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Terrestrial Si dynamics in the Arctic: A study on biotic and abiotic controls

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Abstract

Silicon is the next most abundant element in the Earth's crust and its biogeochemical cycle is linked with that of carbon. Further, silicon is a beneficial nutrient for plants in terrestrial ecosystems and a key nutrient for diatoms in aquatic ecosystems. During the last decade the important role of terrestrial vegetation in controlling Si fluxes downstream aquatic environments, via incorporation of Si into biomass (as amorphous Si) and subsequent storage in soil, has been realized. Due to the high prevalence of high Si-accumulating plants, cold temperatures and perenially frozen soil conditions, Arctic terrestrial ecosystems is hypothesized to store a significant fraction of the global soil ASi stock. The Arctic environment is highly sensitive to climate change, with unknown effects for terrestrial Si cycling.

Hence, in this thesis we utilized archived soil samples collected from different geographical regions of the Arctic tundra and continuous permafrost region. By combining results obtained through soil chemical analysis with literature review this thesis provide a conceptual framework for how climate change may alter the biological component of terrestrial Si cycling in Arctic regions underlain by permafrost. Further, permafrost thaw can mobilize previously frozen soil material initiating biogeochemical processing of the newly thawed material, such as dissolution of plant derived amorphous silica stored in soil. Hence, an additional aspect of this thesis is to shed light on the potential biotic control (i.e. microbial influence) on plant derived ASi dissolution rates during litter degradation. This question was explored by utilization of microcosm laboratory experiments.

Dependent on land cover type, we found total ASi storage to range between 1,030 - 94,300 kg SiO$_2$ ha^{-1} in Arctic shrub/graminoid tundra and peatland ecosystems. Further, the first estimate of total ASi storage (0 - 1 m) in the northern circumpolar tundra regions is presented in this thesis. Our estimates, based on upscaling by vegetation and soil classes provide an estimated storage of 219 to 510 Tmol Si, which represents 2 - 6 % of the estimated global soil ASi storage. The results also show that the majority of the total ASi storage is allocated to the mineral subsoil, indicating that pedogenic rather than biogenically derived Si fractions dominate the ASi pool in the Arctic. Furthermore, the results suggest that at least 30 % of the total ASi pool is allocated to the permafrost layer, thus potentially representing an additional pool of Si that will become available for biogeochemical processing in a future warmer Arctic.

Regarding the influence of microbes (bacteria and fungi) on amorphous silica dissolution during plant litter decomposition, we find that microbes can reduce the apparent release of Si and that the reduction in Si release increases with greater microbial colonization and decomposition of litter. This result is contrary to predicted results and common beliefs (i.e. that microbes can enhance Si release rates during litter decomposition). While the work carried out herein do not allow for the exact mechanism behind this pattern to be resolved, the results indicate that microbes may influence the availability of released Si.

Overall, the work carried out in this thesis fills some of the existing knowledge gaps regarding the size and geographical/landscape distribution of the Arctic ASi pool, its significance in a global context as well as how microbes can influence Si release during plant litter decomposition, which previously were understudied.

Key words: Amorphous silica; Arctic; Litter decomposition; Microbes; Peatlands; Permafrost; Silica dissolution; Tundra;

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"How many years can a mountain exist, before it is washed to the sea?"
- Bob Dylan -

Contents

List of papers

This thesis is based on 3 papers which are listed below. The papers have been appended to the thesis. Paper I is published in the journal Biogeochemistry and reprinted with the permission of Springer. Paper II has been submitted to the indicated journal while Paper III is an unpublished manuscript.

Paper I

Alfredsson H, Hugelius G, Clymans W, Stadmark J, Kuhry P, Conley DJ (2015) Amorphous Si pools in permafrost soils of the central Canadian Arctic and the potential impact of climate change. Biogeochemistry 124:441-459.

Paper II

Alfredsson H, Clymans W, Stadmark J, Conley DJ, Rousk J (submitted) Bacterial and fungal colonization and decomposition of submerged plant litter: consequences for biogenic Si dissolution. Submitted to FEMS Microbiology Ecology.

Paper III

Alfredsson H, Clymans W, Hugelius G, Kuhry P, DJ Conley (manuscript) Estimated storage of amorphous silica in soils of the circum-Arctic tundra region. Intended for submission to Biogeosciences.

Acknowledgments

The time has come to think back of the 4+ past years during which I have worked with this thesis. The road has been paved by both less good times when wanting to quit but also by many good times which made be thankful for continuing. However, this work would not have been possible without the help and support from a number of people which made it all work out in the end.

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To all the past and present PhD students and young researches that I have meet at the department over the years; thank you all for the good times both at fika/lunch while at work as well as outside of office, may it be lunch at Govindas, bowling, curling, bbq´s, ice-cream by the beach or other nice little things and to Nadine, thanks for all the new and tasty New Mexican food experiences. I will sure take a lot of nice memories with me!

During my time as a PhD student I have had the opportunity to meet and work together with people from all over the world as well as taking part in many courses, sometimes very far away. I feel very greatfull for having been given these opportunities with the trips to Svalbard and Alaska being highlights. These trips has made be develop a special interest for Arctic environments and I hope to go back in the future, as a researcher or a tourist.

In addition, I want to thank all the employees at the department for providing a good working environment with special thanks to Gert - for saving my constantly crashing computer, to Git, Åsa and Nathalie - for help with various laboratory things, to the Kansli-staff - for patiently helping out when lost in the maze of administrative things and to Hans - for help with various practicallities. Moreover, I want to thank Carl-Magnus Mörth for running my samples with ICP-OES when the beast gave trouble. Also, many thanks to Gunilla Albertén at MediaTryck for spending 2 h with me explaining InDesign, it was all very helpful and sure made the work much more fun and easy. Further, I thank the Faculty of Science and Lunds Geologiska Fältklubb for providing financial support for trips to Alaska and Svalbard.

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Kramar//Hanna

Photo: H. Genet

Si released by chemical weathering of minerals is carried by rivers and streams through the land-ocean continuum, with terrestrial ecosystems influencing the flux of Si that eventually reach its final destination - the oceans. Here, Si availability play a key role in determining phytoplankton production and community composition.

It follows that alterations of the terrestrial environment, e.g. brought upon by human anthropogenic disturbance, can alter the final delivery of Si to aquatic ecosystems with implications for foodweb dynamics. In its essence, providing one of the rationales for studying the terrestrial Sy cycle as done in this thesis.

Introduction

Biogeochemical cycles describe how elements, such as carbon, nitrogen and silicon, are transformed (i.e. cycled) and moved through the land-ocean continuum by biological, geological, chemical and physical processes. These processes takes place on various time scales, from millions of years to more comprehensible time scales (years).

Found in most minerals, silicon (Si) represents the second most abundant element by weight in the Earth's crust, but its occurrence in nature is not restricted to rocks. In the living biosphere, Si has an important role where it is found incorporated into the biomass of plants, algae and other specific organisms (Clarke 2003; Sommer et al. 2006). On biological time-scales, Si availability has an important role in the functioning of marine food webs (Kristiansen and Hoell 2002), while Si biogeochemistry has influenced the Earth´s climate on geological time-scales (Street-Perrot and Barker 2008). Hence, improved understanding of the biological, geological, chemical and physical processes that governs the transformation and movement of Si in the natural environment becomes important.

The global Si biogeochemical cycle

Chemical weathering of Si-minerals (e.g. quartz) release Si into its dissolved monomeric form H_4SiO_4. For Si-minerals containing calcium or magnesium (e.g. $CaSiO_3$) the result is a net consumption of atmospheric CO_2 via precipitation of carbonates at the deep ocean floor (Sommer et al. 2006; Street-Perrot and Barker 2008; Struyf et al. 2009; Song et al. 2012). This establishes an important link between the global biogeochemical cycles of Si and carbon (C) where chemical weathering of Si-minerals have influenced global climate at geological time scales (Kump et al. 2000). To balance the loss, CO_2 is ultimately returned to the atmosphere via tectonic processes such as volcanism and metamorphism (Berner and Kothavala, 2001) (Fig. 1).

Dissolved Si (DSi) reaching the world's oceans via groundwater flow and rivers is consumed by diatoms, a group of Si-requiring microscopic algae, that frequently dominates the phytoplankton community in temperate and high-latitude marine ecosystems (Lalli and Parsons 1997). DSi availability can control diatom primary productivity in the oceans (Allen et al. 2005) and thus, via the biological carbon-pump (Raven and Falkowski 1999), influence C sequestration in deep ocean sediments (Dugdale et al. 1995; Dugdale and Wilkerson 1998; Bidle et al., 2003; Ragueneau et al. 2006). A biological carbon pump influenced by ocean DSi availability establishes a second link between the global biogeochemical cycles of Si and C (Fig. 1).

In the global Si biogeochemical cycle, terrestrial ecosystems function as large filters (Struyf and Conley 2012) that, via incorporation and storage of Si in biomass and soil (Blecker et al. 2006), influence DSi transport through the land-ocean continuum (Fig. 1). This pivotal role of biological processes in terrestrial ecosystems has become highlighted during the last decade(s) (Bartoli 1983; Conley 2002, Street-Perrot and Barker 2008; Struyf et al. 2009, Carey and Fulweiler 2012; Struyf and Conley 2012; Song et al. 2012; Frings et al. 2014) and forms the basis and scientific motivation for the work carried out in this thesis.

Si biogeochemical cycling within the terrestrial biosphere

The occurrence of Si in soil

Soils are formed by the products of mineral weathering and the input of organic matter from primarily decaying plants (Ashman and Puri 2002). Besides, soils are described as "the main reactor" for biogeochemical processes in terrestrial ecosystems (Sommer et al. 2006). Si occurs in several forms in soil including crystalline, poorly crystalline and amorphous forms as well as Si adsorbed onto Al/Fe hydroxides and dissolved Si (H_4SiO_4) (Sauer et al. 2006; Cornelis et al. 2011).

Crystalline forms represent by far the largest Si pool in soil and are divided into primary (e.g. quartz, feldspar) and secondary (e.g. kaolinite) minerals (Sauer et al. 2006; Blecker et al. 2006). While primary minerals are principally unaltered by chemical weathering, secondary (clay) minerals have been chemically altered (Ashman and Puri 2002). Poorly crystalline forms found in soil include allophane and imogolite and are formed via pedogenic processes (i.e. linked to soil formation) (Cornelis et al. 2011). Allophane and imogolite are commonly found in, but not restricted to, volcanic ash soils (Sommer et al. 2006).

Amorphous forms refer to solids that lack a clearly definable structure (as opposed to crystalline forms) (Ashman and Puri 2002). Depending on origin of formation, this fraction is further divided into either a biogenic or a pedogenic amorphous Si (ASi) pool. The biogenic pool includes plant phytoliths (Clarke 2003), diatom frustules (Kokfelt et al. 2009; Van Kerckvoorde et al. 2000) and the tests of testate amoebae (Aoki et al. 2007; Sommer et al. 2013; Puppe et al. 2014). The pedogenic Si pool is linked to soil formation processes and includes among others Opal-A spheres (formed when DSi concentrations reach saturation) and volcanic glass shards (tephra) (Sauer et al. 2006; Cornelis et al. 2011; Clymans et al. 2015). Compared to crystalline Si, the highly un-

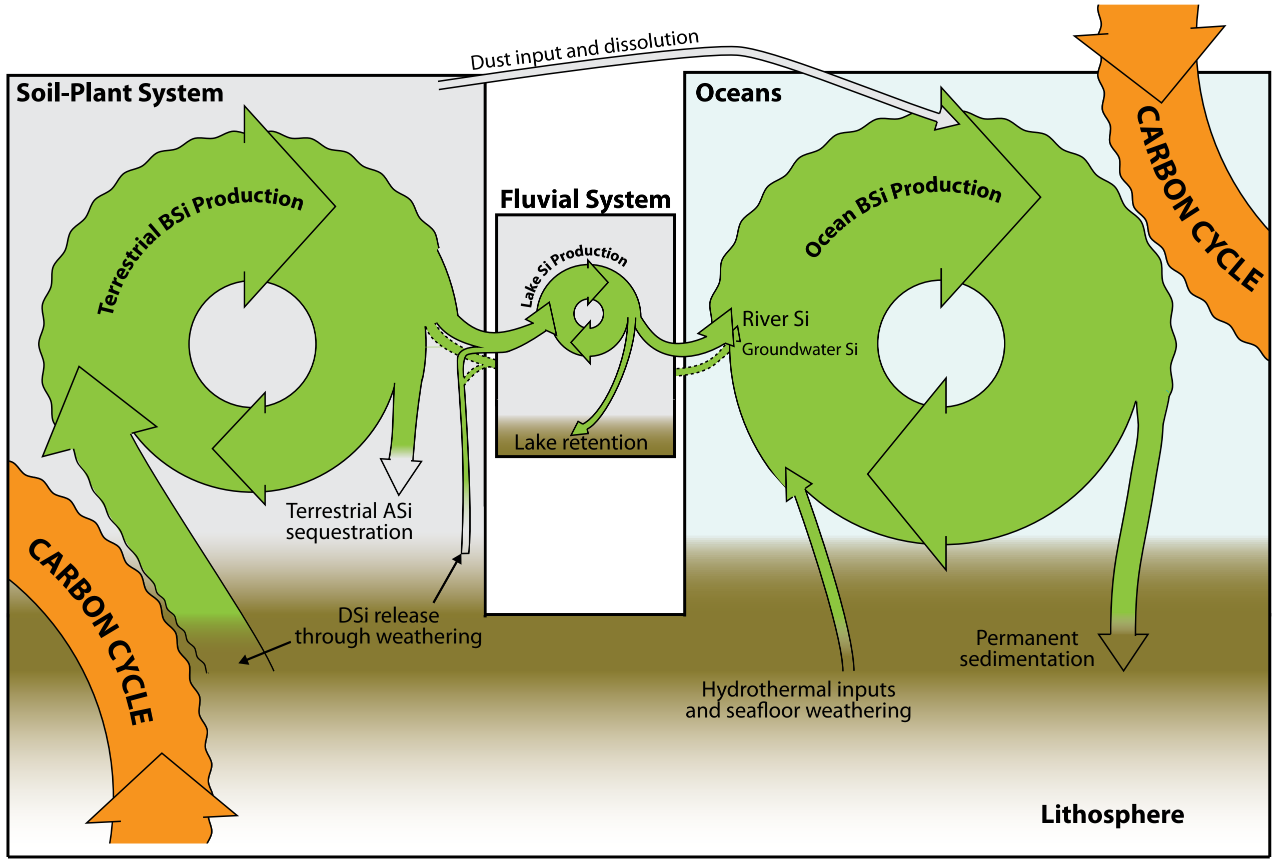


Figure 1. Overview of the global Si biogeochemical cycle where terrestrial (land) processes are linked with the ocean via the fluvial system (i.e. lakes and rivers). The two major connections to the global C cycle are also indicated. Arrow sizes broadly reflects the magnitude of fluxes. Figure from Frings et al. 2014.

structured amorphous forms dissolve more easily (Fraysse et al. 2009) and are the focus of attention in Papers I – III (Fig. 2).

