

Superimposed Ice as Nutrient Storage

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Abstract. Nutrient cycling in the glacial environment is known from the perspective of meltwater release and snowpack elution processes, but the superimposed ice temporary storage remains poorly understood. In this study, the enrichment of superimposed ice in nutrient ions: nitrite, nitrate and ammonium was studied in more detail. The release of these ions from superimposed ice into a supraglacial stream was considered also, additionally considering phosphorus, which was not detected in the snowpack profile, but must have been more abundant elsewhere in the catchment. Nitrite and ammonium were enriched in the superimposed ice layer, and their peak concentrations in discharge formed by melting superimposed ice were also occurring later than for nitrate and phosphate. These two latter species were characterized by another concentration peak, which occurred after the glacial ice became exposed in the catchment.

Keywords: Superimposed ice, nitrate, nitrite, ammonium, phosphate, nutrients.

1. Introduction

Glaciers worldwide undergo rapid melting, releasing the chemical substances stored within them. However, on the glacier surface occur also refreezing processes, that contribute to temporary storage of chemical substances. The delay in the nutrient release is potentially significant to supraglacial and proglacial ecosystems, but little is known about the superimposed ice (refrozen layer) as a nutrient storage medium on glaciers. The investigations concentrate on elution processes in snowpack [1]-[4] and the influence of basal ice formation on runoff [3]. A few other studies [5], [6] address similar processes in Arctic and Antarctic sea ice, but the processes happening there are strongly influenced by the source of brine underneath the ice. No study has yet observed the behaviour of ionic nutrients (nitrogen and phosphorus in ionic forms) in the natural snow column accumulated on the glacier surface as it feeds the superimposed ice forming beneath, to estimate the efficiency of this process and its potential influence on the supraglacial ecosystem. Here, we address this gap by an analysis of a sequence of two snow surveys and a superimposed ice sampling the same location on the glacier surface, as well as the runoff in the nearby stream following the superimposed ice melt.

2. Methods

The study was set up as an experiment in a small supraglacial catchment which was sampled on subsequent occasions during the melt season for the nutrient content of snow, ice and meltwater. Fieldwork was performed in the summer of 2012 on Foxfonna, a small cold-based glacier in the vicinity of Longyearbyen, Svalbard. The study site was chosen in a flat area in the vicinity of supraglacial stream. At the onset of melt, a snow core was retrieved from this location (12th June); afterwards, as the melt proceeded, a snowpit was sampled using a stainless-steel density cutter [7] from its three layers to track processes happening in melting snowpack (11th July). For each snow sample, its snow water equivalent (SWE) was estimated. At the time of the estimated maximum thickness of superimposed ice (28th July), this refrozen layer was cored at the same location (another core, for comparison purposes, was taken 50 m away from this

point). The supraglacial stream in the vicinity of the measurement point was sampled 6 times for ion analysis (between 27th July and 16th August), each sampling followed by a discharge measurement using salt dilution technique.

Snow was sampled into pre-cleaned (with 18 M Ω water) plastic zip-lock bags in the field, melted in low temperature (<10 °C), agitated and transferred into a sampling bottle. All samples were taken into 1 L HDPE bottles, triple-rinsed with sample, and stored in 4 °C until analysis. Before analysis, they were filtered 113A Rotilabo® filter papers (5-8 μ m, 87 g m⁻², Karlsruhe, Germany). Blank samples, standard solutions (Merck, Frankfurt, Germany) and field samples were analysed in triplicates using an ion chromatograph with conductometric detection (Dionex, USA; more detailed methodology described in Polkowska's and Klimaszewska's studies [8], [9]). The nutrient ions analysed were nitrite, nitrate, ammonium and phosphate. Additionally, chloride analysis was included as a conservative hydrological tracer [10]. The limits of detection were: 0.16 mg L⁻¹ for chloride, 0.043 mg L⁻¹ for nitrite, 0.017 mg L⁻¹ for nitrate, 0.015 mg L⁻¹ for phosphate and 0.05 mg L⁻¹ for ammonium ion. In the deposition calculations, values below detection limit were assumed to be equal to a half of the limit level.

