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The effect of warming climate on nutrient and solute export from the Greenland Ice Sheet

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Abstract
Glacial meltwater runoff is likely an important source of limiting nutrients for downstream primary producers. This has particular significance for regions surrounding the Greenland Ice Sheet, which discharges >400 km² of meltwater annually. The Arctic is warming rapidly but the impact of higher discharge on nutrient export is unknown. We present four years of hydrological and geochemical data from a large-Greenland Ice Sheet catchment that includes the two highest melt years on record (2010, 2012). Measurements reveal significant variation in dissolved solute (major ion and estimated dissolved macronutrient (nitrogen, phosphorus and silica) fluxes, with increases in higher melt years. Labile macronutrient fluxes dominate nutrient export, accounting for ~50 % of nitrogen and >80 % of both phosphorus and silica. The response of ice sheet nutrient export to enhanced melting is largely controlled by particle bound nutrients, the future supply of which is uncertain. We propose that the Greenland Ice Sheet provides an underappreciated and annually dynamic source of nutrients for the polar oceans, with changes in meltwater discharge likely to impact marine primary productivity in future decades.

Introduction
Recent estimates predict global mean surface warming of up to 4.8 °C above the 1986-2005 mean by 2100, with the polar regions subject to more extreme increases (Collins et al., 2013). Already, the Greenland Ice Sheet has experienced increased surface temperatures, with the five highest melt seasons on record occurring since 2000 (Tedesco et al., 2013). In 2012, surface melting was the most widespread in over 100 years (Tedesco et al., 2013). By 2100, the annual freshwater flux from the Greenland Ice Sheet could exceed 1000 km² a⁻¹, making it one of the world’s largest sources of freshwater (Fettweis et al., 2013).

Currently, we lack information about the impact of meltwater on downstream biogeochemical cycles, even though the coastal waters surrounding the ice sheet harbour highly productive ecosystems, that are strong CO₂ sinks (Rysgaard et al., 2012). Recent work has highlighted the importance of glacier meltwater, including delivery of essential nutrients to the polar oceans (Bhartia et al., 2013; Wadhams et al., 2013; Hawkings et al., 2014; Lawson et al., 2014). However, whether glacier melting provides an important negative climate feedback through its effect on marine primary production and CO₂ drawdown remains unknown.

Future changes to Greenland Ice Sheet hydrology will probably impact the export of solute and reactive sediments to the polar oceans. Much of the meltwater drains from the surface to the ice sheet bed, chemically weathering the subglacial sediments (Bartholomew et al., 2011). Supraglacial lake drainage events are particularly important because they rapidly channel large quantities of meltwater to the ice sheet bed, flushing out stored, solute-rich, subglacial waters (Bartholomew et al., 2011; Hawkings et al., 2014). Supraglacial lake formation and the migration of drainage systems inland in a warming climate (Leeson et al., 2015) could expose new subglacial areas to meltwater flushing, potentially enhancing solute evacuation. Glaciers are effective at fracturing and grinding bedrock (Cowton et al., 2012), producing turbid meltwaters with abundant, very fine suspended particles, i.e. >1 g L⁻¹ (Cowton et al., 2012). Suspended material has recently been identified as a potential source of labile nutrients to near coastal regions (Hodson et al., 2004; Bhattacharya et al., 2013; Hawkings et al., 2014; Wehrmann et al., 2014) but data are sparse.

In this study, we present a full suite of geochemical and hydrological data from Leverett Glacier, a large (~600 km²), land terminating, outlet glacier of the Greenland Ice Sheet (details in Supplementary Information). The data cover four years (2009-2012) where melting intensity varied (Fig. 1), including the two highest melt seasons on record. This is the most comprehensive dataset yet on major ion and nutrient concentrations from a glacial system.

Results and Discussion
Hydrological data (discharge, electrical conductivity and suspended material concentration) were collected for all four years (2009-2012) at a stable bedrock section ~2.2 km downstream of the glacier mouth. Major ion data are available for 2009, 2010 and 2012 and we used them to interpolate concentrations for 2011. Nutrient flux for 2009, 2010 and 2012 and we used them to interpolate concentrations for 2011. Nutrient flux for 2009, 2010 and 2012 was estimated from 2012 data using a correlation with electrical conductivity. Further details are provided below and in Supplementary Information.

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Hydrology

The 2010 and 2012 ablation seasons produced the largest volumes of meltwater on record (Tedesco et al., 2013). This is reflected in Leverett Glacier discharge (Fig. S-1), which was proportional to annual ice sheet runoff ($R^2 = 0.97$; Fig. 1b). The snowline also reached maximum elevation in 2012, 14 km further inland than in 2010 and 2011 (Table 1; Fig. 1c). 2009 and 2011 can be considered “average” melt years, with discharge proportional to the mean meltwater flux over the past decade. 2010 and 2012, with significantly above average discharge, were “extreme” melt years. This characterisation provides a benchmark for evaluating future trends because the frequency of extreme seasons is likely to increase (Fettweis et al., 2013).

