



Transport and reaction of iron and iron stable isotopes in glacial meltwaters on Svalbard near Kongsfjorden: From rivers to estuary to ocean



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ABSTRACT

Glacial meltwater has been suggested as a significant source of potentially bioavailable iron to the oceans. However, the supply of dissolved iron (dFe) in glacial meltwaters is poorly constrained as few sites have been studied, and because the chemical processing of Fe during transport from glaciers to the adjacent coastal ocean is not well understood. In order to better constrain glacial fluxes of dFe to the ocean, iron concentrations, iron stable isotopes ($\delta^{56}\text{Fe}$), and other supporting chemical and physical measurements were made along a ~4 km long glacial meltwater river on Svalbard and in estuarine waters that it flows into. Dissolved iron concentrations in the Bayelva River decreased from a maximum of 734 nM near the glacier to an average value of 116 nM near the mouth of the river. Measurements in the Kongsfjorden estuary suggest that 3 to 10 nM of dFe from the Bayelva River is stabilized in glacial waters by the time it mixes into the ocean. Incubation of Bayelva River waters over two weeks in both the light and dark show similar results, with the majority of dFe being quickly precipitated and 4 to 7 nM Fe stabilized in the dissolved phase. Evidence suggests that Fe is most likely lost from the dissolved phase by aggregation and adsorption of nanoparticulate and colloidal Fe to particles. Dissolved $\delta^{56}\text{Fe}$ was between -0.11% and $+0.09\%$ for all river samples and did not vary systematically with dFe concentrations. We infer that the Fe is lost from the dissolved phase by a process that fractionates Fe isotopes by less than 0.05‰, indicating that the Fe bonding environment does not change during precipitation. This is consistent with DOC loss that is much faster than predicted photo-oxidation rates, suggesting that DOC is also lost through adsorption and precipitation. Dissolved Fe concentrations in the Bayelva River (15–734 nM), and Fe concentrations which are stabilized in the dissolved phase (4–7 nM) are much lower than some previous estimates of Fe in glacial meltwaters, with roughly 80% of dFe lost during transit in the Bayelva River and roughly 90% of the remaining dFe lost in the estuary. This may mean that glaciers are a less significant source of dissolved Fe to the global oceans than has been previously hypothesized, that cold base glaciers of the type studied here do not contribute significantly to the dissolved Fe flux, or that the flux of reactive particulate Fe to the oceans is more important than the dissolved flux. In Arctic regions with similar proglacial environments, bedrock composition, weathering intensity, and as precipitation of colloidal and nanoparticulate Fe may all play an important role in regulating the glacial meltwater iron flux to the ocean.

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1. Introduction

Despite the high abundance of Fe in the earth's crust (~5%), concentrations of Fe in the modern oxidized oceans are very low (typically <1 nM in the open ocean) due to the low solubility of

Fe in seawater (Bruland and Lohan, 2003). Low Fe concentrations, combined with physiological requirement for Fe by phytoplankton for processes such as photosynthesis and nitrogen fixation, means that Fe is the limiting nutrient for phytoplankton growth in much of the surface ocean (Moore et al., 2002). The residence time of Fe in seawater is much shorter than the timescale of ocean circulation (e.g. Moore et al., 2004; Parekh et al., 2004), meaning that Fe

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concentrations in the ocean are highly dependent on local sources and sinks of the element. Deposition of dust transported from the continents has often been considered the most important source of Fe to the remote oceans (Jickells et al., 2005), though continental-margin sediments (Elrod et al., 2004; Lam and Bishop, 2008) and hydrothermal vents (Saito et al., 2013; Tagliabue et al., 2010) may also represent important sources of biologically available Fe. Recently, glacial Fe inputs in the form of icebergs and glacial meltwater have been proposed as significant sources of bioavailable iron to the ocean (e.g. Bhatia et al., 2013; Death et al., 2014; Smith et al., 2007). As the rate of glacial melting increases due to climate change, this flux of glacial Fe to the oceans may increase, potentially providing an important climate feedback.

Glacial freshwater input to the oceans, in the form of glacial meltwater runoff and iceberg calving, delivers both dissolved Fe (dFe) and particulate Fe to the high-latitude oceans. Dissolved soluble Fe species are typically considered bioavailable, and very small Fe particles within the colloidal (0.02–0.45 μm) or nanoparticulate (0.02–0.1 μm) size range, which can be produced in the glacial environment, are also thought to provide bioavailable Fe because they are more soluble and reactive than larger particles (Raiswell, 2011). Similarly, free drifting icebergs may release iron to support primary production (Smith et al., 2007). These findings have implications for global productivity because Fe is a limiting nutrient throughout the Southern Ocean and large parts of the subarctic Pacific, and there is evidence that Fe may also limit the extent of seasonal nutrient drawdown in the high latitude North Atlantic (Achterberg et al., 2013; Boyd et al., 2007; Nielsdottir et al., 2009). Recently, field observations have supported the idea that glacial Fe is bioavailable by showing that it supports a phytoplankton bloom along a glacier meltwater plume in the Amundsen Sea (Gerringa et al., 2012).

Despite the possible importance of glacial Fe, dissolved Fe supply from glacial meltwaters is poorly constrained due to the limited number of measurements and the great variability in dFe concentrations in these few samples. For example, concentrations of up to 9950 nM were observed at a location in Greenland, leading to an estimated annual flux of biologically available Fe from Greenland meltwater which is comparable to dust-derived soluble iron inputs to the North Atlantic (Bhatia et al., 2013). Just 100 km to the south in Greenland, however, Statham et al. (2008) observed glacial meltwater with an average dFe concentration of 52 nM. At a location 30 km further south at the Leverett Glacier, soluble iron (<0.02 μm) concentrations in meltwater averaged 7 nM, however, iron concentrations in the colloidal size range (0.02–0.45 μm) spanned an order of magnitude, from 232 nM to 4701 nM (Hawkings et al., 2014).

Determining the importance of glacial Fe inputs to the oceans also requires understanding the chemical processing of glacial Fe. Glacial meltwater runoff is characterized by a high physical to chemical erosion ratio (Raiswell et al., 2006), oxygen depletion in the subglacial environment (Hodson et al., 2002), and often by the presence of proglacial basins. Much of the glacial particulate Fe load is in the form of nanoparticulate Fe oxyhydroxides, which have been hypothesized to be directly or indirectly bioavailable, and which may be more easily solubilized in seawater (Raiswell et al., 2006, 2009; Raiswell, 2013). Indeed, glacial meltwaters in western Greenland were found having a much higher percentage of dFe in the colloidal fraction (>98%) (Hawkings et al., 2014) than typical non-glacial rivers (e.g. Dai and Martin, 1995; Escoube et al., 2009; Stolpe et al., 2010). Glacial fed tributaries of the Copper River, Alaska, which were shown to have a higher sediment load than other types of tributaries, also had much higher colloidal Fe concentrations (Schroth et al., 2011).

