Spatial and temporal variation in soil biogenic silicon, total nitrogen, and total carbon over a twenty-one-year period in a hardwood forest of southwestern Quebec

Santiago Ramirez Said

Department of Natural Resource Sciences

McGill University, Montreal, QC.

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Abstract

The biological cycling of silicon (Si) in terrestrial ecosystems is a key driver of long-term carbon sequestration, and terrestrial and marine productivity. A better knowledge of the effects of tree species composition on the spatial and temporal variation of biogenic silicon (BSi) in forest soils is essential to fully understand forests' effects on Si and carbon (C) cycling. In this study, I measured soil BSi concentration in the hardwood forest of the Morgan Arboretum (Montreal, QC, Canada) to understand its relationship with soil fertility parameters (pH, available P, K, Ca, Mg, Al, total C, total N, and water content), soil texture and tree species composition. I hypothesized that BSi would be higher under active Si accumulating species (maples and beech) and in clay textured soils regardless of other soil properties. Additionally, I explored the relationships between the changes in summer rainfall, temperature, and species composition with changes in soil BSi, total N, and total C over the 1998-2019 period. Soil pH and Al, Fagus *grandifolia's* mean weighted DBH, and *Acer rubrum's* mean weighted DBH were the best predictors of soil BSi levels. Although clay content was also a significant predictor of soil BSi, it was more closely associated with soil fertility parameters. Overall, soil BSi tended to decrease with increases in *Acer saccharum* weighted DBH, a species commonly associated with active Si accumulation. I concluded that soil BSi is not necessarily high under active Si accumulating species and that predicting high soil BSi levels requires considering various ecosystem parameters and their interactions.

Total N decreased in the forest from 1998 to 2019, while significant changes in soil BSi and total C were only detected in plots on the glacial till deposit. Extensive *Fraxinus americana* mortality and its replacement by *A. saccharum* drove the decrease in soil BSi. In contrast, soil N decrease was attributed to the significant increase of sugar maple in the forest, which has been associated to increases in nitrate, the form of nitrogen most susceptible to leaching. Finally, soil C decreases

in the till deposit was attributed to soil and canopy changes driven by ash mortality and increases in soil water content and air temperature. Together, our results suggest that changes in the proportion of two species with different BSi uptake mechanisms, increases in water content and in air temperature in the last 21 years (1998-2019) have affected soil BSi, total C, and total N.

Résumé

Le cycle biologique du silicium (Si) dans les écosystèmes terrestres est important dans la séquestration du carbone à long terme et de la productivité terrestre et marine. Une meilleure connaissance des effets de la composition des espèces d'arbres sur la variation spatiale et temporelle du silicium biogénique (SiB) dans les sols forestiers est essentielle pour comprendre pleinement les effets des forêts sur le cycle du Si et du carbone (C). Dans cette étude, j'ai mesuré la concentration de SiB du sol dans la forêt de feuillus de l'arboretum Morgan (Montréal, QC, Canada) pour comprendre sa relation avec les paramètres de fertilité du sol (pH, P, K, Ca, Mg, Al, C total, N et teneur en eau), la texture du sol et la composition des espèces d'arbres. J'ai émis l'hypothèse que le SiB serait plus élevé sous les espèces accumulant du Si activement et dans les sols à texture argileuse indépendamment des autres propriétés du sol. De plus, j'ai exploré les relations entre les changements dans les précipitations estivales, la température et la composition des espèces avec le SiB du sol, le N total et le C total au cours de la période 1998-2019. Cette étude a révélé que le pH, l'Al du sol, le DHP moyen pondérée de *Fagus grandifolia* et le DHP moyen pondérée *d'Acer rubrum* étaient les meilleures variables pour prédire les niveaux élevés de BSi parmi toutes les variables évaluées. Bien que les sols à texture argileuse aient également joué un rôle important dans la prédiction du SiB du sol, ils étaient plus étroitement associés aux paramètres de fertilité du sol. En outre, le SBi avait tendance à diminuer avec les augmentations du DHP pondérée *d'Acer saccharum*, une espèce communément associée à l'accumulation de Si activement. Malgré la découverte que les espèces d'arbres, le pH du sol et Al étaient des prédicteurs significatifs du SiB du sol, ces variables elles-mêmes dépendent de divers facteurs d'interaction comme le dépôt du sol et le matériau d'origine. Ainsi, il existe de nombreuses interrelations entre les prédicteurs significatifs du SiB du sol, rendant le SiB mieux analysé comme une propriété émergente de l'écosystème. Nous avons conclu que le SiB du sol n'est pas nécessairement élevé sous les espèces de Si actif et que la prévision des niveaux élevés de BSi du sol nécessite de considérer les différentes interactions entre les variables significatives identifiées.

Le N total a diminué dans la forêt entre 1998 et 2019, tandis que des changements importants dans le SiB et le C n'ont été détectés que dans les parcelles du dépôt de till glaciaire. La mortalité extensive de *Fraxinus americana* et son remplacement par *A. saccharum* ont entraîné la diminution du SiB du sol. En revanche, la diminution de l'azote dans le sol a été attribuée à l'augmentation significative de l'érable à sucre dans la forêt, qui a été associée à plusieurs reprises à des augmentations de nitrate, la forme de Nitrogène la plus sensible au lessivage. Enfin, la diminution du C du sol dans le dépôt de till a été attribuée aux changements du sol et de la canopée causés par la mortalité des cendres et l'augmentation de la teneur en eau du sol et de la température de l'air. Ensemble, nos résultats suggèrent que les changements dans la proportion de deux espèces avec différents mécanismes d'absorption de SiB, les augmentations de la teneur en eau et de la température de l'air au cours des 21 dernières années (1998-2019) ont affecté le SiB du sol, le C total et le N total.

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Preface

This thesis and the articles to be published from it are the results of the work of S.R Said. It consists of four chapters organized as a classical thesis. The manuscripts will be written separately. The first chapter is a general introduction. The second chapter is a literature review, including the research hypotheses. The third chapter describes the methodological approaches used to meet the research objectives. The fourth chapter is about the effect of tree species on soil biogenic silicon variation and its relative importance compared to soil texture and nutrients. The fifth chapter explores the changes in soil carbon, nitrogen, and biogenic silicon at the study site in the past 21 years in relation to changes in forest species composition, summer rainfall, and temperature.

Contributions of Authors

S.R Said is the first author for all chapters. S.R. Said was responsible for the tree inventory in 2019, the laboratory analysis in 2019, all statistical analyses, and thesis preparation. Benoît Côté, my thesis supervisor, has contributed significantly to the thesis and provided funding for the research. Half of this study is based on Guillaume Larocque's sampling design and effort in 1998 and the laboratory analyses of 1998, making him the third author of this work. Dr. Kallenbach, my co-supervisor, played an essential role in my understanding of soil carbon dynamics and would be the fourth author. Finally, Dr. Fyles was the supervisor of Guillaume Larocque and had a significant role in designing the study and paid for most of the expenses related to Guillaume's work, making him the last author of this work.

1. General introduction

Silicon (Si) is the second most abundant element found in the Earth's crust and the seventh most abundant element in the universe (Tréguer, & De La Rocha, 2013). Its high abundance is related to its chemical affinity to form links with oxygen in a process that generates silicate minerals. Silicate minerals constitute the crust of most planets in the universe, including planet Earth, with over 75% of the Earth's surface composed of silicon dioxide (Fraysse et al. 2009).

An almost omnipresent element on the planet, Si is intertwined with many biogeochemical processes. Due to concerns about the effects of climate change (IPCC,2007) and the relationship of Si with the carbon (C) cycle, the Si cycle is receiving increased attention from researchers. Indeed, the processes involved in the Si cycle consume between 830 megatons (Mt) and 26 gigatons (GT) of carbon dioxide (CO_2) annually (the actual amount varies on whether Si mediated diatom photosynthesis is included in the calculation or not). Here is a summary of these processes:

1. **The weathering of silicates in the bedrock** (Berner, 2008; Caldeira, 2006; Song et al. 2018). Climatic and plant driven processes result in the erosion of bedrock, consuming atmospheric CO_2, and releasing base cations. Each year, continental silicate weathering consumes between 380 and 580 Mt of carbon annually (Meybeck, 1987). The weathering process can be increased twentyfold by plants (Drever, 1994).
2. **The occlusion of carbon in biogenic silicon (BSi) or plant phytoliths** (Song et al., 2017; Parr, & Sullivan, 2005). Plants produce phytoliths through the uptake of dissolved silica. BSi has a multi-porous structure that can occlude soil organic matter and reduce its exposure to decomposers and carbon destabilizing agents. It is estimated that phytoliths sequestrate between 65 and 250 Mt of carbon annually (Song et al., 2017).

3. **The export of silicon from land to ocean**. Forest ecosystems contribute from 40 to 78% of the annual oceanic silica input (Caldeira, 2006). This export of Si allows its incorporation in diatoms, marine algae that are reproductively limited by Si availability (Conley et al., 1993). Diatoms are the most significant contributors to marine photosynthesis (Street-Perrott & Barker, 2008), fixing around 25.6 Gt of C per year, accounting for almost 50% of all marine productivity (Carey & Fulweiler, 2012).
4. **The leaching of base cations produced through bedrock weathering** which are transported to marine ecosystems where they take part in oceanic carbonate precipitation and C sequestration (Street-Perrott & Barker, 2008).

The processes mentioned above make it clear that understanding the Si biogeochemical cycle is relevant for a better understanding of greenhouse gas dynamics and predicting future climates (Struyf et al., 2010).

Of the four processes, the first two occur in terrestrial ecosystems, where plants contribute more than any other organism to the terrestrial Si pools (Alexandre et al., 1997; Fraysse et al. 2009). Based on their important contribution to soil Si, plant species have been categorized into three different groups based on their Si uptake mechanism. Plants can be grouped into active, passive, or excluding Si species. An active Si absorbing plant will spend energy to bring dissolved Si through specialized root channels (Ma et al., 2001), while a passive Si accumulating plant incorporates Si into its tissue by mass flow of soil water through the transpiration stream (Piperno, 2006). Finally, there are Si excluding species, plants that have negligible amounts of Si. Regardless of the uptake process, most Si is stored in the form of hydrated silicon dioxide (SiO_2), with most Si being stored in leaves. Once inside the leaves, this hydrated silica receives the name of phytolith or biogenic silicon (BSi). These phytoliths are returned to the soil through litterfall and then dissolve in soil water in the form of silicic acid (H_2SiO_4), the only form of Si biologically available to plants (Casey et al.,2013). Once dissolved, plants can re-uptake Si and continue the cycle. Considering that plants can differ significantly in their capacity to absorb Si from the soil (active and passive), changes in species dominance may impact soil BSi. Moreover, since plants can only absorb BSi once it is dissolved, soil properties that affect phytolith dissolution may probably affect the amount of BSi in a forest. However, to our knowledge, no research has evaluated the interplay of soil properties, soil texture, and tree species composition in determining the fate of BSi in a deciduous forest.

In eastern North America, leaves of sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), and American beech *(Fagus grandifolia* Ehrh.) are relatively high in Si compared to other hardwoods (Hodson et al., 2005). In non-disturbed forests, the high amounts of Si that active Si species absorb from the soil are balanced by high returns of BSi in litterfall (Gewirtzman et al., 2019), suggesting that active Si accumulating species should present high soil BSi levels. However, in the past 20 years, eastern North America has experienced a series of changes that have potentially modified forest soil BSi dynamics. For instance, Western Quebec has experienced a marked decline of American beech and white ash trees, with the emergence of the beech bark disease and the emerald ash borer, possibly affecting ecosystem services and the mineral cycling capabilities of the forests in the region (Cale et al., 2017).

On the other hand, several research papers (Williamson et al., 2009; Leclerc et al., 2015; D'Orangeville et al., 2015; Menne et al., 2018) agree that climate trends in eastern North America will result in increased temperatures and rainfall. Since soil water content and changes in litterfall decomposition have been hypothesized to affect soil BSi (Nguyen et al., 2019), it is likely that increases in air temperature and rainfall in the last twenty years have already affected soil BSi levels. Moreover, these climatic changes have the potential to affect other forest minerals of importance, like nitrogen and carbon. For instance, Sinha et al. (2015) found that an increase in precipitation alone is enough to generate a robust increase in N leaching. Likewise, the expected increases in precipitation and temperature have the potential to increase litter decomposition (Cisneros et al., 2017) and modify soil C.

Based on the climatic trends of Eastern North America and the decline of beech and ash trees in the past twenty years, I hypothesized that changes in forest species composition, summer temperature, and rainfall could be modifying the amount of soil BSi, total N and total C in the soil. Additionally, since each species has specific soil requirements in terms of soil texture, drainage, and fertility, I will also test the effect of these soil variables on soil BSi. This will allow us to determine if high soil BSi in a deciduous forest is primarily driven by vegetation, soil texture, soil minerals, or a combination of all three.

