Biogeochemistry
DOI 10.1007/s10533-008-9226-3

ORIGINAL PAPER

Speciation, phase association and potential bioavailability of phosphorus on a Svalbard glacier

Marek Stibal · Martyn Tranter · Jon Telling · Liane G. Benning

Received: 25 January 2008 / Accepted: 2 July 2008

Abstract Glacier surfaces are known to harbour abundant and active microbial communities. Phosphorus has been shown to be deficient in glacial environments, and thus is one of the limits on microbial growth and activity. We quantified the phosphorus pool in cryoconite debris and the concentration of dissolved phosphorus in supraglacial water on Werenskioldbreen, a Svalbard glacier. The mean total P content of the cryoconite debris was $\sim$2.2 mg g^{-1}, which is significantly more than would be expected in rock debris from local sources. 57% of this P was present in the fraction defined as organic P. It may account for the P in excess of the rock debris, and could be explained by allochthonous input of organic matter. The concentration of total dissolved P in supraglacial water was very low (5.2–8.5 μg l^{-1}), which was probably caused by efficient flushing and re-adsorption onto mineral surfaces. Dissolved organic P (DOP) was a very important component of the dissolved phosphorus pool on Werenskioldbreen, as concentrations of DOP typically exceeded those of dissolved inorganic P (or SRP) by more than four times in all the glacial water types. It is very difficult to assess whether P was limiting in this environment solely on the basis of the N:P ratios in the debris or biomass. There may be some degree of biological control over the C:N:P ratios in the debris, but the phosphorus cycling in the supraglacial environment on this glacier seems to be mainly controlled by physical and geochemical processes.

Keywords Biogeochemical stoichiometry · Nutrient transformations · Phosphorus · Supraglacial environment · Svalbard

M. Stibal (✉) · M. Tranter · J. Telling
Bristol Glaciology Centre, School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK
e-mail: marek.stibal@bristol.ac.uk

L. G. Benning
Earth and Biosphere Institute, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

Introduction

Glaciers are now established as ecosystems containing various microbial habitats, and glacier surfaces in particular are known to harbour abundant and active microbial communities (Hodson et al. 2008). There are a growing number of biogeochemical studies from glacial ecosystems (Tranter et al. 2004, Hodson et al. 2005, Bagshaw et al. 2007, Barrett et al. 2007), but our knowledge of the interactions between glaciers and their inhabitants is still very limited. The glacier surface, or supraglacial environment, is of great importance for the entire glacial ecosystem since it receives solar radiation, is the locus of melt water production and is a deposition site for windborne debris and aerosol from the atmosphere,

providing an essential source of nutrients, including nitrogen and phosphorus. The debris melts into the glacier ice due to its lower albedo, forming small cylindrical water-filled depressions called cryoconite holes (Wharton et al. 1985). These features represent a relatively favourable aquatic environment, and most life on the glacier surface is contained within them (Stibal et al. 2006).

Phosphorus (hereafter, P) is one of the key macronutrients, accounting for 2–4% of the dry weight of microbial cells (Karl 2000). It is therefore required by all microorganisms in relatively large amounts. It is also the one macronutrient that is primarily rock-derived and cannot be actively fixed from the atmosphere (Walker and Syers 1976). The amount of dissolved inorganic P in glacial waters is very low (usually <5 μg l^{-1}) and the overwhelming majority of P is bound to sediments and soils (Säwström et al. 2002, Hodson et al. 2004, 2005). Phosphorus deficiency in glacial environments can limit microbial growth and activity (Mindl et al. 2007, Säwström et al. 2007, Stibal and Tranter 2007). However, some aspects of P cycling on glaciers have been largely overlooked, including the role of organic P, in situ transformations of P species and adsorption-desorption reactions between the solid and liquid phase. Müller et al. (2006) showed that P adsorption can be significant and affect the fate of P in an oligotrophic environment with high particle contents. The glacier surface is a good example of such environment, and so most bioavailable P may be associated with the debris, rather than dissolved in water. Export of debris from glaciers to downstream aquatic ecosystems, such as lakes, which are also often P limited (Säwström et al. 2007), may be of significance to biogeochemical cycling of P, since microorganisms may be adapted to episodic sediment loading and capable of accelerating their P uptake (Burkholder 1992).

Here we focus on the distribution of P and its availability for microorganisms on the surface of Werenskioldbreen, a high Arctic glacier on Svalbard, that has been shown to contain viable microbial communities both on its surface (Stibal et al. 2006) and at its bed (Kaštovská et al. 2007). The aim of this study is to quantify the P pool in the cryoconite debris and the amount of dissolved P in the supraglacial water, and to elucidate the interactions between these two P pools. We use biogeochemical stoichiometry (C:N:P molar ratios) to assess the availability and limitation of nutrients for microorganisms and discuss the atmospheric import of P to glaciers and potential export to downstream ecosystems following biological and geochemical transformations.

Materials and methods

Field site

Werenskioldbreen (Fig. 1) is a polythermal-based valley glacier in southwest Spitsbergen, Svalbard (77°04′ N; 15°15′ E). It has a total area of $\sim$27 km^2. The altitude ranges from 65 m a.s.l. at the terminus to $\sim$600 m a.s.l. at the highest point of the accumulation area. The equilibrium line altitude lies at $\sim$425 m. Glacial mass balance measurements conducted in 1993/1994 and 1998/1999 were negative, -0.36 m water equivalent and -0.66 m w.e., respectively, and the glacier terminus retreated by 16 and 25 m per year in 2005 and 2006, respectively (Řehák et al. 2007). During the ablation season, $\sim$25% of melt water flows surficially in channels reaching the terminus, while the rest is routed through moulins and englacial conduits to the bed. The subglacial drainage system is channelised during the melt season (Řehák et al. 2007). The adjacent valley slopes that represent the immediate source of debris for the glacier surface are composed of rocks belonging to the Hecla Hoek succession, and are mostly phyllites, quartzites, metaconglomerates, amphibolites, chlorite schists and mica schists (Majka and Budzyń 2006). The distance to the coastline is $\sim$3 km. Precipitation and surficial meltwaters are influenced by sea spray, as suggested by the major ion chemistry (M. Stibal unpublished data).

The glacier surface harbours microbial communities that are mainly concentrated within cryoconite holes (Stibal et al. 2006). They consist of heterotrophic bacteria, photoautotrophic cyanobacteria and microalgae. Other microorganisms, such as fungi and small metazoans, are also present in low amounts. The abundance of heterotrophic bacteria can reach over 1×10^5 cells mg^{-1} (wet weight) of debris. Photoautotrophic microbes are dominated by filamentous cyanobacteria, with up to 8×10^3 cells mg^{-1} (Stibal et al. 2006, Stibal and Tranter 2007).