Iron stable isotope ratios ($\delta^{56}\text{Fe}$) can be a valuable tool for tracking the biogeochemical cycling of Fe in rivers and the ma-

rine environment, though they have so far been minimally applied to the study of glacial systems. The total observed range in riverine $\delta^{56}\text{Fe}$ is between -1.2 and $+2.8\%$, with variations dependent both on river chemistry and filter pore size (e.g. Ilina et al., 2013; Schroth et al., 2011). Continental weathering has been inferred to preferentially release light Fe into the riverine dissolved phase under some conditions (Fantle and DePaolo, 2004). However, the amount of dissolved organic material can also be important in determining $\delta^{56}\text{Fe}$. For example, $\delta^{56}\text{Fe}$ values of $-0.2 \pm 0.1\%$ were measured for dFe in main channel sites of the Amazon River (Bergquist and Boyle, 2006), while isotopically heavy dFe ($+0.30\%$) was measured in waters of an organic-rich tributary. Positive values of dissolved $\delta^{56}\text{Fe}$ have also been reported for the North River, in the United States (Escoube et al., 2009), and some boreal rivers in Russia (Ilina et al., 2013). Recent work on a glacial river showed that the isotopic signature of dFe was found to be similar to crustal values in a glacier fed tributary of the Copper River (Schroth et al., 2011). Better constraints on the $\delta^{56}\text{Fe}$ of dissolved and particulate Fe in glacial meltwaters may make it possible to use Fe isotopes to trace the global distribution of glacial Fe in the oceans, as has recently been done for other Fe sources to the North Atlantic (Conway and John, 2014).

The aim of this study is to investigate the transportation and transformation of dFe between a glacial source and the ocean, via a glacial meltwater river. In addition to measurements of dFe concentration and $\delta^{56}\text{Fe}$, ancillary parameters including dissolved oxygen (DO), dissolved Mn (dMn), dissolved organic carbon (DOC), total suspended matter (TSM), and pH were measured. These data are used to better understand the chemical cycling of glacial Fe in the Bayelva River, and to refine estimates of glacial Fe delivery to the ocean.

2. Materials and methods

2.1. Study area

Sampling for this study was performed in the vicinity of the Ny-Ålesund International Research Facility next to Kongsfjorden, Svalbard (Fig. 1). Svalbard is located in the southern portion of the Arctic Ocean, at the northern end of the Greenland Sea. The region is an important site of North Atlantic Deep Water (NADW) formation, warm North Atlantic waters travel along the western coast of Svalbard before sinking to form NADW (Jungclauss et al., 2005).

About 60% of the land in the Svalbard archipelago is covered by glaciers, with estimated fluxes of meltwater and iceberg calving of $25 \pm 5 \text{ km}^3 \text{ a}^{-1}$ and $4 \pm 1 \text{ km}^3 \text{ a}^{-1}$, respectively (Hagen et al., 2003). The Bayelva River, which this study focuses on, is approximately 4 km long, with a catchment area of 32 km², of which 50% is glaciated by the cold-based valley glaciers Austre and Vestre Brøggerbreen, both of which have thicknesses less than 100 m (Krawczyk et al., 2003). Although meltwater from cold-based glaciers is not typically thought to have subglacial drainage flowpaths, the water chemistry in Bayelva River at the end of ablation season, when our sampling occurred, was found to be similar to that of subglacial meltwaters (Nowak and Hodson, 2014). The Bayelva River catchment is bounded by steep mountain ridges to the south and the Kongsfjorden fjord to the north. The annual discharge of the river is estimated to be $\sim 30 \cdot 10^6 \text{ m}^3$ (Hagen et al., 2003), with suspended sediment transport of between $5.1 \cdot 10^9$ to $22.8 \cdot 10^9 \text{ g}$ per year (Bogen and Bonsnes, 2003).

Sampling expeditions were carried out in August 2012 and 2013. Sampling locations along the Bayelva River were the HBR (head of Bayelva River) site, near the Austre Brøggerbreen glacier and $\sim 0.5 \text{ km}$ downstream from the visible supraglacial output, the MBR (middle-reach of Bayelva River) station located in the middle

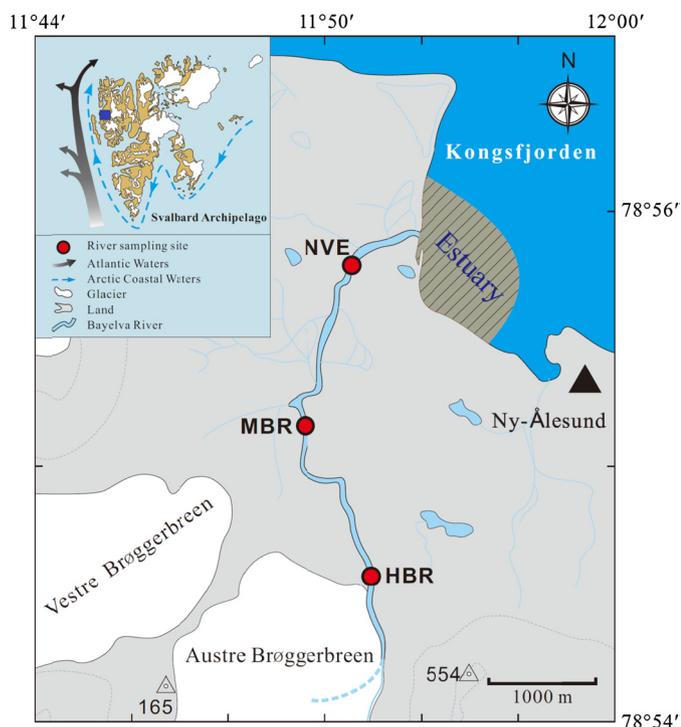


Fig. 1. Map of the study area, with the Bayelva River flowing from supraglacial terrain of the Austre Brøggerbreen glacier for ~4 km through proglacial terrain before draining into Kongsfjorden. Red circles represent sampling sites along the Bayelva River. The hatched region represents the sampling area of Bayelva River estuary. Inset: regional map showing the location of the study area in the Svalbard Archipelago (blue square), with local circulation patterns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reach of Bayelva River, ~1.8 km from glacier, and the NVE (Norwegian Water Resources and Energy Directorate) station situated 2 km northwest of Ny-Ålesund and 300 m from the outlet of the Bayelva River into Kongsfjorden. All three locations were sampled at least once during both the 2012 and 2013 campaigns, and the NVE site was sampled 5 times during 2012. The Bayelva River estuary was sampled only during 2012.

2.2. Sample collection and handling

All plasticware, including high density polyethylene (HDPE) bottles (Nalgene) and Teflon PFA filtration assemblies (Savillex) were cleaned in a class 1000 clean lab at East China Normal University by rinsing with ultrapure water (Milli-Q), soaking in 2% Citranox detergent for 24 h, rinsing five to seven times with ultrapure water, leaching for 7 days in 10% HCl at room temperature or for 2 days in 10% HCl at 60 °C, and rinsing again five times with ultrapure water. In addition to the cleaning steps described above, PFA was boiled in 10% aqua regia for 30 min before Citranox and 10% HCl cleaning steps. HDPE bottles were filled with 0.1% (0.012 M) HCl using acid purified by quadruple distillation in a quartz still (QD HCl), and sealed in double bags until use. Filters (0.4 μm PC membranes, Whatman) were cleaned in 10% QD HCl at 60 °C for 24 h, rinsed ten times with ultrapure water, cleaned at 60 °C for another week in ultrapure water, then rinsed five times with ultrapure water.