2. Literature review

2.1 Importance of the terrestrial Si cycle

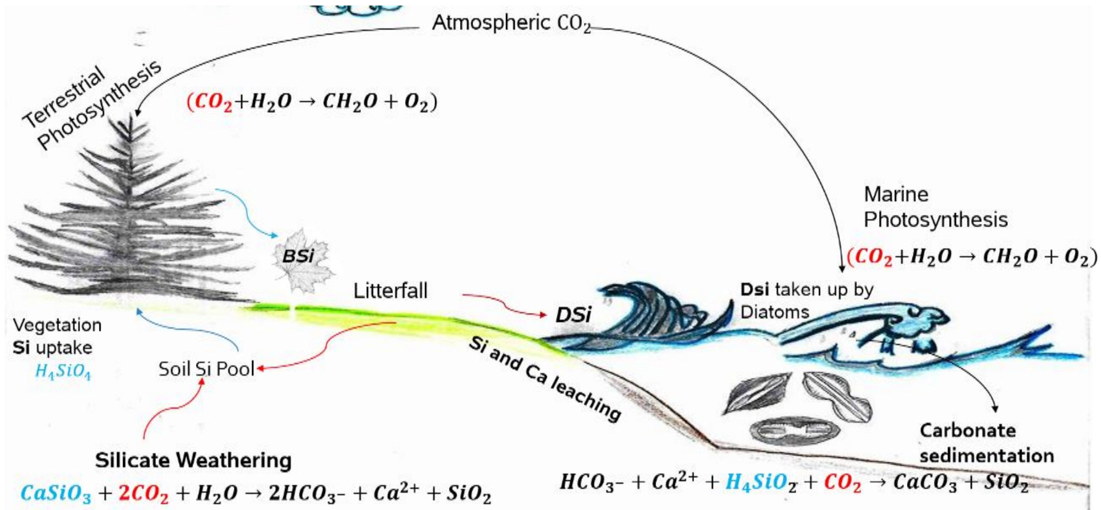
The Si biogeochemical cycle has drawn increased research interest in the last few years due to the relevance of silicate weathering in regulating atmospheric carbon dioxide levels, capable of consuming more than 600 megatons of CO_2 annually (Gaillardet et al. 1999; Song et al. 2018; Tréguer and Pondaven 2000). The cycle has biological and geological drivers; silicate bedrock weathering being the main driver of the geological cycle (Gaillardet et al., 1999) and plant uptake of silicic acid and production of biogenic silica (BSi) being the main drivers of the biological cycle (Cornelis et al., 2010).

2.1.1 Silicate bedrock weathering

The weathering of silicate bedrock is dependent on several factors, such as the type of parent material, precipitation, freezing and thawing, temperature changes, and wind (Krause et al., 2018). Weathering occurs through extended periods and at a slow rate, generating considerable effects at geological timescales (Taylor et al., 2012). However, weathering rates can be increased by biological activity, with plants increasing weathering rates up to 20 times. To do so, plants assimilate atmospheric CO_2 through photosynthesis, then translocate some of the organic C to the roots where it is metabolized, and part of it released as CO_2 through respiration in the soil solution, lowering pH and accelerating weathering (Lucas, 2001). Additionally, plants further affect rock weathering by altering the residence time of water in the soil, inducing mineral chelation and releasing organic acids, (Drever, 1994; Bray et al., 2015; Cornelis et al. 2010). Once weathered, silicate bedrock releases dissolved mono silicic acid (H_2SiO_4) and bicarbonate ions (Berner, 2008;

Struyf et al., 2010), which favor the chemical fixation of atmospheric carbon into this new bicarbonate ion complex (Figure 2-1).

Figure 2-1. Coupled carbon-silicon cycle.



2.1.2 Plant uptake of silicic acid and production of biogenic silica

Plants are some of the few land organisms that convert the silicic acid released through rock weathering to silica (Raven, 2003). Monosilicic acid is the only form of Si that plants can readily incorporate into their tissue since solid forms of hydrated Si are unavailable to plants (Dove & Ienhower, 1997). Once absorbed, silicic acid is precipitated into biogenic silica (BSi) at the end of the transpiration stream in plants (Trembath-Reichert et al., 2015). Once in the transpiration stream, BSi can be stored in leaves or other tissues, including, but not limited to, fruits, flowers, stems, and roots, although most BSi is stored in leaves (Piperno, 2006). Soil restitution of BSi starts with the return of leaf phytoliths through leaf senescence and fall. Thus, factors like litterfall decomposition and stability of phytogenic silica can also affect soil BSi pools. The stability of phytogenic silica depends on environmental conditions like temperature, soil moisture, iron, and aluminum oxides, pH, litterfall chemical characteristics, and species-specific phytolith properties (surface area and pore size) (Bartoli, 1983, Piperno, 2006, Song et al., 2018.)

Because BSi is seven to twenty times more soluble than bedrock silica (Cornelis et al., 2010), it can be quickly re-assimilated by plants. Hence, plants act as filters in the Si cycle (Figure 2-1), changing the amount of soluble silica in soil and affecting the flux rate of Si from land to the ocean (Clymans et al. 2016; Song et al. 2018). The leaching of dissolved silica from forests to oceans can contribute from 40 to 78% of the annual oceanic silica input (Caldeira, 2006; Epstein, 1994; Tréguer & de La Rocha, 2013; Webb & Longstaffe, 2000). Once it reaches the ocean, dissolved silica can be taken up by diatoms (Class: Bacillariophyceae), microscopic algae that can contribute from 30 to 70% of the primary productivity in some parts of the planet (García-Bernal et al., 2017) and 50% of organic C burial in marine sediments (Nelson et al., 1995).

Given the relevance of the terrestrial Si cycle in regulating atmospheric carbon dioxide levels, it is critical to further comprehend the role of plants in the Si cycle. More knowledge into this understudied terrestrial cycle (Tubana et al,.2016) will help develop forest management strategies that promote Si cycling, affecting both the rate of Si rock weathering (Song et al., 2018) and terrestrial exports of Si to the oceans (Lal, 2005; Parr & Sullivan, 2005) where it can be stored for long periods.

2.2 Plants and Si

2.2.1 Plant Si uptake

Silicon has unique characteristics as a “quasi” plant nutrient, being the only element that has never been found to be toxic to plant life, even at high doses (Ma et al., 2001). Furthermore, there is considerable evidence showing that plants can control how much silicic acid is absorbed from the environment (Piperno, 2006). Plants can transfer monosilicic acid from the soil solution into roots and aerial organs through either active transport, by a passive transport mechanism or exclude it almost completely.

In higher plants, the active transport occurs inwards at the plasmalemma of root epidermal and cortical cells (Raven, 2003). Active transport is most often genetically and metabolically mediated, with the plant choosing to allocate a portion of its finite set of resources to silica accumulation. Ma (2006) and Yamaji et al. (2008) identified two genes, *Lsi1* and *Lsi6*, that regulate the active transport mechanisms in rice (*Oryza sativa*). Although transport genes have not been identified in gymnosperms or eudicots, plants that have a concentration of Si above 1% dry weight are classified as active Si accumulators (Ma et al., 2001; Street-Perrott & Barker, 2008).

Passive Si uptake describes the nonselective absorption of monosilicic acid by a plant with Si concentration in the sap being very similar to the concentration in the soil solution. Therefore, the amount of biogenic Si in the plant can be calculated by knowing the concentration of silicic acid in the soil solution and the amount of transpired water (Jones & Handreck, 1967). Because there is always Si in the soil solution, even active Si accumulating species benefit from the passive mechanisms of Si transfer from soil to roots.

Finally, there is a third category of plants coined as Si excluders, plants that have been found to have almost no Si. These plants can prevent the entry of monosilicic acid in the roots. Although not yet elucidated, plants that are Si excluders probably possess a mechanism that produces a thin, fatty substance that encases root hairs and inhibits the entry of monosilicic acid (Parry & Winslow,1997).-

2.2.2. Benefits of silicon incorporation in plants

Silicon has many benefits to plant life, and even if its role as an essential nutrient to plant growth is still debated (Epstein, 1994), there has been thorough research on the beneficial effects it has for plant growth. Silicon has been found to increase resistance to fungal infection in rice (van Bockhaven et al., 2015) alleviate aluminum (Cooke & Leishman, 2016; Hodson et al., 2005; Tikasz, 2016) manganese (Sangster et al., 2001) and cadmium (Liang et al., 2005) toxicities, and augment the tolerance to water stress (Pei et al., 2010). Additionally, Si absorption in young shoots makes the leaf more erect, allowing more sunlight to reach the leaves and thus increasing photosynthesis (Ma & Yamaji, 2006).

Si can also decrease leaf attack by herbivores. The latter is widely recognized and has been a successful evolutionary strategy for plant defense (Katz, 2018). The hypsodont dentition of horses and other herbivores arose as a selective pressure exerted by the hard to chew leaves of prairie grass leaves that are high in Si. Additionally, Si incorporation in seeds and plant tissues has been of increasing interest due to its anti-mycotic properties. Although the mechanisms involved in preventing fungal colonization are still not completely understood (van Bockhaven et al., 2015), it has been shown that Si absorption promotes the formation of a subcuticular layer that acts as a physical barrier against fungal penetration (Ma & Yamaji, 2006), while also boosting and inducing a broad spectrum of immune responses (Fauteux et al., 2005).

2.3. Factors influencing biogenic Si concentration

2.3.1 Forest tree species

Forests store large amounts of Si and export larger amounts of Si than other terrestrial ecosystems (Harvey, 2012; Song et al., 2018). Deciduous forests are of special biogeochemical importance since they are particularly high Si-accumulating ecosystems (Gérard et al., 2008). In eastern North American deciduous forests, American beech (*Fagus grandifolia Marsh.*) trees have among the highest leaf BSi concentrations in the forest (Hodson et al., 2005). The *Acer* genus ranks high among dicots as well, with species like sugar maple (*Acer saccharum* Marsh.) and red maple (*Acer rubrum* L.) having high concentrations of BSi in their leaves. Moreover, Tikasz (2016) identified leaf Si concentrations higher than 1% in beech and sugar maple trees in the Morgan Arboretum (Montreal, Canada), which, according to Carey & Fulweiler, (2014) would make them active Si accumulators. Active Si absorbing species are expected to produce large amounts of phytoliths in almost any environmental condition (Piperno,2006). However, because both active and passive uptake mechanisms are operative in active Si absorbing species, favorable soil conditions can further increase the already high levels of BSi in these plants.

Although a few studies have been conducted to characterize the effect of tree species on soil BSi, very few have been done in a natural environment. Additionally, previous research has focused mostly on European beech (Bayat et al., 2012; Cremer & Prietzel, 2017; Jorgensen et al., 2009). With differences in climatic conditions and soil types, tree species effects on soil BSi could differ in North American forests.

This led me to the formulation of my first hypothesis and objective:

Hypothesis 1: In a natural forest, the concentration of soil biogenic silica (BSi) is higher under *Fagus grandifolia* and *Acer saccharum* than under other tree species.

Objective 1: Identify key tree species that promote the accumulation of soil BSi and soil carbon.

2.3.2 Abiotic factors

The cycling of Si in the plant/soil system depends on how much Si is taken up by the plant, species-specific properties of biogenic silica bodies (e.g., microcavities, the surface to volume ratio), the chemical composition of the plant litter and the environmental conditions that impact leaf decomposition (Penuelas & Matamala, 1990; Alexandre et al., 2015; Tubana et al., 2016). Of particular importance are the abiotic factors that affect BSi solubility, which principally includes soil water content, pH, and aluminum oxides (Song et al., 2018).

Soils with a low pH tend to have less available dissolved silica, since it is known that a low pH can reduce the nucleophilic attack from OH^- ions on silicon dioxide bonds (Dove & Crerar, 1990), preventing the dissolution of phytoliths and increasing soil BSi. Additionally, it is known that soil pH affects microbial decomposition. Since the actual release of BSi from litterfall requires the leaf to be decomposed, any factor that affects decomposition will eventually affect the movement of BSi from biomass to the mineral soil. Thus, trees with an acidic and poor nutrient litter, like that of American beech and sugar maple (Cote & Fyles, 1994; Larocque, 2008) may not only affect soil BSi through an active Si uptake but also due to their soil acidifying effect, affect BSi solubilization and litter decomposition (Schneider et al., 2012; Prieto et al.,2018).

Another important abiotic factor for solubilizing silicates is the presence of aluminum oxides that bind silica (Piperno, 1988). Once aluminum (Al) binds to biogenic Si, it protects it from dissolution, increasing soil BSi significantly (Nguyen et al., 2019). On the other hand, it is acknowledged that Al can be harmful to plant root development once pH drops below five since acidic conditions solubilize Al cations (Dong et al., 1999), which are toxic to plants.

The effects of soil pH and Al on soil BSi highlight the importance of considering soil properties when determining the amount of BSi in soils. Furthermore, because many of the variables that affect soil BSi are related to soil texture (humidity, pH, presence of aluminum oxides), soil BSi has been observed to be higher in clay soils when compared to other soil textures (Henriet et al., 2008). Based on the latter, I propose my second and third hypotheses and my second objective:

1. **Hypothesis 2: Soil BSi levels will be higher in clay soils regardless of forest tree species composition. Thus, soil texture would be a better predictor of soil BSi than tree species composition.**
2. **Hypothesis 3: Soil BSi levels will be higher in forest sites with high Al concentrations. Similarly, plots with low pH will have higher soil BSi.**

Objective 2: Identify the best environmental conditions (soil type and tree species) to maximize the amount of soil BSi and identify soil mineral properties that can predict high amounts of soil BSi.