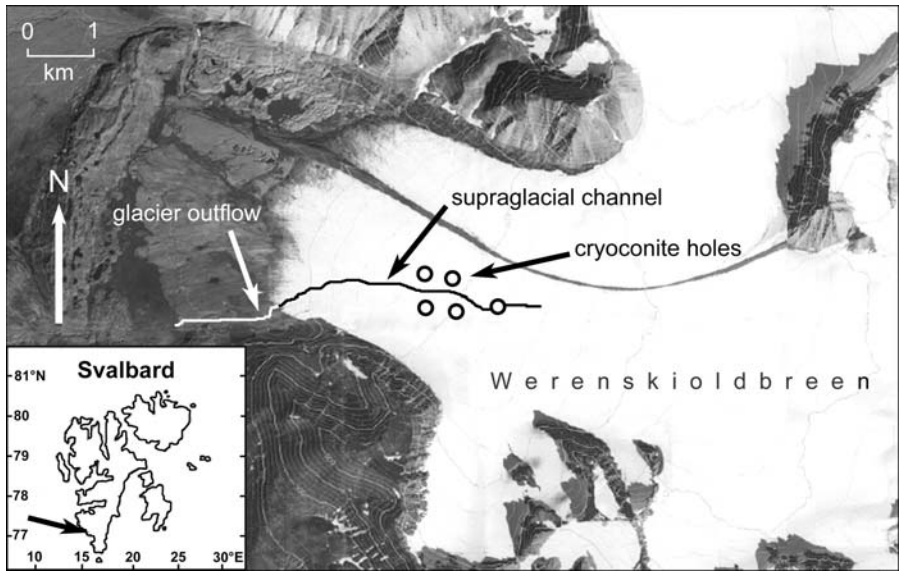

Fig. 1 Map of Werenskioldbreen with schematically marked sampling sites, modified after Jania et al. (2002). The circles show the approximate location of the sampled cryoconites

Sampling

Fieldwork was undertaken from 7 July to 6 August 2006. Samples were collected from cryoconite holes, a representative supraglacial channel and the southern glacier runoff stream (Fig. 1). Six cryoconite holes were randomly selected on the glacier surface and monitored either until the end of the sampling period or until they were destroyed by ablation and melt water flushing. Any hole that dried up or was engulfed by a supraglacial channel was substituted by another randomly selected hole. Samples of water were collected at daily intervals from each cryoconite hole, the supraglacial stream and the runoff stream. The samples were immediately filtered through 0.45 μm Nucleopore filters and placed into clean 60 ml HDPE bottles for nutrient analyses, or filtered through 0.7 μm Whatman glass microfibre (GF/F) filters and placed into clean glass 45 ml bottles for total dissolved carbon (TDC), dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) determinations. The glass bottles were filled completely to avoid headspace and possible CO_2 exchange. All the bottles were rinsed twice with filtrate prior to filling. The samples were stored at ~5°C in the dark, and transported to the UK for chemical analysis. Cryoconite debris was collected from the holes on five occasions during the sampling period (7, 14, 23, and 30 July, and 6 August), placed into sterile polyethylene bottles (200 ml), frozen to −20°C and transported to the UK for analysis. Great care was taken to avoid any chemical or biological contamination by rinsing the bottles twice with cryoconite water and wearing non-powder latex gloves. In situ measurements of water temperature, pH and electrical conductivity (EC) were carried out every day using a Hanna HI 9025 pH meter (Hanna Instruments, Woonsocket, RI) with a pH electrode (HI 1230) and a temperature compensation probe, using the method of McQuaker et al. (1983). EC was measured with a WTW LF 315 conductivity meter with a KLF 315 probe (WTW, Weilheim, Germany). The residence time of water in cryoconite holes was estimated by injecting coloured water into the holes and measuring the time for the colour to disperse.

Water chemistry analyses

Soluble reactive P (SRP), assumed to consist largely of dissolved inorganic species, was determined spectrophotometrically at 880 nm in 1 cm disposable polycarbonate cells in a Shimadzu UV-Mini 1240 spectrophotometer (Shimadzu, Kyoto, Japan), using the standard molybdenum blue method (Murphy and Riley 1962). The detection limit was 0.5 μg l^{-1}. The mean precision of determinations was 4.1%. Samples for total dissolved P (TDP), assumed to be equal to dissolved inorganic and organic P, were acidified with potassium persulfate and autoclaved (Jeffries et al. 1979), and analysed as for SRP above.

Dissolved organic P (DOP) was calculated as the difference between TDP and SRP.

Inorganic nitrogen species (NH_4^+, NO_3^-, and NO_2^-) were determined colorimetrically in a continuous flow stream by an AutoAnalyser 3 (Bran + Luebbe, Norderstedt, Germany). Detection limits were 0.56 μg l^{-1} for NH_4^+–N, 0.21 μg l^{-1} for NO_3^-–N and 0.042 μg l^{-1} for NO_2^-–N. The mean precision of determination was 8.5%, 12% and 5.8% respectively. Determination of TDC, DOC and TDN was undertaken on a Shimadzu TOC-V_{CSN}/TNM-1 analyser (Shimadzu, Kyoto, Japan). DOC was measured as the carbon remaining after acidification with 2 M HCl and sparging for 2 min. Six replicate injections were made. Detection limits were 0.5 mg C l^{-1} for TDC and DOC and 0.1 mg N l^{-1} for TDN. The mean precision of determination was 8.8%, 6.0% and 4.0% respectively. Dissolved organic nitrogen (DON) was calculated as [TDN] − [DIN], where $[DIN] = [NH_4^+ - N] + [NO_3^- - N] + [NO_2^- - N]$. Dissolved inorganic carbon (DIC) was calculated as [TDC] − [DOC].

Cryoconite debris analyses

The mineralogy of the cryoconite debris was determined by X-ray diffraction (XRD) using a Philips PW1050 goniometer with a Philips PW1730 generator CuKα radiation X-ray tube ($\lambda = 1.5418$ Å). The standard power settings were 40 kV and 30 mA and patterns were collected for 2θ between 5° and 70°, at a scan rate of 1° min^{-1}, with a step size of 0.08°. Samples of debris were ground in acetone, placed onto the centre of a low background holder and left to dry prior to analysis. The HBX software (Hiltonbrooks, Cranage, UK) was used for data acquisition, and the TRACES software (GBC Scientific Equipment, Dandenong, Australia), using the ICDD (International Centre for Diffraction Data Powder Diffraction Files) PDF2 database, for phase identification.

