx, the relationship between \(V_b\) and \([\text{Si(OH)}_4^-]\) also supports that Si regulates diatom productivity to some degree (Fig. 4). Our kinetic data demonstrate that in three of four experiments \(K_S\) was ~2.0 µM, but in the Polar Front the \(K_S\) was lower ~0.8 µM. These data are consistent with community kinetic experiments reported in Oslofjorden where \(K_S\) and \(V_{\text{max}}\) were between 1.7–11.5 µM and 0.16–0.64 d\(^{-1}\), respectively, with the lowest \(V_{\text{max}}\) observed during the declining diatom bloom (Kristiansen et al., 2000). These authors concluded that silicon ultimately controlled diatom productivity during this bloom (Kristiansen et al., 2001). In the only other kinetic experiment reported in the northeast Atlantic, Allen et al. (2005), Brown et al. (2003) and Allen et al. (2005) observed a linear response in \(V_b\) between ambient and 5 µM \([\text{Si(OH)}_4^-]\), which suggests uptake did not show any degree of saturation at this concentration (Note: the single experiment reported in Allen et al. (2005) is one of four experiments originally reported in Brown et al. (2003)). These field-based \(K_S\) values are considerably higher than parameters used in Barents Sea models, e.g. 0.5 µM (Slagstad and Støle-Hansen, 1991), 0.05 µM (Wassmann et al., 2006) which reflect the high-efficiency Si uptake reported for cultures (Paasche, 1975). Fitting a regression to the \(V_b V_{\text{max}}^{-1}\) as a function of \([\text{Si(OH)}_4^-]\) (line shown in Fig. 5B) suggests that 2.3–2.8 µM is the best constrained half-saturation concentration (i.e. concentration where \(V_b V_{\text{max}}^{-1} = 0.5\) for the regional assemblage. This empirical value, however, this excludes the Hornsunddjupet assemblage (white symbols, Fig. 5B), their inclusion decreases and this aggregated half-saturation would increase to 2.58 µM if those data were not considered. Unlike diatoms in the north Atlantic Subtropical Gyre, e.g. Sargasso Sea (Krause et al., 2012), regional diatoms do not appear well-adapted for maintaining \(V_b V_{\text{max}}^{-1} > 0.5\) at low \([\text{Si(OH)}_4^-]\). Instead, diatoms during the spring season appear to be best adapted for concentrations exceeding 2.3 µM, which suggests that as \([\text{Si(OH)}_4^-]\) is depleted, diatoms may slow growth both from severe limitation of Si uptake (Fig. 5B) and/or biomass yield (i.e. stock of diatom bSiO\(_2\) far exceeds \([\text{Si(OH)}_4^-]\)).