DSi in soil solution, originating from dissolution of the above solid fractions, mainly occurs in its uncharged monomeric form ($H_4SiO_4^0$) (Wonisch et al. 2008) but can also form polymers (Sommer et al. 2006). Further, DSi can be adsorbed onto solid surfaces of mainly Al and Fe hydroxides (Cornelis et al. 2011).

The role of Si in terrestrial biology

Plants take up Si from the soil solution in its uncharged monomeric form H_4SiO_4 (Casey et al. 2003). During transport in the plants xylem, H_4SiO_4 monomers starts to polymerize to eventually form solid precipitates of amorphous Si (opal-A or $SiO_2 \times nH_2O$) (Epstein 1994; Currie and Perry 2007) commonly termed phytoliths (Clarke 2003). Deposition of phytoliths typically occurs at transpiration sites, such as around the stomata of leafs (Fig. 3), (Sommer et al. 2006; Trembath-Reichert 2015) but also in plant roots (Watteau and Villemin 2001). The degree of ASi accumulation in plants typically varies between 0.1 – 10 % by dry weight (Epstein 1994) and is dependent on species, with grasses (Poaceae), sedges (Cyperaceae) and horse-tails (Equisetaceae) (Hodson et al. 2005; Carnelli et al. 2001) being known Si-accumulators. Conversely, many shrubs such as *Vaccinium* spp., *Salix* spp. and *Calluna* spp. accumulate low amounts of ASi (Carnelli et al. 2001). Fixation of Si by plants is suggested to have evolved at least 400 million years ago (Trembath-Reichert 2015).

Uptake of DSi from the soil solution is thought to occur either through passive flow via the transpiration stream or by an active uptake mechanism (Epstein 1994; Prychid et al. 2004; Meunier et al. 2008). A gene responsible for the active uptake of DSi has been identified in rice (Ma and Yamaji 2006). In addition to uptake by plants, Si is consumed by diatoms and testate amoebae that also occur in the terrestrial environment (Van Kerckvoorde et al. 2000; Kokfelt et al. 2009; Sommer et al. 2013; Puppe et al. 2014).

At present, Si is not regarded as being essential for plant growth. Instead, Si is observed to exert several positive effects including improved growth (Meena et al. 2014) and resistance to biotic (e.g. pathogens) (Fauteux et al. 2005; Shetty et al. 2011; Guntzer et al. 2012) and abiotic stress (e.g. drought, metal toxicity) (Kidd et al. 2001; Guntzer et al. 2012) as well as providing structural support (Schoelynck et al. 2010) and defense against grazing herbivores (Massey et al. 2006, 2007, 2008). Today many crop fields are therefore supplied with Si fertilizers (Meena et al. 2014; Haynes et al. 2014).

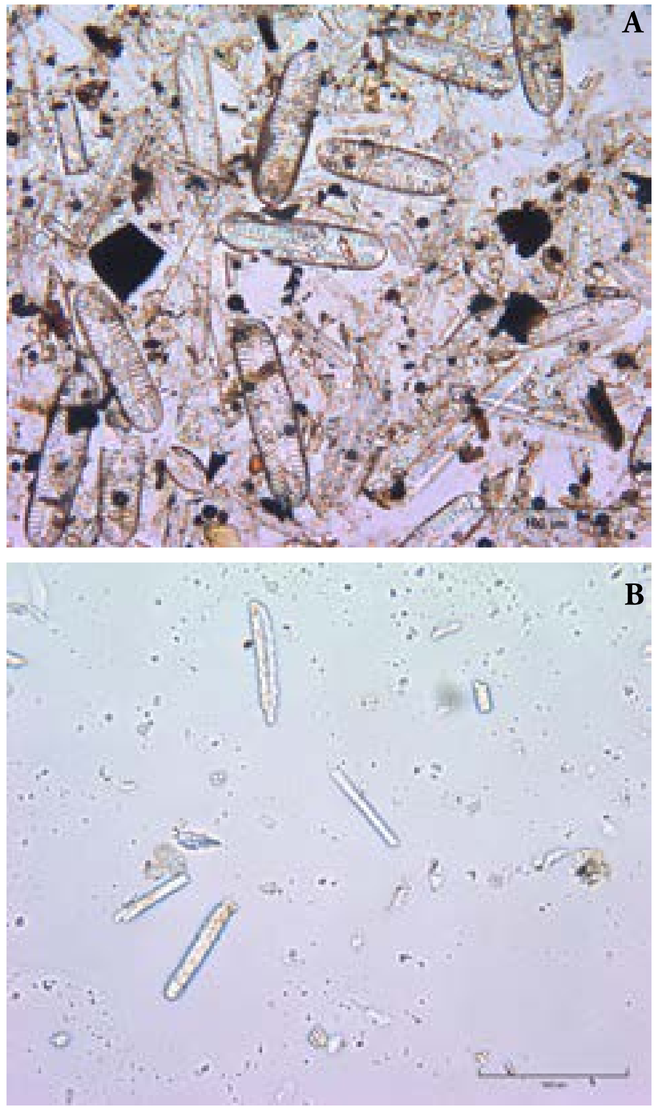


Figure 2. Examples of biologically derived amorphous Si fractions found in soil including **a**) pennate diatoms and **b**) plant phytoliths. Photos: Belinda Alvarez.

The terrestrial Si filter

Uptake and fixation of Si by terrestrial plants on a global scale is estimated to range between 55 – 200 Tmol Si year (Conley 2002; Laruelle et al. 2009; Carey and Fulweiler 2012) which is similar to the estimate of Si fixed by diatoms in the global ocean (240 ± 40 Tmol Si year; Tréguer et al. 1995; Tréguer and De La Rocha 2013). Note that these estimates for terrestrial vegetation do not include Si fixed by diatoms and Si requiring organisms found in terrestrial habitats.

Through litterfall, phytoliths are returned to the top soil. This pool of biologically fixed ASi is commonly much larger (orders of magnitude) than that stored in aboveground biomass (Markewitz and Richter 1998; Blecker et al. 2006; Sommer et al. 2013) and forms a pool of higher reactivity than that of crystalline Si (Fraysse et al. 2009) and, thus, increases its bioavailability to plants (Gocke et al. 2013). Diatoms and testate amoebae also contribute to this ASi pool (Van Kerckvoorde et al. 2000; Kokfelt et al. 2009; Sommer et al. 2013). Estimates of ASi storage in soil, based on either extracted phytolith content or alkaline extractable Si, range between 963 – 800,000 kg SiO_2 ha^{-1} (Struyf and Conley 2012; Paper I). The size of the soil ASi pool is dependent on several interacting factors, including aboveground net primary productivity (Blecker et al. 2006; Melzer et al. 2010), type of vegetation (Cornelis et al. 2010, 2011b; Alexandre et al. 2011), climate (Blecker et al. 2006), lithology (Melzer et al. 2012), weathering degree of parent material (Henriet et al. 2008) and human perturbations (e.g. deforestation and agricultural practices; Conley et al. 2008; Clymans et al. 2011; Keller et al. 2012; Vandevenne et al. 2015).

Dissolution of phytoliths takes place in the top soil (Sommer et al. 2013) and released DSi can either continue to be cycled within the plant-soil continuum, precipitate and form pedogenic ASi (Sauer et al. 2006; Cornelis et al. 2011, 2014) or contribute to the leaching of DSi out of the soil environment (Bartoli 1983; Sommer et al. 2013). Alternatively, phytoliths and diatoms can be preserved in the soil on centennial to millennial time-scales (Meunier et al. 1999; Clymans et al. 2014; Paper I).

By regulating Si fluxes through the land-ocean continuum, via a plant-soil Si cycle, terrestrial ecosystems including wetlands have been termed the "ecosystem Si filter" (Struyf and Conley 2012). Depending on dominant plant species (low vs. high Si-accumulators), the "efficiency" of this filter can vary between land-cover types. For example, Cornelis et al. (2010) found the output of DSi in deep mineral horizons to be negatively correlated with the annual DSi uptake by different tree species. In

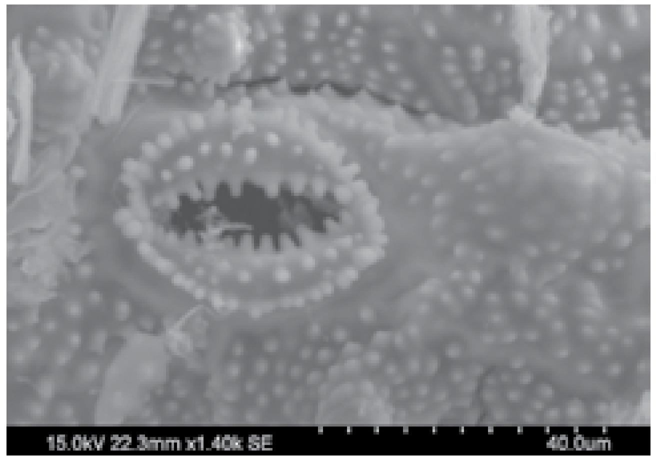


Figure 3. Scanning electron microscope image of silicified plant tissue (*Equisetum arvense*) including stomatal complexes after removal of organic matter. This illustrates how the deposition of silica mimics the different plant cell structures.

addition, lakes are important sinks for retaining Si at the continents (Frings et al. 2014; Tallberg et al. 2014).

Anthropogenic perturbations

A change in the river load of dissolved and amorphous Si ultimately reaching coastal zones will influence DSi availability for marine diatoms. This will have implications for marine primary productivity, phytoplankton community composition, the food-web and associated C-cycle dynamics (Kristiansen and Hoell 2000, Tréguer et al. 1995; Tréguer and De La Rocha 2013). Today we know that several anthropogenic activities including construction of river dams (Triplett et al. 2012), deforestation (Conley et al. 2008), land-use change (Struyf et al. 2010; Carey and Fulweiler 2012b) and agricultural practices (Clymans et al. 2011; Keller et al. 2012; Vandevenne et al. 2012, 2015) cause perturbations to the global Si cycle such as alterations in soil ASi storage and DSi river fluxes. Ongoing climate warming can be expected to alter global Si biogeochemistry in multiple and intricate ways, which has yet remained largely unexplored (Laruelle et al. 2009). The majority of the above studies have been carried out in mid-latitude regions with high-latitude regions, such as the Arctic, receiving less attention (Pokrovsky et al. 2013).

The Arctic perspective

In the Arctic, warming of surface air temperatures are occurring at a rate twice that of the global average (Anisimov et al. 2007) which makes the region particularly sensitive to climate change. Reduced permafrost extent and a thickening of the active layer depth will follow with warmer temperatures (Vaughan et al. 2013). Together with more abrupt permafrost degradation processes, such as thermokarst formation (Sannell and Kuhry 2011), previously frozen material will become available for biogeochemical reactions. In response to these processes, hydrological flow paths will be altered (Lawrence and Slater 2005; Andresen and Lougheed 2015) as well as vegetation cover (Johansson et al. 2006; Tape et al. 2006; Myers-Smith et al. 2011) which may influence Si biogeochemistry. Compared to an increasing number of studies reporting soil organic carbon (SOC) storage in permafrost terrain during the last decade (Zimov et al. 2006; Ping et al. 2008; Tarnocai et al. 2009; Hugelius et al. 2010, 2014; Michaelson et al. 2013; Strauss et al. 2013; Palmtag et al. 2015) no estimates, to my knowledge, has earlier been reported concerning ASi soil storage.

Permafrost thaw combined with alterations in hydrology and vegetation cover will alter Si fixation by plants, subsequent soil ASi storage and Si delivery to aquatic ecosystems, including the Arctic Ocean, in yet uncertain ways. Studying the link between changes in terrestrial landscape processes and their impact on downstream aquatic environments (Vonk et al. 2015) is a highly relevant research field regarding Si biogeochemistry. Further, whether soil microbes influence phytolith dissolution during organic matter decomposition is uncertain (Fraysse et al. 2010) but gained knowledge can improve our understanding regarding fate of biogenically derived ASi that is mobilized by permafrost thaw. This since rate and type of microbial litter decomposition could alter rates of ASi recycling within the vegetation-soil continuum.

A potential role of soil microbes

Bacteria and fungi are key regulators of biogeochemical cycles (Rousk and Bengtson 2014). It is well established that bacteria enhance dissolution of diatom frustules (ASi) in aquatic ecosystems (Bidle and Azam 1999, 2001; Bidle et al. 2002, 2003; Roubeix et al. 2008; Holstein and Hensen 2010) by ectoenzymatic decomposition of an outer organic coating (Bidle and Azam 1999, 2001). Based on their role as primary decomposers of organic matter, it is commonly anticipated that microbes will enhance dissolution of phytoliths embedded in an organic matrix (Sommer et al. 2006; Schoelynck et al. 2010; Struyf and Conley 2012; Schaller and Struyf 2013). While the interactions between soil microbial colonization and release of nutrients during decomposition of plant litter are well studied for C, other plant material constituents, such as Si, have not received equal attention. Struyf and Conley (2012) proposed this to be one of the key aspects needing further attention to better understand the function of the terrestrial ecosystem Si filter.

Few studies designed to investigate Si release from plant litter in the presence of a live microbial decomposer community are available (Struyf et al. 2007; Fraysse et al. 2010) and they were not designed to explicitly investigate the role of microbes. These studies indicate no or a slight enhancement of phytolith dissolution rates during microbial litter decomposition, but methodological limitations make interpretation less straightforward. For instance, both studies (Struyf et al. 2007; Fraysse et al. 2010) evaluated the influence of an actively degrading microbial community indirectly, without confirming the presumed difference in colonization between controls and inhibited or sterilized treatments. Hence, the question whether microbes enhance phytolith dissolution during plant litter degradation remains unclear. Improved understanding of this matter would provide insight into how biotic factors control Si release into pore water and how DSi-fluxes are influenced by the rate and type of microbial decomposition of submerged plant litter.