Table 1  Flux and hydrological data.

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenland Ice Sheet runoff *</td>
<td>km$^3$</td>
<td>348</td>
<td>559</td>
<td>466</td>
<td>665</td>
</tr>
<tr>
<td>Leverett Glacier discharge</td>
<td>km$^3$</td>
<td>0.94</td>
<td>1.79</td>
<td>1.10</td>
<td>2.03</td>
</tr>
<tr>
<td>Snowline above catchment</td>
<td>est. days</td>
<td>45</td>
<td>100</td>
<td>73</td>
<td>85</td>
</tr>
<tr>
<td>Snowline retreat from margin</td>
<td>km</td>
<td>125</td>
<td>135</td>
<td>135</td>
<td>149</td>
</tr>
<tr>
<td>Solute Flux</td>
<td>eq</td>
<td>3.0 x 10$^8$</td>
<td>5.6 x 10$^8$</td>
<td>3.2 x 10$^8$</td>
<td>5.6 x 10$^8$</td>
</tr>
<tr>
<td>Sediment Flux</td>
<td>t</td>
<td>3.7 x 10$^8$</td>
<td>2.6 x 10$^8$</td>
<td>3.0 x 10$^8$</td>
<td>2.2 x 10$^8$</td>
</tr>
<tr>
<td>Dissolved inorganic nitrogen †</td>
<td>t</td>
<td>25</td>
<td>46</td>
<td>26</td>
<td>48</td>
</tr>
<tr>
<td>Dissolved silica †</td>
<td>t</td>
<td>130</td>
<td>230</td>
<td>120</td>
<td>230</td>
</tr>
<tr>
<td>Dissolved inorganic phosphorus†</td>
<td>t</td>
<td>6.2</td>
<td>12</td>
<td>6.7</td>
<td>12</td>
</tr>
<tr>
<td>Dissolved inorganic nitrogen ‡</td>
<td>t</td>
<td>22</td>
<td>41</td>
<td>25</td>
<td>47</td>
</tr>
<tr>
<td>Dissolved silica ‡</td>
<td>t</td>
<td>110</td>
<td>220</td>
<td>130</td>
<td>240</td>
</tr>
<tr>
<td>Dissolved inorganic phosphorus‡</td>
<td>t</td>
<td>7.8</td>
<td>15</td>
<td>8.9</td>
<td>16</td>
</tr>
<tr>
<td>Exchangeable NH$_4$**</td>
<td>t</td>
<td>19-58</td>
<td>13-41</td>
<td>15-47</td>
<td>11-35</td>
</tr>
<tr>
<td>Amorphous silica**</td>
<td>t</td>
<td>18,000-44,000</td>
<td>12,000-31,000</td>
<td>14,000-36,000</td>
<td>11,000-26,000</td>
</tr>
<tr>
<td>NaOH extractable phosphorus**</td>
<td>t</td>
<td>20-130</td>
<td>14-92</td>
<td>16-110</td>
<td>12-78</td>
</tr>
</tbody>
</table>

All estimates are shown to Decimal Day 230/231, i.e. 17 August. Estimates are reported with 2 significant digits.

* Greenland Ice Sheet runoff estimates from Tedesco et al. (2013).
† Sediment fluxes given as range based on minimum and maximum extractable nutrient concentrations.
‡ Fluxes estimated using discharge weighted mean.

Solutes Flux

We estimated total solute export for all years from the electrical conductivity (EC) of the meltwater (Fig. S-3). The major ion (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$) concentrations are a linear function of conductivity with $R^2 = 0.87$ (2009), 0.77 (2010) and 0.98 (2012) (Figs. S-3 and S-4). We have a full hydrological dataset (discharge, EC and suspended material) from 2011 but major ion data are missing so using the concentration-conductivity correlation for data from 2009, 2010 and 2012 (n = 368; $R^2 = 0.89$), we estimated 2011 solute concentrations (Fig. S-3). Solute flux was estimated by cumulatively summing the total solute concentration.
at each conductivity measurement time step (Fig. 2). We differentiated supraglacial solute from the total solute flux to assess the importance of subglacial sources (Fig. 2a). The estimates suggest that flushing of stored subglacial waters and rapid weathering of subglacial sediments by dilute supraglacial meltwater account for >95% of the solute export from the catchment.