The content of P associated with different fractions of the debris was determined spectrophotometrically in samples obtained from sequential extractions of the debris. We used a sequential extraction scheme that can be seen in Fig. 2. The debris was first dried at 105°C for 16 h, and 0.2 g of dried debris was weighed into pre-cleaned polypropylene tubes. The first extraction ('loosely adsorbed P') was undertaken

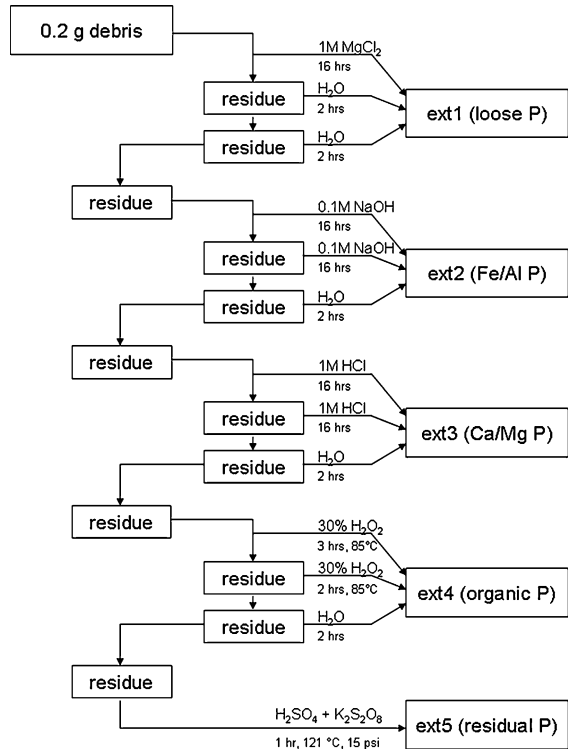

Fig. 2 Sequential extraction scheme for different P forms in cryoconite debris. All steps were done under laboratory temperature and pressure unless stated otherwise

by adding 12 ml of 1 M $MgCl_2$ to the tubes, and agitating them at 200 rpm on a reciprocating shaker for 16 h. Finally, the mixture was centrifuged at 2600 rpm for 12 min. The supernatant was collected into pre-cleaned HDPE bottles (Extract 1), and the debris was retained in the tubes. 12 ml of deionised H_2O was added to the debris in tubes, shaken for 2 h, centrifuged, and the supernatant was collected and added to Extract 1. The latter step was repeated one more time. It should be noted that each extraction is operationally defined, and that more reactive components of a given P-containing phase may contribute to an earlier extraction, while less reactive components may contribute to a later extraction. 'Fe- and Al-bound' P (Extract 2) was determined by adding 12 ml of 0.1 M NaOH to the retained debris and treating the mixture as for Extract 1. 'Ca- and Mg-bound' P (Extract 3) was determined by adding 12 ml of 1 M HCl to the retained debris and treating as above. 'Organic bound' P (Extract 4) was determined by adding 12 ml of 30% H_2O_2 to the retained debris and heating to 85°C in a hot bath for 3 h with

occasional agitation. The mixture was allowed to cool slowly, was centrifuged, and the supernatant was collected. Another 12 ml of 30% H_2O_2 was added to the debris in tubes, and heated to 85°C in a hot bath for 2 h with occasional agitation. It also was allowed to cool, centrifuged at 2600 rpm for 30 min, and the supernatant was collected. Finally, 12 ml of deionised H_2O was added to the debris in tubes, shaken for 2 h, centrifuged, and the supernatant collected. 'Residual' P (Extract 5) was determined by transferring the remaining debris into a pre-cleaned autoclavable HDPE bottle, to which 15 ml of sulphuric acid/potassium persulphate reagent (55 ml concentrated H_2SO_4 and 60 g $K_2S_2O_8$ in 1 l of deionised water; Jeffries et al. 1979) was added. The mixture was autoclaved for 1 h at 121°C and 15 psi, after which it was allowed to slowly cool. All extracts were filtered through 0.45 μm Nucleopore filters immediately after collection. The debris in the tubes was refrigerated at 5°C between extraction steps. Five replicates of each sample were extracted, and five control tubes without debris were also processed. The content of P in the extracts was then determined as SRP as described above (Murphy and Riley 1962). Extracts 1 and 2 could be measured directly using this method. Extracts 3 and 5 were diluted 1:1 and 1:14, respectively, with deionised water prior to measurement. Extract 4 required boiling for 5 h with 1 M NaOH (pH = 10.5) in order to eliminate residual hydrogen peroxide.

The total carbon (TC) and nitrogen (TN) contents of the debris were determined using a EuroVector EA3000 Elemental Analyser (EuroVector, Milan, Italy). Inorganic carbon (IC) was measured on a Strohlein Coulomat 702 analyser (Strohlein Instruments, Kaarst, Germany) adapted for this purpose. Both analysers were calibrated using certified standards. Detection limits were 10 ppm for both elements, and the precision of determinations was 0.3%.

Results

Glacial water

Water originating from snow and ice melt in the ablation area constantly flowed down the glacier, mainly in supraglacial channels. Consequently, the cryoconite holes were continuously flushed with meltwater. Most of this water eventually drained to the glacier bed through moulins (vertical shafts formed by the action of melt water) and crevasses. The remainder drained from the glacier surface in the vicinity of the terminus. The residence time of water in the cryoconite holes was very variable, ranging from minutes to tens of minutes in hydrologically connected holes, and up to several hours in more isolated holes. Supraglacial water was cold (~0.1°C) and very dilute (3–10 μS cm^{-1}), in comparison to glacier runoff, which was warmer (~3–5°C), more turbid and more concentrated (EC = 46 ± 7.4 μS cm^{-1}). The water in supraglacial channels had a relatively stable EC of ~5 μS cm^{-1}, whereas the EC of waters in cryoconite holes dropped significantly from ~9 to ~4 μS cm^{-1} over the ablation season ($p < 0.001$; Pearson's correlation coefficient $r = 0.79$; Fig. 3).

The pH was lowest in supraglacial channel water and highest in the glacier runoff stream. There were no significant trends in the pH values over the course of the sampling season (Table 1). The runoff had significantly higher concentrations of DIC, and consequently a lower proportion of DOC. There were no significant differences in the concentrations of DOC, DIN and DON in the supraglacial channel, cryoconite holes and the runoff. C:N ratios were significantly higher in the runoff than in supraglacial waters, and in all samples exceeded the molar ratio of 6.6:1 which is typically required for balanced microbial metabolism (Redfield et al. 1963). About 70% of

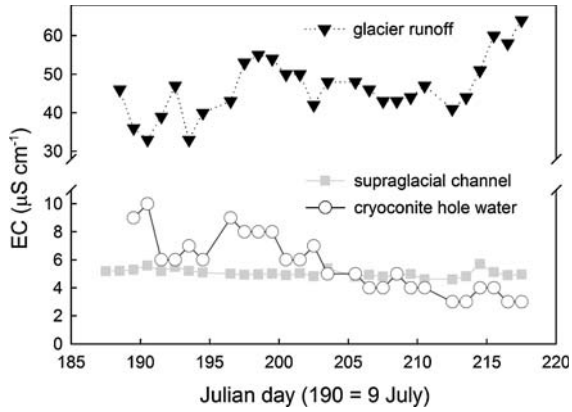

Fig. 3 Electrical conductivity (EC) of glacial waters of Werenskioldbreen during summer 2006

Table 1 pH, carbon and nitrogen in glacial waters of Werenskioldbreen (mean ± SD)

	pH[A]	DIC[A] (mg l^{-1})	DOC[A] (mg l^{-1})	DOC (%TDC)	DIN[A] (μg l^{-1})	DON[A] (μg l^{-1})	DON (%TDN)	DIC:DIN	DOC:DON
Supraglacial channel	5.1 ± 0.27a	1.3 ± 0.52a	1.8 ± 1.2a	58 ± 15a	48 ± 17a	130 ± 87a	68 ± 20a	34 ± 20a	22 ± 15a
Cryoconite holes	5.4 ± 0.19b	1.3 ± 0.93a	2.1 ± 1.6a	59 ± 19a	49 ± 22a	130 ± 95a	68 ± 17a	34 ± 23a	26 ± 27a
Glacier runoff	6.9 ± 0.33c	4.1 ± 0.57b	3.4 ± 3.5a	38 ± 18b	55 ± 15a	180 ± 130a	72 ± 13a	85 ± 36b	30 ± 31a