2.4. Changes in forest species composition and climatic trends between 1998 and 2019

2.4.1 Changes in species composition

The deciduous forest of southern Quebec is a diverse forest made up of many tree species with different Si accumulation strategies. Any change in species composition is, therefore, likely to affect Si cycling. It has been shown that changes in forest cover brought by deforestation lead to sustained BSi leaching, decreasing soil BSi, and increasing exports of Si from land to waterways (Clymans et al., 2011). Furthermore, the BSi leaching generated by deforestation can perdure for more than 50 years, since tree death removes the Si cycling capacity of trees in the ecosystem (Conley et al., 2008: Clymans et al., 2016). Although large scale perturbations in forest cover have been evaluated for their effect on soil BSi, to our knowledge, no study considers the impacts of selective tree mortality and the resulting composition change in soil BSi. Even if trees' selective mortality can have a smaller impact than clear-cutting, the death of active Si accumulators or the replacement of dead trees by active Si accumulating trees may be equally as significant to BSi pools as large scale deforestation has been proven to be.

2.4.1.1. Change in American beech

The beech scale insect is a European hemipter first observed on the island of Montreal between 1995-2000 (Cale et al., 2017). Although not deadly by itself, the insect only kills trees due to the invasion of the wounds left by the hemipter with the airborne pathogenic fungus *Neonectria spp*. The fungus destroys protective, vascular, and storage tissues of adult beech tree trunks. The latter leads to the progressive death of trees, which can take several years (Ehrlich, 1934). However, dying beech trees can still reproduce vegetatively through the production of root suckers (Jones & Raynal, 1988), with beech trees arising from root suckers having superior growth rates than beech seedlings (Beaudet & Messier, 2008). Due to the low economic value of beech timber, the scope of beech mortality and its effects on the ecosystem have not been thoroughly studied (Cale et al., 2017). As mentioned earlier, beech trees are known as a Si accumulating species, implying that a marked decrease in beech trees could affect soil BSi.

2.4.1.2. Change in white ash

Likewise, ash trees have been decimated during the same period (last 20 years) due to the emerald ash borer. This Asian insect was first reported in North America in 2002 and has since killed more than 20 million ash trees (Robinett & McCullough, 2019), putting several North American ash species in the critically endangered category (Herms & McCullough, 2014). Although not an active Si accumulator, extended ash mortality may generate space for other tree species to take over, with possible repercussions on the Si cycle. Therefore, I hypothesize that changes in forest species composition in the Morgan Arboretum are affecting the amount of soil BSi , especially in plots with extended beech and ash mortality. My fourth hypothesis is:

> **Hypothesis 4: There has been a decrease in soil biogenic silica (BSi) concentration after 21 years (1998-2019) of changes in tree species composition.**

2.4.2. Climatic trends

Predicted increases in rainfall and temperature in eastern North America have the potential to intensify the increases in soil water and temperature generated by selective tree mortality (Kolka et al., 2011; D'Orangeville et al., 2015). For instance, southern Quebec's historical climate data has indicated an upward trend for spring and summer rainfall between 1970 and 2015 (Leclerc et al.,2015). Similarly, Menne et al. (2018) have found rapid warming trends in the past 30 years in eastern North America, with temperatures increasing an average of 0.4 C per decade since 1988.

Changes in forest composition could exacerbate these changes in temperature and precipitation. Selective tree mortality has been shown to increase soil temperature significantly due to canopy gaps left by dead trees and increased soil water content due to changes in root biomass (Cazzolla Gatti et al., 2014). Similarly, several studies that have evaluated the effects of the emerald ash borer have associated ash death with increases in soil water saturation and mineral leaching (Flower et al., 2013; Kappler et al., 2018; Kolka et al.,2018).

Based on the observed climatic trends and the potential effects of ash mortality, we argue that increases in water content could impact soil N after twenty years of increased tree mortality. Sinha et al. (2015) have shown that increases in precipitation alone are enough to generate robust increases in N leaching. Similarly, Wang et al. (2019) observed that removing plant species can further increase N leaching since there are no trees present to capture soil N. Therefore, I hypothesize that potential increases in soil water content due to decreases in white ash and the predicted increases in summer rainfall could affect the amount of soil N. Thus, my last hypothesis and research objective are:

Hypothesis 5: Soil N has decreased in stands with elevated ash mortality over the period of 1998-2019

Objective 3: Assess the relationship between changes in mean summer temperature and rainfall and soil N, C , and C:N ratio.

2.5. HYPOTHESES

To sum up, the following five hypotheses were tested in this study

i. **In a natural forest, the concentration of soil biogenic silica (BSi) is higher under *Fagus grandifolia*, and *Acer saccharum* than under other tree species**.

ii. **Soil BSi levels will be higher in clay soils regardless of forest tree species composition. Thus, soil texture would be a better predictor of soil BSi than tree species composition.**

iii. **Soil BSi levels will be higher in forest sites with high Al concentrations. Similarly, plots with low pH will have higher soil BSi.**

iv. **There has been a decrease in the amount of soil biogenic silica (BSi) after 21 years (1998-2018) of changes in tree species composition.**

v. **Soil N has decreased in stands with elevated ash mortality over the period of 1998-2019.**

2.6. RESEARCH OBJECTIVES

To complement these hypotheses, the following objectives were formulated:

Objective 1: Identify key species that promote the accumulation of soil BSi.

Objective 2: Identify the best environmental conditions (soil type and tree species) to maximize the amount of soil BSi and identify soil mineral properties that can help predict high amounts of soil BSi.

Objective 3: Assess the relationship between changes in mean summer temperature and rainfall, and soil N, C and C:N ratio.

3. Methods

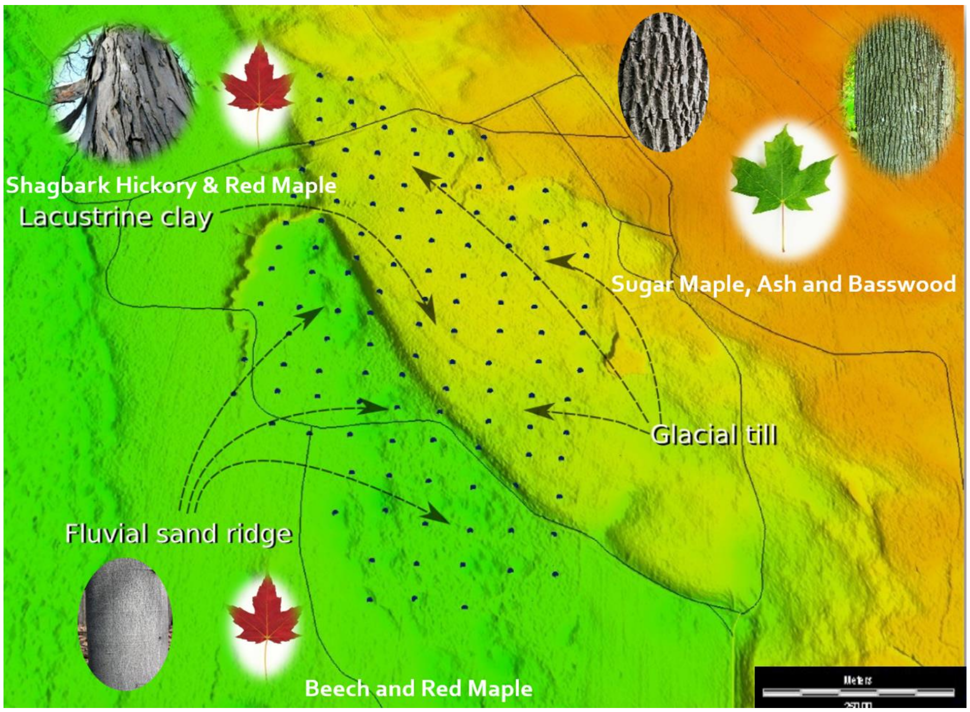
3.1 Site description

The soil samples for this study were collected at the Morgan Arboretum, a 245-hectare forest located in the Saint-Lawrence River valley in Montreal, Quebec (45º 25’N, 73º 57’W; 30m above sea level). The average temperature is 12 °C, with highest mean temperatures in July and August (average 26°C) and lowest temperatures in January and February (average -5°C). The forest stands range from pioneer to climax forests typical of the Great Lakes-Saint Lawrence forest region of eastern North America (Rowe, 1972). Stand age ranges from 60 to 150 years (Morgan Arboretum, 2014). Soils in the forest are derived from fluvial and marine sediments to glacial till and can range from dystric brunisols to sombric brunisols (Côté & Fyles, 1994).

3.2 Data Set

In the fall of 1998, a systematic sampling grid was established (500 x 2300 m), composed of 209 points spaced every 50 m. The plot centers' geographical coordinates were recorded with a global positioning system and marked with iron pigtail sticks (Larocque, 2008). The sampling grid covers a gentle topographical gradient associated with different geomorphological conditions and forest cover types. Figure 3-1A summarizes the three different areas of interest in the forest. The first one is a sub-mesic to sub-hygric fluvial sand deposit, underlain by a lacustrine clay layer. This deposit supports forest stands dominated by American beech, with a smaller abundance of red maple and yellow birch (*Betula alleghaniensis* Britton). The second area is a mesic glacial till deposit derived from a calcareous bedrock, where silt textured soils are dominant and with a mature forest dominated by sugar maple and with a smaller abundance of white ash, bitternut hickory (*Carya cordiformis* K. Koch) and American basswood (*Tilia americana* L.). It is the area with the highest amount/proportion of sugar maple and white ash. Finally, the central portion of the grid is characterized by a sub-hygric lacustrine clay deposit with a diverse forest, with red maple, beech, and shagbark hickory (*Carya ovata* K. Koch) appearing more frequently than other species.

Figure 3-1. *Three-dimensional LIDAR map of the study site showing the three types of soil deposit, their corresponding dominant tree species and the systematic sampling grid where soil samples were taken in 1998 and 2019. Map adapted from Larocque. (2008)*



Other species commonly found on this deposit include basswood, silver maple *(Acer saccharinum* L.), white ash, and black ash (*Fraxinus nigra* Marsh.). To the southwest of the sampling grid, there is a coniferous plantation with a mixture of Norway spruce (*Picea abies* L.), red pine (*Pinus resinosa* Sol.) and white pine (*Pinus strobus* L.). The nine most common tree species in the arboretum are listed in Table 3-1 with some characteristics.

Table 3-1 *Most frequent species inventoried in 2019 in the Morgan Arboretum.*

Scientific name	**English name**	**Average Weighted DBH (WDBH)**	**sites where found (%)**
Acer saccharum Marsh.	sugar maple	0.288	43
Fagus grandifolia Ehrh.	beech	0.213	24
Acer rubrum L.	red maple	0.134	14
Quercus rubra L.	red oak	0.072	5.7
Carya cordiformis K.Koch	bitternut hickory	0.061	5.3
Fraxinus americana L.	white ash	0.056	3.3
Carya ovata K.Koch	shagbark hickory	0.021	2.2
Tilia americana L.	American basswood	0.042	1.5
Betula alleghaniensis Britton	yellow birch	0.007	0.24

3.3 Soil sample collection and forest inventory (1998 and 2019)

GPS coordinates were used to locate plots in 2019. In many cases, the plot centers still had the pigtail sticks installed in 1998. The latter allowed sampling in 2019 to be done at the same location most of the time. The sampling procedure used in 2019 was the same used in 1998. At each sampling point, the mineral topsoil was collected by coring to a depth of 0-15 cm. This depth was considered appropriate since, in most ecosystems, the top 15 to 20 cm of soil include well over 60% of total soil phytolith assemblage (Saccone et al., 2007). At each plot, four cores were collected around the pigtail stick following a cardinal point scheme. The cores were mixed in a plastic bag. Samples were kept on ice packs in a cooler until brought to the laboratory. Soil samples were air-dried for three days at 25^{o}C and gently grounded and sieved to pass through a 2 mm mesh. Soil samples from 1998 were preserved in glass jars at room temperature, which allowed their reutilization in 2019.