Water samples were collected using a custom made “pole sampler” consisting of a PVC holder attached to the end of a fishing rod. This 2 m long rod made it possible to avoid contamination from the side of the ship when sampling in Kongsfjorden, and allowed samples to be taken from the middle of the main stream of the Bayelva River. To collect samples, a 1 L HDPE bottle was attached to the pole sampler, rinsed several times with the natu-

ral waters, and submerged until full. After sampling, bottles were sealed and stored in double plastic bags in a dark cool box until filtration in an onshore lab in Ny-Ålesund.

Samples were filtered through a 0.4 μm pore size membrane, meaning our samples included both soluble Fe (<0.02 μm) and colloidal Fe as typically defined operationally in the chemical oceanography literature (0.02–0.45 μm) (Wu et al., 2001). These samples will also include a portion of the Fe occurring in the size range typically described as nanoparticulate (0.02–0.1 μm) (Raiswell and Canfield, 2012). Samples were filtered in a class 100 portable clean flow bench (Air Control). The filtration system was rinsed with copious quantities of 0.1% QD HCl, ultrapure water, and a small amount of sample, before filtering the bulk of the sample. Subsamples were collected in cleaned 30 mL or 500 mL HDPE bottles and acidified to pH 2 with QD HCl before storage.

2.3. Meltwater incubation experiment

Incubation of meltwater was carried out at the Ny-Ålesund research labs in order to determine how dFe changed over time and to investigate the role of light and DOC on dFe. Five liters of meltwater were collected at the NVE station by pole sampling from the main channel of the Bayelva River. These samples were filtered and homogenized, then 1 L was added to each of four 2 L acid-cleaned PTFE-lined plastic bags, sealed with a PTFE plastic rod sealer, and incubated on an exterior balcony. Two incubations were performed in the dark and another two incubations were exposed to natural sunlight, which was visible 24 h a day. Samples were exposed to ambient temperature fluctuations (0–6 °C). From each sample bag, 100 ml subsamples were taken on days 0, 2, 6, 8, and 13, filtered, and stored for analysis of dissolved Fe and DOC.

2.4. Fe concentration analyses

Dissolved iron concentrations were analyzed by ICPMS after single-batch extraction onto a nitrilotriacetate resin (NTA, Qiagen) according to the procedures of Lee et al. (2011). Briefly, samples were spiked with an enriched ^{54}Fe solution, oxidized with H_2O_2 , and extracted onto ~100 clean NTA resin beads. After separating Fe from other ions on the NTA resin, samples were reconstituted in 0.5 M HNO_3 for analysis on a multi-collector ICPMS (Neptune, Thermo) at East China Normal University. The Neptune was operated in high-resolution mode with a minimum resolution of 6000 in order to separate ^{54}Fe and ^{56}Fe beams from $^{40}\text{Ar}^{14}\text{N}$ and $^{40}\text{Ar}^{16}\text{O}$ interferences, respectively. Three replicates from each 30 ml subsample were prepared for analysis, and in rare cases where the three replicates did not agree another 3 replicates were prepared. The typical procedural blank was 0.15 nM, with a detection limit of ~0.12 nM (based on three-times the standard deviation of the procedural blank). Accuracy of the method was tested by analysis of three SAFe open ocean intercalibration samples, and our measurements compared favorably with the consensus values (provided by Ken Bruland, April, 2013). Our measured Fe concentrations for SAFe S, SAFe D1 and SAFe D2 were 0.094 ± 0.019 , 0.68 ± 0.07 and 0.94 ± 0.07 nM compared to consensus values of 0.094 ± 0.008 , 0.70 ± 0.03 and 0.95 ± 0.02 nM, respectively. Measurements of two high concentration certified reference materials (both NRC, Canada) also compared favorably: estuarine water SLEW-3 (10.4 ± 0.2 vs 10.2 ± 1.2 nM) and river water SLRS-5 (1.25 ± 0.10 vs 1.62 ± 0.12 μM). We suspect that the relatively lower accuracy of our technique for samples with higher Fe concentrations is due to low spike/sample ratios. Therefore, Fe concentrations for meltwater samples with high concentrations of dFe were obtained from double-spike Fe isotope analyses (see below).

2.5. Fe isotope analysis

Iron stable isotope analyses were carried out using a double-spike technique according to previously published methods (Conway et al., 2013). Briefly, samples were spiked with an iron double spike consisting of roughly equal amounts of ^{57}Fe and ^{58}Fe at a sample:spike ratio of 1:2. Samples were then dried down in clean PFA vials, reacted with 200 μL each of clean concentrated HNO_3 and H_2O_2 (Aristar, VWR) to dissolve any organic material, and dried down again. Samples were then purified by anion exchange chromatography according to methods developed for marine particulate Fe (Revels et al., 2015). Samples were first reconstituted in 0.2 mL 10 M HCl and 0.001 M H_2O_2 , then loaded onto 135 μL AG-MP1 resin. After rinsing with 0.5 mL 10 M HCl and 0.001 M H_2O_2 , iron was eluted from the resin with 0.8 mL 1 M HCl. The eluent was then dried down and reconstituted in 2 mL 0.1 M HNO_3 for isotopic analysis on a Neptune multi-collector ICPMS at the University of South Carolina Center for Elemental Mass Spectrometry. In addition to stable isotope ($\delta^{56}\text{Fe}$) data, the double spike method also allowed for the calculation of ultra-precise Fe concentration data for all Bayelva River samples.

2.6. Analysis of other physical and chemical parameters

Temperature, pH, dissolved oxygen (DO), and salinity were measured in situ with a WTW multiline F/sets3 multi-parameter probe. Total suspended material (TSM) was determined by filtering onto pre-weighed Whatman GF/F filters, which were then freeze dried and reweighed. Dissolved organic carbon (DOC) was analyzed by the high-temperature catalytic oxidation (HTCO) method with a Shimadzu TOC analyzer (Model TOC-CPH) according to the methods of Wu et al. (2013). The method used for determination of dissolved manganese (dMn) is modified from the methods of Resing and Mottl (1992), which determined dMn concentrations by leucomalachite green–sodium periodate catalytic kinetic spectrophotometry (Wang et al., in press).

3. Results

3.1. Bayelva River

3.1.1. Bayelva River transect

During both the 2012 and 2013 field seasons, samples were taken from three stations along the Bayelva River on the same day (Fig. 2). In both years, the highest dFe concentrations were observed in samples taken closest to the glacier output (734 nM in 2012 and 401 nM in 2013) with decreasing concentrations downstream. During 2012, dFe was approximately twice as high at all three stations compared to 2013, though the rate of dFe loss was similar both years with a 71% decrease in dFe between HBR and NVE stations in 2012 and an 84% reduction in dFe between the same stations in 2013. Additionally, dFe was measured in two samples taken from tributaries to the Bayelva River in 2012, with 226 nM in a supraglacial tributary and 157 nM in a tributary near NVE station.