C:N ratios are in mol/mol. Values with the same letter are not significantly different at $p = 0.01$ (one-way ANOVA with Tukey's honest significant difference test)

DIC dissolved inorganic carbon

DOC dissolved organic carbon

TDC total dissolved carbon

DIN dissolved inorganic nitrogen

DON dissolved organic nitrogen

TDN total dissolved nitrogen

[A] Stibal et al. (2008)

Table 2 Phosphorus in glacial waters of Werenskioldbreen (mean ± SD)

	SRP (μg l^{-1})	DOP (μg l^{-1})	DOP (%TDP)	DIC:SRP ($\times 10^3$)	DIN:SRP	DOC:DOP	DON:DOP
Supraglacial channel	0.91 ± 0.80a	5.9 ± 1.0a	87 ± 12a	6.4 ± 4.7a	204 ± 160a	890 ± 640a	59 ± 51a
Cryoconite holes	0.75 ± 0.47a	6.1 ± 0.9a	89 ± 6.8a	6.7 ± 9.3a	202 ± 130a	990 ± 780a	58 ± 39a
Glacier runoff	0.80 ± 0.83a	5.7 ± 1.1a	88 ± 13a	24 ± 12b	240 ± 150a	2400 ± 4200a	97 ± 130a

C:P and N:P ratios are in mol/mol. Values with the same letter are not significantly different at $p = 0.01$ (one-way ANOVA with Tukey's honest significant difference test)

SRP soluble reactive phosphorus

DOP dissolved organic phosphorus

TDP total dissolved phosphorus

DIN, DIC, DON—see explanation in Table 1

all dissolved nitrogen was present in the form of DON (Table 1).

The total dissolved P was between 5.2 and 8.5 μg l^{-1}. SRP was very low (<0.5–3.6 μg l^{-1}), and there were no significant differences in its concentrations between the water types (Table 2). Concentrations of DOP were considerably higher (2.6–8.2 μg l^{-1}) than those of SRP in all samples, and DOP accounted for almost 90% of all dissolved P. The DIC:SRP and DIN:SRP ratios in all water types considerably exceeded the Redfield ratios (106:1 and 16:1, respectively)(Table 2). The molar ratios of DOC:DOP in supraglacial waters were ~10 times higher than the balanced ratio, while DOC:DON and DON:DOP exceeded the respective Redfield ratios roughly by a factor of three (Tables 1, 2). No significant trends or peaks in the concentrations of SRP and DOP over the course of the ablation season were apparent in any of the waters, with the exception of the initial peak in SRP and coincident low DOP value in the glacial runoff stream (Fig. 4).

Cryoconite debris

The cryoconite debris on Werenskioldbreen mainly consisted of silicates, such as chlorite, muscovite, quartz, feldspars (albite), amphiboles (edenite) and amorphous materials, indicated by the high background under the main peaks between ~18° and ~35° 2θ (Fig. 5). There was some input of new chlorite and edenite over the season as seen in Fig. 5,

while the overall debris composition remained very similar. No phosphate minerals, such as apatite, were detected.

The mean total P content in the cryoconite debris was 2.2 ± 0.53 mg g^{-1}. Most P (57 ± 6.4%) was present in Extract 4 ('organic bound'), followed by Extract 3 ('Ca- and Mg-bound': 20 ± 3.3%), Extract 5 ('residual': 17 ± 3.9%), and Extract 2 ('Fe- and Al-bound': 6.3 ± 0.99%). Very little P was detected in Extract 1 ('loosely adsorbed' P: 0.22 ± 0.04%). Hence, some 0.98 ± 0.12 mg g^{-1}, or ~43%, of the total P was present in fractions operationally defined as inorganic, with the P either bound within or adsorbed onto minerals (Fig. 6). No significant changes in the concentration of P or the relative percentage of each P fraction were found over the course of the ablation period, with the exception of Extract 2 ('Fe- and Al-bound' P), where the P content was significantly higher at the end of

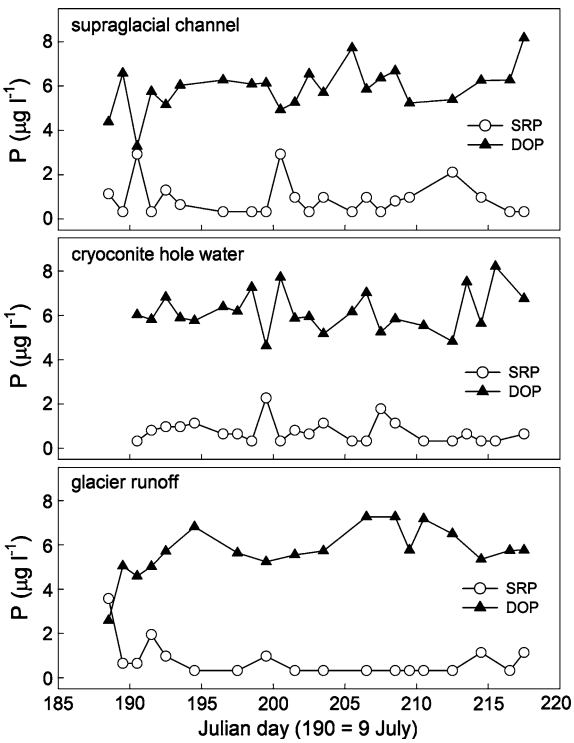

Fig. 4 Soluble reactive phosphorus (SRP) and dissolved organic phosphorus (DOP) in glacial waters of Werenskioldbreen during summer 2006

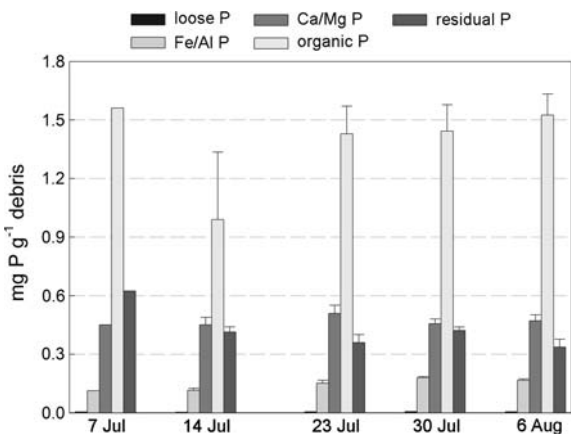

Fig. 6 Distribution of phosphorus in the different extractions in cryoconite debris collected on Werenskioldbreen on the five dates shown during summer 2006 (mean ± SD)