Scope of thesis

With the presented background in mind, the general scope of this thesis was to investigate size and land-cover partitioning of ASi storage in Arctic permafrost affected soils. An additional aim is to shed light over the potential influence of microbes on phytolith dissolution during plant litter decomposition. The recently improved understanding of the importance of biological processes in terrestrial Si cycling provides the rationale for this thesis.

The general working hypotheses were that 1) Arctic tundra and peatlands underlain by permafrost represents hotspots of soil ASi storage due to high prevalence of Si-accumulating plant species and cold climates favoring preservation and 2) microbes enhance phytolith dissolution during plant litter mineralization, thus playing a key role with regards to Si cycling within the plant-soil continuum.

In specific terms, the aims of this thesis were to:

- Quantify ASi storage (0 – 1 m) and investigate partitioning between land-cover types, soil type and active layer versus permafrost. This was achieved by, together with own samples, taking advantage of archived soil samples collected from several contrasting regions in the circum-Arctic region (Paper I and Paper III).

- Based on our results combined with literature review discuss potential impacts of climate change and permafrost thaw with regards to the biological part of the terrestrial Si cycle. The goal is to provide a framework for future research to build on (Paper I).

- Based on thematic upscaling provide a first estimate of soil ASi storage (0 – 1 m) in the circum-Arctic tundra region (Paper III).

- With laboratory incubation experiments containing submerged plant litter test whether microbes influence phytolith dissolution during microbial decomposition (Paper II).

Study sites

A map (Fig. 4) showing the location of all study sites, together with photos (Fig. 5) depicting the common landscape at most sites, is provided.

Tulemalu Lake, central Canadian Arctic

The Tulemalu Lake study site (Paper I) is located in the central Canadian Arctic close to the shore of Tulemalu Lake (Fig. 4; 62°55'N, 99°10'W). The climate is continental with mean annual air temperature (MAT) ranging between -9.4 to -14.3 °C and total annual precipitation (MAP) being < 300 mm of which 40 % falls during the winter period (mean temperature < 0 °C) (Hugelius et al. 2011). The area is located within the continuous permafrost zone, meaning that > 91 % of the land area is underlain by permafrost (Tarnocai et al. 2009). Elevation in the study area range between 281 and 303 meter above sea level (a.s.l). The bedrock is dominated by granite and is overlain by quaternary deposits from previous glaciations in the area. Quaternary deposits are glacial till (sandy loam to loamy sand) and glaciofluvial materials (sandy). In depressions, thick peat deposits have accumulated over time. Soils developed on glacial till are classified (World Reference Base of Soil Terminology; WRB) as Turbic (or Histic) Cryosols while soils developed on glaciofluvial materials are classified as Cambic or Haplic Cryosols (Hugelius et al. 2011). Where thick peat deposits have developed, soils are classified as Cryic Hemic Histosols (bog peatland) or Histic Cryosol/Cryic Histosol (fen peatland) (Hugelius et al. 2011).

Vegetation cover in the study area consists of bog- and fen peatlands intermixed with shrub tundra having different drainage conditions depending on slope position. Bog peatlands (typically occurring in high-centered ice wedge polygons) are dominated by mosses, lichens and prostrate shrubs (*Vaccinium* spp., *Ledum palustre*, *Rubus chamaemorus*) whereas fen peatlands are dominated by graminoids (*Eriophorum* spp.) and mosses (*Drepanocladus* spp., *Sphagnum* spp.). Shrub tundra sites are dominated by *Salix* spp. and *Betula nana* shrubs while lichen tundra is dominated by lichens (*Cladonia* spp.) together with *Empetrum* spp. and *Vaccinium* spp. shrubs (Hugelius et al. 2011). According to the Circumpolar Arctic Vegetation Map (CAVM Team 2003; see Walker et al. 2005) the vegetation in the region is dominated by erect dwarf-shrub tundra (S1), low-shrub tundra (S2) and sedge, moss, low-shrub wetland (W3).

Adventdalen, Svalbard

The Adventdalen study site (Paper III) is a U-shaped valley located in a mountainous landscape nearby the

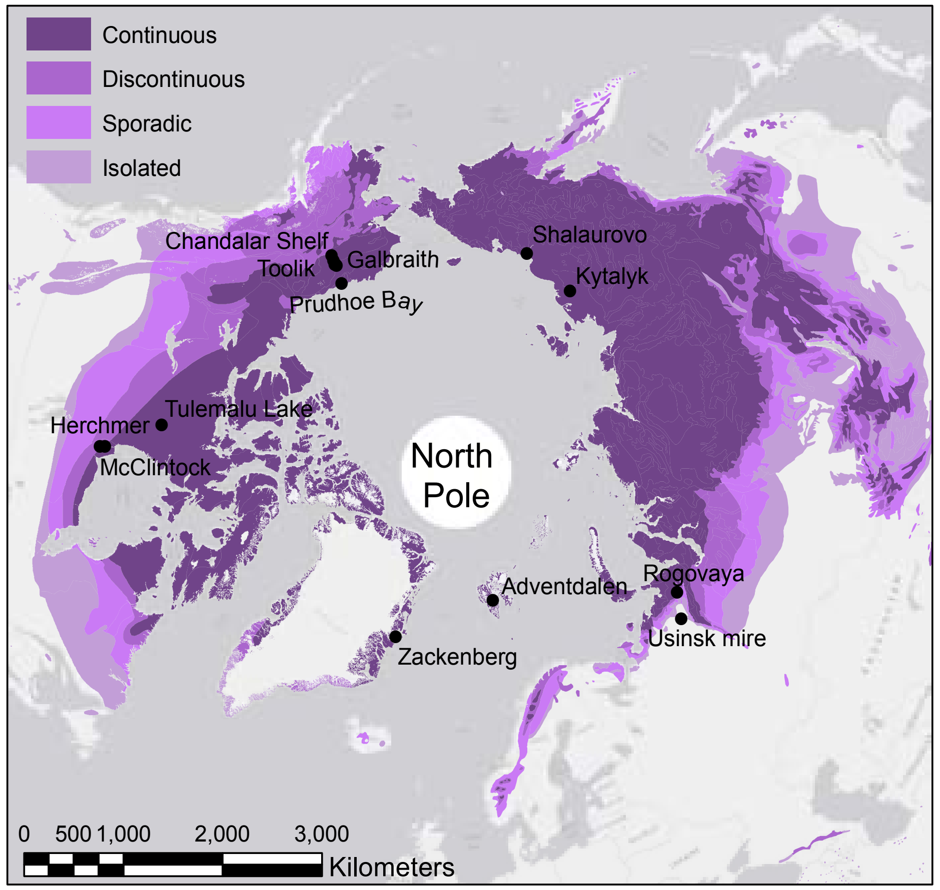
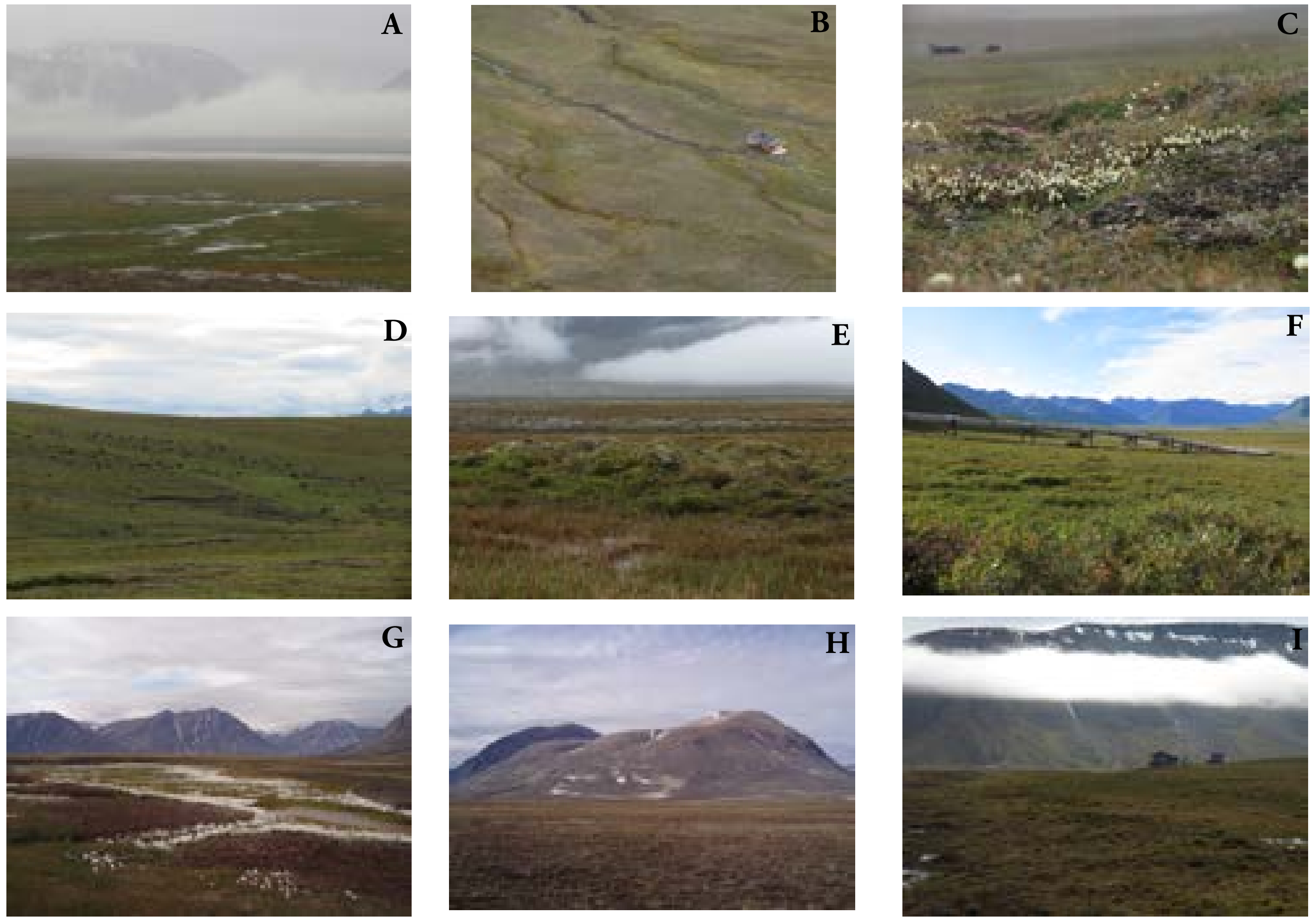


Figure 4. Location of study sites in the circum-Arctic permafrost region from which soil samples were retrieved in Paper I and III. Permafrost zonation is following Brown et al. (1998).



<Figure 5. Selected pictures showing different Arctic land covers from some of the study sites included in this thesis. Picture **a-c**, **e**, **i**) Adventdalen, Svalbard, **d, e**) Arctic Foothills, Alaska and **g-h**) Zackenberg, NE Greenland (Photos from Zackenberg: C. Stiegler).

community of Longyearbyen in central Svalbard (Fig. 4; 78°12´N, 16°20´E). The climate is high-Arctic with a MAT of -6 °C and a MAP of 190 mm of which most falls as snow (Christiansen 2005). Adventdalen is situated within the continuous permafrost zone and the area consists of sedimentary rocks of Early Permian to Eocene age (Dallman et al. 2001). The area has been glaciated and the valley is covered by glacial till, fluvial sediments and eolian material.

According to CAVM, the vegetation cover in Adventdalen is dominated by rush/grass, forb, cryptogam tundra (G1) and sedge, grass, moss wetland (W1). Presence of low-centered ice wedge polygons are common which leads to a distinct vegetation zonation with tall grasses in troughs, sparsely vegetated rims and an extensive moss cover in the low-polygonal centers (Christiansen et al. 2005).

Zackenberg, NE Greenland

The Zackenberg study site (Paper III) is located in the surrounding area of the Zackenberg Research Station situated by the coastline of NE Greenland (Fig. 4; 74°28´N, 20°34´W). The area is mountainous and the study site is located in a broad, flat central valley (altitudinal range; 0 – 1372 m a.s.l). The climate is high-Arctic with MAT of -9.2 °C and MAP of 200 mm with approximately 10 % falling as rain during summer (June – September) (Hansen et al. 2008). A large fault system dividing Caledonian gneiss/granite bedrock (west) and Cretaceous-Tertiary sedimentary rocks (east) have created the Zackenberg valley (Escher and Watt 1976), which has been glaciated. The valley is covered by quaternary glaciofluvial, deltaic, eolian and glacial till deposits while solifluction material is dominant on slopes. The dominant soil type in the Zackenberg central valley has been classified as Typic Psammoturbel (Elberling et al. 2008). On hill slopes, the dominant soil type is Gelorthents whereas fen peatlands are classified as Hemistels or Histoturbels (Palmtag et al. 2015).

The vegetation in Zackenberg forms a zonal pattern ranging from fell fields at the hilltops to fen peatlands in the lowland areas of the central valley. In the lowland valley, *Cassiope tetragona* heaths, *Salix arctica* snow beds, grasslands and fen peatlands are intermixed with each other whereas *Dryas* spp. heaths are common at higher elevations (Elberling et al. 2008). Fen peatlands, located in depressions and dominated by grasses (e.g. *Eriophorum scheuchzeri*), are typically surrounded by grasslands, which are common on slightly sloping terrain. The grasslands are dominated by *Eriophorum triste*, *Arctagrostis latifolia* and *Alopecurus alpine* with a moss cover of approximately 55 % (Elberling et al. 2008). According to CAVM the area surrounding Zackenberg is dominated by prostrate shrub tundra (P1 and P2).

Shalaurovo, NE Siberia

The Shalaurovo study site (Paper III) is located in the Kolyma Lowlands of NE Siberia (Fig. 4; 69°27´N, 161°48´E). The region has a continental climate with a MAT of -11.3 °C and MAP of 290 mm of which 50 % falls during the summer months. Compared to the three previous field sites, the area stayed largely unglaciated during the Last Glacial Maximum (LGM) (Brubaker et al. 2005). The parent material comprises late Pleistocene Yedoma Ice Complex (IC) deposits. Yedoma IC deposits consist of fine grained silty material with a high content of ground ice (up to 80 % by volume) that can rise 30 m above the neighboring terrain (Schirrmeister et al. 2011). Histoturbels represent the dominant mineral soil type at tundra sites while Haploturbels are dominating on floodplains. Bog peatlands and fen peatlands in the area are classified as Folistels and Hemistels, respectively (Palmtag et al. 2015).