A variety of other physical and chemical parameters were also measured along the transect. Little variation of pH was observed, with an average pH of 8.23 ± 0.41 in 2012 and 8.27 ± 0.68 in 2013. Dissolved oxygen (DO) increased slightly with distance from the glacier during both years, from 12.6 mgL^{-1} at HBR to a supersaturated value of 20.1 mgL^{-1} at NVE in 2012, and an increase from 12.5 mgL^{-1} to 15.3 mgL^{-1} at the same stations in 2013. DOC and dMn both decreased away from the glacier in 2012, from 275 nM to 153 nM for dMn and from 167 μM to 98 μM for DOC. TSM increased 17% from 389 mgL^{-1} at station HBR to 455 mgL^{-1} at station MBR, then decreased to a value of 115 mgL^{-1} at station

NVE. Dissolved $\delta^{56}\text{Fe}$ did not vary in any systematic fashion along the transect, with all values between -0.11‰ and 0.09‰ .

3.1.2. Bayelva River temporal variability

Over twelve days in August 2012, the same parameters which had been measured on the transect were monitored at the NVE station (Fig. 2). Over this time, discharge rates varied from 0.8 $\text{m}^3 \text{s}^{-1}$ to 6.4 $\text{m}^3 \text{s}^{-1}$ (Fig. 3). Dissolved Fe concentration varied from 15 nM to 213 nM, with an average value of 116 ± 84 nM ($n = 5$). These dFe values were similar to the range observed at this station during the transect sampling, and all values were lower than dFe measured closer to the glacier, at station HBR. No clear relationship was found between dFe and discharge at the NVE station.

3.2. Kongsfjorden estuary

Dissolved Fe concentrations were measured at a variety of salinities in the Bayelva River estuary where fresh glacial waters mix with saline coastal seawater (Fig. 4). Assuming that the average dFe concentration measured at the NVE station, ~ 300 m upstream from Kongsfjorden, represents the freshwater end-member (116 nM), there is a significant loss of Fe immediately upon mixing of fresh and saline waters, with dFe of 27.4 nM at a salinity of 1.5, dFe of 11.3 nM at a salinity of 6.9, and an average dFe of 4.7 ± 1.6 nM ($n = 7$) at salinities $\sim >10$.

3.3. Freshwater incubations

Incubations of Bayelva River waters were performed for two weeks in both natural light conditions and in the dark, during which time dFe and DOC concentrations were monitored (Fig. 5). dFe in filtered waters from the NVE station at the beginning of the experiment (incubation day 0) was 15 nM. This decreased sharply to ~ 7 nM by day 2 in both dark and light incubations. Subsequently, dFe concentrations in the dark incubations remained relatively constant, decreasing only ~ 1 nM over the next 12 days of the incubation experiment, with differences between the two replicate dark incubations within analytical error. In contrast, dFe in the light incubations decreased further, to about 5 nM by the end of the experiment. DOC also decreased dramatically within the first 2 days of the experiment from 75 μM at day 0 to ~ 15 μM at day 2. Between days 2 and 12 there did not appear to be much further loss of DOC, though it is possible that samples were contaminated during filtration, especially considering the low DOC present. Nonetheless, the $\sim 75\%$ loss of DOC at the beginning of the experiment was observed in all four samples and therefore appears robust.

4. Discussion

A primary aim of this study is to investigate the transportation and transformation of dFe between a glacial source and the ocean, via a glacial meltwater river, and to evaluate the importance of glacial meltwaters as a source of Fe to the oceans. To do so requires both a quantitative measure of the amount of dissolved Fe which is stabilized in glacial meltwaters, where it can ultimately be delivered to the oceans, and an understanding of the chemical transformations by which Fe is lost from glacial waters. Below we discuss both our observations about Fe concentrations in the Bayelva River and estuary, and hypothesize about the processes responsible for Fe precipitation or stabilization.

4.1. Sources of water and Fe to the Bayelva River

Though we regard the Bayelva River as being mostly closed to new inputs along its course to the ocean, there are likely small