To avoid growth limitation under conditions of kinetic limitation (i.e. suboptimal \([\text{Si(OH)}_4^-]\)), diatoms can reduce their silicon per cell when \([\text{Si(OH)}_4^-]\) is suboptimal. An important principal from culture work is that diatoms can alter their silicon per cell by a factor of four (Martin-Jézéquel et al., 2000). Thus, when uptake is reduced to <25% of \(V_{\text{max}}\) (i.e. concentration which promotes uptake at half the half-saturation level), diatoms must slow growth to take up enough Si to produce a new cell. Using the empirical half-saturation constant range (2.3–2.8 µM) calculated from Fig. 5B and using Eq. 1 to solve for the concentrations where \(V_b V_{\text{max}}^{-1} = 0.25\) (\(V_{\text{max}}\) is a constant), suggests that when \([\text{Si(OH)}_4^-]\) is below 0.3–0.8 µM, the degree of kinetic limitation could force diatoms to slow growth in response. This type of limitation could occur even if diatom bSiO\(_2\) stock was not sufficiently high to induce yield limitation, e.g. it could not deplete all \([\text{Si(OH)}_4^-]\) from the assemblage undergoing one division. Such a range could be biased low given the influence of the highly efficient Hornsunddjupet assemblage (which was associated with warmer Atlantic waters). But at these \([\text{Si(OH)}_4^-]\) there would also be up to 0.8 µM \([\text{NO}_3^- + \text{NO}_2^-]\) remaining (Fig. 5A), is lower than the common interpretation of the Egge and Aksnes (1992) data set showing diatoms may be outcompeted by flagellates when \([\text{Si(OH)}_4^-] = 2\) µM, a value which is more reflective of an ecological niche opposed
to a physiological threshold as has been purported in numerous citations of these data. At these inferred limiting [Si(OH)\textsubscript{4}] there would be up to 0.8 µM [NO\textsubscript{3} + NO\textsubscript{2}] remaining (Fig. 5A), which would allow a secondary group of non-siliceous phytoplankton to draw down the remaining N. Therefore, under shallow stratified conditions which favor diatoms over Phaeocystis (sensu Reigstad et al. (2002)), [Si(OH)\textsubscript{4}] may regulate regional diatom productivity during spring consistent with similar results from southern Norway fjords (Kristiansen et al., 2001) through either yield- or severe-kinetic limitation. This provides the most direct assessment to date supporting the general ideas proposed for that Si regulation of may limit regional diatom productivity (Rey, 2012; Rey et al., 1987; Reigstad et al., 2002).

4.3 Diatom contribution to primary production

Among the six sites with paired PP and \( \rho \) measurements, the bloom phase can be inferred from the magnitude of nutrient drawdown, [Chl \textsubscript{a}], PP, and pCO\textsubscript{2} (data not shown). Bredjupet appeared to be a pre-bloom station given the high surface nutrient concentrations, while the van Mijenfjorden station also appeared to be in an early bloom phase based on relative high nutrients and moderate [Chl \textsubscript{a}]. The Erik Eriksenstretet station represented a peak bloom condition, whereas assemblages at Hornsundjupet and Edgeøya appeared to be post bloom and in a stage of decline. The Polar Front station represented the end or late-phase bloom condition; however, at this station Phaeocystis was abundant (data not shown), suggesting it may have dominated the bloom dynamics instead of diatoms.

The diatom contribution to PP was highly variable. Among the stations with high [NO\textsubscript{3} + NO\textsubscript{2}] (van Mijenfjorden, Bredjupet) the diatom contribution to PP (e.g. Eq. 2) was low, 52–63%. At two stations, Hornsundjupet and the Polar Front, the diatom contribution to PP increased to 4825–5730%. In the Edgeøya, and Erik Eriksenstretet stations, diatoms accounted for all a majority or all of PP, 70430% and 180240%, respectively. Such unrealistic value at Erik Eriksenstretet could imply a potential issue with the Si:C ratio (Eq. 2), specifically an increase in Si per cell and/or lower C per cell due to reduced growth rate associated with the peak/end of the bloom. Given that diatoms can reduce their cellular Si in response to kinetic limitation (Paasche 1973, McNair et al. in press), the Si:C ratio of 0.25 based on nutrient-replete diatoms in culture may systematically underestimate diatom contribution to PP using our approach. For example, if kinetic limitation reduced Si per cell by 50% (i.e. \( \nu_s \nu_{\text{max}}^{-1} \approx 0.50 \), Fig. 5B) but did not affect cellular C, then the Si:C ratio would be 0.13 (i.e., temperate Si:C diatom value), and nearly all the calculated diatom contributions would double. Considering the degree of kinetic limitation at most stations (Fig. 5B), this suggests our estimates are conservative except at Erik Eriksenstretet. Such an unrealistic value at Erik Eriksenstretet could imply a potential issue with the Si:C ratio (Eq. 2), however, adjusting Si:C downward would increase the diatom contribution. Thus, there may have been lower C per cell for diatoms at this station due to other factors, such as reduced growth rate associated with the peak/end phase of the bloom and/or the different assemblage, e.g. Porosira glacialis dominant at this station and has a large vacuole which could lower C content thereby increasing Si:C (data not shown).