At Shalaurovo, upland areas are dominated by shrubby tussock tundra while areas with gentle slopes are dominated by shrubby grasslands. Depressions of low lying areas are characterized by sedge fen and willow communities while steep slopes are primarily dominated by *Equisetum* spp. (Lashchinskiy et al. 2013). According to CAVM, the vegetation in the region is dominated by tussock-sedge, dwarf-shrub, moss tundra (G4), low-shrub tundra (S2) and sedge, moss, shrub wetlands (W2 and W3).

Kytalyk, NE Siberia

The Kytalyk study site (Paper III) is located in the Indigirka Lowlands of NE Siberia (Fig. 4; 70°49´N, 147°28´E) and is situated in the continuous permafrost zone. The region has a continental climate with a MAT of -10.5 °C and MAP of 212 mm of which approximately 50 % falls during the summer months (Van der Molen et al. 2007). Similar to Shalaurovo, the region stayed mostly unglaciated during the LGM and the parent material comprises late Pleistocene Yedoma IC deposits.

According to CAVM, the vegetation in Kytalyk is dominated by tussock-sedge, dwarf-shrub, moss tundra (G4), low-shrub tundra (S2) and sedge, moss, shrub wetlands (W2 and W3). Blok et al. (2010) described moist tussock tundra in Kytalyk to be dominated by *Eriophorum vaginatum* and shrubs of *Betula nana*, *Salix pulchra* and *Ledum palustre* whereas wet areas are dominated by *E. angustifolium*, *Carex aquatilis* and *Sphagnum* mosses.

Alaska, USA

Soil samples were collected in Alaska during a field study course ("Alaska Soil Geography Field Study", University of Alaska Fairbanks, Fairbanks, Alaska) in July/August 2012. The field course followed the route of Dalton Highway starting in Fairbanks of interior Alaska, going north through the Brooks Range toward the Arctic coastal plains and ending in Prudhoe Bay (Fig. 4) located at the coastline of the Beaufort Sea. Stops were made along the route where soil pits were dug. The climate changes from continental in interior Alaska (Fairbanks) to high-Arctic in the coastal plains.

While travelling from interior Alaska toward the Arctic coastal plain, the landscape changes from spruce dominated forests (*Picea glauca*, *Picea mariana* intermixed with e.g. *Alnus* spp., *Betula* spp. and *Salix* spp.) to shrub and graminoid tundra. The permafrost zonation changes from discontinuous permafrost in interior Alaska to continuous permafrost in the high-Arctic regions.

Other sites

In addition to the above described field sites, data retrieved from two soil pedons collected in Hudson Bay Lowlands, central Canada (Kuhry 1998, 2008) and two soil pedons collected from the European Russian Arctic (Oksanen et al. 2001, 2003) were included in Paper III. All four soil pedons were retrieved from raised bog peatlands (palsas and peat plateaus) consisting of meter thick *Sphagnum* spp. and *Carex* spp. peat.

Materials and Methods

Soil material

Field campaigns to the described study areas (except Alaska) in late summer were originally conducted to study storage and landscape distribution of soil organic carbon (SOC) in Arctic permafrost terrain (Hugelius et al. 2010, 2011; Palmtag et al. 2015; Siewert et al. in review). These samples are archived at the Department of Physical Geography, Stockholm University, Sweden. Subsamples were retrieved from these sites for the purpose of investigating ASi storage and landscape distribution in permafrost terrain (Paper I and Paper III).

A transect based sampling method has been used at all study sites for the collection of soil pedons. When using this approach, initial scouting of the field is performed to establish transects that are representative for the investigated study area. After this, the sampling of soils is made at equidistant intervals (Hugelius et al. 2010; Palmtag et al. 2015; Siewert et al. in review). Such a sampling approach leads to a combination of subjective selection of sites (thought to be characteristic for the investigated landscape) and a degree of randomness (represented by small-scale vegetation and micro-topography patterns) (Hugelius et al. 2011).

At each site, soil cores were retrieved by hammering steel tubes into the frozen ground (Fig. 6) in ~ 0.05 – 0.10 m vertical depth increments after cutting out blocks of the top organic layer. At tundra sites (but not for peatlands) three randomly selected replicates of the top organic layer were cut out. This was done since spatial fine-scale variability of the top organic layer thickness can vary greatly. In some cases, soil samples were collected using fixed volume cylinders inserted horizontally at unfrozen exposed surfaces (e.g. at exposed erosion sites or dug soil pits) while a Russian peat corer was sometimes used to collect unfrozen peatland deposits. Depth of the top organic layer and active layer together with a description of the vegetation cover and other parameters (e.g. slope, aspect) was recorded while sampling.

For some of the study sites (e.g. Tulemalu Lake in Paper I and Adventdalen in Paper III) field work was carried out in late June and July. At this time of the season, the maximum seasonal thaw depth of the active layer is not yet reached. Therefore, the estimates made for ASi stored in permafrost do not entirely correspond to the maximum seasonal thaw depth.

Soil sampled during the field study course along the Dalton Highway, Alaska, was collected by digging soil pits (using jackhammers when reaching permafrost) and a sample was collected from each described soil horizon.

Quantification of ASi in soil and vegetation

To quantify the content of ASi in soil (Paper I and Paper III) and vegetation (Paper II) samples, a wet alkaline digestion method was used. The digestion method applied here was originally described by DeMaster (1981) to quantify ASi in marine sediments but have been evaluated for and widely applied to soil samples (Sauer et al. 2006; Saccone et al. 2007; Melzer et al. 2010, 2012; Struyf et al. 2010; Clymans et al. 2011; Cornelis et al. 2011b; Opdekamp et al. 2012).

In this procedure, a 30 mg dried and homogenized soil (or plant) sample is digested in 1 % Na_2CO_3 (pH=11.2) at 85 °C while shaken (100 rpm) for 5 h. During digestion, a 1 mL subsample is collected and neutralized with 0.01 M HCl after 3, 4 and 5 h, respectively. DSi extracts are colorimetrically analyzed using the molybdate-blue methodology (Paper I and Paper III) in which DSi reacts with molybdate to form a yellow complex, in turn reduced to a silicomolybdenum blue complex (by ascorbic acid) for which the absorbance is measured at 660 nm. To avoid potential interference from dissolved phosphate present in the extracts, oxalic acid is added to the reaction mixture (Amornthammarong and Zhang 2009). In Paper II, DSi extracts (obs. *not* from soil) had to be analyzed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) due to interference from very high phosphate concentrations.

Figure 6. Field work in Adventdalen, Svalbard. The collection of soils is carried out by hammering a fixed volume steel tube into the frozen ground.

The method to determine ASi described by DeMaster (1981) relies on two basic assumptions: 1) ASi of biogenic origin is nonlinearly and completely dissolved within the first 2 h of extraction and 2) increasing DSi concentrations after 3 h is solely due to a continued dissolution of clay minerals and primary silicates which follows a linear pattern over time. These two assumptions allows for a mineral correction to be made (Fig. 7), where the fraction of DSi released from amorphous components (as opposed to mineral Si) is determined by linear extrapolation of the slope to time zero for the three time-course measurements at 3, 4 and 5 h (DeMaster 1981). For digestion of pure plant material (Paper II) no mineral correction is necessary, instead an average value of DSi for the three time-course measurements is used. This method allows for a relatively large number of samples (ca. 150 – 200 samples) to be analyzed during a relatively short time-span (1 week) compared to other methods (e.g. Georgiadis et al. 2013, 2014; Barão et al. 2014, 2015).

Methodological considerations

The presence of different Si fractions in soil, forming a continuum from highly ordered crystalline (less dissolvable) to amorphous forms (more dissolvable) (Sauer et al. 2006), complicates the quantification of biologically formed ASi in soil. Several methods have been used to quantify ASi in soil including digestion in 1 % Na_2CO_3 (DeMaster 1981), NaOH (Saccone et al. 2007) or Tiron (Meunier et al. 2014), a sequential separation procedure suggested by Georgiadis et al. (2013, 2014) and continuous extraction of Si and Al in NaOH (Koning et al. 2002; Barão et al. 2014, 2015). Extraction in Na_2CO_3, NaOH and Tiron is not phase specific. While a mineral correction is made for the simultaneous Si release from clay minerals and crystalline Si (DeMaster, 1981), no separation can be made between Si released from biogenic and pedogenic amorphous Si and other poorly crystalized Si fractions.

Digestion in Na_2CO_3, Tiron and NaOH produces comparable results when applied on fresh phytolith material and organic top soils (Saccone et al. 2007; Meunier et al. 2014; Barão et al. 2015), whereas incomplete digestion of ASi (in Na_2CO_3) can occur in samples containing aged phytoliths having a lower reactivity (Meunier et al. 2014). The incomplete digestion of biogenic ASi within 2 h violates the first assumption which the method by DeMaster (1981) relies on. The use of a stronger solvent, such as NaOH, may thus be a better choice to avoid underestimations of biogenic ASi. However, compared to Na_2CO_3 the use of NaOH can result in higher Si release, especially when applied on deep mineral samples (Saccone et al. 2007; Barão et al. 2015). This may result from enhanced dissolution of other non-biogenic Si fractions present in mineral soils. Moreover, dissolution of pedogenic amorphous Si, other poorly crystalline forms and clay minerals can release Si in a non-linear pattern during digestion in both Na_2CO_3 and NaOH (Barão et al. 2015; Clymans et al. 2015). This violates the second assumption made by DeMaster (1981) leading to potential overestimation of the biogenic ASi fraction.

In a method tested by Barão et al. (2014, 2015), the extraction of Si and Al from soil is continuously monitored during digestion in NaOH. By fitting the measured concentrations to mathematical models, a distinction can be made between Si released from clay minerals and ASi of biogenic or pedogenic origin based on their Si/Al ratios. In Paper I and Paper III, we suggest that ASi of biogenic origin contribute to a larger relative fraction of the ASi pool in top organic layers as compared to mineral soils. This since alkaline extraction was combined with microscopic investigation of selected soil samples which clearly indicated a high relative abundance of biogenic ASi in organic top soils (Paper I and Paper III), while no (or very few) traces of biogenic ASi were seen in the deeper mineral soils. A higher contribution of biogenic ASi in organic top soils and a higher contribution of pedogenic ASi in deeper mineral soils were found for other mixed soils analyzed with the phase specific method described in Barão et al. (2014, 2015). Other studies support this pattern with depth between biogenic and pedogenic Si fractions (Blecker et al. 2006; Saccone et al. 2007; Sommer et al. 2013; White et al. 2012; Georgiadis et al. 2014). Moreover, Si extracted from various soil types using three different methods (digestion in 1 % Na_2CO_3, digestion in 0.5M NaOH, and digestion in 0.5 M NaOH with continuous monitoring of Si and Al) showed good agreement between methods (Barão et al. 2014). Extracted Si concentrations, as well as the vertical distribution pattern of extracted Si concentrations, agreed well between soils and methods (Barão et al. 2014). In summary, the 1 % Na_2CO_3 method used in Paper I and Paper III works well when applied to top soil and organic samples containing fresh phytoliths. In deep mineral soils, a dominant contribution of Si release from pedogenic and other non-amorphous fractions is expected. We therefore performed spot checks on soil samples under a microscope to better evaluate the contribution of biogenic versus pedogenic ASi in the different soil layers.

Evaluating the contribution of biogenic Si

Since no distinction between biogenic or pedogenic ASi can be made with the applied alkaline digestion method (DeMaster 1981) selected soil samples were investigated under a microscope to evaluate the composition of ASi. Soil samples from both the top organic layer, intermediate depth and the deeper mineral horizons of soil profiles were evaluated under microscope. No quantitative enumeration of the biogenic fraction was made.

In Paper I, soil samples were investigated with both light- and scanning electron microscope (SEM). Prior to analysis, organic matter was removed by treating the samples with H_2O_2 at ~ 80 °C (light microscopy) or by ignition at 550 °C (SEM). In Paper III, organic material was removed with H_2O_2 (~ 80 °C) and followed by heavy liquid separation using polytungstate (SPT; relative density 2.3 g cm^{-3}) (Morley et al. 2004) in order to obtain the concentrated biogenic ASi fraction. This approach was selected since the large contribution of silt to the mineral soils of the Yedoma IC could potentially mask the presence of any biogenic Si remains. Samples were viewed under a light microscope (40 x magnifications) (Fig. 2).

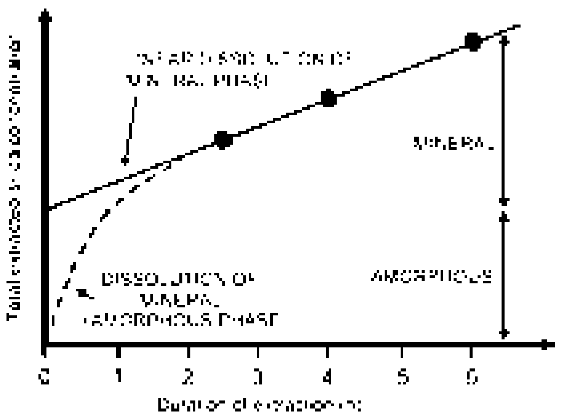


Figure 7. Summary of the method used to correct for the simultaneous dissolution of mineral Si during extraction of ASi from soil samples. Figure from DeMaster (1981) and Koning et al. (2002) as modified by Clymans et al. 2011b.

Storage calculations and upscaling

The storage of ASi in each soil sample is calculated by using the DBD (kg m^{-3}), the concentration of [Si] (g SiO_2 kg^{-1} dry weight) and the depth (d; m) of the sampled horizon (i):

$$\text{Storage}_i = \text{DBD}_i * [\text{Si}]_i * d_i * (1 - \text{CF})_i * 10$$

A correction factor of (1 – CF) was applied to take the percent stone content (CF; course fraction > 2 mm) of each horizon into account. The factor 10 is to convert g m^{-2} to kg ha^{-1}. In Paper I, no correction for the CF was made in the storage calculations since particle-size separations (sieving) were not conducted on these archived soil samples. This would result in potential overestimation of the calculated pools. However, descriptions of % CF were made for a limited number of soil pedons in the field and showed a negligible contribution of stones in the top organic layer of peatlands and shrub tundra. In the shrub tundra mineral soils, stone content varied between 2 to 100 % with an average of 12 ± 17 %, resulting in an average uncertainty range of 1,100 to 9,000 kg SiO_2 ha^{-1}. In Paper III, no CF needed to be included in the storage calculations for the Shalaurovo and Kytalyk study sites since no large stones were encountered in these soils.