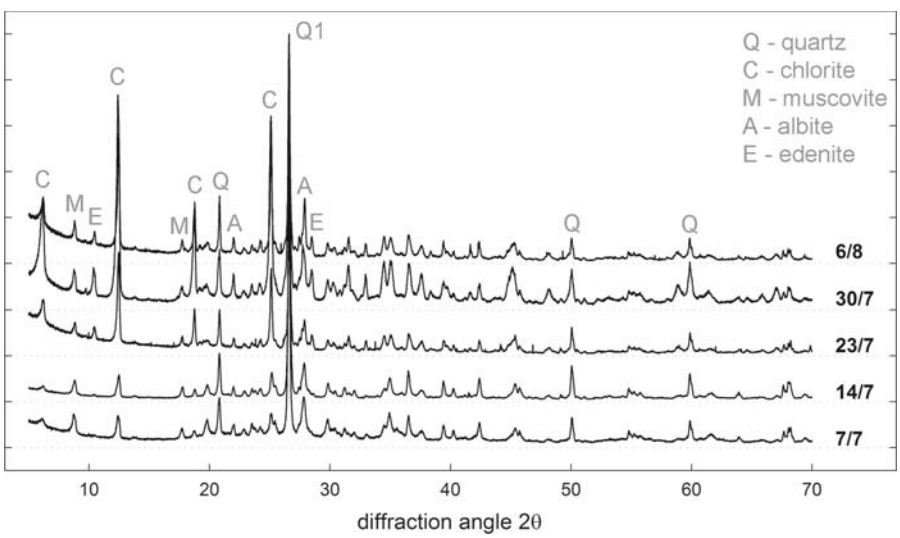

Fig. 5 XRD trace of cryoconite debris collected from a single cryoconite hole on Werenskioldbreen on the five dates shown during summer 2006. Peaks are normalised to Q1. All the peaks have been identified, but only distinctive peaks are labelled

Table 3 C:N:P ratios (mol/mol) in cryoconite debris from Werenskioldbreen

	TC:TP	OC:OP	TN:TP	TN:OP	TC:TN	OC:TN
7 July (day 188)	43 ± 0.23a	74 ± 2.8ab	3.8 ± 0.01a	6.7 ± 0.02ab	11 ± 0.03a	11 ± 0.01a
14 July (day 195)	47 ± 4.1a	110 ± 28a	3.6 ± 0.17a	8.9 ± 2.0a	13 ± 0.51a	12 ± 0.31a
23 July (day 204)	20 ± 3.4b	33 ± 4.6b	1.7 ± 0.18b	2.9 ± 0.20b	12 ± 0.70a	11 ± 0.81a
30 July (day 211)	21 ± 0.63b	34 ± 0.74b	1.8 ± 0.09b	3.1 ± 0.32b	11 ± 0.92a	11 ± 0.87a
6 August (day 218)	20 ± 0.47b	32 ± 1.3b	1.7 ± 0.05b	2.7 ± 0.12b	12 ± 0.11a	12 ± 0.06a

Values with the same letter are not significantly different at $p = 0.01$ (one-way ANOVA with Tukey's honest significant difference test)

TC total carbon

OC organic carbon

TN total nitrogen

TP total phosphorus

OP organic phosphorus

TC, OC and TN from Stibal et al. (2008)

the ablation season than at the beginning ($p < 0.01$, one-way ANOVA with Tukey HSD test; Fig. 6).

The average C:P and N:P molar ratios within the cryoconite debris showed great variability over time, and were 30 ± 13 (TC:TP), 57 ± 35 (OC:OP), 2.5 ± 1.0 (TN:TP) and 4.9 ± 2.7 (TN:OP). Both C:P and N:P ratios decreased considerably between 14 and 23 July, whereas C:N ratios remained constant (Table 3).

Discussion

P in cryoconite debris

The supraglacial environment receives P from a variety of sources, including the rock debris from surrounding valley slopes and aeolian dust. The rock debris contains mainly primary lithospheric P, while the wind-borne debris may contain biological material and thus secondary biospheric P (Marshall and Chalmers 1997). Glacier surfaces may receive an important component of their P supply from aeolian dust, as has been suggested for other environments by Chadwick et al. (1999). The resulting cryoconite debris may then comprise two components, one which is primary lithospheric and another that is secondary biospheric, including microbial biomass and dead organic matter (Hodson et al. 2008, Stibal et al. 2008).

The mean total P content of the cryoconite debris on Werenskioldbreen was ~2.2 mg g^{-1} (Fig. 6), which is significantly more than would be expected in average rock debris. The global mean P content of Earth surface rocks is ~0.7 mg g^{-1} (Rudnick and Gao 2004). Local rocks, the most likely source for cryoconite debris, are mostly metamorphic, with various P contents (Majka and Budzyń 2006). Metabasalts are also present in the vicinity (Majka and Budzyń 2006). The typical P content of metamorphic rocks is 0.5–0.7 mg g^{-1} (Rösler and Lange 1972, Slansky 1986), but it may be higher in basic rocks (1.1–1.4 mg g^{-1}; Rösler and Lange 1972). Hence, the cryoconite debris contains approximately twice as much P as local rocks. We noted earlier that ~43% (~0.98 mg g^{-1}) of the total P in the cryoconite debris was present in fractions defined as inorganic and associated with minerals. This lies comfortably within the range found within metamorphic rocks. Approximately half (~57%) of the P in the cryoconite debris was present within the organic phase (Fig. 6).

There are two possible ways to explain this excess P. First, aeolian input may have contained rock debris with a higher P content than the local rocks. For example, phosphogenic marine sediments have been found ~20 km SSE from Werenskioldbreen with P contents of up to 30% P_2O_5 (Krajewski 2000). This P could be taken up by active microorganisms and transformed into organic P. However, we think that this is unlikely because microbial primary production, and thus an autochthonous organic matter source, seems to be relatively insignificant on this

glacier compared to the total organic matter found in the cryoconite debris (Stibal et al. 2008). Further, the P associated with inorganic phases was not significantly depleted by microbial activity during the ablation season, suggesting that conversion of inorganic to organic P was not a major process within the cryoconite holes. Second, the organic C in the debris is largely derived from atmospheric deposition. An allochthonous source of organic matter, including microbial biomass, has been shown to make the dominant contribution to the organic carbon budget of the cryoconite holes (Stibal et al. 2008), and hence it is also likely that an allochthonous source of organic P explains the high overall P content of the cryoconite debris. The mean C:P ratio (57 ± 35) of the organic phase is typical of soil microbial biomass (60; Cleveland and Liptzin 2007), and so may be of terrestrial origin. Some of this organic debris is likely to be wind-blown microbial and plant biomass and/or peat, which may partially degrade and dissolve in water to provide the relatively high DOP concentrations in the supraglacial waters (see below).