A key discovery is that solute flux during the two extreme melt years was ~90% higher than for the average years, indicating that solute export scales with discharge. Thus, it is likely that increased melting will increase solute fluxes from the Greenland Ice Sheet. Most of the solute is delivered during peak melt periods during the ablation season (Fig. S-5). Solute pulses are also released during supraglacial lake drainage events (Fig. S-5; Bartholomew et al., 2011). Enhanced solute discharge during extreme years likely results from i) drainage of concentrated subglacial waters stored in poorly connected regions, e.g., deeper into the ice sheet, ii) higher flushing rates and iii) rapid weathering of reactive subglacial sediments by large volumes of supraglacial meltwater. We next ascertain if nutrient fluxes follow the same trend.

**Dissolved nutrient fluxes**

Nutrient fluxes for all years were estimated from the 2012 dataset, the only complete macronutrient record available. For the most common, namely NH$_4^+$, NO$_3^-$, Si and PO$_4^{3-}$, we also estimated annual flux by correlation with conductivity, as for major ion concentrations. This is justified by the good correlation of conductivity with nutrient concentrations (Fig. S-6). If the function holds for 2012, we assume it also holds for the other years. Si and P are released during rock weathering and dissolved inorganic nitrogen is also enhanced by subglacial biogeochemical processes, such as microbially mediated nitrification (NO$_3^-$) and mineralisation of organic matter (NH$_4^+$; Wynn et al., 2007). For example, mean nitrogen concentrations attributable to subglacial processes (~1 μM) are similar to supraglacial processes (~1.3 μM). Nitrogen correlates linearly with conductivity ($R^2 = 0.74$; Fig. S-6). To account for the seasonal evolution in meltwater composition, we used two regressions (Fig. S-6) for dissolved silica ($R^2 = 0.72$ for early season and $R^2 = 0.34$ for bulk season runoff), and phosphate ($R^2 = 0.61$ and 0.59, respectively). We propose that these differences arise from the change in source of the subglacial water as the melt season progresses, i.e., close to ice margins early in the season to more isolated inland subglacial waters as the season progresses. The source influences the subglacial flowpath length, hence water residence times and pH/redox conditions.

Higher dissolved nutrient flux correlates with higher discharge years. Inorganic nitrogen (86% ± 9.8%), dissolved silica (85% ± 0.1%) and phosphate (86% ± 11.9%) are higher in extreme melt years than for average years. This is significant and demonstrates the potential for nutrient release by a warming climate.

A different approach for estimating nutrient flux is to combine discharge weighted mean concentrations and total discharge flux (Hawkins et al., 2014). Estimates from this method and the EC-based method are similar (Table 1). The weighted mean dissolved nitrogen and silica fluxes were marginally lower (~7% and ~5%) and phosphate flux was higher (~23%), probably because of late melt season influence, when phosphate concentrations were high and where the bulk of the discharge occurred.
An important assumption is that the correlation of nutrient concentration with conductivity is consistent over the years. We have a limited dataset for NO$_3^-$ and Si from 2009. Results are sparse so estimates are crude but they serve as a benchmark for comparison. Flux derived from 2009 data for NO$_3^-$ N is 12 tons, compared with 15 tons estimated using 2012 data. Flux for dissolved Si is 180 tons, compared with 130 tons estimated using 2012 measurements (Table 1). Both are well within an order of magnitude, which offers confidence that our estimates from 2012 data are reasonable.

**Nutrient flux on particles**

Glaciers effectively fracture and grind bedrock into high surface area, highly reactive, clay and silt sized particles, some of which are transported in runoff as suspended material (Gurnell and Clark, 1987; Brown et al., 1996). By using data derived from the labile nutrients in the 2012 suspended material (n > 25), we estimated the range of nutrient concentrations associated with the particulate fraction (Table 1; Fig. 3). We assumed that the 2009-2011 mean extractable nutrient concentrations lie within the 2012 minimum and maximum concentrations, which is reasonable because the runoff comes from the same catchment and the mineral composition is relatively constant (Hawkings et al., 2014).

![Graph showing particulate and dissolved nutrient flux](image)

**Figure 3** Estimated nutrient flux. Minimum (left column), mean (middle) and maximum (right) possible values give an impression of the range for phosphate, silicate and nitrogen compounds. Dissolved flux was determined using the electrical conductivity correlation.

Particulate bound nutrients account for a large portion of the estimated nutrient flux (Table 1; Fig. 3), which is significant in all years. The particulate transported fraction correlates with the nutrient source (lithogenic or atmospheric) and the tendency for the ion to complex. Nutrients derived directly from rocks associate more with solids, i.e. for Si, >99 % and for P, ~80 % of the total flux. Nitrogen, which has a supraglacial component, is transported less on solids, i.e. <50 %. Our results are consistent with the low solubility of Si and the high affinity for P absorption onto solids, such as iron (oxyhydr)oxides. Ammonium is only weakly absorbed and nitrate remains preferentially in solution. This suggests that annual nitrogen flux is more sensitive to changes in ice sheet water discharge than particle flux.