Data needed for storage calculations (DBD, % CF) were retrieved from Hugelius et al. (2010), Palmtag et al. (2015) and Siewert et al. (in review). Where values of DBD and/or [Si] were missing, extrapolation was made by taking a mean from the sample directly above and below in the soil horizon. Total storage was calculated by summing the values of all soil horizons corresponding to the depth interval of interest. Extrapolation to 1 m depth was made from the last sample in the mineral horizon. Such extrapolation can lead to overestimation of the pool at depth. The triplicate top organic layers collected at tundra sites (not peatlands) were used to calculate a mean storage for the organic layer at each site. Regarding the Alaskan soil samples, sampling in the field were carried out without taking the volume of the sampled soil into account. Hence, no estimates of the DBD could be made for these samples. However, DBD and percent CF of soil profiles collected from the same soil type and area were available from previous investigations (Michaelson et al. 2013) and this data was used in Paper III to estimate ASi storage at these sites.

In Paper III, we apply thematic upscaling to provide an estimate of ASi storage (Tmol Si) in the circum-Arctic tundra region. In thematic upscaling, the mean ASi storage for a specific thematic class is multiplied with the total areal coverage of that class. This approach relies on the assumption that the assigned thematic classes provide a correct representation of the diverse natural environment in the landscape of interest (Hugelius et al. 2011). To estimate ASi storage on a circum-Arctic scale we applied two upscaling scenarios based on available spatial data for the circum-Arctic region. The first scenario is based on vegetation classification using the Circumpolar Arctic Vegetation Map (CAVM) available at a 1:7,500,000 scale (CAVM Team 2003; see Walker et al. 2005). The CAVM map includes 15 different vegetation types occurring between the Arctic Ocean to the north and the northern limit of forests (treeline) to the south. The entire area is underlain by continuous permafrost. The second scenario is based on soil classification using the "Northern Circumpolar Soil Database (NCSCDv2) (Tarnocai et al. 2009; Hugelius et al. 2014). The upscaling using soil classification (henceforth referred to as "CASM") was restricted to the same area covered by the CAVM map. Based on available site descriptions, all soil pedons were assigned a vegetation class (following CAVM) or soil type (following CASM).

Investigating the role of microbes - study approach

Commonly either laboratory batch (Struyf et al. 2007; Fraysse et al. 2010; Schaller and Struyf 2013) or flow-through experiments (Fraysse et al. 2006, 2009, 2010) are used to study phytolith and diatom dissolution kinetics. We used laboratory batch experiments to assess whether microbes (bacteria and fungi) influence the rate of phytolith dissolution during plant litter mineralization (Paper II). In such experiments, a siliceous material (here phytoliths) is suspended in a liquid that is originally free from Si and the subsequent release of DSi is then observed over time. Of course, such experiments do not fully depict the complex natural environment but it enables the variable of interest (here phytolith dissolution) to be studied under controlled conditions. Compared to flow-through experiments, batch experiments are simpler to perform which allows for more replication of treatments. However, a potential drawback of using batch cultures (as opposed to flow-through experiments) is that the composition of the solution continuously changes over time (Loucaides et al. 2011).

To distinguish between biotic (i.e. microbial) and abiotic factors, phytolith dissolution in the presence of a microbial decomposer community need to be compared with a sterile control (all other conditions being equal) (Fig. 8). This necessitates the use of sterilization techniques; hence, autoclavation of plant litter was performed in Paper II to obtain sterile litter for use in the experiments. After inoculation with either a live microbial community (live soil) or a sterilized soil, batch cultures were incubated at room temperature for 1 month with microbial growth and DSi concentrations being monitored over time. The applied sterilization approach proved to be efficient for our purpose. However, sterilization by different means (autoclaving, ɣ-irradiation) may alter the physical properties and chemical composition of the sterilized material (Berns et al. 2008). An initial pilot experiment testing a range of sterilization methods was therefore conducted, with litter being either heated at 80 °C or autoclaved (assumed to be more "harsh"). Both methods used to sterilize litter resulted in similar patterns of Si release from litter and the bacterial use of plant litter was identical between the two methods of sterilization. Together, this suggests that the sterilization of litter did not fundamentally alter the used plant material´s susceptibility to microbial degradation. Additionally, pure phytoliths heated to 450 °C showed similar or slightly higher Si release rates when compared to unheated phytoliths over a range of different pH conditions (Fraysse et al. 2006).

Soil microbial parameters

To verify the presence of growing microbes in live batch experiments, and their absence in sterile controls, measurements of bacterial growth and fungal abundance were performed over time (Paper II). Bacterial growth was estimated by Leucine incorporation which estimates the rate of protein synthesis as a proxy for bacterial growth. Leucine incorporation was initially used to estimate bacterial growth in aquatic sciences (Kirchman et al. 1985) but later modified and widely used for soil systems (Bååth 1994, Bååth et al. 2001; Rousk et al. 2009). In the method, radioactively labeled Leucine, [^{3}H]Leu, is added to a bacterial suspension followed by a 1 h incubation at room temperature without light. The incubation is terminated by addition of 100 % trichloroacetic acid (TCA). Samples are washed from non-incorporated [^{3}H]Leu by a set of centrifugation steps (Bååth et al. 2001). Radioactivity is then measured using a liquid scintillation analyzer to determine the incorporated radioactivity and estimate the leucine incorporation rate. Methodological considerations include potential uptake of [^{3}H]Leu by fungi. Though, fungi are mainly expected to be associated with the litter rendering their presence in the bacterial suspension likely insignificant (Rousk and Bååth 2011).

Fungal abundance was estimated by extracting ergosterol from freeze dried and homogenized plant litter (Rousk and Bååth 2007; Rousk et al. 2009). Ergosterol is a membrane lipid specific to fungi and is widely used for studies in soil systems (Rousk and Bååth 2011). Ergosterol was extracted, separated and analyzed as previously described (Bååth et al. 2001; Rousk et al. 2009). The extracts are analyzed by high performance liquid chromatography (HPLC) using methanol as the mobile phase and a UV detector (282 nm). Since ergosterol is extracted from collected plant litter, it was only estimated for the experiments final day and not followed over time as for bacteria.

Figure 8. Microcosm systems containing submerged *E. arvense* litter inoculated with a sterile soil (left) or a live microbial inoculum (non-sterilized soil) (right). Note the difference in transparancy between the sterile and live treatment. Photo: Wim Clymans.

Summary of Papers

Author contributions to the following papers are given in Table 1.

Paper I

Alfredsson H, Hugelius G, Clymans W, Stadmark J, Kuhry P, Conley DJ (2015) **Amorphous silica pools in permafrost soils of the Central Canadian Arctic and the potential impact of climate change.** Biogeochemistry 124:441-459

In Paper I, we present the first estimate of vertical distribution, storage and landscape partitioning of amorphous Si (ASi) in Arctic permafrost terrain. Archived soil samples were retrieved from the Tulemalu Lake study area, central Canadian Arctic, where a detailed study of soil organic carbon (SOC) storage had been previously performed (Hugelius et al. 2010).

We found two basic patterns describing the vertical distribution of ASi in the investigated study area. First, declining ASi concentrations with depth were found in shrub tundra and fen peatlands indicating addition of ASi rich material to the top soil and dissolution in deeper soil horizons. Contrary, bog peatlands showed variable ASi concentrations with depth.

Total ASi storage (0 – 1 m) ranged between 9,600 – 83,500 kg SiO_2 ha^{-1} dependent on landscape type (Fig. 9b) and these values fall within the mid-range of previous estimates from different temperate and tropical regions. Similar to SOC (Fig. 9a), ASi storage appears to decline along the shrub tundra moisture gradient (from wet to dry). Biologically derived ASi (phytoliths and diatoms) contributes to the ASi pool in peatlands and organic top soils of shrub tundra while we suggest that pedogenic ASi fractions contribute significantly to the ASi pool in mineral soils.

In summary, we conclude that bog peatlands underlain by permafrost can act as sinks for ASi, where ASi of biological origin (primarily diatoms) is preserved over millennia rather than being cycled through the plant-soil continuum or being leached out from the soil.

Additionally, by combining our results with a literature review we furthermore discuss the potential effects of climate change on terrestrial Si cycling in Arctic permafrost terrain. Our sole attempt is to provide a conceptual framework for future studies to build on. Focus is directed toward the biological part of the terrestrial Si cycle and the changes that may follow as a result of permafrost thaw, altered hydrology and changes in vegetation cover. In the framework, we suggest that climate change can cause mobilization of previously frozen ASi, altered soil storage of biologically fixed ASi and an increased Si-flux to the Arctic Ocean.

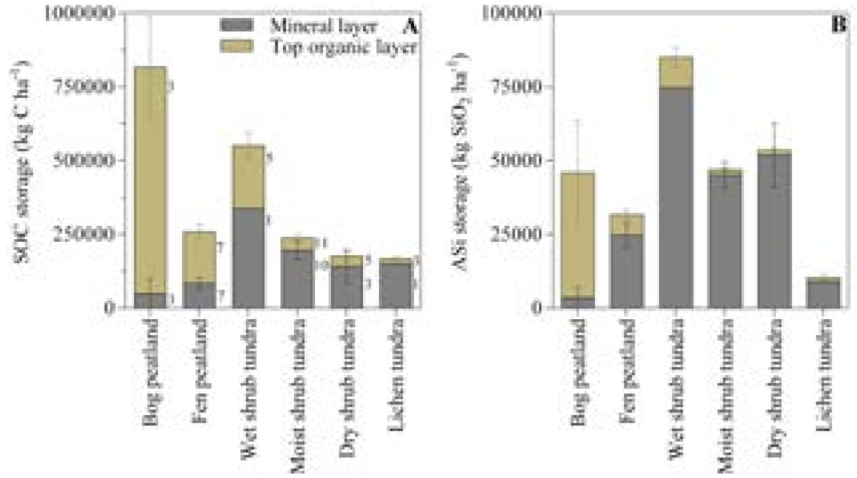


Figure 9. Mean **a**) soil organic carbon (SOC) and **b**) amorphous Si (ASi) storage for peatland and shrub tundra land cover classes. Total storage (0-1 m) is partitioned between the top organic and mineral layer. Error bars show standard error (SE) of the mean, while numbers to the right of bars show the number of sites used to calculate average storage (the numbers for ASi are the same as for SOC).

Paper II

Alfredsson H, Clymans W, Stadmark J, Conley DJ, Rousk J (submitted) **Bacterial and fungal colonization and decomposition of submerged plant litter: consequences for biogenic silica dissolution.** Submitted to FEMS Microbiology Ecology

Paper II explores the potential influence of microbes on phytolith dissolution during microbial decomposition of submerged plant litter (*Equisetum arvense*). Release of DSi together with parameters indicative of microbial growth were monitored for one month, with live microbial treatments compared to sterile controls. By combining the litter with nitrogen (N) and phosphorous (P) supplements at four different levels the rates and level of microbial production was varied. This allowed us to study the effect of varying degree of litter decomposition on Si release.

Bacterial production responded positively to increasing levels of N and P supply while fungal abundance, however, remained unresponsive. The achieved differences in microbial utilization of litter between treatments allowed us to study its effect on Si release. Contrary to hypothesized results, a general reduction in total Si release from plant litter was observed in the presence of a live microbial community when compared to sterile control treatments. Higher levels of microbial growth corresponded with a larger reduction in total Si release, though, after 1 month only 10 – 15 % less of the total plant Si pool was dissolved in the presence of a live microbial community when compared to sterile treatments. The exact mechanism(s) causing this apparent reduction in total Si release is uncertain and cannot be evaluated by our experiments (which was beyond the goal of this study). However, we conclude our results to suggest that the microbial role in litter associated Si turnover is much smaller than what is commonly anticipated. Rather than resulting in a net release of Si from litter, it results in reductions through microbial immobilization (Fig. 10).

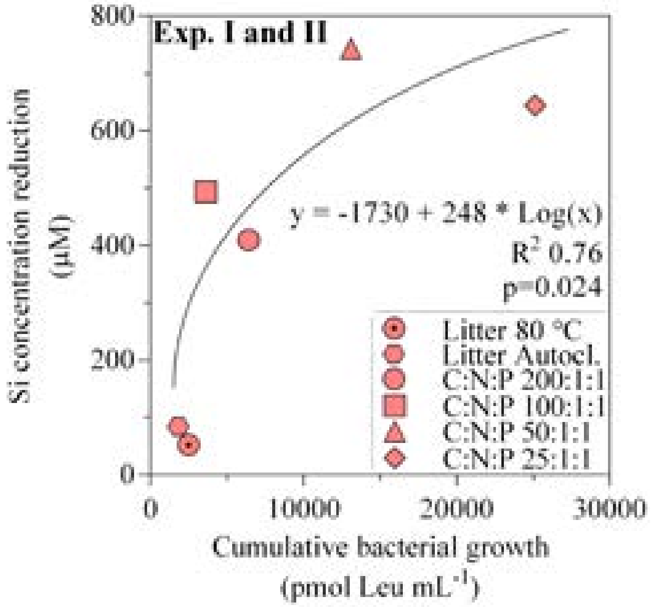


Figure 10. Relationship between Si concentration reduction and total cumulative bacterial growth for the different treatments in Experiments I and II. The Si concentration reduction represents the reduction of DSi by a live microbial community and is obtained by, at equal C:N:P level, subtracting the total DSi at live conditions from total DSi at sterile conditions. The line was fitted with a log-linear relationship.

Paper III

Alfredsson H, Clymans W, Hugelius G, Kuhry P, Conley DJ (manuscript) **Estimated storage of amorphous silica in soils of the circum-Arctic tundra region.** Manuscript intended for submission to Biogeosciences.

Continuing on the topic of Paper I, we investigated vertical distribution, landscape partitioning and spatial variability of ASi storage in permafrost terrain at four contrasting sites. Archived soil samples were retrieved from Adventdalen (Svalbard), Zackenberg (NE Greenland), Shalaurovo (NE Siberia) and Kytalyk (NE Siberia). Together with additional upscaling sites from European Russian Arctic, Alaska and the central Canadian Arctic (Paper I) we provide a first estimate of total ASi storage (0 – 1 m) for the circum-Arctic tundra region using thematic upscaling based on vegetation and soil classifications.