The potential sources of bioavailable P in Werenskioldbreen cryoconite debris are the more readily extractable portions of the inorganic phases in the debris (Extracts 1 and 2). The majority of inorganic P resides in the residual (Extract 5) and the acid-extractable Ca- and Mg-bound (Extract 3) phases. The former phase probably includes apatite and other aluminosilicates, while the latter contains carbonates and other poorly crystalline phases (Reddy et al. 1999). The fact that no apatite was found in the mineralogical analyses is consistent with the low inorganic P content of the debris. These sparingly soluble phases lock up P in their structure and only some of the P on the surface of the minerals will become available for microbial use via desorption or dissolution (Welch et al. 2002). The P contained within carbonates can become bioavailable if pH conditions in the debris promote carbonate dissolution. However, the only source of readily bioavailable P is the loosely bound P (Extract 1), which accounts for only ~0.22% of all P present in the debris (i.e. ~5 μg g^{-1}). The base-extractable Fe- and Al-P (Extract 2) probably represents adsorbed P, for example on poorly ordered iron and aluminium oxyhydroxide phases (Ruttenberg 1992), and is potentially bioavailable (Hodson et al. 2004). Hence, ~6.5% of the total P (~15% of IP) within the debris (~0.16 mg g^{-1}) is potentially readily bioavailable. This is well in excess of the P microbes need for primary production on the glacier. The average in situ microbial primary production was ~0.4–2 μg C l^{-1} h^{-1}, equivalent to 0.002–0.01 μg C g^{-1} h^{-1}, over the summer 2006 (Stibal et al. 2008), and typical bacterial secondary production rates on other Svalbard glaciers were between 0.016 and 0.051 μg C g^{-1} h^{-1} (Anesio et al. 2007, Hodson et al. 2007). If the potential microbial demand of P is assumed to follow the carbon uptake rate in a balanced molar ratio (106:1 after Redfield et al. 1963; ~60:1 if terrestrial after Cleveland and Liptzin 2007) for ~720 h (30 days) over the summer, then the microbial demand for P is ~2 μg P g^{-1} at maximum, about 1.2% of the potentially bioavailable inorganic P calculated above. Conversion of IP to OP, therefore, seems inefficient in this system.

The input of new P sources to the supraglacial environment may be seasonal. Small inputs of rock debris from adjacent slopes occur during the ablation season (Fig. 4), consisting mainly of chlorites and amphiboles (Majka and Budzyń 2006). This source of primary P contains relatively little readily bioavailable P. Aeolian import of new biological materials is probably insignificant during the ablation season, since fresh biomass is fixed in the wet soils and/or wetlands. The main input is likely to occur when ambient temperatures fall below freezing in autumn, when the surface biomass desiccates and can be easily lofted and transported by wind (Marshall and Chalmers 1997, Stibal et al. 2008).

Biogeochemical stoichiometry in the debris

C:N:P molar ratios are more variable in soils and sediments than in the sea (Cleveland and Liptzin 2007), but are still useful for assessing the relative influence of biotic and abiotic controls on biogeochemical cycling, nutrient availability and limitation in glacial environments (Barrett et al. 2007). The global ratios of total C:N and N:P in the soils and sediment of terrestrial ecosystems are typically in the range of 2–30 and 1–77 respectively, with the modal value of 8 for both ratios (Cleveland and Liptzin 2007). The element ratios within the cryoconite debris on Werenskioldbreen fall within these ranges (C:N 11–13; N:P 1.7–3.8), which may suggest some degree of biological control. The total N:P ratios are

at the low end of the range, probably due to the young age of the debris and the subsequent high relative P content compared to N (Chadwick et al. 1999). The C:N and N:P ratios of microbial biomass in soil/sediment are relatively constrained, despite the high heterogeneity of soil ecosystems, with mean ratios of 8.6 and 6.9 respectively (Cleveland and Liptzin 2007). We calculated the C:N and N:P ratios in our cryoconite debris by assuming that microbial C and P were represented by OC and OP, and that TN was almost exclusively associated with biomass (Table 3). This is an approximation, as it is likely that other types of biomass (plant, peat) were also present, but microbial biomass is the most abundant in glacial ecosystems (Hodson et al. 2008). The obtained OC:TN (11–12) and TN:OP (2.7–8.9) ratios agree quite well with the global stoichiometry in soil microbial biomass.

The significant decrease in both C:P and N:P ratios over the season (Table 3) was probably the result of the decreasing the C and N content of the debris (Stibal et al. 2008), while the content of P remained virtually unchanged. The greatest decrease in C and N contents took place between 14 and 23 July (Days 195–204 in Fig. 3), which also marked the end of the period of higher EC in the cryoconite waters, indicating the flushing of solute from the holes (Fig. 3). An explanation for this is that most of the C and N originating from decaying biomass was solubilised during the high flushing period, as is evident from the relatively high concentrations of DOC and DON, and was flushed down glacier, whereas most of the P was readsorbed to mineral surfaces (see below).

Caution should be exercised when using these elemental ratios to determine whether or not P or N were limiting. A large proportion of the biomass is allochthonous and inactive, and its stoichiometry is primarily determined by its original environment, rather than controlled by biological activity in the cryoconite debris. Preferential flushing of carbon and nitrogen from the cryoconite debris may distort the ratios over the ablation season. The biomass N:P ratio is $\sim$7–8 at the beginning of the season, but then markedly decreases to $\sim$3, which would indicate N deficiency. Laboratory studies in which the cryoconite environment was simulated showed P limitation of bacterial growth (Mindl et al. 2007, Säwström et al. 2007) and DIC uptake (Stibal and Tranter 2007). However, only cryoconite water was analysed in these studies, and no systematic flushing of water occurred.

Dissolved P in supraglacial water

Most P in Arctic glacial ecosystems is bound within rock debris or sediment, and dissolved P is present only in very low amounts in glacial waters (Hodson et al. 2005). The concentration of SRP detected in the supraglacial channel water on Werenskioldbreen ranged from <0.5 to 2.9 μg l^{-1}, and in cryoconite holes from <0.5–2.3 μg l^{-1} (Table 2). These values are similar to those found in glacial runoff (0.9–1.0 μg l^{-1}; Mindl et al. 2007) and cryoconite holes (0.9–9.0 μg l^{-1}; Säwström et al. 2002, Anesio et al. 2007) on another Svalbard glacier (Midtre Lovénbreen) or in cryoconites on the White Glacier in the Canadian High Arctic (0.6–13.5 μg l^{-1}; Mueller and Pollard 2004). The low concentrations measured during this study were probably caused by several factors. First, the leaching of P from P-containing minerals may be slow due to the short residence time of water (Hodson et al. 2004) even in deep cryoconite holes. Hence, any SRP produced is more rapidly diluted and flushed down glacier. Second, any available dissolved P will quickly re-adsorb onto mineral surfaces—primarily poorly ordered iron or aluminium rich oxides or hydroxides. Finally, SRP may be consumed by active microorganisms (Stibal and Tranter 2007), particularly within the debris where the microbial abundance is high (up to 1×10^5 cells of heterotrophic bacteria per milligram of debris, and 8×10^3 of cyanobacterial cells per milligram; Stibal et al. 2006, Stibal and Tranter 2007). However, the uptake rates of P are likely to be much lower than the rate of adsorption.