We have demonstrated that, as in riverine systems (Mayer et al., 1998; Ruttenberg, 2014), a high fraction of ice sheet nutrient export is associated with suspended material. This is consistent with previous research from Arctic glaciers (Hodson et al., 2004) and supports recent assertions that the impact of terrigenous material on the oceans is underestimated in global element cycling (Jeandel and Oelkers, 2015). Our results underline the need for more information about ice sheet sediment flux dynamics. As in previous studies, we observed highly variable annual sediment fluxes, which do not correlate well with discharge on a catchment basis (Fig. 2; Gurnell and Clark, 1987). Sediment flux might be less influenced by total meltwater discharge and more sensitive to meltwater access to fresh, subglacial sediment sources (Cowton et al., 2012). However, evidence from past deglaciation events indicates that climate warming increases sediment export (Jeandel and Oelkers, 2015) and analysis of sediment plumes from meltwater rivers demonstrates a higher sediment flux in recent years (Hudson et al., 2014).

The extent of biological consumption of the nutrients bound to particles before deposition and subsequent burial is unknown. Particulates from meltwater are extremely fine, e.g., >95 % of particles can be <32 μm in size (Brown et al., 1996), so surface area is high and nutrient transport in the buoyant, fresh water plumes in near coastal regions is likely to be significant. Evidence from recent polar studies shows that particle borne nutrients are carried far offshore (Schrøth et al., 2014; Wehrmann et al., 2014) and nutrients deposited with glacial sediments in fjords can be resuspended in the water column (Wehrmann et al., 2014). However, the scarcity of data means that the contribution of particle bound nutrients on oceanic productivity near Greenland remains uncertain.

Terrestrial and marine studies have shown that large fractions (75-95 %) of amorphous Si can be dissolved and recycled (Treguer et al., 1995; Gibson et al., 2000). Amorphous Si is an order of magnitude more soluble in saline solutions than in fresh water (Icenhower and Dove, 2000; Loucaides et al., 2008) and recycling is favoured in estuaries (Loucaides et al., 2008). NaOH extractable phosphate is commonly termed “algae available” (DePinto et al., 1981) and its bioavailability has previously been demonstrated (Bostrom et al., 1988). High salinity in ocean and fjord waters also favours P and NH$_4^+$ desorption (Garner et al., 1991; Hodson et al., 2004; Zhang and Huang, 2011), enhancing their bioavailability. Thus, annual sediment flux is an important factor in downstream productivity.
Conclusions

Changes in the hydrological output from the Greenland Ice Sheet in a warming climate could have significant effect on solute and nutrient delivery to near coastal regions. Our data, from Leverett Glacier, a large representative ice sheet catchment, indicate that bulk solute and dissolved nutrient fluxes will increase as “extreme” melt year frequency increases. A significant fraction of nutrients, especially silica and phosphorus, will be transported by suspended particles. The extent of their influence depends on desorption before burial, bioavailability and change in the ice sheet particulate flux, which are currently uncertain. Our study demonstrates that retreating snowline and higher meltwater input into less efficiently drained subglacial regions are likely to increase the dissolved macronutrient flux. Particle bound nutrients have been largely overlooked but contribute significant mass to nutrient cycling. Increased warming, thus increased meltwater runoff, will likely impact regional nutrient availability, and thus, the carbon cycle.

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Supplementary Information

This letter accompanies this letter at www.geochemicalperspectivesletters.org/article1510

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HUDSON, B., OVEREEM, I., McGRAVES, D., SYTVIS, I.P.M., MIRKESSEN, A., HASHOLD, B. (2014) MODIS observed increase in duration and spatial extent of sediment plumes in Greenland fjords. The Cryosphere 8, 1161-1176.

Author Contributions

All authors contributed. JLW and MT conceived the project. JRH, EL, AS, TC, IB, AT, PN, DC and JLW collected field data. JRH, JRH, EL and JT undertook the lab analysis. JRH, JLW and MT wrote the paper.

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Study Site and Methods

Sediments were collected at Leverett Glacier (LG; Fig. 1a; 67.06°N, 50.17°W), a large supraglacial lake on the Greenland ice sheet advance inland under warming climate. Nature Climate Change 5, 51–55.

Figures S-1 to S-6

The Supplementary Information includes:

- Data on the hydrological monitoring of discharge, electrical conductivity (EC) and turbidity (suspended particulate matter), recorded at 5-10 minute intervals (Fig. S-1).
- The hydrological and climatic record was maintained during the 2009-2012 summer ablation seasons, with a significant increase in rainfall and streamflow during the latter years.
- The catchment hydrology is typical of large Greenland outlet glaciers and is described elsewhere (Chandler et al., 2009). Catchment hydrology is typical of large Greenland outlet glaciers and is described elsewhere (Chandler et al., 2009).

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