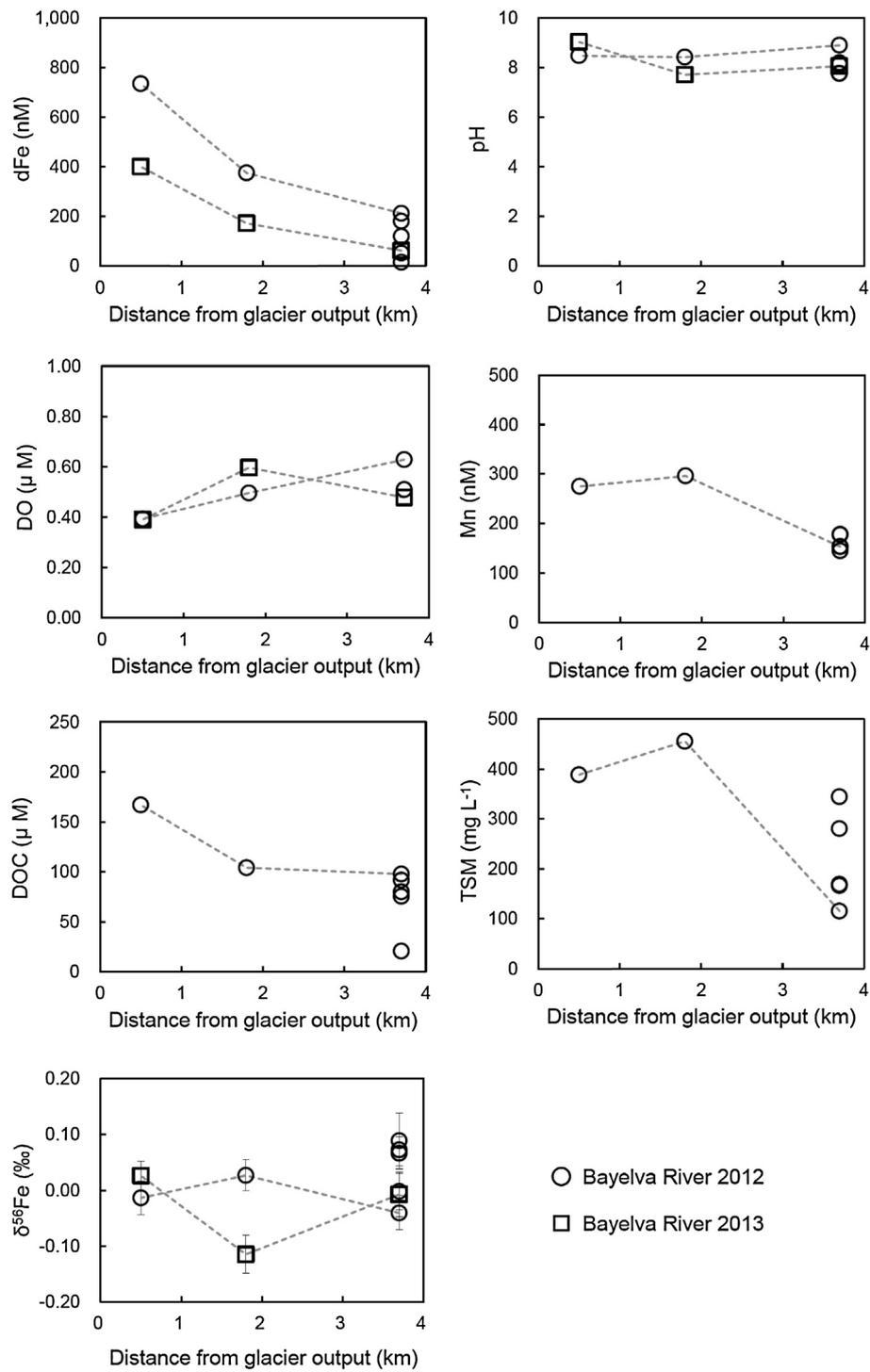


Fig. 2. Dissolved Fe (dFe) concentrations, $\delta^{56}\text{Fe}$ values, and ancillary parameters including pH, dissolved Mn (dMn), dissolved oxygen (DO), dissolved organic carbon (DOC), and total suspended matter (TSM) in the Bayelva River. Open circles represent data from 2012 and open squares represent data from 2013. Dashed grey lines connect data from samples taken during the same day.

inputs from groundwater and tributary streams. For example, Mn concentrations were $\sim 8\%$ higher at the MBR station compared to HBR, suggesting either rapid timescale variability in Mn output from the glacier or input from hyporheic groundwater (Green et al., 2005). Inputs from longer residence-time groundwater to the Bayelva are not thought to be significant (Nowak and Hodson, 2013). During the sampling period, we did not observe any large tributaries to the main stream of Bayelva River. dFe concentrations in the two tributaries which we measured (~ 200 nM) were

not low enough to account for the loss of Fe along the path of the Bayelva by dilution alone. Discharge data from many different years has suggested that meltwater from Austre Brøggerbreen contributes $>50\%$ of total discharge in Bayelva River (Hodson et al., 1998). We therefore conclude that while lateral inputs of both water and Fe to the Bayelva River may occur, they are not a dominant factor in dFe and cannot explain the dramatic dFe decrease observed downstream in the Bayelva River.

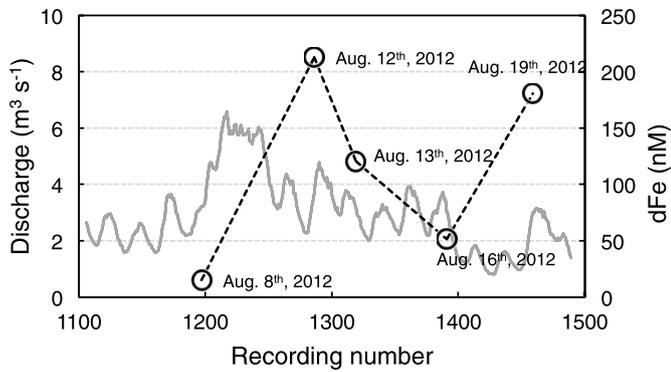


Fig. 3. Dissolved iron concentrations (open circles) and discharge (grey line) monitored at NVE station on the Bayelva River in August 2012. Sampling date for each dFe measurement is given beside dFe data symbols.

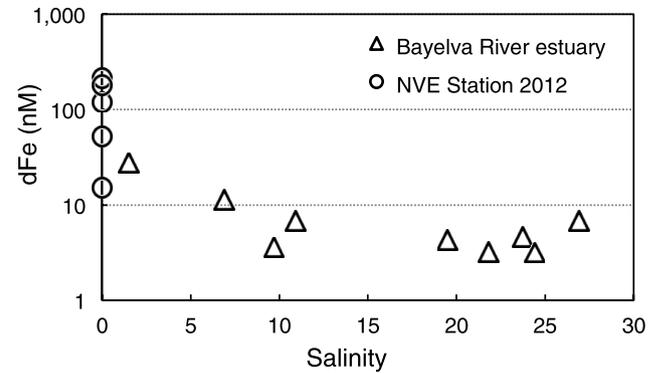


Fig. 4. Dissolved Fe (dFe) concentrations compared to salinity in Bayelva River estuary (triangles) and in the Bayelva River roughly 300 m upstream of the estuary (circles).

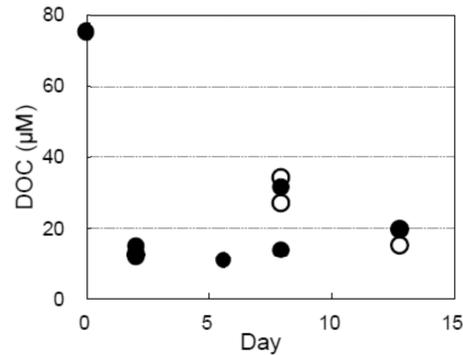
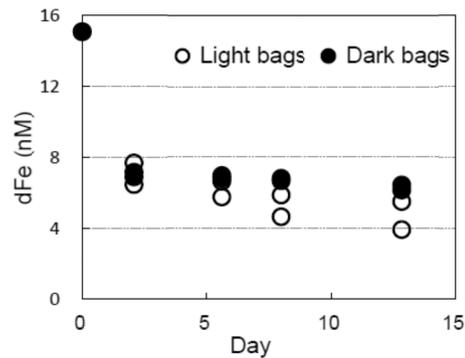


Fig. 5. Dissolved Fe and DOC concentrations in light and dark incubations in duplicates. Open circles are bags incubated in daylight, while solid circles represent bags kept in the dark.

4.2. Rates of Fe precipitation from Fe in glacial meltwaters

Several lines of evidence suggest that most dissolved Fe is quickly precipitated within hours after emerging from the glacier, but that a small fraction (4–7 nM) is present in a chemical form that is stable over a period of days to weeks. In both 2012 and 2013, Fe concentrations decreased markedly downstream in the Bayelva River (Fig. 2). Estimates of river velocity suggest that water travels the entire ~4 km from the glacier to Kongsfjorden in 1 to 3 h (Hodson et al., 2005), suggesting that the half-life for dFe in the river is about an hour or less. While most of the dFe was precipitated from river waters during this short transect, significant quantities remained even in the samples taken downstream at the NVE station (15–213 nM). Considering that our first sampling site located at the highest accessible location was still ~0.5 km from the glacier output, our measurements of dFe and our estimates of Fe loss in the proglacial environment represent likely minimum values.