3. Results

During melt, ionic content of snowpack was slowly removed and partly trapped in the superimposed ice layer (Table 1). If the initial deposition of nutrients in snow is compared to superimposed ice storage (in relation to the water equivalent ratio of 37.3% between the two), the nitrite and ammonium became relatively enriched in superimposed ice (38.6% and 461.6%, respectively), while nitrate and chloride became less concentrated in the refrozen layer (17.1% and 23.6% of the initial deposition retained, respectively). Hence, if compared to the chloride concentration, both nitrite and ammonium experienced strong enrichment in the ice. Nitrate and ammonium ions have shown higher deposition variability between superimposed ice sampling locations, which were separated by 50 m distance (53.4% and 69.6% difference, respectively, as compared to only 17.0% difference for chloride and 2.0% for nitrate). In the melting snowpack (Fig. 1), increasing concentrations of all detected ions were noted towards the bottom of the profile, nitrate dominating the ionic nutrient composition. All the snowpack concentrations of chloride, nitrate and ammonium were within the range reported on other glaciers (see [11] and citations therein).

Initially, as the leftover snow was disappearing from the catchment, both chloride and all nitrogen containing ions were removed rapidly (Fig. 2); another peak in ionic concentration followed as the superimposed ice started melting (31st July - 8th August). Phosphate and nitrate have been removed faster than ammonium and nitrite. Phosphate and nitrate showed another concentration peak upon transition to glacial ice melt also (12th-16th August), which has not been observed for nitrite and ammonium, but occurred with a lower magnitude for chloride.

Table 1: Ionic deposition [mg m⁻²] in the snow profile before and during melt, and in refrozen form as superimposed ice (mean concentrations [mg L⁻¹] in the corresponding samples reported in brackets).

Medium / ion	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺
Initial snowpack	1331 (3.20)	97 (0.23)	314 (0.75)	46 (0.11)
Metamorphosed, melting snowpack	760 (2.95)	25 (0.10)	168 (0.66)	7 (0.03)
Superimposed ice	314 (2.02)	37 (0.24)	54 (0.35)	211 (1.36)

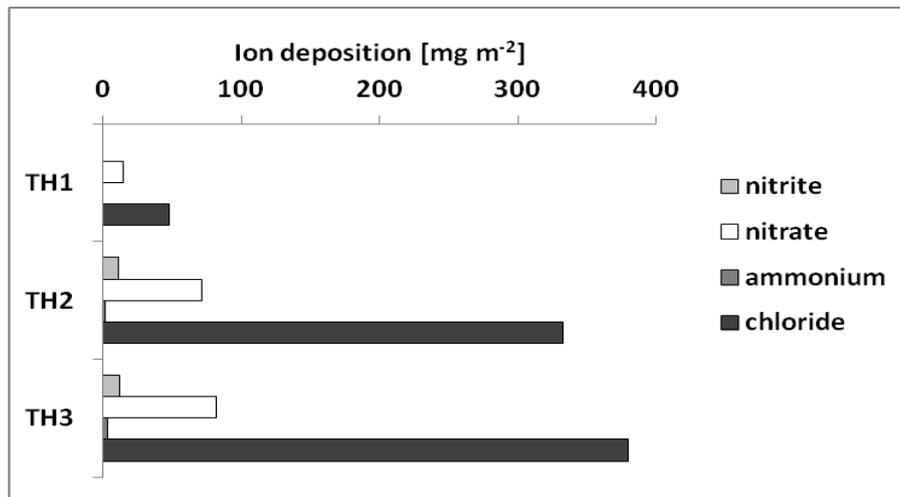


Fig. 1: Distribution of ions (each bar corresponding to deposition in a 10 cm layer) in the melting snow profile taken at the study site on 11th July 2012.