The basal area of each plot was determined using a factor-two prism, with DBH being recorded for trees that were more than nine cm in diameter (DBH at 1.3 m aboveground). The distance of trees to the center of the plot was measured in 2019 but not in 1998 due to different research goals. The trees' distance to the center of the plot was determined to allow the calculation of a weighted effect of tree species on soil BSi. This weighted effect is also known as a distance-dependent competition index (CI), which allows to better assess the individual contribution of a tree on soil properties (Contreras et al., 2011). The weighted DBH (wDBH) was calculated as following:

$$Weighted\ DBH\ (wDBH) = \frac{DBH\ (cm)}{distance\ to\ center\ (cm)}$$

3.4 Laboratory analysis

3.4.1 Extraction of soil biogenic Si

Soil biogenic Si was measured following a wet alkaline chemical extraction (Saccone et al., 2007). Ten mg of soil was placed in a flat-bottomed polyethylene tube with 15 ml of 0.5M NaOH solution. The tubes were placed in a block digester at 85 °C for five hours. Aliquots were taken after 2, 3, 4, and 5 hours. To neutralize the solution, 0.75 ml of 0.5M sulphuric acid were added to each aliquot, followed by 1 ml of 0.03 M ammonium molybdate and 1.25 ml of 0.04M oxalic acid. Silicon concentration was measured with the molybdate blue method using the reducing agent ANSA (aminonaphthol sulfonic acid) (Directorate, 1979). The absorbance of the blue colour produced by the reagent was measured at 560 nm using an LKB Pharmacia 4050 UltroSpec II UV-Vis spectrophotometer. BSi concentration was determined by plotting Si concentration in the extract against extraction time and determining the y-intercept of the linear model for the four sampling times, as suggested by DeMaster (1981) and Saccone et al. (2007). Standards were made with sodium hexafluorosilicate.

3.4.2 Soil properties and nutrients

Particle size analysis was carried out in 1998 with a pre-treatment for organic matter removal. Thus, the categorization of the study plots within a given soil deposit (lacustrine clay, fluvial sand ridge, or glacial till) followed the classification done by Larocque (1998). For total organic carbon and total nitrogen analysis, a flash combustion analysis followed by separation through a GC column and detection by a thermal conductivity detector was carried out using a Thermo Fisher Flash elemental analyzer (Verardo et al., 1990; Krotz et al., 2016). Available Ca, K, P, Mg, and Al were determined following the Mehlich-III extraction (Sen Tran & Simard, 1993) with K, Ca, Mg, and Al being determined by atomic absorption spectrometry and P by spectrophotometry. Soil pH was determined in solution with a soil-to-water ratio of 1:5 using a Denver Instrument model 250 electrochemical multimeter (Hendershot et al., 1993). Soil volumetric water content (VWC) was measured in all plots to a depth of 15 cm using a Spectrum Technologies FieldScout TDR150 Soil Moisture Meter. VWC for all plots was measured in the same day to ensure there were no rain events between measurements that could drastically change VWC among plots. Furthermore, the VWC measurements were taken by following a randomized pattern produced on R. Five VWC measurements were taken per plot, and the average was used in the statistical analysis.

3.5. Climate data

Climate data was extracted from the historical climate database freely accessible at the Canadian government page: https://climate.weather.gc.ca/historical_data/search_historic_data_e.html. Based on its proximity to the study area and on the total number of reported days, the climate station from the West Island of Montreal- “Pierre Elliott Trudeau international airport”, was chosen (Climate ID: 702S006). Climate data were downloaded from 1988 to 2019 and separated in two-time intervals: ten years before the first sampling year (1988-1998) and ten years before the last sampling year (2009-2019). Finally, the average summer maximum, minimum and mean temperature were calculated for each time interval as well as the mean summer rainfall.

3.6. Data analysis

To assess the contribution of tree species and soil variables to soil BSi as well as to evaluate the change in soil fertility and species composition over time, I performed both univariate (ANOVA, Spearman correlation and Wilcoxon T-test) and multivariate (Multivariate linear regressions and principal component analyses (PCA)) analyses using statistical packages in R. Since the statistical analyses differ slightly between chapter 4 and chapter 5, I divided the statistical section per chapter.

3.6.1 Evaluating the effects of tree species and soil properties on soil biogenic Si

3.6.1.1 Selection of variables

To assess the effect of tree species on soil BSi, the average wDBH per plot of each species was included in the dataset as a surrogate of the species biomass in the plot.

For the effect of soil texture, only clay content was included to avoid problems related to collinearity. Moreover, while a total of 35 tree species were inventoried in the study area, only species with pure stands were included in the analysis, pure stands being defined as plots having more than 70% of their wDBH attributed to the same species. Only three species were abundant enough to produce more than ten pure plots: red maple, sugar maple, and beech. All measured soil variables were included in the analysis (C, N, pH, Ca, Mg, Al, P, K, VWC, and pH).

3.6.1.2 Univariate analysis- ANOVA and Spearman correlations

The Shapiro-Wilk test of normality was applied to verify if the data were normally distributed. All the null hypotheses were accepted, indicating that the data were from normal distributions. Furthermore, univariate Spearman correlations were performed to explore the individual relationship between the predicting variables and soil BSi. Additionally, an ANOVA test was performed to determine if there were significant differences in soil minerals between the three soil deposits and between species pure plots.

3.6.1.3 Principal component analysis (PCA)

PCAs were used for characterization of the study area according to its soil properties, species composition and phytolith content. The PCA's in this thesis were carried out with the **dplyr, factoextra, FactoMineR, ggpubr,** and **psych** packages. The **dplyr** package is a grammar module for data management (Francois et al., 2020). The **FactoMineR** module is used to make PCA rotations and produce factor loadings that **factoextra** will use for plotting (Le & Husson, 2008). The **factoextra** module is especially useful because it can be used with different multivariate tests to highlight the most important variables based on the quality of their representation and can also be used to create figures (Kassambara & Mundt, 2019). Finally, **psych** allows the calculation of the loadings of individual variables and calculating the total contribution of the variables in several PCA dimensions (Revelle, 2019). A critical loading factor of 0.5 was used to eliminate variables with low contributions and only components with an eigenvalue of more than 1.0 were used.

3.6.1.4 Multivariate linear regressions (MVLR)

Dependence of soil BSi on the various selected soil properties and tree species wDBH was described through multivariate linear regressions. The multivariate linear regressions were done with R's base code (lm). Using R's base code command allowed to eliminate problems like collinearity and selection of models based solely on high adjusted R^2 values. Once a model was selected, a relative importance test was carried out on the parameters to assess their contribution to the R^2 or, in this case, the amount of variability of BSi described by a given variable. The relative importance test was carried out using the free online statistical tool from Davidson University (https://relativeimportance.davidson.edu/) .

3.6.2 Temporal changes in soil biogenic Si, total nitrogen and total carbon after 21 years of tree species composition change

3.6.2.1 Identifying variables that changed over time through univariate Wilcoxon tests

For evaluating the change of BSi, C, and N over time (1998-2019), I first tested which species basal area and which soil minerals had a significant change between 1998 and 2019. To do so, a Wilcoxon signed test was performed between the 1998 data and the 2019 data. Likewise, to test whether the two-time intervals (1988-1998 & 2009-2019) differed in temperature and average rainfall, a Wilcoxon signed test was performed, and significance was reported at the 0.05 level. Since volumetric water content (VWC) was not measured in 1998, we compared the changes in VWC between plots where tree BA decreased and plots where tree BA increased and performed a Wilcoxon test to evaluate significance.

3.6.2.2 Principal component analysis (PCA)

PCAs were carried out with the same packages explained in section 3.6.1.3. PCAs were used for characterization of the glacial till deposit only since it was the only deposit to show significant changes in species composition as well as soil BSi, N and C. Only species whose basal area changed significantly in the twenty years were included in the PCA along with the soil variables.

3.6.2.3 Multivariate linear regressions (MVLR)

MVLR was used to explore the dependence of the change of soil BSi on the change of soil variables and species basal area. Similar to the PCA, the MVLR only analyzed data from the glacial till deposit.

3.6.2.4 Visualization of the change in species composition in ArcGIS

ArcGIS was used to illustrate the change in species composition in the study area, (de Filippis et al., 2019). First, the latitude and longitude of all plots were plotted over a base map of the West Island of Montreal. Since only the decrease in white ash was significant as well as the increase of sugar maple (Table 4-3), only these two species were included in the map. Each plot was represented by a point in the map. If the increase of sugar maple basal area overlapped with a decrease in white ash, the plot was colored in red. If white ash basal area decreased but no sugar maple increase was associated with it, the plot was colored in green.

4. Evaluating the effects of tree species and soil properties on soil biogenic Si

4.1.Results

4.1.1 Effect of tree species on soil BSi

Soil BSi concentration was significantly correlated with the weighted DBH (wDBH) of red maple (r = 0.55) and sugar maple (r = -0.59) (Figure 4-1). Beech wDBH was not significantly correlated with soil BSi but was significantly correlated with soil Ca ($r = -0.59$), Mg ($r = -0.56$) and, Al (r =0.52). Sugar and red maple wDBHs were not significantly correlated with any other soil parameter but were negatively correlated with each other ($r = -0.68$).

The comparison of the pure plots dominated by sugar maple, red maple, and beech (Table 4-1) shows a significantly lower soil BSi and Al concentration under sugar maple. In contrast, sugar maple plots had the highest soil pH, followed by red maple and beech. Beech pure plots had the highest C:N ratio and soil Al, while having the lowest pH, Ca, Mg and K concentrations. Finally, red maple pure stands had significantly higher soil C and volumetric water content (VWC). All three species had different concentrations of soil Al with beech having the highest, followed by red maple and sugar maple. There were no significant differences in soil BSi between pure beech and pure red maple plots.

Table 4-1. *Soil fertility parameters of pure stands of the three most common species in the Morgan Arboretum (Mean $\pm$ SE). Means within a column with different letters are significantly different for $p < 0.05$.*

Pure stand	Most common Deposit	BSi (mg/g)	C (mg/g)	N (mg/g)	C:N ratio	VWC (%)	pH	Al (ug/g)	K (ug/g)	P (ug/g)	Mg (ug/g)	Ca (ug/g)
Red maple (n=10)	7 out of 10 plots on clay	6.7 ±1.5 a	4.5 ±0.5 b	0.3 ±0.03 a	14.7 ±0.61 a	37.3 ±3.6 b	5.43 ±0.25 a	1099 ±117 a	90.6 ±17 a	20. ±4.2 a	237 ±66 a	1341 ±299 a
Beech (n=21)	19 out of 21 plots on sand	5.4 ±0.50 a	3.8 ±0.19 a	0.24 ±0.01 a	18.7 ±0.51 b	11.2 ±1.6 a	4.9 ±0.1 b	1591 ±100 b	42.1 ±6.8 b	30.8 ±10.4 a	66 ±20 b	329 ±110 b
Sugar maple (n=32)	All plots on glacial till	2.8 ±0.20 b	3.7 ±0.14 a	0.27 ±0.01 a	13.2 ±0.19 a	15.4 ±1.1 a	6.0 ±0.11 c	725 ±36 c	76.1 ±5.4 a	20.4 ±3.4 a	289 ±37 a	1963 ±181 a

4.1.2 Effect of soil fertility parameters on soil BSi.

Soil pH, the only soil parameter negatively correlated with soil BSi (Figure 4-1), did not show a strict linear pattern when plotted against soil BSi (Figure 4-2).

Figure 4-1. *Spearman correlation coefficients for soil fertility parameters, proportion of soil particle sizes (sand, silt and clay) and weighted basal area (wDBH) for beech, sugar maple and red maple. Significant correlations for p <0.05 are indicated by an asterisk.*