Clearly, diatoms can play a significant role in local productivity, but these data demonstrate a “bloom and bust” nature. At stations at or near peak bloom levels (e.g. Edgeøya, Erik Eriksenstretet), diatoms could account for nearly all primary production. However, they may also conduct a small percentage of primary production prior to the onset of the bloom (e.g. van Mijenfjorden, Bredjupet). But even when physical conditions...
may favor Phaeocystis blooms, diatoms appear to be significant contributors to primary production (Polar Front station). In such a situation, N would be predicted to be the limiting nutrient as it will be consumed by both Phaeocystis and diatoms whereas Si will only be consumed by the latter.

In the European Arctic, shifts in summer-period phytoplankton communities away from diatom-dominated conditions have been observed in numerous studies. One of the dominant features has been the increasing abundances of Phaeocystis in ice-edge (Lasternas and Agustí, 2010) or under-ice blooms (Assmy et al., 2017). These changes have corresponded with larger-scale shifts in the export of diatoms to depth in the Fram Strait (Nöthig et al., 2015; Lalande et al., 2013; Bauerfeind et al., 2009). The timing of these shifts, e.g. mid-2000s, correspond with the broader regional reduction in winter mixed-layer [Si(OH)₄] concurrent with the shift to negative gyre-index state in the latter half of the decade (Hátún et al., 2017). With a reduction in pre-bloom Si(OH)₄ supply, diatoms may run into limitation sooner during the bloom cycle and thus leave more residual nitrate for non-diatom phytoplankton. Degerlund and Eilertsen (2010) also demonstrate a dynamic temperature niche for individual diatom groups/species. Coello-Camba et al. (2015) showed that temperature induced a shift in the Arctic phytoplankton community, with diatoms declining as temperature increased and thereby favoring dominance of flagellates. Given the highly variable contribution of diatoms to primary productivity in this system in spring and the effects which carry over into summer, should climate change or natural physical oscillations affect diatoms in this system resolving a climate change or natural physical oscillation such a signal will be challenging. A similar conclusion about detecting a climate-change signal was made in the eastern Bering Sea by Lomas et al. (2012) given the natural variability in primary production.

### 4.4 Diatoms and export

The bSiO₂ export rates observed during ARCEx were significant relative to the standing stocks. At van Mijenfjorden, the rate of export in the upper 40 m represented 39% of the bSiO₂ standing stock (23.3 mmol Si m⁻², integral of data in Fig. 2C) in the same vertical layer. This quantity was much higher than at Erik Eriksenstretet, where the 40-m export rate was <11% of the bSiO₂ in the upper water column (note: no samples were taken deeper than 20 m, thus, additional bSiO₂ between 20–40 m would lower the 11% estimate). Given that the van Mijenfjorden site was located within shallow fjord waters (bottom depth approximately 60 m), such a high proportion export relative to standing stock may suggest either lateral focusing processes (e.g. discussed by DeMaster (2002)) and/or resuspension of sediment bSiO₂ into the water and resettlement. The rate of bSiO₂ export among all export- and production stations was also at least a factor of four higher than \( \rho \) in the upper 20 m (Table 1). The rate of bSiO₂ export was also at least a factor of four higher than \( \rho \) in the upper 20 m. It is likely that some fraction of \( \rho \) was missed due to lack of sampling between 20–40 m, but with a lack of less light at these depths, it is unlikely systematic underestimates of \( \rho \) caused the disparity. Given the deeper water at the Erik Eriksenstretet and Atlantic stations, such high bSiO₂ export may be driven by previously high \( \rho \) and bSiO₂ standing stock which accumulated in the overlying waters or given the dynamic circulation in the region, this signal may have been laterally advected to these station locations.