Most studies conducted so far have overlooked the role of DOP in nutrient fluxes from glacial ecosystems. Our results show that DOP is a very important component of the dissolved P pool on Werenskioldbreen, mostly exceeding those of SRP (<0.5–3.6 μg l^{-1}) by at least four times (2.6–8.2 μg l^{-1}) in all the glacial water types (Fig. 4). DOP enters the P cycle after microbial and biochemical transformations (Stewart and Tiessen 1987). Rapid recycling of DOP is not likely to occur in cryoconite holes due to the virtual absence of direct consumers, but it can be taken up after mineralisation or by microbes

possessing alkaline phosphatases (Stewart and Tiessen 1987). Phosphatase activity has been detected in cryoconite samples from Werenskioldbreen (M. Stibal, unpublished results) and also reported from Antarctic cryoconite holes (Foreman et al. 2007), and may be an efficient means of coping with P deficiency.

The small initial SRP peak accompanied by low DOP in the glacier runoff may represent an early P mobilisation from the snowpack, when melt waters interact less with the cryoconite ecosystem. Otherwise, neither SRP nor DOP showed any trend in concentrations over time (Fig. 4), unlike the total EC (Fig. 3). This may be because of the very low values in the case of SRP, which are near the detection limit. The lack of a trend in DOP may suggest that decomposition of organic matter occurs at a relatively constant rate throughout the ablation season. However, this was not tested quantitatively, and the lack of a trend might also have occurred due to the low values.

Both the total dissolved C:P and N:P ratios are far above the balanced values (C:P $\sim 1400 \pm 780$; N:P $\sim 60 \pm 29$; balanced values 106 and 16 respectively; Redfield et al. 1963). This apparent lack of biological control over the biogeochemical stoichiometry in the water is consistent with the microorganisms being primarily associated with the debris, and with the very low microbial abundance and activity in the unstable water column (Säwström et al. 2002, Hodson et al. 2007).

Adsorption of organic P on minerals

Dissolved organic P in the water is likely to originate from slowly decaying biomass that is concentrated within the debris in cryoconite holes. Hence, the concentration of DOP should approximately follow the balanced molar ratio of DOC:DOP (106:1 after Redfield et al. 1963; $\sim$60:1 if terrestrial after Cleveland and Liptzin 2007). However, the actual DOC:DOP ratios determined in the cryoconite water were $\sim 10 \times$ higher (Table 2), suggesting a loss of DOP from the water column. The loss of DOP can be partly explained by microbial uptake, but this is thought to be insignificant, as stated above. A more likely alternative is the adsorption of dissolved P species onto mineral surfaces, by a process where the reactive $-OPO_3^{2-}$ groups bind to positively charged sites on minerals, mainly amorphous Fe and Al oxyhydroxides (Stewart and Tiessen 1987, Reddy et al. 1999). This is supported by the fact that base-extractable P was the only fraction from the sequential extractions whose content within the debris significantly increased over the course of the season, by ~ 60 μg g^{-1} (Fig. 6). In a previous in vitro study we found a P loss from the water at DIC uptake rates close to in situ ones, without any replenishing of P from water inflow (Stibal and Tranter 2007). Therefore, we believe that the adsorption of P is more rapid than leaching.

Significance for downstream environments

Export of P from the glacier surface may be beneficial to some nutrient-limited downstream environments, such as proglacial lakes (Säwström et al. 2007), where P concentrations are extremely low. The inorganic P content in the cryoconite debris from Werenskioldbreen was approximately twice as high as that of glaciofluvial sediment from another Svalbard glacier (Hodson et al. 2004), and the base-extractable (Fe- and Al-bound) P was 1–2 orders of magnitude higher. The difference in total inorganic P was relatively small and may be explained by differences in the mineralogy of the sediments and debris of the two glaciers. However, the high content of base-extractable P may have been caused by rapid adsorption of SRP and/or DOP from the degrading organic matter. The total amount of P in the primary minerals of subglacial and proglacial sediments is much higher than in supraglacial debris, but the latter is more labile and thus more readily bioavailable than the primary P (Hodson et al. 2004). Therefore, there is the potential for P fertilisation of ultraoligotrophic proglacial lakes and other aquatic environments via export of cryoconite debris from the glacier surface.

Conclusions

The mean total P content of cryoconite debris on Werenskioldbreen was ~ 2.2 mg g^{-1}, which is significantly more than would be expected in rock debris from local sources, estimated as 0.7–1.1 mg g^{-1}. Some 57% of the P (~ 1.2 mg g^{-1}) was present in the fraction defined as organic P. The remainder (~ 0.98 mg g^{-1}) present in the inorganic fractions

was similar to that estimated in local sources. The excess P in the organic phase can be explained by allochthonous input of microbial and other biomass. The amount of readily available P for microbes within the debris was relatively small ($\sim$0.16 mg g^{-1}), but probably more than sufficient given the low production rates. The concentration of total dissolved P in supraglacial water of Werenskioldbreen was very low (5.2–8.5 μg l^{-1}), which was probably caused by efficient flushing and re-adsorption onto mineral surfaces. DOP was a very important component of the dissolved P pool on Werenskioldbreen, as concentrations of DOP often exceeded those of SRP by a factor of four in all the glacial water types. It is difficult to assess whether N or P was limiting in this environment solely on the basis of the N:P ratios in the debris or biomass. There may be some degree of biological control over the C:N:P ratios of the cryoconite debris, but cycling of P in waters within the supraglacial environment on this glacier seems to be mainly controlled by physical and geochemical processes.

Acknowledgments This work was supported by BIOTRACS, an EU funded EST fellowship for MS. Jenny Mills (Bristol) is thanked for help with carbon and nutrient determinations, and Lesley Neve (Leeds) for XRD analyses. We thank Alexandre Anesio for comments on an earlier draft of the manuscript, and Andy Hodson and the associate editor Scott Bridgham for insightful comments which greatly improved our manuscript.

References

Anesio AM, Mindl B, Laybourn-Parry J, Hodson AJ, Sattler B (2007) Viral dynamics in cryoconite holes on a high Arctic glacier (Svalbard). J Geophys Res 112:G04S31. doi:10.1029/2006JG000350

Bagshaw EA, Tranter M, Fountain AG, Welch KA, Basagic H, Lyons WB (2007) Biogeochemical evolution of cryoconite holes on Canada Glacier, Taylor Valley, Antarctica. J Geophys Res 112:G04S35. doi:10.1029/2007JG000442

Barrett JE, Virginia RA, Lyons WB, McKnight DM, Priscu JC, Doran PT et al (2007) Biogeochemical stoichiometry of Antarctic Dry Valley ecosystems. J Geophys Res 112:G01010. doi:10.1029/2005JG000141

Burkholder JM (1992) Phytoplankton and episodic suspended sediment loading: phosphate partitioning and mechanisms for survival. Limnol Oceanogr 37:974–988

Chadwick OA, Derry LA, Vitousek PM, Huebert BJ, Hedin LO (1999) Changing sources of nutrients during four million years of ecosystem development. Nature 397:491–497. doi:10.1038/17276

Cleveland CC, Liptzin D (2007) C:N:P stoichiometry in soil: is there a "Redfield ratio" for the microbial biomass? Biogeochemistry 85:235–252. doi:10.1007/s10533-007-9132-0