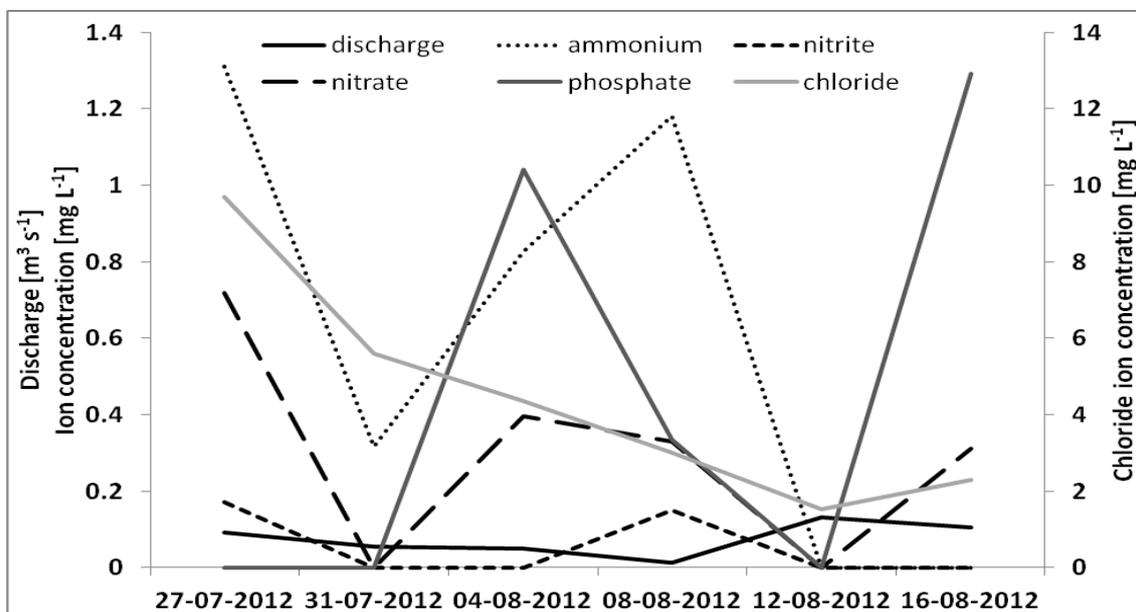


Fig. 2: Ionic nutrient concentration change in the supraglacial stream during and briefly after superimposed ice melt period. For comparison, chloride ion concentration has been plotted on the secondary axis.

4. Discussion

Elution processes were active for all nitrogen ions: ammonium, nitrite and nitrate, as well as chloride, which is included here as a conservative comparison. Ammonium and nitrite were both observed to be captured in the superimposed ice more effectively and removed with a longer delay in the supraglacial stream. The removal of chloride was more uniform than for any of the nutrient species, however ecosystem activity could be involved in the temporal depletion in nutrient levels as well. The nitrate detected in runoff might be partly a result of ammonium ion oxidation, if nitrifying bacteria are present. An interesting feature observed for all studied nutrient ions, but not for chloride, is their rapid increase in concentration upon superimposed ice melt commencement. For nitrate and phosphate, this was also observed in glacial ice melt. The possibility cannot be excluded that ammonium and nitrate concentration increase would follow the pattern established in superimposed ice if the glacial ice was melting for longer.

The increase in ammonium concentration beyond the initial deposition level might be a feature of its mobility in the basal water in snowpack, which would enable its transfer into the flat part from the snowpack above the study site. However, this goes against the argument of Li and others [1] about the relative

immobility of ammonium ion in snowpack, and the usually reported position of ammonium ion in the end of the elution sequence. It can be argued, that the relatively immobile species are therefore captured in the superimposed ice more effectively, while those readily eluted are immediately removed with the meltwater drainage. The diversification of nutrient species supply to ecosystem might be, therefore, increased by the presence of superimposed ice. That could result in different cell communities dominating the supraglacial ecosystem structure in the beginning and end of the melt season. This would also result in diversification of the nutrient supply to downstream ecosystems provided the limited uptake of the nutrients *in situ*.

On the other hand, the emerging pattern might be a result of the existing microbial communities distribution in those media. Nitrate reducing bacteria have been detected in glacial ice [12], [13], while the ice surface (cryoconite debris) has been shown to contain nitrifying communities [14]. This would corroborate with the high spatial variability in ammonium and nitrite concentrations in superimposed ice. Therefore, the refrozen layer might be a source of *in situ* ammonium and nitrite, and the glacier surface a source of nitrate. Thus, the formation of superimposed ice above cryoconite would contribute significantly to its nutrient supply and support its productivity.

5. Conclusion

Nutrient ions can be divided in two groups in terms of their mobility of transfer into and from refrozen ice layer. The oxidized species: nitrate and phosphate were released more readily, less abundant in superimposed ice and experienced a secondary concentration peak in meltwater stream after glacial ice exposure. Ammonium and nitrate were released later from the superimposed ice, perhaps in connection to their relative abundance in this medium. This may influence the supply of nutrients to the supraglacial ecosystem, diversifying periods of favorable conditions for nitrifying and denitrifying bacteria. However, the bacterial communities may be responsible themselves for the distribution of nitrogen species in ice and meltwater, the feedback mechanisms connected to superimposed ice formation and melting remaining underexplored. The noticeable feature of the superimposed ice is its ability to store nutrients while forming and release them while melting, forming peak concentrations in supraglacial runoff.

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