Relative to previous studies, the bSiO₂ export rates were also high. During May 2012 in Kongsfjorden, Lalande et al. (2016) reported bSiO₂ export rates between 0.2–1.3 mmol Si m⁻² d⁻¹ in the upper 100 m, a similar range was observed by Lalande et al. (2013) in the eastern Fram Strait using moored sediment traps (2002–2008) collecting at depths between 180–280 m. Lalande et al. (2013) concluded that, despite warm anomaly conditions, pulses of bSiO₂ export were
positively correlated to the presence of ice in the overlying waters which stratifies the water and helps initiate a diatom bloom. However, if the light was insufficient to stimulate a bloom, Lalande et al. (2013) suggested much of the pulse of bSiO$_2$ exported to depth may have originated in the ice and sank during melting. Indeed, the low V$_b$ (<0.01 d$^{-1}$) observed at the Hinlopen station (ice algae), despite the moderate $p$ measured (0.12 µmol Si L$^{-1}$ d$^{-1}$), suggests that most of the ice-associated bSiO$_2$ was detrital and not associated with living diatoms. Thus, the recent ice retreat observed prior to the ARCEx cruise was a potential source of such high bSiO$_2$ export to depth despite the considerably lower $p$ in the upper 20 m.

Among the groups examined, the most important diatom genera for standing stock and export were *Thalassiosira* and *Fragilariopsis*, suggesting these groups are important drivers of bulk bSiO$_2$ fluxes. Given the large-size and chain-forming life histories for the dominant species within each genus, it is likely that their dominance in the trap abundances helps explain the high correlation ($r = 0.67$, p<0.01; Spearman’s Rho Test) between bSiO$_2$ and diatom export. Given this degree of correlation, it would be expected that both bSiO$_2$ and diatom export would be similarly enhanced relative to previous studies; however, this was not observed. Comparing the magnitude of bulk bSiO$_2$ export and the export of diatom cells suggests significant food web repackaging occurred. The export of diatom cellular export in Kongsfjorden (Lalande et al., 2016) were similar-to or a factor of three lower than rates quantified during ARCEx (Table 1, Fig. 3E), whereas bSiO$_2$ export during ARCEx was over an order of magnitude higher than bSiO$_2$ export in Kongsfjorden. One possible explanation for the higher degree of bSiO$_2$ export enhancement, relative to diatom cellular export, between studies is that more exported material during ARCEx was repackaged and modified in the food web. For instance, in Erik Erikssenfjord gel traps confirm the presence of aggregates and mesozooplankton fecal pellets (Wiedmann et al. in prep), and in van Mijenfjorden detrital particles and sediment material were most prominent on the gel traps opposed to clearly recognizable material (e.g. diatom valves). These observations suggest the potential for considerable modification of diatom organic matter prior to export (diatoms in fecal pellets, fragments associated with aggregates, etc.). This repackaging is consistent with previous observation in the Barents Sea showing high potential for copepod fecal pellets to be exported in the Polar Front and Arctic-influenced regions during spring (Wexels Riser et al., 2002). And supports the general ideas for the importance of diatom organic matter in fueling secondary production regionally during this season (Degerlund and Eilertsen (2010) and references therein).

4.5 **Conclusion**

This is the first regional data set with contemporaneous measurements of diatom bSiO$_2$ standing stock, production, export and assessment of kinetic limitation by [Si(OH)$_4$] in the European Arctic. Among stations and depths there was widespread limitation of diatom bSiO$_2$ production rates by ambient [Si(OH)$_4$] during spring-bloom conditions. The kinetic parameters for diatom Si uptake (e.g. $K_s$) quantified in our study are significantly higher than rates used in regional models and quantified in polar diatom cultures; therefore, these data will help future modeling efforts better simulate diatom/Si dynamics. Given the trajectories of Si and N consumption, diatom-dominated blooms (vs. *Phaeocystis*-dominated) could deplete Si(OH)$_4$ prior to nitrate yield limitation; and at some stations, the degree of kinetic limitation by ambient [Si(OH)$_4$] could have resulted in diatom growth being slowed. Diatom contribution to PP was highly variable, ranging from <10% to ~100% depending on the bloom stage; but even when *Phaeocystis* appeared to be favored, diatoms still had a significant (~50%) contribution to PP.
While there was agreement with previous regional studies regarding the export rate of diatom cellular export, we observed significantly elevated bSiO\textsubscript{2} export. Such a discrepancy can be resolved if a higher fraction of the diatom material exported during our study was modified by zooplankton grazers, relative to previous studies, or if much of this bSiO\textsubscript{2} was derived from melting ice and/or advection.