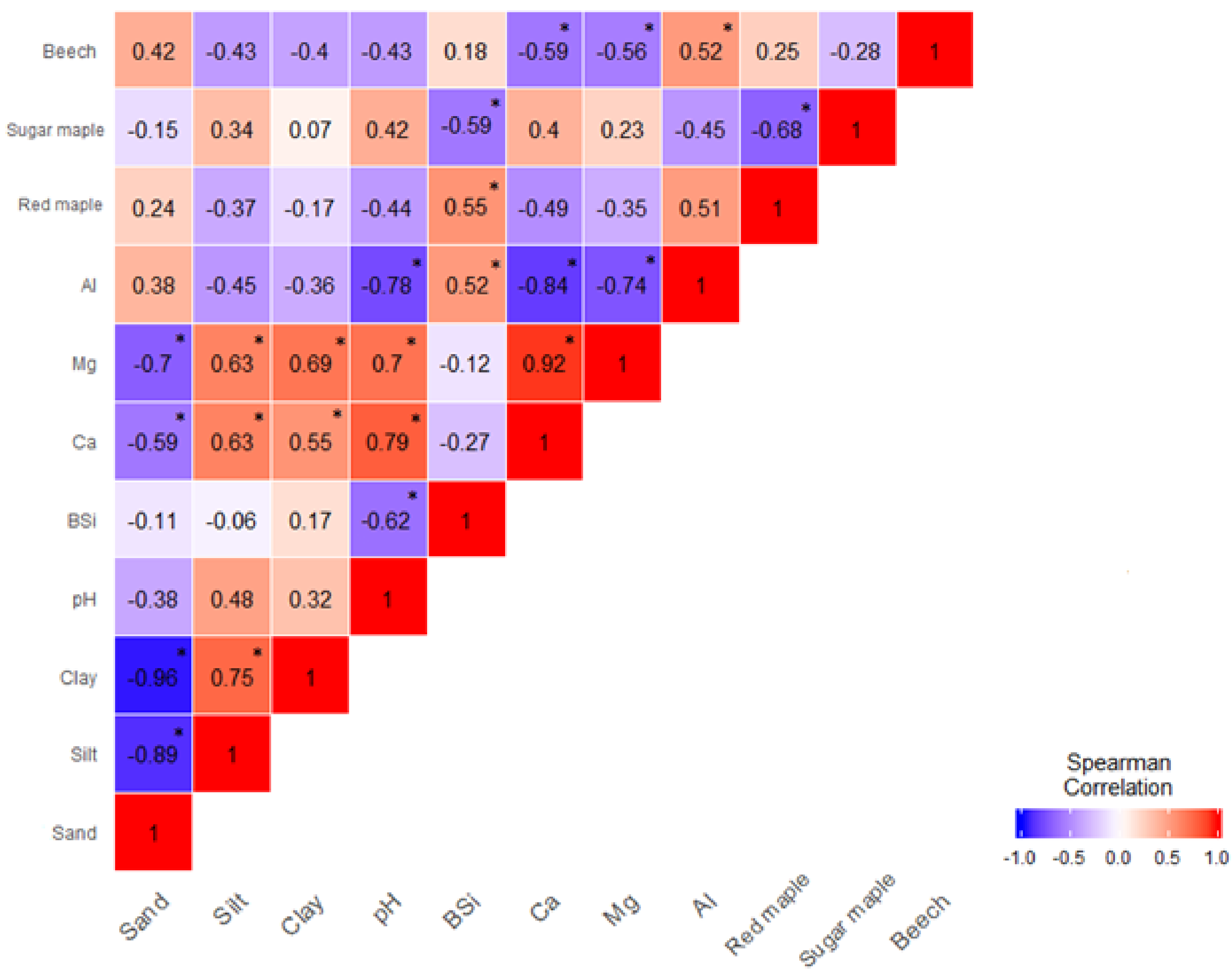
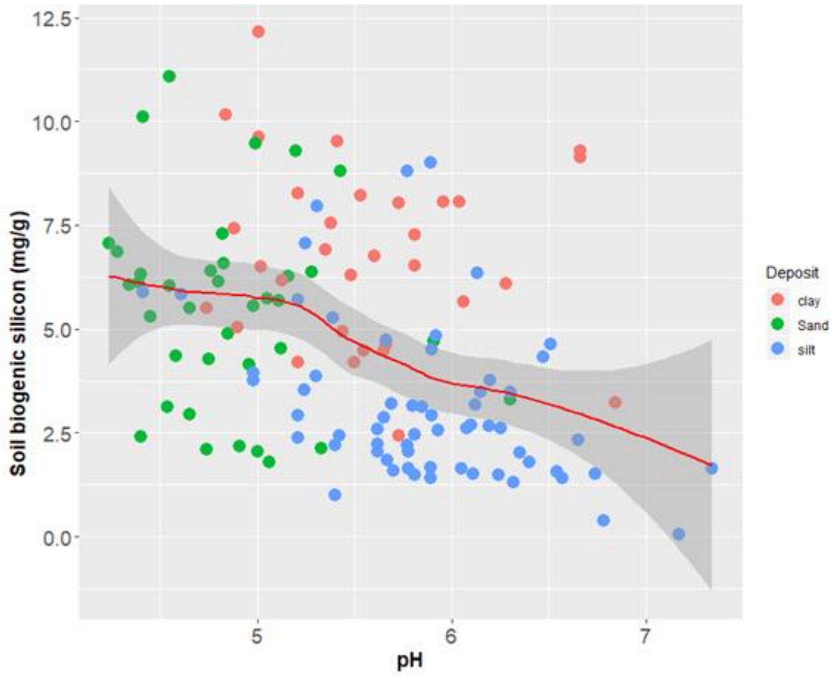
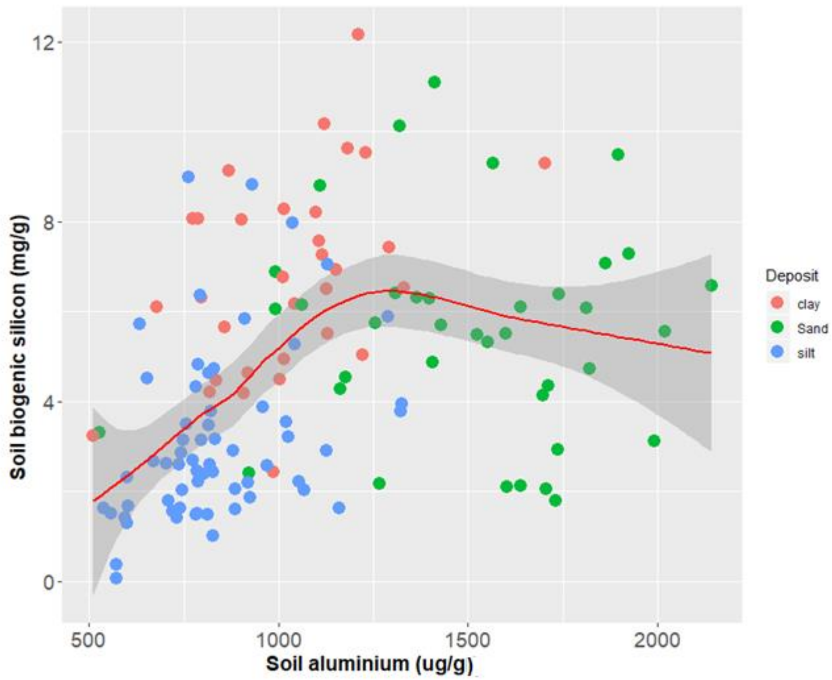


Figure 4-2. *Locally weighted scatterplot of soil pH vs soil BSi.*



Soil BSi concentration was relatively stable below pH = 5 and decreased steadily at higher soil pH. Most plots with pH values lower than five were on the sand deposit, while the highest pH occurred in the glacial till deposit. Aluminium, the only soil mineral with a significant positive correlation with soil BSi (Figure 4-1), showed two different patterns when plotted against soil BSi (Figure 4-3).

Figure 4-3. *Locally weighted scatterplot of soil Al vs soil BSi.*



Soil BSi steadily increased with Al until it reached a plateau around 1250 ug/g of soil Al. Concentrations of soil Al higher than 1250 ug/g occurred exclusively on the sand deposit.

4.1.3 Effect of soil deposit and texture on soil BSi

The clay deposit had the highest concentration of soil BSi, total soil C, and volumetric water content. The sand deposit had the lowest soil pH and available K, Mg and Ca, while having the highest soil Al. Finally, the glacial till deposit had the highest soil pH and available Ca while having the lowest Al and soil BSi (Table 4-2). All three deposits were significantly different for soil BSi, pH, Ca, and Al with soil BSi concentration decreasing as follows:

$$clay > sand > till$$

Table 4-2. *Comparison of soil biogenic silicon (BSi) and fertility parameters for the three soil deposits sampled in 2019 (Mean ± SE) Means within a column with different letters are significantly different for p < 0.05. (VWC=Volumetric Water Content)*

Variable/ Deposit	BSi (mg/g)	Carbon (mg/g)	Nitrogen (mg/g)	C:N Ratio	VWC (%)	pH	Al (ug/g)	K (ug/g)	P (ug/g)	Mg (ug/g)	Ca (ug/g)
Clay (lacustrine clay)	7.0 ±0.55 a	5.4 ±0.23 a	0.31 ±0.02 a	15.5 ±0.27 b	21.3 ±1.60 a	5.2 ±0.24 b	1139 ±38.00 b	125 ±7.20 a	20.6 ±2.01 a	365 ±44 a	1546 ±174 b
Sand (fluvial sand ridge)	5.5 ±0.35 b	3.8 ±0.22 b	0.22 ±0.01 b	18.1 ±0.39 a	16.6 ±1.75 b	4.7 ±0.14 c	1543 ±29. a	39.1 ±3.8 b	28.9 ±7.2 a	43.2 ±7 b	183 ±25 c
Silt (glacial till)	3.05 ±0.24 c	3.83 ±0.14 b	0.29 ±0.01 a	14.4 ±0.13 b	17.4 ±1.0 b	5.8 ±0.11 a	729 ±22 c	94.3 ±5.8 a	20.0 ±2.1 a	332 ±255 a	2014 ±126 a
All deposits	4.5 ±0.22	4.3 ±0.11	0.27 ±0.08	15.9 ±0.23	17.4 ±1	5.5 ±0.09	1093 ±34	85 ±4.5	23.0 ±2.5	257 ±20	1388 ±102

Despite the significant differences observed in soil BSi among the different deposits, no significant correlation was observed between the proportion of clay, silt and sand particles and soil BSi concentration (Figure 4-1).

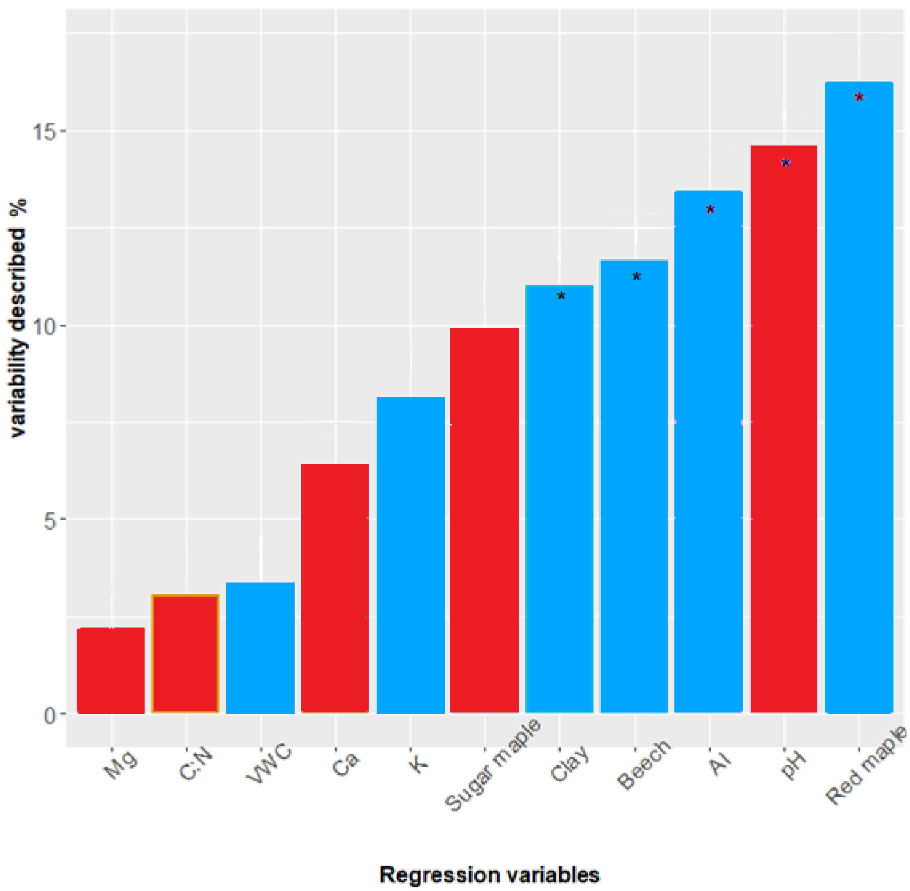
4.1.4 Overall contribution of selected variables to soil biogenic silica

The multivariate linear regression used to describe the variation of soil BSi accounted for almost 50% of the variation in soil BSi ($p < 0.0001$). Of the total variation explained by the model, the relative contribution test (Figure 4-4) showed that 53.4% was attributed to clay textured soil, soil Al, beech and red maple wDBH, which were the only significant positive descriptors of the variation in soil BSi, explaining respectively, 11.0, 13.4, 11.7 and 16.2% of the variation. Soil pH was the only significant variable that had a negative relationship with soil BSi, describing 14.6% of the variation. None of the other variables used (sugar maple wDBH, soil K, Ca, Mg, and C:N ratio) in the model had a significant contribution. The equation obtained to predict soil BSi concentration, using only the significant variables was:

$$soil\ BSi\ \left(\frac{mg}{g}\right) = -0.989pH + 1.651Al\left(\frac{mg}{g}\right) + 0.044Clay\ (\%) + 2.455Redmaple(wDBH) + 1.286Beech(wDBH\ ) \quad \textbf{(Eq.1)}$$