Foreman CM, Sattler B, Mikucki JA, Porazinska DL, Priscu JC (2007) Metabolic activity and diversity of cryoconites in the Taylor Valley, Antarctica. J Geophys Res 112: G04S32. doi:10.1029/2006JG000358

Hodson A, Mumford P, Lister D (2004) Suspended sediment and P in proglacial rivers: bioavailability and potential impacts upon the P status of ice-marginal receiving waters. Hydrol Process 18:2409–2422. doi:10.1002/hyp.1471

Hodson AJ, Mumford PN, Kohler J, Wynn PM (2005) The high Arctic glacial ecosystem: new insights from nutrient budgets. Biogeochemistry 72:233–256. doi:10.1007/s10533-004-0362-0

Hodson A, Anesio AM, Ng F, Watson R, Quirk J, Irvine-Fynn T et al (2007) A glacier respires: quantifying the distribution and respiration CO_2 flux of cryoconite across an entire Arctic supraglacial ecosystem. J Geophys Res 112:G04S36. doi:10.1029/2007JG000452

Hodson A, Anesio AM, Tranter M, Fountain A, Osborn M, Priscu J et al (2008) Glacial ecosystems. Ecol Monogr 78:41–67. doi:10.1890/07-0187.1

Jania J, Kolondra L, Aas HF (2002) Werenskioldbreen and surrounding areas, Spitsbergen, Svalbard, Norway. Orthophotomap 1:25,000. University of Silesia, Sosnowiec, Poland

Jeffries DS, Dieken FP, Jones DE (1979) Performance of the autoclave digestion method for total phosphorus analysis. Water Res 13:275–279. doi:10.1016/0043-1354(79)90206-9

Karl DM (2000) Phosphorus, the staff of life. Nature 406:31–33. doi:10.1038/35017683

Kaštovská K, Stibal M, Šabacká M, Černá B, Šantrůčková H, Elster J (2007) Microbial community structure and ecology of subglacial sediments in two polythermal Svalbard glaciers characterized by the epifluorescence microscopy and PLFA. Polar Biol 30:277–287. doi:10.1007/s00300-006-0181-y

Krajewski KP (2000) Phosphorus and organic carbon reservoirs in the Bravaisberget Formation (Middle Triassic), Hornsund, Spitsbergen. Stud Geol Pol 116:175–209

Majka J, Budzyń B (2006) Monazite breakdown in metapelites from Wedel Jarlsberg Land, Svalbard—preliminary report. Miner Pol 37:61–69. doi:10.2478/v10002-007-0006-9

Marshall WA, Chalmers MO (1997) Airborne dispersal of Antarctic algae and cyanobacteria. Ecography 20:585–594. doi:10.1111/j.1600-0587.1997.tb00427.x

McQuaker NR, Kluckner PD, Sandberg DK (1983) Chemical analysis of acid precipitation—pH and acidity determinations. Environ Sci Technol 17:431–435. doi:10.1021/es00113a013

Mindl B, Anesio AM, Meirer K, Hodson AJ, Laybourn-Parry J, Sommaruga R et al (2007) Factors influencing bacterial dynamics along a transect from supraglacial runoff to proglacial lakes of a high Arctic glacier. FEMS Microbiol Ecol 59:307–317

Mueller DR, Pollard WH (2004) Gradient analysis of cryoconite ecosystems from two polar glaciers. Polar Biol 27:66–74. doi:10.1007/s00300-003-0580-2

Müller B, Stierli R, Wüest A (2006) Phosphate adsorption by mineral weathering particles in oligotrophic waters of high particle content. Water Resour Res 42:W10414. doi:10.1029/2005WR004778

Murphy J, Riley JP (1962) A modified single solution method for determination of phosphate in natural waters. Anal Chim Acta 26:31–36. doi:10.1016/S0003-2670(00)88444-5

Reddy KR, Kadlec RH, Flaig E, Gale PM (1999) Phosphorus retention in streams and wetlands: a review. Crit Rev Environ Sci Technol 29:83–146. doi:10.1080/10643389991259182

Redfield AC, Ketchum BH, Richards FA (1963) The influence of organisms on the composition of seawater. In: Hill MH (ed) The sea, vol 2. Wiley, New York, pp 26–77

Řehák J, Řehák S, Stibal M, Řeháková K, Šabacká M, Kostka S (2007) Glacier caves and drainage systems of the northern part of Hornsund area, southwest Spitsbergen, Svalbard. In: Abstracts of the 8th GLACKIPR Symposium, Sosnowiec, Poland, p 111

Rösler HJ, Lange H (1972) Geochemical tables. Elsevier, Amsterdam, 468 pp

Rudnick RL, Gao S (2004) Composition of the continental crust. In: Holland HD, Turekian KK (eds) Treatise on geochemistry, vol 3. The Crust Elsevier, Amsterdam, pp 1–65

Ruttenberg KC (1992) Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol Oceanogr 37:1460–1482

Säwström C, Mumford P, Marshall W, Hodson A, Laybourn-Parry J (2002) The microbial communities and primary productivity of cryoconite holes in Arctic glacier (Svalbard 79°N). Polar Biol 25:591–596

Säwström C, Laybourn-Parry J, Granéli W, Anesio AM (2007) Heterotrophic bacterial and viral dynamics in Arctic freshwaters: results from a field study and nutrient-temperature manipulation experiments. Polar Biol 30:1407–1415. doi:10.1007/s00300-007-0301-3

Slansky M (1986) Geology of sedimentary phosphates. North Oxford Academic, London, 210 pp

Stewart JWB, Tiessen H (1987) Dynamics of soil organic phosphorus. Biogeochemistry 4:41–60. doi:10.1007/BF02187361

Stibal M, Šabacká M, Kaštovská K (2006) Microbial communities on glacier surfaces in Svalbard: impact of physical and chemical properties on abundance and structure of cyanobacteria and algae. Microb Ecol 52:644–654. doi:10.1007/s00248-006-9083-3

Stibal M, Tranter M (2007) Laboratory investigation of inorganic carbon uptake by cryoconite debris from Werenskioldbreen, Svalbard. J Geophys Res 112:G04S33. doi:10.1029/2007JG000429

Stibal M, Tranter M, Benning LG, Řehák J (2008) Microbial primary production on an Arctic glacier is insignificant in comparison to allochthonous organic carbon input. Environ Microbiol. doi:10.1111/j.1462-2920.2008.01620.x

Tranter M, Fountain AG, Fritsen CH, Lyons WB, Priscu JC, Statham PJ et al (2004) Extreme hydrochemical conditions in natural microcosms entombed within Antarctic ice. Hydrol Process 18:379–387. doi:10.1002/hyp.5217

Walker TW, Syers JK (1976) The fate of phosphorus during pedogenesis. Geoderma 15:1–19. doi:10.1016/0016-7061(76)90066-5

Welch SA, Taunton AE, Banfield JF (2002) Effect of microorganisms and microbial metabolites on apatite dissolution. Geomicrobiol J 19:343–367. doi:10.1080/01490450290098414

Wharton RA Jr, McKay CP, Simmons GM Jr, Parker BC (1985) Cryoconite holes on glaciers. Bioscience 35:499–503. doi:10.2307/1309818