Similar to Paper I, we found the vertical distribution of ASi concentrations to follow two major patterns reflecting 1) declining concentrations with depth or 2) increasing/maxima concentrations with depth. These results suggest that a set of processes, including solifluction/slope processes, cryoturbation and formation of inorganic precipitates, influence vertical distribution of ASi in permafrost terrain, with the capacity to retain stored ASi on centennial to millennial time scales. At the four study sites, total ASi storage (0 – 1 m) ranged between 18,400 – 73,900 kg SiO_2 ha^{-1}, with ASi storage generally being higher in graminoid tundra compared to fen peatlands. ASi of biogenic origin (diatoms and phytoliths) contributed importantly to the ASi pool, particularly in the top organic layer of soils. Further, we present the first estimate of ASi soil storage (0 – 1 m) in circum-Arctic tundra terrain. Based on thematic upscaling using both vegetation (CAVM) and soil (CASM) classifications, total storage is estimated to range between 219 ± 28 (CAVM) to 510 ± 59 (CASM) Tmol Si, of which at least 30 % is stored in permafrost. This estimate would account for approximately 2 – 6 % of the current estimate of global soil ASi storage, while covering an area of 4 – 6 % of the global land surface. Using soil classifications, maps describing the spatial variability of ASi storage in the circum-Arctic tundra region was produced (Fig. 11). Opposite to our hypothesis, the soil ASi reservoir of the circum-Arctic tundra region cannot be considered a hotspot in a global context. Nevertheless, climate warming has the potential to alter the future ASi storage and terrestrial Si cycling in the Arctic.

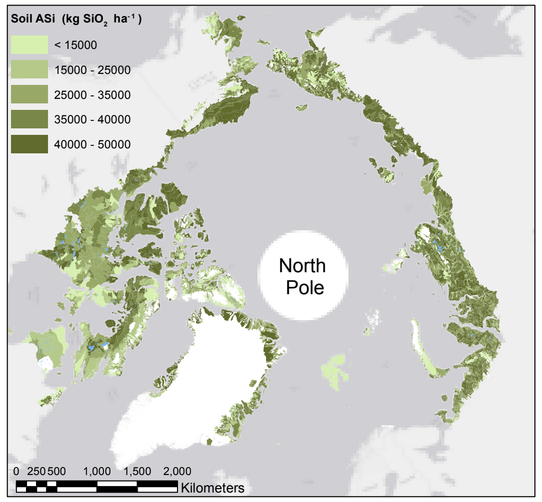


Figure 11. Spatial distribution of ASi storage (0 - 1 m) in soils of the northern circumpolar tundra region produced using soil classifications following Tarnocai et al. (2009) and Hugelius et al. (2014).

Discussion

This PhD project was initially set out to explore the size and landscape distribution of ASi in Arctic permafrost soils. In a later stage, the project was extended to also explore the role of microbes (bacteria and fungi) in turnover of biologically fixed ASi. The outcome of this thesis have filled some of the existing knowledge gaps regarding terrestrial Si cycling in permafrost terrain, which can provide the basis for future research concerning what the effects of climate change will be. Further, this work provides new insights into how Si release from degrading plant litter is affected by the presence of a live microbial community that stand in contrast to common beliefs.

Global context of the northern circumpolar ASi reservoir

Paper I and Paper II represent the first reports of ASi storage (0 – 1 m) in Arctic permafrost soils. In Paper I, estimated total ASi storage range between 9,600 – 83,500 kg SiO_2 ha^{-1} in a shrub tundra and peatland dominated landscape, while in Paper II total ASi storage range between 18,400 – 73,900 kg SiO_2 ha^{-1} in graminoid tundra and fen peatlands across diverging landscape types. Further, the additional upscaling sites in Paper III provide estimated total ASi storage in the range of 1,030 – 94,300 kg SiO_2 ha^{-1}.

In the literature, a range of methods are applied to quantify soil ASi storage, such as alkaline digestion (Clymans et al. 2011; Melzer et al. 2012; Paper I; Paper III) and physical separation (Blecker et al. 2006). While the former will release Si from both biogenic and pedogenic Si fractions, estimates based on the latter method usually only considers the biogenic fraction. Together with differences in reported depth intervals, this makes direct comparisons between our estimates (Paper I and III) and the full range of reported literature values not always straightforward. Focusing on reports of total soil ASi storage based on comparable methodological approach (e.g. alkaline digestion methods) and calculated using similar depth intervals (0.85 – 1 m), our estimates from Arctic permafrost soils are placed within the same range as those reported from other regions, including temperate forests (66,900 – 104,000 kg SiO_2 ha^{-1}; Clymans et al. 2011; Sommer et al. 2013), North American grasslands (221,000 kg SiO_2 ha^{-1}; White et al. 2012) and agricultural land (21,500 – 72,000 kg SiO_2 ha^{-1}; Clymans et al. 2011, 2014), with the exception of South African savannahs having a considerably larger storage (300,000 – 800,000 kg SiO_2 ha^{-1};Melzer et al. 2012).

Table 1. Author contributions for Papers I to III. Names within brackets are non-author contributions.

	Paper I	Paper II	Paper III
Concept and study design	H. Alfredsson D.J. Conley	H. Alfredsson J. Rousk	H. Alfredsson P. Kuhry D.J. Conley
Field sampling of soils	P. Kuhry		H. Alfredsson P. Kuhry with others
Laboratory work	H. Alfredsson (C. Funkey)	H. Alfredsson (C. Funkey)	H. Alfredsson W. Clymans (C. Funkey)
ArcGis work/ soil classifications			W. Clymans G. Hugelius
Data interpretation	All authors	H. Alfredsson J. Rousk W. Clymans	H. Alfredsson W. Clymans
Writing of manuscripts	H. Alfredsson	H. Alfredsson	H. Alfredsson
Comments on manuscript	All authors	All authors	All authors

Estimates based on phytolith extracted content, interpolated over the 0 – 1 m depth interval, range between 14,300 – 45,000 kg SiO_2 ha^{-1}, 15,000 kg SiO_2 ha^{-1} and 21,600 kg SiO_2 ha^{-1} for North American grasslands (White et al. 2012), African savannah´s (Alexandre et al. 2011) and tropical rainforest (Alexandre et al. 1997), respectively. Using a continuous extraction method, the contribution of biogenically derived ASi in temperate forest soils is found to range between 8,600 – 54,600 kg SiO_2 ha^{-1} (Barão et al. 2014; Vandevenne et al. 2015). If comparing these latter literature values with our estimates of top organic soils (assumed to largely consist of biogenic components), ASi storage is comparable with regards to peatlands and wet shrub tundra (3,400 – 45,400 kg SiO_2 ha^{-1}; Paper I and III) while storage of biogenic components in graminoid tundra and drier shrub tundra classes is considerably lower in Arctic regions than other temperate and equatorial regions (510 – 1760 kg SiO_2 ha^{-1}; Paper I and III).

Taken together, ASi storage in Arctic permafrost terrain do not stand out in comparison to other non-permafrost regions. Furthermore, in Paper III the first estimate of total ASi storage (0 – 1 m) in circumpolar tundra terrain is provided, which amounts to 219 ± 28 to 510 ± 59 Tmol Si while covering an area of 4 – 6 % of the global land surface. In comparison, North American grasslands are estimated to contain 130 Tmol Si while covering an area of 1 % (Blecker et al. 2006) of the global land surface (Jobbágy and Jackson 2000). Hence, ASi storage in the northern circumpolar tundra region is of similar magnitude to that estimated to be stored in North American grasslands alone. Besides, the estimate by Blecker et al. (2006) is based on phytolith content while only considering the 0 – 0.5 m depth interval and is therefore likely underestimated. Moreover, estimated amounts of Si fixed by the major biome types temperate steppe (13 Tmol Si yr^{-1}) and savannah (22 Tmol Si yr^{-1}) is nearly as high as that fixed by cultivated crops (29 Tmol Si yr^{-1}) (Carey and Fulweiler 2012). This provides a large input of biogenically fixed ASi to the top soil. Despite high Si-accumulating graminoids (Hodson et al. 2005) being a dominant feature of the tundra biome, only 3 Tmol Si yr^{-1} is estimated to be fixed by vegetation on a yearly basis in part due to low terrestrial net primary productivity (Carey and Fulweiler 2012). Therefore, temperate grasslands together with savannah´s, which stand out by having a notably large ASi soil reservoir (Melzer et al. 2010, 2012), may instead contribute significantly to the global stock of soil ASi. In contrast, although being responsible for 35 % of the Si fixed by vegetation per year (Carey and Fulweiler 2012) ASi storage in crop lands is usually lower (Haynes 2014) since agricultural practices tend to deplete soils of biogenically derived ASi (Clymans et al. 2011; Guntzer et al. 2012b; Vandevenne et al. 2012; 2015).

The estimates of 219 ± 28 to 510 ± 59 Tmol Si being stored in circumpolar tundra (Paper III) represents 2 – 6 % of the current global estimate (8,250 Tmol Si; Laruelle et al. 2009). In Paper III, we suggest the current global estimate to be an underrepresentation and that a reassessed estimate should take into account spatial variability of ASi storage between different biomes (Carey and

Fulweiler 2012), make use of public soil data bases for estimates of basic soil properties (bulk density, soil depth etc.) as well as assessing the available data of soil ASi concentrations quantified by means of different methods. This would allow for a better evaluation of the significance of the Arctic soil ASi reservoir in a global context. Considering that the global estimate of 8,250 Tmol Si may be underestimated, this implies that the significance of the Arctic tundra biome in storing ASi could be even less. Nonetheless, ongoing climate change has the potential to alter future soil ASi storage and terrestrial Si cycling in the circumpolar region.

Soil storage as an indicator of biological Si cycling?

In a global context, our knowledge concerning storage and distribution of ASi in soil has improved during the last decade since the early work by Bartoli (1983) showed the importance of considering biological Si cycling in terrestrial ecosystems. Studying soil ASi pools and the relative contribution of biogenically derived Si fractions can be indicative of the extent by which biology influence terrestrial Si cycling. Though, to fully comprehend the dynamics of Si cycling and the influence of biology in terrestrial landscapes additional information is needed.

When formulating the basic ideas that provided the rationale for this project, the concept of "hotspots" was used to describe Arctic tundra as an important region of high ASi accumulation in soil. If defining the concept of Si hotspots to describe the importance of biological cycling of Si within the plant-soil environment and its effects on Si fluxes through the landscape, the solitary study of soil pools will not necessarily indicate the complete picture. Instead, pool sizes may reflect a difference in preservation regimes (i.e. turnover rates) between different landscapes, which Paper III as well as the work of others clearly indicates. For instance, Blecker et al. (2006) studied phytolith storage in both soil and aboveground vegetation across a bioclimatic sequence along the coastal plains of North America. In their study, an increased degree of Si plant fixation (i.e. exerting a biological control on Si cycling) was coherent with a decreasing degree of soil phytolith storage. This was explained by considerably shorter turnover rates due to wetter climatic conditions. It follows that soil storage alone do not provide enough detail to unravel the importance of biological cycling in a studied system. Further, in Paper III we find clear differences in ASi storage between graminoid tussock vs. non-tussock forming tundra with storage being higher in the former. We attributed these dissimilarities to differences in soil pH where tussock-tundra is characterized by lower pH (Ping et al. 2005), which enhance ASi preservation (Fraysse et al. 2006). Although we have not provided estimates of Si fixation by the two plant communities (tussock vs. non-tussock tundra), the importance of biological Si cycling is likely to be similar due to the prevalence of high Si accumulating grasses and sedges at both sites. However, it can be hypothesized that the slow turnover rate of the ASi pool in tussock-tundra stimulates chemical weathering of the lithogenic Si pool to meet the demand of bioavailable Si (Blecker et al. 2006).

Biotic components of phytolith turnover – controlling factors

To understand how terrestrial Si cycling is altered by environmental change, such as global warming, it becomes important to study its controlling factors. How biological factors can influence turnover rates of ASi stored in soil is especially interesting in the perspective of permafrost thaw that will initiate the biogeochemical processing of recently thawed material. Turnover rates for phytoliths stored in temperate soils are estimated to range between 19 – 1300 years (Blecker et al. 2006; Sommer et al. 2013) and providing that a microbial influence on phytolith turnover during soil organic matter decomposition exists, the response of the microbial community to permafrost thaw (Jansson and Tas 2014) could have an important influence. For instance, recent results suggest that the function of microbial communities directly upon permafrost thaw may be low, resulting in a time lag between thaw and decomposition of the newly available material (Ernakovich and Wallenstein 2015). Microbes are known to play different roles in Si biogeochemistry and includes 1) aiding smectite dissolution through reduction of iron (Kim et al. 2004; Vorhies and Gaines 2009), 2) production of exogenous metabolites enhancing dissolution rates of non-biogenic Si materials (Bennett and Siegel 1987, Bennett et al. 1988, 2001; Welch and Ullman 1993; Ullman et al. 1996; Pokrovsky et al. 2009) and 3) accelerating diatom dissolution in aquatic systems (Bidle and Azam 1999, 2001). Additionally, in agricultural systems, certain bacteria enhancing mineral Si dissolution ("silica solubilizing bacteria") are used as bio-fertilizers to improve crop yields (Meena et al. 2014). Taken together the results of Paper II may seem unexpected, where a higher degree of microbial litter decomposition resulted in greater reductions in total Si release from plant litter.

A set of different mechanisms for this observation is discussed in Paper II, of which two deserves additional attention. First, it is well studied that several organic compounds, analogous of microbial exudates, cell surface components and dissolved organic matter, can exhibit either an inhibiting or a rate enhancing effect with regards to Si dissolution (Bennett et al. 1988; Ullman et al. 1996; Pokrovsky et al. 2009). Production of inhibiting metabolites thus offers one explanation to our results. The effects of organic metabolites are commonly studied individually (Pokrovsky et al. 2009) while this scenario seem unlikely in the presence of a microbial community (Paper II). It is therefore unclear what the net outcome would be when a combination of organic compounds acting both enhancing and inhibiting on dissolution is present simultaneously. The concentrations and composition of such compounds (e.g. acetate, oxalate and glucose) in our experimental units are unknown (Paper II), but would need to be high (10^{-1} – 10^{-3} M; Pokrovsky et al. 2009) to have a significant effect on Si dissolution rates. The concentrations found in bulk soil are usually lower than this (Pokrovsky et al. 2009) and the importance of this process in the natural soil environment is therefore also uncertain. Although, it can be speculated that high enough concentrations may develop at microsites in the soil, such as around roots and where bacteria grow in biofilms.