Data availability. All data are available upon request to the authors or are available through the UiT research data bank (https://dataverse.no/dataverse/uit).

Author contributions. JK, CMD, SA conceived/designed the study and conducted analysis. JK, CMD, IM, PA, MFM, IW, SA conducted the fieldwork. PW and SK conducted analysis. All co-authors contributed to the writing of the paper, led by JK.

Competing interests. The authors declare that they have no conflict of interest.

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References


McNair, H. M., Brzezinski, M. A., and Krause, J. W.: Diatom populations in an upwelling environment decrease silica content to avoid growth limitation, Environmental Microbiology, in press.


Tsuji, T., and Yanagita, T.: Improved fluorescent microscopy for measuring the standing stock of phytoplankton including fragile components, Marine Biology, 64, 207-211, 1981.


Wassmann, P., Slagstad, D., and Ellingsen, I.: Primary production and climatic variability in the
European sector of the Arctic Ocean prior to 2007: preliminary results, Polar Biology, 33, 1641-1650,
2010.

Wexels Riser, C., Wassmann, P., Olli, K., Pasternak, A., and Arashkevich, E.: Seasonal variation in
production, retention and export of zooplankton faecal pellets in the marginal ice zone and central

Wiedmann, I., Reigstad, M., Sundfjord, A., and Basedow, S.: Potential drivers of sinking particle's size
spectra and vertical flux of particulate organic carbon (POC): Turbulence, phytoplankton, and
Table 1 – Station properties including surface temperature, nutrients and chlorophyll a (± standard deviation), 20-m biogenic silica stock (∫bSiO2), production (∫p) and depth-weighted specific production (VAVE), 40-m integrated diatom abundance (∫Diatom) and export of bSiO2 and diatoms at 40 m. The disparity between the integration depths for bSiO2 standing stock and diatom abundance reflects the lack of bSiO2 samples to 40 m depth and that the latter are used to compare with diatom export (Discussion). Note: Hinlopen (ice) station not included. The Polar Front ∫Diatom is the mean of two profiles.