Incubation experiments also suggest that a small portion of glacial meltwater Fe is present in a stable dissolved form, regardless of whether samples are exposed to sunlight or not. When Bayelva River waters were incubated, a rapid loss of Fe was observed over the first two days of the experiment. In the dark incubations, very little additional Fe was lost from the dissolved phase. The rate of Fe loss from the dissolved phase in the light incubations was also quite slow from days 2 to 12, compared to rates of Fe loss in the Bayelva River and during the first two days of incubation. The slight loss of Fe in the light incubations is consistent with the work of Shiller et al. (2006), who found that photooxidation could destroy Fe binding organic ligands leading to precipitation of Fe(III). We cannot rule out the possibility that the rapid loss of dFe over the first two days was due to Fe adsorption to the

PTFE bag lining, though PTFE is not very surface reactive to either inorganic Fe oxyhydroxides or organically bound Fe. Even if a significant amount of Fe was lost by adsorbing to the bag walls, rather than by precipitation and removal during filtration, this may still reflect a large pool of surface-reactive Fe in the Bayelva River that would be lost either by precipitation or adsorption during transit or during flocculation upon mixing with the estuary. The relative surface area in the incubation bags is not much different from the surface area exposed within the stream bed. Thus, we expect that ~4–7 nM of Fe which remained dissolved in the incubation experiments would also remain dissolved under natural conditions.

A similar pattern is observed in the Kongsfjorden estuary, with ~90% of the dissolved Fe present at the NVE station in the Bayelva River lost during the early stages of estuarine mixing (based on an average ~120 nM dFe at the NVE station). This amount of loss is similar to other, non-glacial river systems and mixing experiments, where much of the riverine Fe is lost as the ionic strength of the waters increase (Bergquist and Boyle, 2006; Buck et al., 2007; Dai and Martin, 1995; Krachler et al., 2005; Laglera and van den Berg, 2009). Fe concentrations in the estuary were not significantly different between salinities of 7 to 11 (7.3 ± 3.9 nM, $n = 3$) compared to salinities of 19 to 27 (4.4 ± 1.5 nM, $n = 5$). This suggests mixing of brackish water ($S = 7$ –11) with seawater ($S = 34$), both of which had Fe concentrations of about 5 nM, with little loss or addition of Fe during mixing. During 2012 an endmember seawater sample was collected from the mouth of the Kongsfjorden bay, where it enters the Arctic Ocean, which contained ~3 nM dFe at a salinity of 34 (data not shown).

Considering together all incubation samples after 2 days of incubation, and all estuarine samples at salinities $\sim > 10$, we suggest that between 4 nM and 7 nM of glacial Fe in the Bayelva River is

stabilized in the dissolved phase (5.8 ± 1.4 nM, $n = 20$). This represents roughly 1% of the Fe concentrations measured near to the glacial outflow.

4.3. Mechanism of Fe precipitation

4.3.1. Chemical form of Fe in meltwaters

The high dissolved Fe concentrations observed near the glacial outlet may be either truly dissolved chemical species (<0.02 μm), or small particles which fall in the size range typically described as colloidal or nanoparticulate. One possible mechanism by which Fe may dissolve underneath the glacier or within the moraines of the glacial forefield is by the formation of reduced, soluble Fe(II) from sulfide oxidation, weathering, or microbial respiration (Wadham et al., 2013). Because Austre Brøggerbreen is a cold-based glacier there will be a minimum of delayed subglacial meltwater, though even in cold-based glaciers there can be temperate ice and thin films of water at the ice–rock interface (Raiswell and Canfield, 2012). Observations of water chemistry in Bayelva River have suggested the meltwater does have a subglacial signature during the late ablation season (Nowak and Hodson, 2014). The oxidation half-life of Fe(II) in natural fresh water is typically seconds to minutes (Davison and Seed, 1983), however Fe(II) may be stabilized by complexation with organic ligands (Statham et al., 2012). While we do not observe consistently lower dissolved oxygen concentrations near the glacier, we do observe high dissolved Mn concentrations (153–296 nM) that persist for 4 km downstream of the glacier output (Fig. 2). Reduced Mn(II), like Fe(II), is easily water soluble while oxidized Mn(III) is particle reactive, however the oxidation half-life of Mn is significantly longer than for Fe (Morgan, 2005). Higher dissolved Mn concentrations near the glacier may therefore be indicative of reducing conditions in subglacial waters. Dissolved Fe in meltwaters could be comprised either of dissolved Fe(II), or of nanoparticulate Fe(III) minerals formed after oxidation of the river waters. Alternatively, iron in the dissolved fraction may be present as nanoparticulate minerals, such as the schwertmannite, which can form directly under glaciers when oxic waters weather Fe sulfides (Raiswell et al., 2009).

4.3.2. Mechanism of Fe loss

The study of Fe isotopes can help to constrain the mechanism by which Fe is lost from the dissolved phase. The average $\delta^{56}\text{Fe}$ was statistically equivalent at stations HBR, MBR and NVE, $0.01 \pm 0.03\text{‰}$, $-0.04 \pm 0.10\text{‰}$ and $0.02 \pm 0.02\text{‰}$, respectively, and there was no apparent relationship between dFe and $\delta^{56}\text{Fe}$ in the Bayelva River. Assuming that the Bayelva River is a closed system, the relationship between dFe and $\delta^{56}\text{Fe}$ can be modeled by Rayleigh distillation as:

$$\delta^{56}\text{Fe}_{\text{river}} = \delta^{56}\text{Fe}_{\text{glacier}} + \Delta\delta^{56}\text{Fe}_{\text{precipitate-dissolved}} \cdot \ln(F) \quad (1)$$

where $\delta^{56}\text{Fe}_{\text{river}}$ is the Fe isotope composition measured in the Bayelva River, $\delta^{56}\text{Fe}_{\text{glacier}}$ is the dissolved $\delta^{56}\text{Fe}$ at the glacier output, $\Delta\delta^{56}\text{Fe}_{\text{precipitate-dissolved}}$ is the isotope effect of Fe precipitation, and F is the fraction of Fe remaining in the dissolved phase. Doing so, we find that all of the $\delta^{56}\text{Fe}$ data can be fit with Rayleigh distillation curves assuming that the process by which Fe precipitates fractionates Fe isotopes by less than -0.05 to $+0.05\text{‰}$ from a starting dFe of 700 nM and a starting $\delta^{56}\text{Fe}_{\text{glacier}}$ of -0.02‰ (Fig. 6). Dissolved $\delta^{56}\text{Fe}$ is also similar to the crustal average of around 0.07‰ (Poittrasson, 2006), suggesting that Fe isotopes were not greatly fractionated during dissolution under the glacier before entering the Bayelva River.