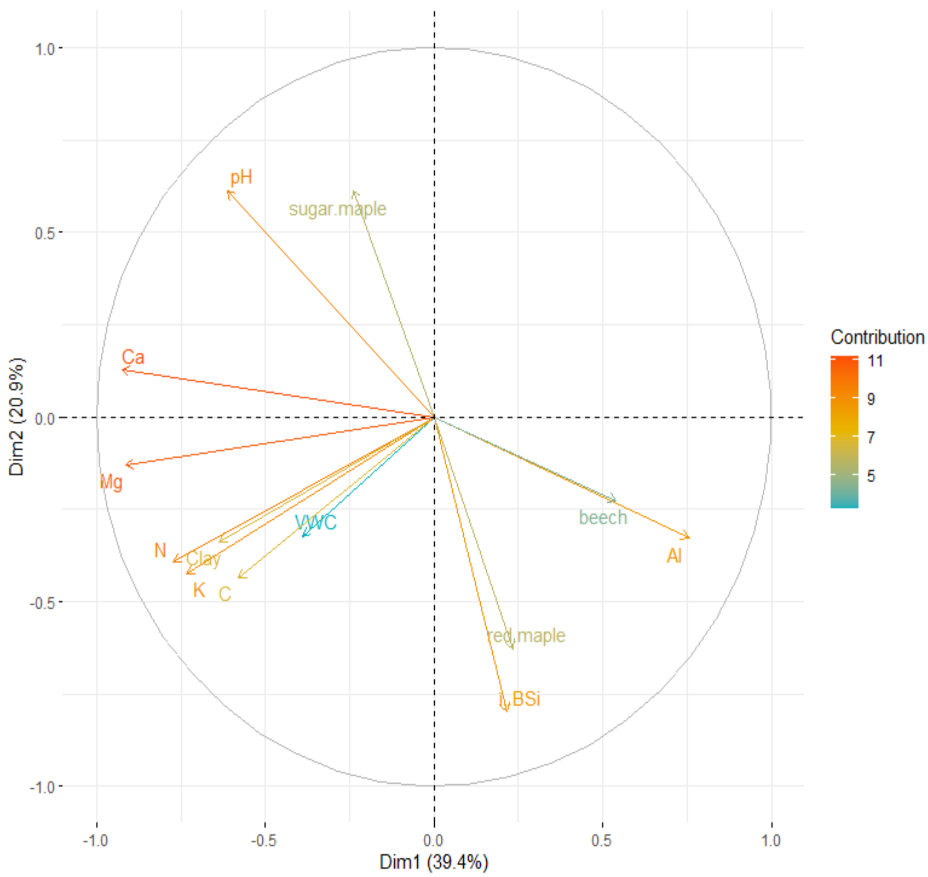
Overall, tree species wDBH and soil variables, excluding soil texture, explained 37.8 and 52.2 % of the variation in soil BSi. The percentage of clay particles explained the remaining 11 %.

Figure 4-4. *Relative contribution of variables to the* R^2 *of the multiple regression for soil BSi in the Morgan arboretum. Asterisks denote variables that were significant in the regression for p <0.05. (*$model\ R^2 = 0.49,\ p\ value < 0.0001$ *). Blue and red columns represent positive and negative correlations, respectively.*



The first two components of the PCA using soil BSi, the selected soil parameters, and tree species wDBH (Figure 4-5) explained 60.3% of the variation. Variables contributing the most to the first dimension were total soil N (0.77), clay % (0.65), K (0.73), Mg (0.91), Ca (0.93), Al (-0.76) and beech wDBH (-0.64), while BSi (0.8), pH (0.65), red maple wDBH (0.68) and sugar maple wDBH (-0.71) contributed the most to the second dimension of the PCA

Figure 4-5. *PCA of the soil variables and species composition (wDBH) for 2019. Significant loadings > 0.65).*



4.2. Discussion

4.2.1. Differences in BSi among pure plots

Contrary to what was initially hypothesized, sugar maple plots did not have the highest concentration of soil BSi. All the tests in this study indicate that sugar maple wDBH was negatively correlated with soil BSi. Moreover, despite beech being a significant variable in the regression to predict soil BSi, and its BSi concentrations not differing from red maple pure plots in the ANOVA, the PCA suggested that beech is more closely associated with soil fertility parameters than with soil BSi. Conversely, red maple had the highest contribution in the regression among all variables and had significant positive loadings in the same dimension as BSi in the PCA. Hence, our results suggest that even if BSi did not differ between beech and red maple plots, red maple was a slightly better predictor of soil BSi.

According to Maguire et al., (2017), sugar maple accumulates relatively high amounts of BSi in its vegetative tissue. Both sugar maple and beech shoot BSi concentrations are higher than that of red maple (Hodson et al., 2005) with a BSi concentration higher than 1% in sugar maple and beech being associated with active Si accumulation. If plant production of BSi was the most important factor when determining soil BSi, sugar maple pure plots would have had high soil BSi, given the high amounts of BSi produced in sugar maple leaves. Considering that this was not the case, it is reasonable to suggest that the presence of active Si absorbing species does not necessarily imply soil BSi will always be high. Thus, apart from a species effect, there must be other factors contributing to the high amounts of BSi under red maple and the low amounts of BSi under sugar maple. This study also found that pH and Al were significant predictors of soil BSi, highlighting their importance when prediction high soil BSi. However, if we consider that most of the red maple pure plots were on the lacustrine clay deposit while all sugar maple plots were on glacial till and all pure beech plots were on the fluvial sand ridge, it is therefore likely that the soil deposit and parent material were also relevant drivers of soil BSi concentration in our study area. Thus, we argue that BSi is influenced by various interacting factors in the ecosystem.

4.2.2. Effect of soil pH and decomposition on soil BSi

Soil pH can affect the concentration of soil BSi in several ways. Acidity levels like those observed in the clay and sand deposits are known to reduce the nucleophilic attack from OH^{-} ions on silicon dioxide bonds (Dove & Crerar, 1990), protecting soil BSi from dissolution and increasing the soil BSi pool. Thus, the higher soil pH measured under sugar maple on the glacial till deposit, would make soil BSi more exposed to nucleophilic attacks, increasing its rate of dissolution. More dissolved BSi would result in lower soil BSi when sampling late in the growing season, thus, partly explaining the higher soil BSi under red maple and beech and the low soil BSi under sugar maple.

Moreover, it is acknowledged that sufficiently low pH values, like those observed in the pure beech plots, can decrease the rate of litter decomposition through its effect on fungal biomass (Griffith & Perry, 1994). With tree litter contributing up to 98% of the annual BSi input to forest soil (Clymans et al., 2016), a slower rate of leaf decomposition could in turn slow down the release of BSi into the soil (Sommer et al., 2006). The fact that pure beech plots had a significantly higher soil C:N ratio along with the most acidic soil is in support of a slower rate of litter decomposition. This suggests a slower but longer lasting release of Si from BSi under beech than under sugar or red maple (Manzoni et al., 2008).

Apart from the effect of soil acidity on litter decomposition, the absence of endogeic earthworms like *Lumbricus terrestris*, a keystone species in the sugar maple/hardwood on glacial till system

(Larocque,2008) may have also contributed in slowing down decomposition. Earthworms are major consumers of leaf litter and play an essential function in mixing organic matter into the mineral soil, producing the characteristic mull humus form with a thick Ah horizon (Zanella et al., 2011). These earthworms are basically absent in the beech stands on the fluvial sand system and variously present in the clay system forests. Research suggests that earthworms do not do well on sand because of the abrasiveness of the sand particles and do poorly on clay because of the seasonal high-water table of the lacustrine deposit (Singh et al., 2016). Earthworm activity in the till deposit would allow for a faster BSi leaf release and, coupled with the high pH of this deposit, more dissolution of soil BSi in the till deposit, which would have resulted in lower soil BSi levels when sampling.

4.2.3. Effect of Al on soil BSi

Acidic soils like those found under red maple and beech tend to have high levels of available Al, which facilitate the production of Si-Al complexes that protect BSi from dissolution (van Cappellen & Qiu, 1997). More specifically, Al adsorption and incorporation into biogenic silica can influence phytolith solubility, dissolution rates, and hence modify tree Si uptake and dissolved silica profiles in soil (van Bennekom et al., 1991; van Cappellen & Qiu, 1997). However, this study showed that there is a limit to the continuous increase of soil BSi with increasing Al. Based on the plots of soil pH and Al vs. soil BSi, there seems to be a threshold where if pH continues to decrease, and Al continues to increase, soil BSi stops increasing. For this study, this threshold occurred at pH 5, a pH level occurring exclusively in the sand deposit. It is widely acknowledged that high concentrations of Al in acidic soil conditions can be harmful to plants. Dong et al. (1999) found a marked increase in Al uptake by vegetation at pH below five since soluble Al^{3+} cations are the main form of Al at that pH. It is known that Al^{3+} is toxic to plants and can reduce root nutrient uptake, which may slow down BSi uptake and turnover rate (Zhao & Shen, 2018). Red maple pure plots had a mean pH and Al concentration of 5.4 and 1099 ug/g, respectively, which would imply that the BSi protection effect of pH and Al was maximized while Al toxicity was minimal.

4.2.4. Sampling season and the species effect of sugar maple

Sampling for this study was done in late summer, by the end of the growing season. If we consider that Si is only available for tree uptake once BSi has dissolved into silicic acid and that most soil BSi had already been solubilized in the glacial till deposit due to the high rate of litter decomposition associated with the high soil pH, presence of earthworms and low Al concentration, most Si would have probably been absorbed by sugar maple and immobilized in its tissues by the time of sampling. Since the return of BSi occurs when leaves senesce and fall, most of it occurs during the fall season with BSi being released through the subsequent leaf decomposition (Yang & Zhang, 2018). Hence, sugar maple plots on the till deposit may not have the lowest BSi content when considering plant and soil pools, as most of this BSi could have been inside sugar maple tissue at the time of sampling. This seasonal variation of BSi has been observed in other tree species of the North American deciduous forest. Gewirtzman et al., (2019) found that leaf BSi content of red maple and red oak increases as summer progresses, reaching peak amounts in August. The opposite is true for soil BSi, which reaches the lowest values in August. Thus, sampling in the month with the lowest amount of soil BSi, plus the ideal soil conditions for BSi solubilization and a high abundance of active Si accumulating sugar maple, made the glacial till deposit the lowest in soil BSi. Future studies should measure soil BSi levels not only during summer but also during spring and fall. This would account for the seasonal variation in soil BSi and allow to test for the full effect of sugar maple on soil BSi. Another approach to test for the effect of tree species composition would be to study red maple and sugar maple monocultures growing on the same soil to determine if the relationships observed in this study can be confirmed.

4.2.5. Soil texture, tree species and interrelationship of variables

Despite finding that BSi was significantly higher in the clay deposit, the proportion of clay, silt, and sand particles were not as good predictors of soil BSi as tree species composition or soil pH and Al, as shown by the correlations and PCA. For instance, none of the soil texture classes were correlated with soil BSi in the univariate correlations, while soil pH, Al, sugar maple, and red maple wDBH had strong correlations with soil BSi. Soil texture was, in fact, more closely associated with soil fertility, being associated in the PCA with variables like soil Ca, K, and Mg. Furthermore, the total contribution of soil texture to the description of the variation of soil BSi (11.0%) in the multiple linear regression was less than half the contribution of red maple and beech together (27.9%) or the contribution of soil pH and Al (28.0%).

Although our results at first glance would suggest that tree species, pH, and soil Al are the best predictors of soil BSi, it is critical to consider how these variables interact with other ecosystem components before concluding about causalities. For instance, each soil deposit's parent material has several features that variously influence water drainage, primary soil nutrients, and root permeability (Anderson, 1988). These features, in turn, influence the plant and animal species that can thrive in each deposit and the biological activity of these organisms via production, uptake, decomposition, and nutrient cycling. These biological activities interact again with the soil, to different extents, to produce the set of soil conditions identified in this study. Hence, soil development and chemistry can never be truly independent of vegetation, soil fauna or other soil properties (Maxwell et al., 2018)

The significant predictor variables of BSi identified in this study (pH, Al, beech, and red maple wDBH) are themselves influenced by these interrelationships arising from soil deposit development. For instance, the till deposit, apart from favoring earthworms, is a deposit derived from limestone, which imparts a high pH, a high cation status and gives an advantage to sugar maple and other tolerant hardwoods, rather than to red maple and beech (Larocque,2008). By favoring high pH, low Al and abundance of both sugar maple and earthworms, many variables favor BSi dissolution and its subsequent uptake by vegetation, resulting in the low BSi values observed. Conversely, red maple seldom occurs in mixture with sugar maple in this forest, as amply demonstrated by the PCA's opposite arrow direction, since red maple is favored by the mineral and drainage features of the clay textured soils in the lacustrine clay deposit. Beech trees on the other hand thrive in acidic and fast drained soils of the fluvial sand ridge, with the characteristic acidity and decomposition rates of this deposit affecting soil BSi as previously stated Thus, pH, Al and tree species interact and are affected by the deposits' parent material, texture and drainage, and might best be viewed as emergent properties of the ecosystem. Likewise, BSi, having these variables as significant predictors, should also be considered as an emergent property of the ecosystem and dependent on the interrelationships previously mentioned.