Second, potential formation of organo-Si precipitates in the presence of a microbial community is briefly discussed in Paper II. Formation of Si nanoparticles, aided by bacterial and fungal extracellular proteins, is shown for submerged plant litter exposed to bacterial (Bansal et al. 2006) and fungal (Singh et al. 2008) cultures. Further, the production of exopolysaccharides (EPS) is stimulated when bacteria are growing attached to surface particles, as shown for sand grains (Vandevivere and Kirchman 1993). Adsorption of Si ions onto the surfaces of EPS macromolecules, resulting in lowered Si concentrations in the aqueous phase, is further demonstrated (Malinovskaya et al. 1990). In line with this, Pokrovsky et al. (2009) observed no clear differences in Si release from wollastonite (a Si mineral) in the presence of live bacteria having poor formation of EPS upon comparison to a sterile control, while presence of live bacteria having abundant EPS formation showed increased Si release rates when compared to the sterile control. Though, poor replication makes direct conclusions less straightforward. Stimulation of bacterial EPS production in the presence of solid surfaces, provided by amorphous Si particles in our experimental units (Paper II), is therefore hypothesized as one potential explanation for the apparent reduction in Si release in presence of a microbial community. As hypothesized in Paper II, filtering of the aqueous phase prior to DSi analysis could remove such clusters providing they are of a size ≥ 0.45 µm. This would cause an apparent reduction in Si release, which innately suggests that the actual Si release in the presence of a microbial community was either similar to or higher than that in sterile controls. In either case, this suggests that the presence of a microbial community can influence availability of released DSi by locking up Si in different precipitates. Though, this is a highly speculative hypothesis and in order to be significant such complexes need to be stable on longer time scales. Future investigation concerning this theory represents an exciting task and could aid in resolving the question whether microbes can accelerate phytolith dissolution during litter decomposition or not.

Terrestrial Si cycling and climate change: an Arctic perspective

In the northern circumpolar region, soils influenced by permafrost covers an area of 17.8×10^8 ha (Hugelius et al. 2014), representing approximately 15 % of the global land area (1.21×10^{10} ha; Jobbágy and Jackson 2000). Anthropogenically induced climate warming is projected to cause extensive reductions in permafrost coverage during the coming century (Anisimov et al. 2007; Vaughan et al. 2013), followed by associated changes in hydrological flow paths (Lawrence and Slater 2005; Smith et al. 2005; Keller et al. 2010; Walvoord et al. 2012), mineral weathering (Keller et al. 2007; Pokrovsky et al. 2013) and vegetation cover (Tape et al. 2006). Such alterations will undoubtedly influence the biogeochemical cycles of various elements in different ways. For C, a major concern is that previously frozen organic matter will become available to microbial mineralization following permafrost thaw, which can generate a positive feedback to global warming (Schuur et al. 2008, 2013, 2015). Alterations in the terrestrial environment (such as permafrost degradation) can influence downstream aquatic ecosystem processes (Ball et al. 2010; Vonk et al. 2015) (Fig. 12) via alterations in river geochemistry (Frey et al. 2007; Frey and McClelland 2009), such as changed fluxes of Si reaching downstream lakes, rivers and eventually coastal zones. The Arctic Ocean receives nearly 10 % of the global river discharge, while only representing 1 % of the global ocean volume (Dittmar and Kattner 2003). DSi availability governs diatom primary productivity in lakes and coastal zones (Kristiansen and Hoell 2002; Allen et al. 2005) with implications for marine food web dynamics and C cycle dynamics. Hence, a conceptual framework intended to spur future research on the effects of climate warming on terrestrial Si cycling in the circumpolar region was presented in Paper I. The framework primarily focuses on the biological components of terrestrial Si cycling and how permafrost thaw and changes in hydrological flow paths and vegetation cover can come to alter Arctic Si biogeochemistry.

The results presented in Paper III suggest that between 219 ± 28 to 510 ± 59 Tmol Si is stored in the 0 – 1 m depth interval of circumpolar tundra soils. The majority (~ 70 %) of this ASi is allocated to the active layer and, hence, already subject to annual freeze-thaw cycles. It must be noted, however, that the actual timespan for the entire active layer being in a thawed state is limited considering that the full thaw depth is usually reached first at the end of summer (late August). Combined with generally low ground temperatures during the thawed state, the dissolution of ASi stored in the active layer is expected to be slow (Van Cappellen and Qiu 1997). This is illustrated by presence of diatom and phytolith remains, preserved on centennial to millennial time scales (Palmtag et al. 2015), also in the active layer of e.g.

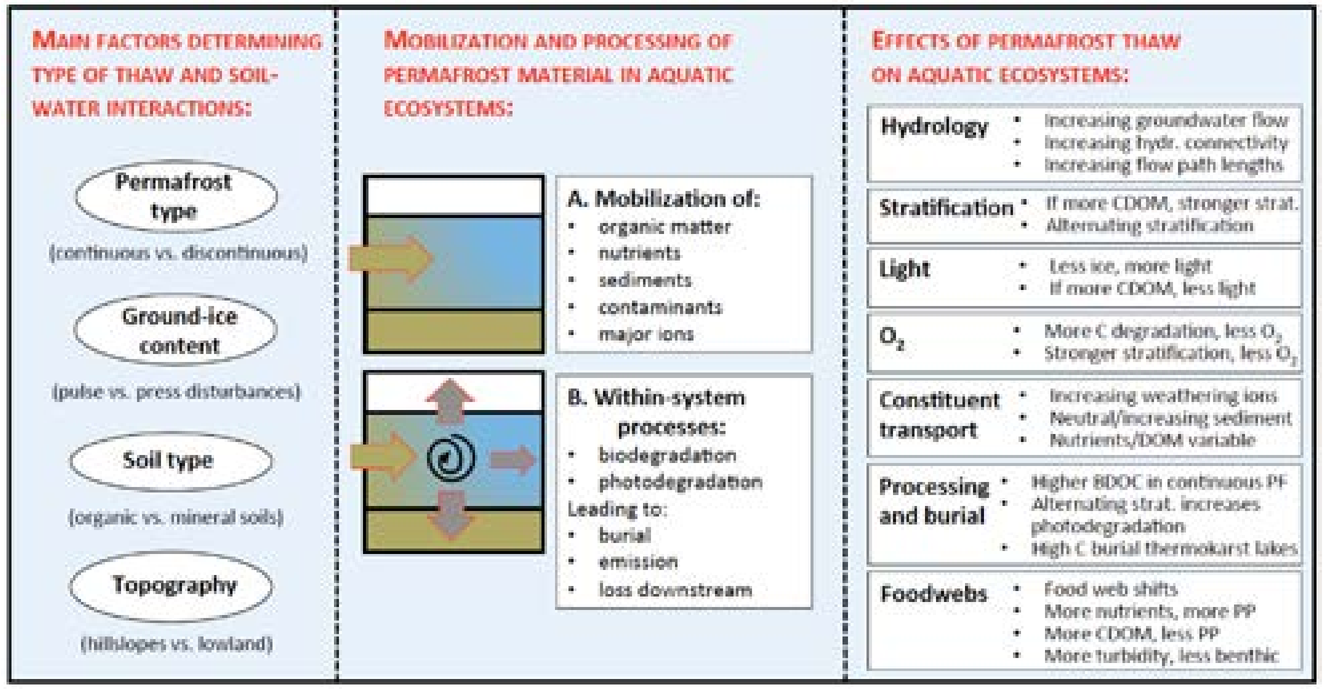


Figure 12. Conceptual scheme of factors determining permafrost thaw type and soil-water interactions (left panel), mobilization and processing of material released from thawing permafrost in aquatic ecosystems (center panel) and the resulting effects on aquatic ecosystems (right panel). The response of downstream aquatic ecosystems (e.g. foodwebs) to permafrost thaw depicted in the right panel can, in part, depend on how Si fluxes through the terrestrial landscape is influenced. Figure from Vonk et al. 2015.

fen peatlands (Zackenberg; Paper III). At least 30 % of the estimated circumpolar ASi storage is allocated to the perennially frozen ground (Paper III), which will become available for biogeochemical cycling upon permafrost thaw (Fig. 13) as extensively discussed in Papers I and III. The dissolution rates of ASi stored in the active layer are likely to become elevated in response to increased ground temperatures (Van Cappellen and Qiu 1997), combined with a new source of biogeochemically available ASi (i.e. recently thawed material) and increased deep mineral soil-water interaction (due to permafrost thaw; Lawrence and Slater 2005; Frey and McClelland 2009) is suggested to create a "pulse" of elevated DSi concentrations toward aquatic systems, followed by a new steady state of likely higher DSi concentrations. However, what quantity of this newly available DSi that will actually reach the coastal zones of the Arctic Ocean is uncertain, due to multiple fates of the released DSi.

Released DSi may continue to be recycled within the plant-soil continuum (Sommer et al. 2013) with the importance of this pathway being dependent on whether permafrost thaw is associated with a shift in vegetation, to e.g. greater abundance than before of high Si-accumulating plants and vice versa (outlined in Paper I). Additionally, a prolonged season of warmer temperatures can stimulate plant productivity overall leading to enhanced Si fixation by plants without a necessary shift in dominant vegetation cover. Elevated atmospheric CO_2 concentrations, causing enhanced plant net primary productivity, is indeed recently shown to also elevate Si fixation by plants (Fulweiler et al. 2015). Alternatively, released DSi can precipitate to form pedogenic Si fractions (Barão et al. 2014, 2015; Cornelis et al. 2014). More importantly, the amount of released DSi ultimately reaching rivers is highly dependent on the hydrological connectivity between thaw-impacted areas and aquatic systems (Olefeldt and Roulet 2014; Vonk et al. 2015). For instance, Si can be mobilized through abrupt permafrost degradation processes, such as thermokarst lake formation (outlined in Paper I), which commonly have poor hydrological connectivity (Vonk et al. 2015) resulting in low impact on downstream river biogeochemistry. Instead, released DSi may be utilized locally by diatoms and high Si-accumulating plants colonizing the newly formed wet areas (Paper I). In areas where permafrost thaw (through active layer deepening) will positively influence hydrological connectivity, more of the DSi can be transported downstream. Indeed, sediments of high-latitude lakes are found to contain a high proportion of terrestrially derived biogenic Si fractions (Tallberg et al. 2014). Further, increased temperatures and a longer growing season combined with elevated nutrient supply is anticipated to lead to higher levels of primary productivity in Arctic ponds, lakes and streams (Prowse et al. 2006; Bowden et al. 2008; Vonk et al. 2015). This implies that elevated sequestration of Si in water bodies (Frings et al. 2014) may occur in response to increased diatom production, hence, applying a reductive influence on the amounts of DSi reaching coastal zones. However, the effect may be offset by increased delivery of dissolved and particulate organic carbon to aquatic systems by diminishing light availability needed for photosynthesis (Vonk et al. 2015) and, hence, diatom productivity.

Figure 13. Permafrost thaw feature at the northern foothills of Alaska. The peat mound is formed due to aggradation of ground ice that pushes the top soil upwards.

Overall, rates of coastal erosion appear to be increasing in the northern circumpolar region (Günther et al. 2013) but being particularly important in the regions of the Yedoma IC which drains into the East Siberian Seas/Laptev Sea (Rachold et al. 2000; Vonk et al. 2012). Thawing of the high and ice rich deposits, accompanied by reduced period of sea ice extent, promote the direct slumping of material into the coastal zone (Vonk et al. 2012). Such processes are likely to not only transport considerable amounts of C into the waters (Vonk et al. 2013), but would also provide an additional source of ASi (Paper III) to the coastal zone. Due to higher salinity conditions ASi of biogenic origin (Loucaides et al. 2011) would quickly become a bioavailable source of Si for coastal diatoms. The sediment input by coastal erosion into the Laptev Sea is estimated to be 58.4×10^6 ton yr^{-1} (Rachold et al. 2000). Combined with an average ASi storage of 7.65 ± 4.7 g SiO_2 kg^{-1} in Yedoma IC deposits (Paper III), annual delivery of ASi into the Laptev Sea by coastal erosion is estimated to be in the order of 0.0074 ± 0.0046 Tmol Si yr^{-1}.

The results presented in Paper I and III also indicate that the majority of ASi stored (0 – 1 m) in circumpolar tundra is allocated to the mineral layer, especially so concerning graminoid and shrub tundra that are a dominant feature of the tundra landscape (CAVM Team 2003). This also implies that pedogenic ASi fractions, rather than biogenic ones, contribute significantly to the total ASi pool (Paper I and III). A consequence of permafrost thaw (active layer thickening) is increased deep subsurface flow on the expense of surface flow (Lawrence and Slater 2005; Keller et al. 2010). This means a reduced contact time between soil water and organic top soils (dominated by biogenic Si sources), while an increased interaction will occur with mineral soils (dominated by lithogenic/pedogenic Si sources) (Harms and Jones 2012). This implies that dissolution of Si from lithogenic and pedogenic Si fractions can become more important in the future (Pokrovksy et al. 2013), especially in soils having thin top organic layers. Investigating the reactivity of non-biogenic versus biogenic Si sources and determine their respective role in short-term Si cycling thus becomes important (Barão et al. 2015; Vandevenne et al. 2015). Whether the DSi released from weathering of lithogenic Si sources in deep mineral soil will be fed into a biological plant-soil cycle may depend on rooting depth of the vegetation cover, which may be relatively shallow if considering e.g. moss dominated wetlands. Contrary, elevated weathering of pedogenic Si sources may as well contribute to the new formation "tertiary" Si fractions as the "weathering front" keeps progressing downward (Cornelis et al. 2014), thus influencing the flux of Si through the land-ocean continuum.

An aspect not discussed in the conceptual framework presented in Paper I includes the potential effect of fire with regards to soil ASi storage and terrestrial Si cycling. Tundra wild fires (Mack et al. 2011) might become more common in a warmer Arctic climate (Grosse et al. 2011). Fire is suggested to indirectly stimulate Si storage in plant biomass and soil by its positive influence on aboveground net primary productivity (Melzer et al. 2010). Recently, post-burning or organic top soils were found to alter both phytolith structure and structure (Unzué-Belmonte et al. 2015). The authors found that while an apparent crystallization of phytoliths occurred for some types of litter, solubility were still clearly enhanced with increasing degree of burning. In a future Arctic, an increased fire frequency is thus expected to exert a greater influence on terrestrial Si cycling and fluxes through the land-ocean continuum.