In many natural environments, Fe precipitation occurs by processes that are associated with large Fe isotope fractionations, a pattern that is inconsistent with Bayelva River $\delta^{56}\text{Fe}$ measurements. For example, Fe(II) is roughly 3‰ lighter than Fe(III) at

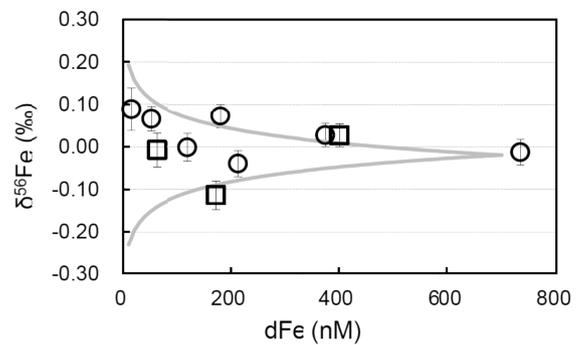


Fig. 6. $\delta^{56}\text{Fe}$ versus dFe concentration. Open circles represent data from 2012, while open squares are data from 2013. Error bars show the 2σ standard analytical errors. Grey line represents the Rayleigh distillation curves for closed system isotope fractionation from an initial glacial outflow with 700 nM dFe and $\delta^{56}\text{Fe} = -0.02\text{‰}$.

isotopic equilibrium (Johnson et al., 2002; Welch et al., 2003), and environments where Fe(II) and Fe(III) are both present are generally characterized by large variations in $\delta^{56}\text{Fe}$ of up to several permil. Examples include reducing sediment porewaters (Severmann et al., 2006; Severmann et al., 2010), hydrothermal vents (Bennett et al., 2009; Severmann et al., 2004), and submarine groundwaters (Rouxel et al., 2008), all of which exhibit $\delta^{56}\text{Fe}$ at least several permil different from the crustal average. Non-redox chemical changes in Fe speciation are also typically associated with large kinetic isotope effects. For example, a series of inorganic Fe(III) precipitation experiments exhibited isotopic fractionations from -0.22 to -2.12‰ with an average $\delta^{56}\text{Fe}$ of -0.95‰ (Balci et al., 2006). Kinetic isotope effects associated with the binding and unbinding of Fe to organics have not been well studied, but organic complexation of Fe by the organic siderophore DFB leads to an equilibrium isotope offset of 0.6‰ fractionation in $\delta^{56}\text{Fe}$ compared to inorganic Fe, suggesting that the kinetic isotope effects associated with binding and unbinding may be even larger (Dideriksen et al., 2008). We cannot rule out the possibility that Fe precipitation in the Bayelva River involves a change in Fe speciation associated with a very small kinetic or equilibrium isotope effect. However, we consider it more likely that Fe speciation does not change during precipitation.

Two processes by which Fe could precipitate without any change in Fe bonding environment (speciation) are the adsorption of organically bound Fe to particles, and the aggregation of nanoparticulate/colloidal Fe. Complexation of Fe by organic ligands is common in natural environments, and such complexes are known to keep Fe(III) dissolved in solution (Rue and Bruland, 1995). Both dFe and DOC are present at much higher concentrations close to the glacier, and concentrations of both decrease downstream (Fig. 2, Fig. 7). However, given a DOC photodegradation rate of ~ 0.25 $\mu\text{M h}^{-1}$ (Mostofa et al., 2007; Shiller et al., 2006) and the short water travel time (1–3 h, Hodson et al., 2005), there should be minimal loss of DOC by photodegradation in the Bayelva River. Instead we presume that the DOC is lost predominantly by adsorption onto particulates. This is supported by the finding that particulate organic carbon increased by $\sim 80\%$ during the transit from station HBR to station NVE, suggesting that DOC loss and dFe precipitation may occur simultaneously. The relationship between DOC and dFe is not entirely linear however, suggesting either that the organics which bind Fe are precipitated more quickly than bulk DOC, or that dissolved Fe is not bound to organics. Alternatively, much of the dissolved Fe may be present as nanoparticulate/colloidal minerals. Operationally, colloidal materials are those in the 0.02 to 0.4 μm size range, meaning that they can pass through a filter to be included in the dissolved phase but still have relatively high molecular weights compared to most “truly dissolved” species. Chemically, colloids are large

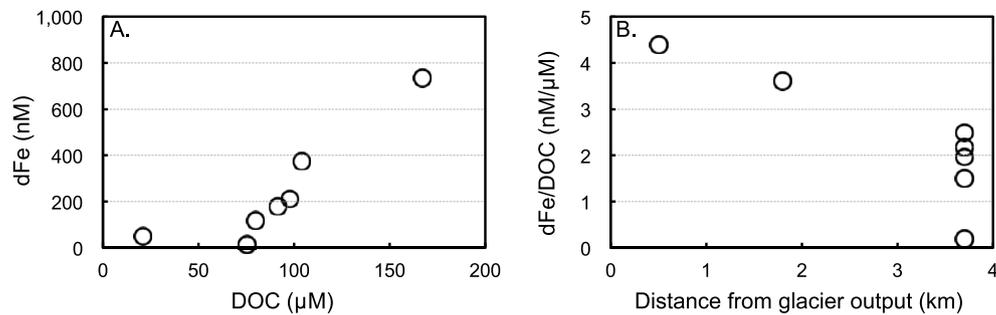


Fig. 7. A. dFe versus DOC in Bayelva River. B. dFe to DOC ratio versus distance from glacier output.

enough that atoms on their interior do not chemically interact with the environment. Thus, aggregation and precipitation of nanoparticulate/colloidal Fe is a pathway by which Fe could leave the dissolved phase without any significant change in Fe bonding environment. Considering the lack of isotopic fractionation during Fe precipitation in the Bayelva River, we propose that precipitation of nanoparticulate/colloidal Fe is the most likely pathway for the loss of dissolved Fe. The suggestion that much of the dFe in Bayelva River meltwaters occurs as nanoparticles/colloids matches similar findings from Greenland (Hawkings et al., 2014) and Alaska (Schroth et al., 2011).

4.4. Glacial Fe contribution to the global marine Fe budget

The dissolved Fe concentrations measured here are on the low end of the global average. The total range for glacial waters reported from previous studies is from a minimum of 20 nM to a maximum of 9950 nM, with an average concentration of $\sim 1000 \pm 1600$ nM for all published meltwater concentrations ($n = 110$) (Bhatia et al., 2013; Green et al., 2005; Hawkings et al., 2014; Statham et al., 2008). The average dFe concentration for all glacial river samples from this study was 233 ± 218 nM ($n = 10$), which is at the lower end of the global range. Some of this variability may be driven by differences in sampling protocol. The highest previously reported Fe concentrations were for samples filtered directly in the field (Bhatia et al., 2013), while lower Fe concentrations were observed by Statham et al. (2008) and in this study, where filtration occurred in the lab several hours after sampling. However, no observable precipitate observed during filtration of samples in this study. Also, if such rapid precipitation were occurring it would be consistent with our overall finding that the half-life for dFe in glacial meltwater is quite short.

Crucially for estimating the flux of glacial Fe to seawater, we hypothesize that dissolved Fe in the Bayelva River occurs in two very different forms. Most of the dissolved Fe measured near the glacier outflow is precipitated within hours to days, and does not enter the Kongsfjorden estuary where it might ultimately mix into the North Atlantic. We propose that this Fe is predominantly Fe nanoparticles/colloids. A second species of Fe, present at concentrations of 5–10 nM appears to be stable on timescales of days to weeks. We propose that this portion of Fe is organically complexed. Thus, when attempting to calculate glacial Fe fluxes to the ocean we suggest that total dissolved Fe concentrations may be a much less important parameter than the concentration of Fe which is stabilized in the dissolved phase for long enough to be mixed into the coastal ocean.