4.2.6. Possible overestimation of BSi in clay soils

The interpretation of the results relative to the contribution of clay texture and therefore of red maple to soil BSi may be made difficult by a possible interference in the measurement of soil BSi. Barão et al. (2015) found that BSi extractions performed with strong solvents like NaOH may dissolve clay minerals and result in an overestimation of the concentration of BSi in clay samples. Although possible, significant overestimations of BSi in clay soil samples are unlikely due to the approach used in my study. Indeed the purpose of using the intercept of the linear regression of the amount of BSi measured after 2, 3, 4 and 5 h of extraction is to correct for the amount of Si released by more resistant fractions of Si materials such as clay once all of the BSi has been dissolved. The only instance when Si could be overestimated would be for samples with clay that would dissolve completely like soil BSi within the first two hours, which is very unlikely. Regardless of whether BSi was overestimated or not in the clay deposit, all statistical analyses (correlations, regression, PCA) except the ANOVA indicate that tree species composition is better than soil texture at predicting soil BSi. In fact, if there is indeed an overestimation of BSi in clay soils, that would imply that the actual BSi values in clay textured soils are lower than the ones reported in this study, which would make clay an even weaker predictor of soil BSi than tree species composition. Nevertheless, future studies of soil BSi levels across different soil textures should incorporate both NaOH and Na_2CO_2 extractions to correct for this potential interference.

5. Temporal changes in soil biogenic Si, total nitrogen, and total carbon after 21 years of tree species composition change

5.1 Results

5.1.1. Changes of soil properties from 1998 to 2019

Soil BSi and total C only decreased in glacial till plots with a dominance of sugar maple. All three deposits had a significant decrease in soil N and a significant increase in C:N ratio. By pooling the three deposits to get an overall estimate of the changes for the entire sampled area, we observed significant decreases in soil BSi and total N and a significant increase in the C:N ratio (Table 4-3).

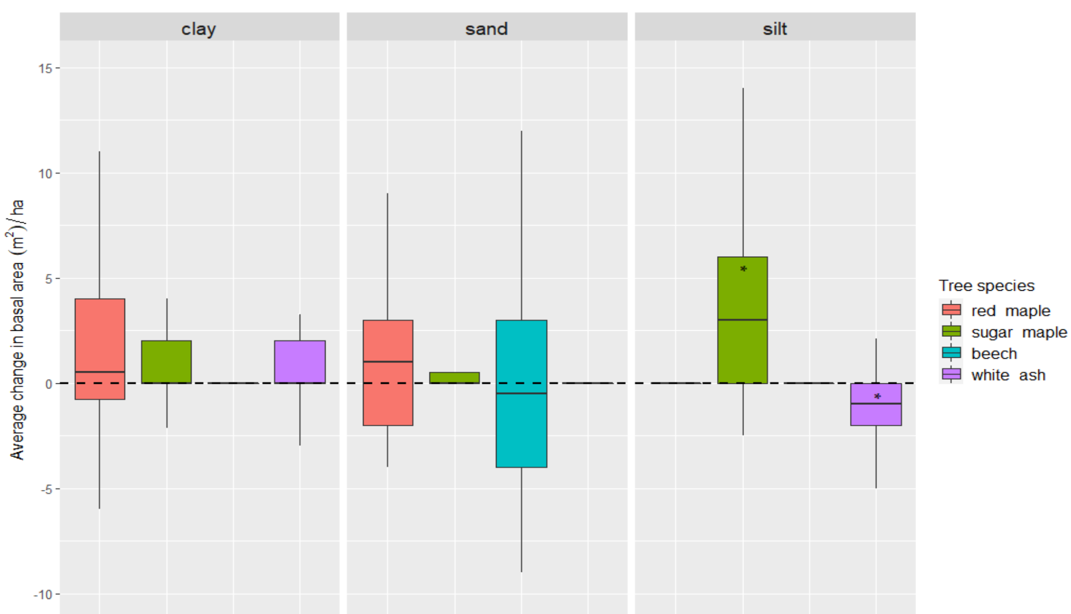
***Table 5-1** Comparison of soil parameters and basal area for sugar maple and white ash on different soil deposits for 1998 and 2019. (Mean ± SE) Significant differences are in bold; *** < 0.001, ** < 0.01, * < 0.05, ^ <0.1.*

Variable/Deposit	Lacustrine Clay Dominated by red maple		Fluvial Sand ridge Dominated by beech		Glacial Till. Dominated by sugar maple and white ash.		Entire forest	
Year	1998	2019	1998	2019	1998	2019	1998	2019
Biogenic silicon (mg/g)	7.7 (0.54)	7.4 (0.55)	5.8 (0.4)	5.5 (0.35)	**4.0*** (0.29)**	**3.0 (0.25)**	**5.1* (0.194)**	**4.5 (0.22)**
Carbon (mg/g)	4.6 (0.14)	5.4 (0.23)	3.5 (0.15)	3.8 (0.22)	**4.6*** (0.13)**	**3.8 (0.14)**	4.3 (0.09)	4.3 (0.11)
Nitrogen (mg/g)	**0.39** (0.03)**	**0.31 (0.02)**	**0.36** (0.08)**	**0.22 (0.01)**	**0.43*** (0.02)**	**0.29 (0.01)**	**0.42*** (0.03)**	**0.27 (0.008)**
C:N	**11.4*** (0.8)**	**15.5 (0.27)**	**13.9*** (1.7)**	**18.0 (0.39)**	**11.0*** (0.73)**	**14.4 (0.13)**	**12.1*** (0.53)**	**15.9 (0.23)**
Sugar maple (m^2/ha)/ distance	1.2 (0.82)	1.6 (0.8)	6.4 (1.3)	8.8 (1.4)	**9.1^ (1.2)**	**13.0 (1.6)**	6.9 (0.7)	9.3 (0.9)
White ash (m^2/ha)/distance	0.088 (0.001)	0.91 (0.17)	**2.2* (0.3)**	**1.6 (0.42)**	**3.5 (0.5)**	**2.2 (0.4)**	1.9 (0.26)	1.5 (0.2)

5.1.2 Species composition change

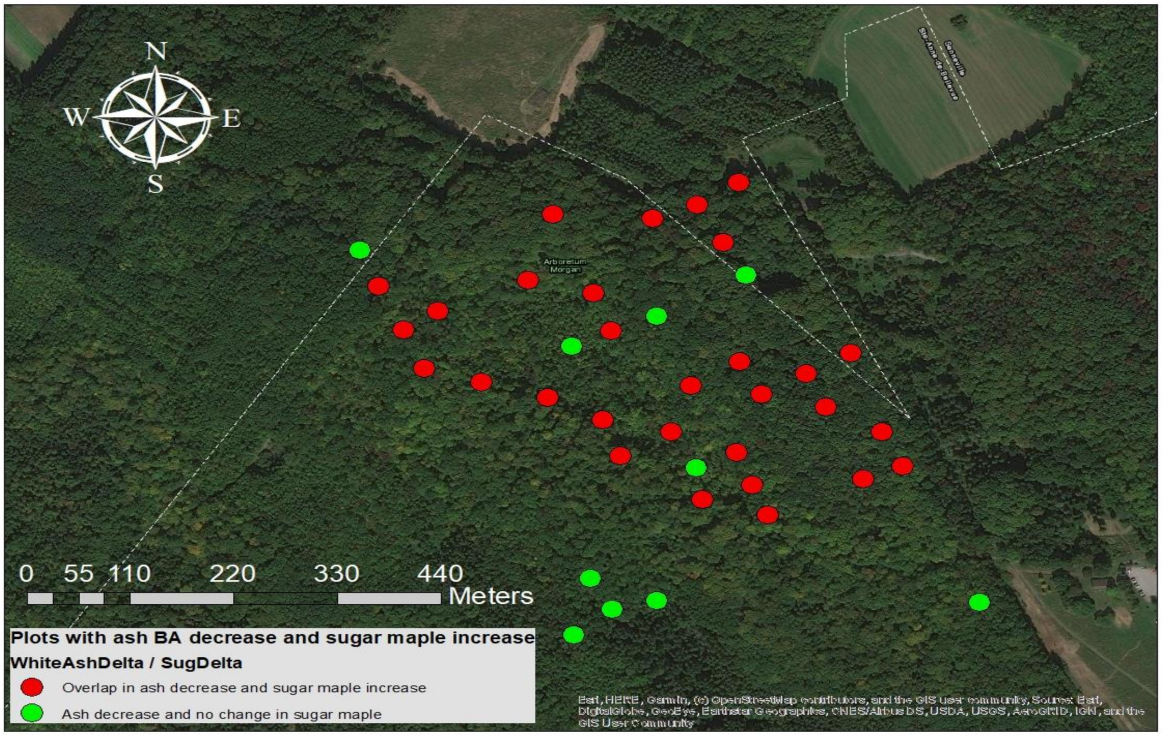
The only tree species to significantly decrease in basal area from 1998 to 2019 was white ash on the till deposit (*$p<0.05$*) (Figure 4-6). Sugar maple basal area increased on average by 43%, while most other species show changes not different than zero. Overall beech basal area did not change significantly over time on the sand deposit but great variability was observed among plots. Altogether, the sand deposit had the smallest increase in average tree basal area (0.18 m^2/ha) followed by clay (0.98 m^2/ha) and then till (1.11 m^2/h).

Figure 5-1 *Average change in tree basal area (BA) from 1998 to 2019 on the clay, sand and till deposits; significant differences for p < 0.05 indicated with an **



The increase in sugar maple basal area was generally concurrent with a decrease in ash basal area, with sugar maple basal area increasing in 31 out of the 41 plots that registered a decrease in white ash basal area (Figure 4-7).

Figure 5-2. *Image of the study area in the Morgan Arboretum showing plots where decrease in white ash overlapped with increase in sugar maple basal area. Red points represent plots with the overlap while green points represent white ash decrease but no increase in sugar maple. Every point indicates a plot.*

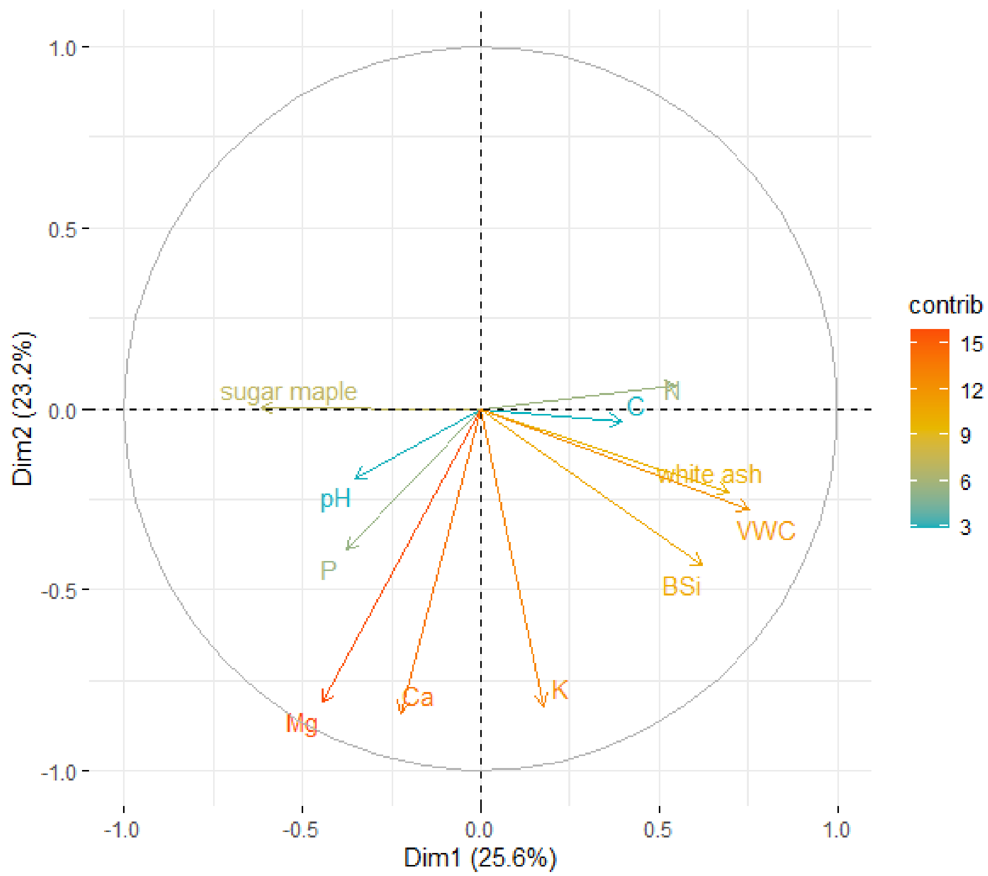


5.1.3 Study site factors associated with the change in soil biogenic silica.

The multivariate regression using site factors to predict the change of soil BSi (Annex 1) showed that only sugar maple and white ash basal area were significant descriptors of the variation in the change in soil BSi on the till deposit. The model described 28.5% of the change in soil BSi after 21 years.

The first two components of the PCA using only the deposit plots (Figure 4-8) described 48.8% of the variation. Among the most contributing variables for the first dimension was the change in basal area of sugar maple and white ash, the change in soil BSi and the volumetric water content (VWC) with loadings of -0.65, 0.7, 0.68 and 0.75, respectively. For the second dimension, the change in soil Mg was associated with the change in soil P and Ca.