It follows that the processes able to impact Si biogeochemistry in a changing Arctic are several and interact in intricate ways (Fig. 14), complicating interpretation of possible net outcomes for how Si fluxes to the Arctic Ocean will be altered in the future. The different scenarios presented in the conceptual framework of Paper I only depict a simplified view of how climate change can come to alter terrestrial Si cycling. Nonetheless, the hope is that the results presented in this thesis will ultimately stimulate further research related to Si biogeochemistry in permafrost terrain and the impacts of climate change. Indeed, the Arctic Ocean exemplifies an area of high productivity during the Arctic summer with populations of migrating birds, mammals and fish schools returning every year to take advantage of the short peak in high productivity (Lalli and Parsons 1997), where Si availability plays a key role at the base of the food web.

Conclusions and future research prospects

The outcome of this thesis has enhanced our understanding of two yet relatively unexplored research fields; storage of ASi in permafrost terrain and the influence of a microbial community on phytolith dissolution during plant litter degradation. Based on the discussion and three appended papers the main conclusions of this thesis, together with future research prospects, are summarized below:

- Vertical distribution of soil ASi concentrations in permafrost terrain was found to largely follow two patterns, the first being declining concentration with depth while the second represents increasing or maxima concentrations with depth (Paper I and III). The first case is commonly described by others (e.g. Blecker et al. 2006) and show that biological and pedogenic processes together govern vertical distribution of elements is soil. In the latter case, our results indicate that several processes are involved in vertical redistribution of ASi in permafrost terrain, including slope processes/solifluction in mountainous regions, cryoturbation and the potential precipitation of pedogenic ASi near the permafrost table as a result of repeated freeze-thaw cycles.

- Rather than being cycled through the soil-plant continuum or contribute to the leaching of DSi into the hydrosphere, ASi of biological origin can be preserved on centennial to millennial time scales both in the perennially frozen ground as well as in the seasonally thawed active layer. In Paper I, this was particularly observed in bog peatlands of high centered ice-wedge polygons. Paper III showed that this can also occur in other land cover types than bog peatlands, such as fen peatlands and graminoid tundra.

- Combining the results of Paper I and III, we find ASi storage in Arctic permafrost soils to range widely between 1,030 – 94,300 kg SiO_2 ha^{-1} depending on land cover type. This range corresponds to those generally found in the literature, with the exception of savannah´s having a considerably higher soil ASi reservoir (Melzer et al. 2010). Furthermore, Paper III illustrate that common patterns in total ASi storage exist between similar land cover types dispersed across different geographical locations supporting the use of thematic classes for upscaling (e.g. vegetation).

- Through application of thematic upscaling, following vegetation and soil classification, a first estimate of total ASi storage (0 – 1 m) in circumpolar tundra is provided (Paper III). Depending on classification method, we provide an estimate of 219 ± 28 to 510 ± 59 Tmol Si, which correspond to ~ 2 – 6 % of the current estimate of global ASi soil storage (Laruelle et al. 2009) while covering an area of 4 – 6 % of the global land surface. Hence, we cannot currently conclude that this soil ASi reservoir represents a hotspot in a global context, as shown for SOC storage.

- Furthermore, the upscaling results presented in Paper III show that most ASi is allocated to storage in the mineral horizon, rather than to top organic soils. This is especially true for soils having thin organic surface horizons, such as for drier graminoid and shrub tundra. Among the investigated land cover types, peatlands generally have the largest relative storage of ASi allocated to top organic soils.

- As supported by microscopy and analysis of mineral dissolution slopes (MDS; Paper III), biogenically fixed ASi contribute majorly to the total ASi pool in top organic soils, while pedogenic Si fractions dominate in mineral soils (although biogenically derived ASi fractions are still present). Being that the majority of the total ASi storage is allocated to mineral soils (Paper I and III), pedogenic Si fractions, rather than biologically derived ones, dominate the ASi pool. Due to potential differences in reactivity this is of importance when predicting how climate change will impact terrestrial Si cycling in the future, especially considering that permafrost thaw will shift hydrological flow paths from being dominated by surface flow through organic soils toward deeper subsurface flow through mainly mineral soils.

- Most ASi harbored within the circumpolar tundra soil reservoir (0 – 1 m) is allocated to the seasonally thawed active layer, rather than being perennially frozen. We estimate that at least 30 % is allocated to permafrost (Paper III), which upon thaw will become available for biogeochemical cycling.

- Hence, a conceptual framework for how climate change may alter Si biogeochemical cycling in Arctic permafrost terrain is provided in Paper I. For example, we hypothesize that climate change will lead to altered soil ASi storage and Si fluxes through the land-ocean continuum via alterations in hydrology and dominant vegetation caused by permafrost thaw. The sole purpose of the framework is to spur future research within this currently understudied field.

- In addition, the outcome of Paper II shows how Si release from phytoliths appears to be reduced in the presence of a live microbial community during plant litter decomposition. This result stands in sharp contrast to common anticipations and previous results reported in the literature showing no or slight enhancement of Si release during microbial litter decomposition.

The contribution to improved understanding of terrestrial Si cycling provided by this thesis inevitably also raises a set of new questions to be answered. First, an obvious continuation is to further improve the estimate of total ASi reservoir in the northern circumpolar tundra region. An overarching goal is to collect more soil pedon data that are representative of the full range of land cover and soil types represented in the Arctic, while simultaneously having a broad geographical coverage. For Si this type of research is just initiated, while compared to investigations of soil organic carbon storage (0 – 1 m) the latest circumpolar estimate is based on 1778 individual soil pedons (Hugelius et al. 2014). Moreover, to improve our understanding regarding the contribution of biogenically derived Si sources a different technique than the alkaline digestion method by DeMaster (1981) should be utilized where a distinction between biogenic and pedogenic Si fractions can be made. The continuous extraction of Si and Al in NaOH represents valuable approach, which have been applied in studies of temperate soils (Barão et al. 2014, 2015; Vandevenne et al. 2015). This would be especially important if considering extending the estimate of total ASi storage beyond the 0 – 1 m depth range, since lithogenic/pedogenic Si fractions will dominate in mineral soils. Also, the estimate of ASi storage should be extended to also include the entire area of the northern circumpolar permafrost region (i.e. below the treeline), which represents 15 % of the global land area(!).

While providing estimates of ASi pools in Arctic permafrost terrain has filled some of the existing knowledge gaps regarding terrestrial Si cycling, an improved understanding of the real dynamics of Si cycling and the impacts of climate change requires additional approaches. This since studying pools does not fully reflect the dynamics of Si cycling within the plant-soil system as discussed previously. For instance, the hypotheses put forward in our conceptual framework (Paper I) can be studied by the application of catchment scale mass-balance studies which in addition to soil pools also considers to the various sources of input and output of Si to a system (e.g. Sommer et al. 2013). Such studies could be carried out by comparing catchments within nearby geographical regions that have varying degree of permafrost extent (e.g. MacLean et al. 1999), or by e.g. studying transects representing chronosequences across collapse-scar bog peatlands (Pokrovsky et al. 2011; O´Donnell et al. 2012). Other techniques include the utilization of Si stable isotopes (Opfergelt et al. 2011; Pokrovsky et al. 2005, 2013) and geochemical traces (e.g. Ge/Si ratios; Derry et al. 2005) as tools to study Si dynamics between the different components of a landscape (i.e. vegetation/litter, soil, pore water, river inflow- and outflow to a catchment). The application of such a tool box to study Arctic catchments influenced by e.g. different degrees of permafrost thaw would offer a nice addition to the work carried out in this thesis.

Additionally, the incorporation of Si in the study of elemental stoichiometry (C, N, P) of peatlands and other soils (Wang et al. 2014) can provide useful insights of how Si of biogenic origin (e.g. quantified by means of Barão et al. 2015) is recycled within the soil in relation to other nutrients.

Revealing the mechanisms by which microbes can result in apparent reductions in Si release during litter decomposition represent an interesting future task as well. One of the suggested hypotheses involves formation of complexes between microbial exogenous metabolites and Si, which may cluster into larger aggregates. It follows that future experiments, looking at the interactions between Si release, microbial growth and decomposition of submerged litter should also take the particulate fraction into account when collecting and analyzing Si in the aqueous phase. Potential Si aggregates/particles could be retrieved through phase-separation techniques (Bansal et al. 2006) and identified by microscopy techniques. Another approach includes studying Si release from submerged plant litter in the presence of a microbial community, that dependent on nutrient conditions, show varying degrees of EPS production (see Pokrovsky et al. 2009).

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Svensk sammanfattning

Inom forskningsområdet biogeokemi studerar man hur naturens olika grundämnen, såsom kol, kväve, fosfor och kisel ändrar form och transporteras genom landskapet för att via bäckar och vattendrag till slut nå havet. Tillsammans beskriver dessa olika processer, som sker på olika tidsskalor, från sekunder till flera miljoner år, ett grundämnes kretslopp (eller biogeokemiska cykel).

Grundämnet kisel (Si) är det näst vanligaste i jordskorpan, efter syre, och därför ingår det också i de flesta mineraler och bergarter som exempelvis granit. När mineraler och bergarter vittrar sönder frigörs kisel och blir löst kisel som sedan transporteras via vattendrag och grundvatten genom landskapet. På vägen mot kust och hav tas en del av detta lösta kisel upp av vegetation och av små mikroskopiska organismer, t.ex. kiselalger, som lever i jorden, för att bilda så kallat amorft kisel. När växter och kiselalger dör, ackumuleras sedan detta amorfa kisel till olika grad i jorden där det kan bevaras i tusentals år. Sammanfattningsvis innebär detta att biologiska processer på land kan reglera flödet av löst kisel till akvatiska ekosystem nedströms. Hur mycket löst kisel som når akvatiska ekosystem har stor betydelse för produktionen av kiselalger som utgör en av de vanligaste grupperna av växtplankton i sjöar och hav. Förändringar i flödet av löst kisel till akvatiska ekosystem kan därmed ha inverkan på näringsväven i sjöar och hav. Många av människan orsakade processer, som t.ex. byggande av dammar för vattenkraft, kan minska flödet av löst kisel som når havet. Förändringar i landskapet, såsom vegetationsskifte och förändringar i hur vattnet rinner till följd av klimatförändringar, kan också påverka flödet av löst kisel till akvatiska miljöer.

I stort syftar denna avhandling till att öka vår förståelse kring hur mycket amorft kisel som lagras i jord och hur det skiljer sig mellan olika landskapstyper, med speciellt fokus på Arktis permanent frusna jordar, det vill säga områden med permafrost. Inom detta område har det hittils saknats kunskap och det är ett viktigt forskningsområde, speciellt då uppvärmingen av klimatet sker mycket snabbare i Arktis jämfört med i övriga världen. Dessutom belyser denna avhandling hur bakterier och svamp kan påverka upplösningen av det amorfa kisel som finns lagrat i jord. Avhandlingen utgörs av tre delstudier (Paper I, II och III) som är sammanfattade nedan.

I den första delstudien tittade vi på hur mycket amorft kisel som finns lagrat i jorden hos arktiska tundra- och torvmarker. För denna studie samlades jordprover in från en region i centrala Kanada. Vi fann att moss-torvmarker lagrade en stor andel amorft kisel av biologiskt ursprung (kiselalger) som bevarats, istället för att ingå i ett kretslopp, under tusentals år. Baserat på våra resultat i kombination med en litteraturöversikt, presenterar vi också en föreställningsmässig konceptuell modell för hur global uppvärmning kan komma att påverka kisels kretslopp i framtiden. Vi föreslår att klimatförändringar kan komma att sätta delar av det amorfa kisel som idag är lagrat i permafrost i rörelse, vilket kan leda till förändrade flöden av kisel till nedströms akvatiska miljöer.

I den andra delstudien undersökte jag hur mikrober, i form av bakterier och svampar, påverkar upplösningen av amorft kisel under nedbrytningen av organiskt material. Till detta experiment inkuberade vi växtmaterial med hög halt av amorft kisel, i frånvaro av eller tillsammans med levande mikrober. I motsats till vår hypotes, så kunde vi inte påvisa att upplösningshastigheten av amorft kisel ökar i närvaro av levande bakterier. Istället såg vi det motsatta, det vill säga att levande bakterier minskar mängden kisel som kan frigöras. Vårt experiment tillåter dock inte några slutsatser gällande möjliga mekanismer som kan förklara detta, och det var heller inte huvudsyftet med studien. Detta kan betyda att levande bakterier kan påverka tillgängligheten av löst kisel, men detta måste testas vidare för att några större slutsatser ska kunna dras.

Den tredje och sista delstudien bygger vidare på de resultat vi erhöll i delstudie ett, detta genom att inkludera jordprover från fler områden i Arktis (Svalbard, Grönland och Sibirien) för analys av amorft kisel. Dessa resultat användes sedan för att uppskatta mängden amorft kisel som totalt finns lagrat (0 - 1 m) i marken i Arktis tundraregion. Vi uppskattar att det finns mellan 219 och 474 Tmol (T=terra, 10^{12}) kisel vilket motsvarar 70 - 160 gånger mer kisel än det som uppskattas bindas utav växter årligen. Denna pol av amorft kisel kan komma att bli tillgänlig för det biogeokemiska kretsloppet när permafrosten tinar, vilket kan få konsekvenser (bra eller dåliga?) för akvatiska ekosystem nedströms.

Sammanfattningsvis presenterar denna avhandling de första studierna av hur mycket amorft kisel som finns lagrat i Arktis frusna marker samt hur det är fördelat i landskapet. Det arbete som presenteras i denna avhandling kan utvecklas vidare genom ytterligare studier och då leda till ännu bättre uppskattningar av mängden amorft kisel som finns lagrat i Arktis permafrost. För detta krävs ett större antal jordprover från fler typer utav mark samt från fler olika lokaler än de som den nuvarande studien bygger på.

Vidare påvisar vi att levande mikrober kan minska mängden kisel som frigörs under nedbrytning av kiselrikt växtmaterial. Med tanke på att klimatet blir varmare med smältande permafrost till följd, utgör detta en huvudfråga för framtida undersökningar som ämnar bättre förstå de processer som påverkar kretsloppet av kisel.