In contrast to previous studies, extrapolating the lower dFe concentrations found in the Bayelva River to global glacial meltwaters would not support glaciers as being an important source of Fe to the North Atlantic. Based on dFe concentrations of 3.7 µM in glacial meltwaters measured in Greenland, and assuming a 90% loss of dFe during estuarine removal processes, Bhatia et al. (2013) extrapolate

to the 0.5 Tm³/y Greenland Ice Sheet runoff volume and predict an annual flux of ~ 0.01 Tg of dissolved iron from the Greenland ice sheet to the North Atlantic. In contrast, applying the same calculations to our average Bayelva River dFe concentration of 223 nM, we would predict fluxes more than an order of magnitude lower ($6 \cdot 10^{-4}$ Tg/y). Similarly, applying our 223 nM to the global glacial meltwater discharge of 1.4 Tm³/y (Raiswell et al., 2006), we would calculate a global dFe input (before accounting for estuarine removal processes) of 0.017 Tg/y, which is insignificant compared to other global total Fe fluxes (iron present in different forms), calculated to be of the order of ~ 1 –100 Tg/y (Jickells et al., 2005). Furthermore, the decrease in dFe concentration between our mean glacial runoff samples (223 nM) and concentrations measured in mid salinity estuarine waters (a mean of 4.4 nM over a salinity range of 19 to 27) suggests that the assumed 90% attenuation of dFe due to estuarine removal processes may be an underestimate. If we were to extrapolate from the ‘stabilized dFe’ (Fe which is assumed to remain in the dissolved phase following the increase in salinity as it is delivered to the ocean) concentrations of 4–7 nM from the Bayelva River to Greenland, we would estimate a glacial flux of dFe from the Greenland Ice Sheet of between $1.4 \cdot 10^{-4}$ and $2.8 \cdot 10^{-4}$ Tg/y, which represents a very small proportion of the soluble Fe to the global iron fluxes (Boyd et al., 2010; Fan et al., 2006).

However, there are several reasons why the dFe measurements from the Bayelva River in Svalbard may not be globally representative. First, The Bayelva River originates from a cold-base glacier where the subglacial processes may be very different from larger ice sheets in Greenland and Antarctica (Nowak and Hodson, 2014). Second, there is large variability in glacial bedrock types, catchment size, and meltwater residence time, and these factors can affect Fe concentration and speciation in meltwaters (e.g. Hawkings et al., 2014). Third, we find that processing in the proglacial environment has a large impact on Fe concentrations and speciation, and considering that our first sample was taken ~ 500 m from the outflow of the glacier there might be much higher dFe in anoxic englacial meltwaters, which in Antarctica and Greenland can be delivered directly into the ocean providing both soluble and reactive nanoparticulate Fe (Raiswell and Canfield, 2012). Finally, even though we observed precipitation of dissolved Fe, the Bayelva River may still be delivering high quantities of reactive particulate Fe to the ocean. Phytoplankton may acquire Fe directly from such particles to support their growth (e.g. Thuróczy et al., 2012). Alternatively, reactive particulate Fe can be dissolved from within the sediments to contribute Fe to the overlying water column (Wehrmann et al., 2014). While our data add significantly to the global dataset on glacial Fe delivery to the oceans, and provide some of the first measurements of Fe delivery from cold-based glaciers, studies with greater spatial and temporal coverage will be needed to fully constrain the possible importance of glacial Fe to the oceans.

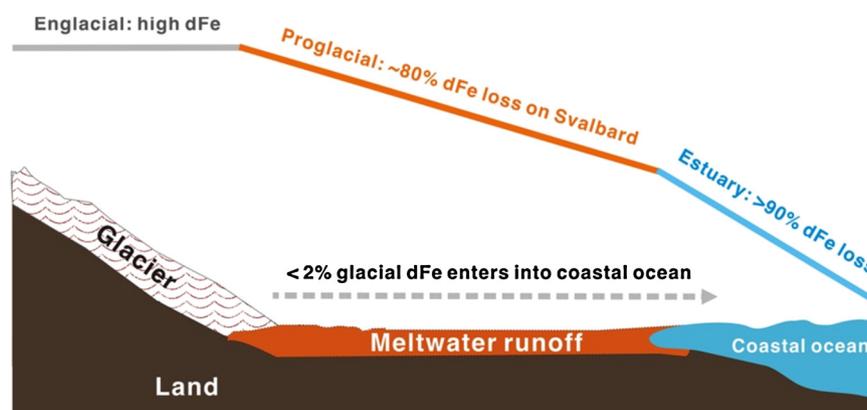


Fig. 8. Schematic diagram of dFe transportation from glacier to coastal ocean on Svalbard.

While the concentration measurements made here cannot directly support glaciers as a significant source of Fe to the North Atlantic, it is intriguing to note that the $\delta^{56}\text{Fe}$ data may be consistent with a large glacial input. Measurements of seawater dissolved $\delta^{56}\text{Fe}$ from the North Atlantic show a distinct isotope signature in Upper Labrador Sea Water (ULSW) near 0 to +0.2‰ (Conway and John, 2014). This Fe isotope signature was originally proposed to result from the interaction of ULSW with resuspended oxic seafloor sediments. However this $\delta^{56}\text{Fe}$ also matches our measurements of glacial $\delta^{56}\text{Fe}$, suggesting that glacial meltwater input may be contributing to North Atlantic dFe.

5. Conclusions

Our data represent the first study of the transport of dissolved Fe in meltwaters all the way from a glacier through a marine estuary (Fig. 8). In this study, a significant loss of dFe in a glacial meltwater runoff was observed during transport through the proglacial environment. In the Bayelva River, roughly ~80% of Fe was lost between a station 0.5 km from the glacial outlet and a station 3.2 km further downstream. A further ~90% of the remaining dFe was lost in the Kongsfjorden estuary. Overall, only ~2% of the Fe output from the Austre Brøggerbreen Glacier was stabilized in the estuary where it could eventually mix into the North Atlantic, excluding the possible redissolution of particulate Fe within estuarine sediments. Based on analyses of various physical and chemical parameters, especially DOC and $\delta^{56}\text{Fe}$, we propose that most of the dissolved Fe in the Bayelva River near the glacial output is in a colloidal/nanoparticulate phase which rapidly precipitates from solution, while roughly 4–7 nM Fe is stabilized by complexation with organic ligands and can be delivered into the Kongsfjorden estuary and eventually the North Atlantic. Given the great variability in glacial Fe fluxes and glacial Fe geochemistry observed to date, our results do not necessarily mean that glaciers are not an important source of Fe to the oceans. However they do suggest that cold-based glaciers contribute relatively low concentrations of dFe, and that bedrock type, weathering intensity below the glacier, and the character of the proglacial environment will all have a significant impact on Fe concentration and speciation in meltwater, complicating efforts to extrapolate the global flux of glacial Fe to the oceans from a limited number of measurements.

Anthropogenic climate change and global warming are predicted to greatly impact the Arctic. Under such conditions, proglacial process will play an important role in controlling the amount of Fe that is delivered to the oceans. Our study implies that accurate estimation of glacial Fe fluxes depends both on sampling a wide variety of glacial locations, and on understanding more fully the processes which lead to the precipitation and stabilization of Fe in proglacial environments.

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