<table>
<thead>
<tr>
<th>Station Name</th>
<th>T (°C)</th>
<th>[NO3 + NO2] (µM)</th>
<th>[Si(OH)4] (µM)</th>
<th>[Chl a] (µg L⁻¹)</th>
<th>20-m ∫bSiO2 (mmol Si m⁻²)</th>
<th>20-m ∫p (mmol Si m⁻² d⁻¹)</th>
<th>20-m VAVE (d⁻¹)</th>
<th>20-m ∫Diatom abundance (10⁹ cells m⁻²)</th>
<th>40-m bSiO2 export (mmol Si m⁻² d⁻¹)</th>
<th>40-m Diatom export (10⁶ cells m⁻² d⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>‡van Mijenfjorden</td>
<td>-0.43</td>
<td>8.1</td>
<td>3.8</td>
<td>1.84 ±0.19</td>
<td>10.8</td>
<td>-</td>
<td>7.67</td>
<td>9.03</td>
<td>769</td>
<td></td>
</tr>
<tr>
<td>‡Bredjupet</td>
<td>4.72</td>
<td>9.4</td>
<td>4.5</td>
<td>0.72 ±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Bellsund Hula</td>
<td>0.69</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>2.66 ±0.05</td>
<td>15.3</td>
<td>0.49</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Hornsund</td>
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<td>1.6</td>
<td>1.1</td>
<td>2.50 ±0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.97</td>
<td>1180</td>
<td></td>
</tr>
<tr>
<td>‡Hornssunddjupet</td>
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<td>&lt;0.1</td>
<td>0.4</td>
<td>2.43 ±0.17</td>
<td>42.2</td>
<td>1.46</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>‡Edgeøya</td>
<td>-0.70</td>
<td>0</td>
<td>0.7</td>
<td>1.99 ±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>‡Erik Eriksenstretet</td>
<td>-1.58</td>
<td>0.4</td>
<td>0.4</td>
<td>4.77 ±0.31</td>
<td>34.9</td>
<td>1.03</td>
<td>0.04</td>
<td>252</td>
<td>4.00</td>
<td>436</td>
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<td>‡Polar Front Station</td>
<td>2.19</td>
<td>&lt;0.1</td>
<td>1.1</td>
<td>3.00 ±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>527</td>
<td>-</td>
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<tr>
<td>Atlantic</td>
<td>4.10</td>
<td>3.3</td>
<td>1.4</td>
<td>6.66 ±0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.20</td>
<td>2380</td>
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‡Surface value
*25 m depth
‡Denotes concurrent primary production and biogenic silica production measurements at one depth
Figure Captions:

Figure 1: Surface properties during 2016 ARCEx cruise including A) NO3 + NO2 (µM), B) dissolved silicic acid (µM), C) biogenic silica (µmol Si L⁻¹), D) Chlorophyll a (µg L⁻¹) and E) Temperature (°C) overlaid on station map. Station names are denoted on the map and colored arrows generalize the flow of Atlantic-influenced (red) and Arctic-influenced (blue) waters.

Figure 2: Vertical profiles for A) dissolved silicic acid, B) NO3 + NO2 + NOC, C) biogenic silica standing stock, D) biogenic silica production rate, and E) biogenic silica export. Symbols are associated by station, and line connectors are used to denote profile data opposed to individual symbols noting samples at one depth.

Figure 3: Diatom abundance (A) and assemblage composition (B–D) in the water column, and diatom export (E) and assemblage composition (F–H) within sediment traps. Note – taxonomy information only shown for stations where both water-column and sediment-trap data were available (see text for species). Resting spores (e.g. Chaetoceros, Thalassiosira) were absent from the 40-m sediment traps; thus, proportional abundances for spore-producing taxa are entirely for vegetative cells. For panel A, there are replicate diatom abundance measurements (from separate hydrocasts) for the Polar Front station.

Figure 4: Assessment of Si uptake limitation by available silicic acid during ARCEx. A) 8-point kinetic experiments taken at four stations (legend next to panel B). Data were fit to a Michaelis-Menten hyperbola using SigmaPlot 12.3 software. B) Enh. ratio profiles (i.e. Vb in +18.0 µM [Si(OH)₄] treatment relative to Vb in the ambient [Si(OH)₄] treatment) at four stations.

Figure 5: Diagnosis of potential silicon limitation for diatom production during ARCEx. A) Nitrate + Nitrite drawdown as a function of dissolved silicic acid. B) The ratio of Vb at ambient [Si(OH)₄] to Vmax versus dissolved silicic acid. In both panels, linear regressions were done using a Model II reduced major axis method, for panel B the regression line does not include the Hornsunddjupet station (open circles). For comparison, the same relationship for the Sargasso Sea in the North Atlantic subtropical gyre, as synthesized in Krause et al. (2012).
Figure 1:
Figure 4:

A) 

B) Enh. Ratio

Depth (m)

- Bellund Hula
- Breidjupet
- Hornsundjupet
- Erik Eriksen Strait
- Edgeoya
- Polar Front
- Atlantic
- Hinlopen (Ice Algae)