Figure 5-3. *PCA showing the relationships between soil fertility parameters and species basal area change on the till deposit. Significant loadings (> 0.65).*

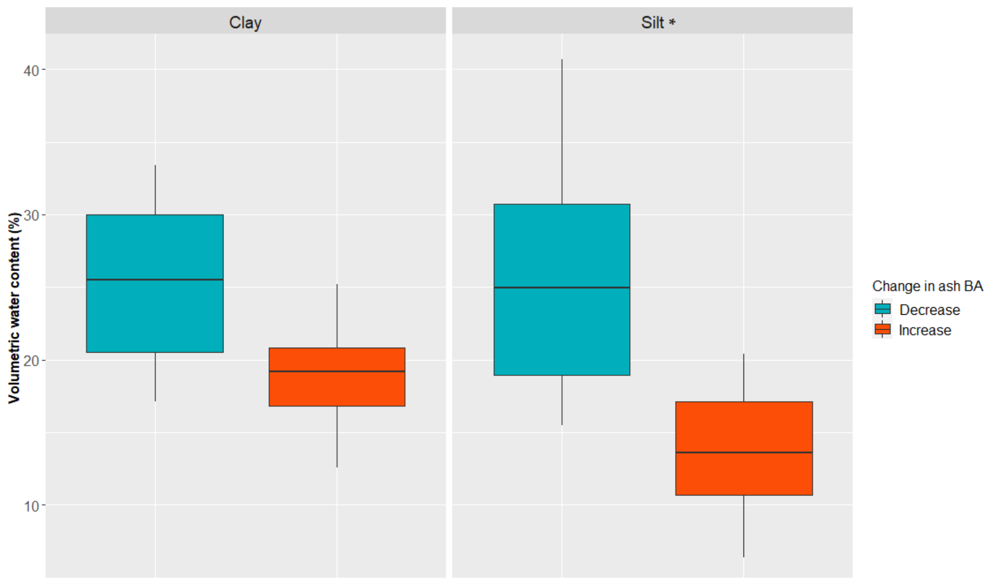


5.1.4 Differences between soil water content

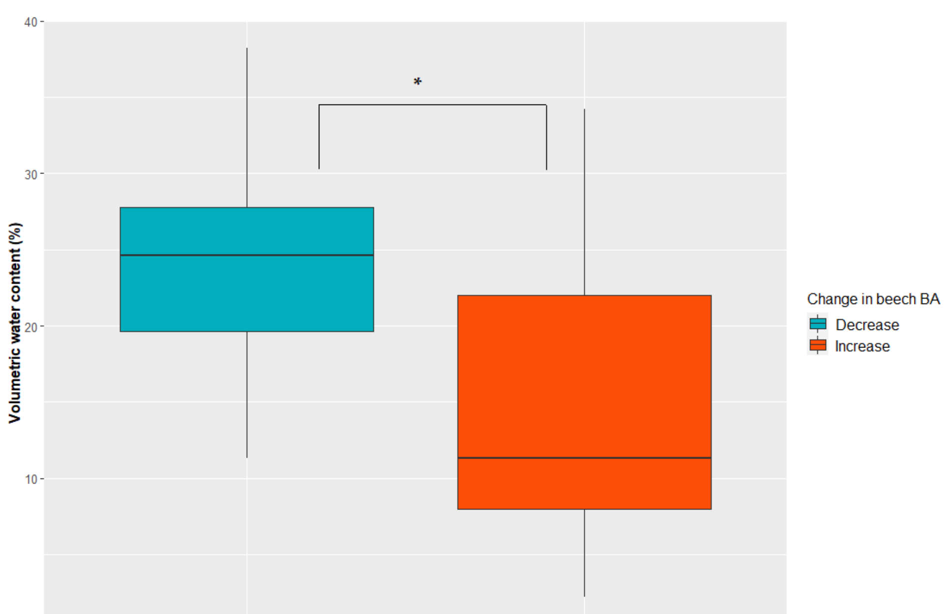
Plots on till with a decrease in white ash basal area (Figure 4-9. A) and plots on sand with a decrease in beech basal area (Figure 4-9. B) had a significantly higher soil water content compared to plots where the two species increased. The increases in water content on the clay deposit was not significant ($p = 0.07$)

Figure 5-4. Differences in volumetric water content in plots with either ash (A) or beech (B) mortality. Significant differences for p <0.05 indicated with an *

(A).



(B).

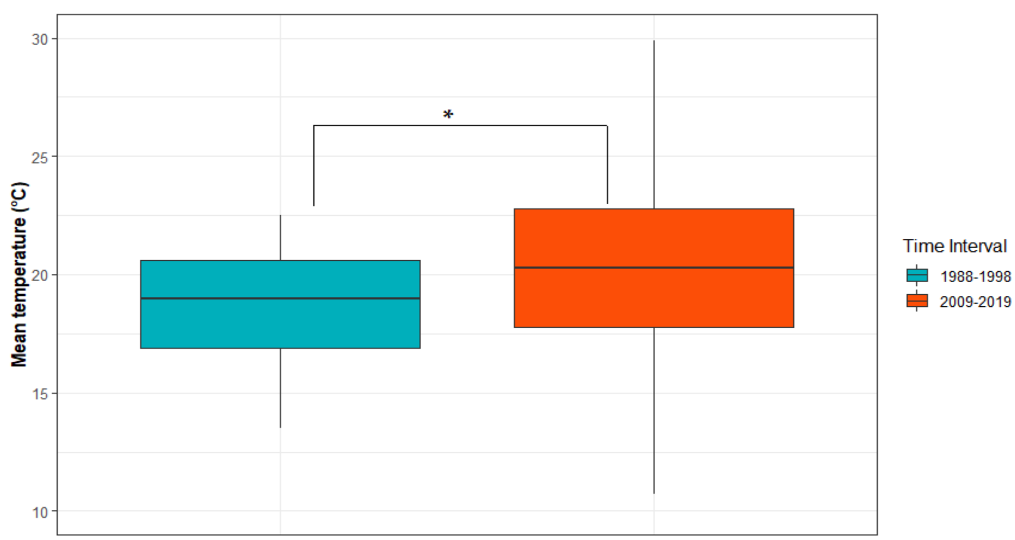


5.1.5 Change in average summer temperature and rainfall

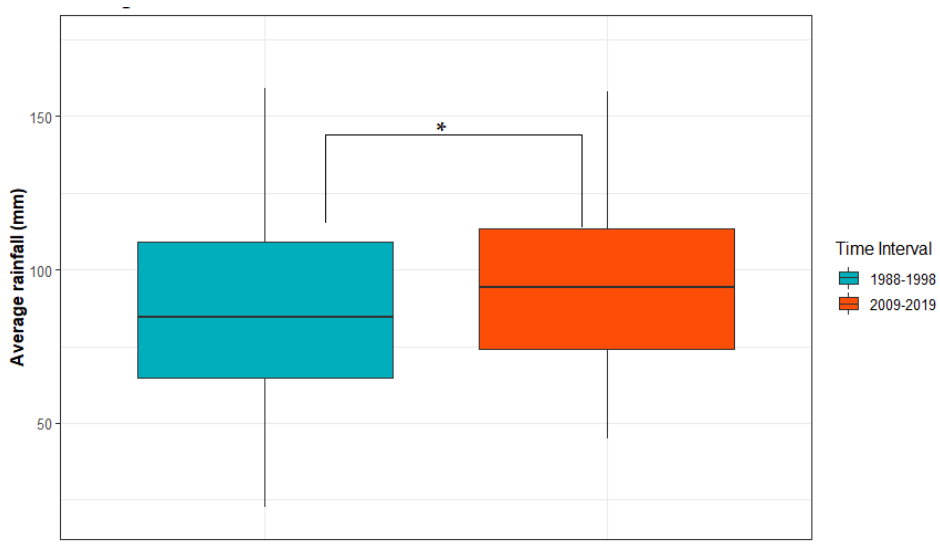
The mean summer temperature ten years before the first sampling season (1988-1998) differed significantly ($p = 0.02$) from the mean summer temperature ten years before the last sampling season (2009-2019) (Figure 4-10. A). Mean summer temperature increased 0.91°C, from 18.6 °C for the 1988-1998 decade to an average of 19.6 °C for the 2009-2019 decade. The average summer rainfall (Figure 4-10. B) increased from the first sampling decade to the second sampling decade ($p = 0.05$). Average summer rainfall increased an average of 18.8 mm, from an average of 85.9 mm for the 1988-1998 decade to 104.7 mm for the 2009-2019 decade.

Figure 5-5. Differences in mean summer temperature (A) and mean summer rainfall (B), ten years before the first sampling season and ten years before the last sampling season.

(A).



(B).



5.2. Discussion

5.2.1. Change in sugar maple and white ash basal area

Several studies have demonstrated that soil BSi can be lost from the ecosystem when subjected to forest cover changes such as sustained agricultural cultivation (Struyf et al. 2010), pasture sites (Clymans et al. 2011), and deforestation (Guntzer et al. 2011; Clymans et al., 2016;). However, my study suggests that smaller-scale changes, like changes in the dominance of sugar maple and white ash, can be enough to induce decreases in soil BSi.

Regarding the change in sugar maple dominance in the forest, several articles have reported that trees of the *Acer* genus frequently take over sites with high ash mortality, taking advantage of the resulting increased availability of light and water (Flower et al., 2013; Kolka et al., 2018). This is consistent with the significant increase in sugar maple's basal area measured in my study. In the previous section, we observed that the dominance of sugar maple, along with the sampling season and the many interacting variables in the till deposit, resulted in this deposit having the lowest soil BSi concentration since most BSi was already absorbed into tree tissue at the time of sampling.

Hence, an increase in sugar maple in 2019 would imply that larger amounts of soil BSi are being transferred from the soil to sugar maple tissue, suggesting that reduced soil BSi in 2019 is not due to BSi being lost from the ecosystem but rather because of increased immobilization in tree tissue.

Another possible explanation for the decrease of soil BSi in plots with high ash mortality is the lack of a concomitant increase in sugar maple. Ash mortality would initially lead to an increase in soil BSi since the decomposition of dead plant matter allows the release of the BSi stored in plant tissue. However, since there are no trees to uptake this released BSi, BSi can accumulate in the soil (Struyf & Conley 2012). With the increase in soil water content in plots with ash mortality, increased BSi leaching was likely, since increases in soil water content are known to leach surplus soil minerals that are not incorporated into plant tissue (Landbord, 1996; Sinha et al., 2018). Although we did not measure BSi in soil solution below rooting depth, it is relevant to consider the possibility of this happening in the Arboretum. Various reports of extended tree mortality in North American deciduous forests have shown that the increases in available soil Si following tree decomposition lead to Si building-up in soil and thus, its leaching (Struyf, et al., 2010; Clymmans, et al., 2011; Clymmans et al.,2016). Whether the reductions in soil BSi identified in this study can be attributed to the transfer of BSi from soil to sugar maple, to the removal of BSi from the ecosystem by leaching or to both mechanisms, it cannot be determined with the experimental design used. Regardless, our study highlights that a change in the proportion of biomass of only two tree species can affect soil BSi. It has been suggested that because of the large stocks of BSi in deciduous forest soils, detecting a change in soil BSi concentrations would require at least 15 years (Harmon et al., 2009; Geiwartzen, 2019). My results for 21 years of change in tree species composition and soil water content suggest that 15 years may indeed be enough to detect changes in soil BSi.

5.2.2. Change in American beech basal area

As seen in Figure 4-6, changes in beech basal area were characterized by large increases in some plots and large decreases in others. In turn, these extremes balanced each other out and did not allow the detection of any significant change in beech basal area after 21 years. If the decreases in basal area are attributed to beech mortality, the observed increases in basal area can be mainly attributed to the generation of root suckers, a vegetative reproduction mechanism in trees with aboveground mortality (Jones & Raynal, 1988). Beaudet & Messier (2008) reported that beech trees arising from root suckers develop faster than seedlings, growing up to 5 times faster. A faster growth rate, in turn, could explain why after 21 years of beech trees dying, the overall basal area of beech trees did not change significantly since tree suckers would have compensated the observed beech mortality. Like sugar maple, beech is an active Si accumulating species, and a change in beech composition would have possibly generated a change in soil BSi as was the case for sugar maple in the till deposit. However, given the lack of a significant change in beech basal area, no significant changes in soil BSi were detected.

5.2.3. Changes in soil N and water content

In contrast with the change in soil BSi, total N decreased in the entire study area after 21 years. Although decreases in total soil N can be attributed to many forest changes, several research articles have attributed N decreases in deciduous forests to species composition changes, increased soil water content, and the associated increase in nutrient leaching. (Landbord, 1996; Speight,2008; Kolka et al., 2011; Sinha et al., 2015).

The decrease in total soil N can be linked to a change in tree species composition. Significant increases in sugar maple dominance, like the one reported in this study, can lead to lower N retention in soils by favoring nitrate production, the form of inorganic N most susceptible to leaching (Lovett & Mitchell,2004). Despite high net nitrification and nitrate production rates, sugar maple does not readily take up nitrate, which leads to its build up in the soil profile (Rothstein et al. 1996; Templer 2001). Due to this nitrate build up, several research articles studying changes in sugar maple dominance in eastern North American forests have shown that increases in sugar maple can produce significant shifts in forest N cycling (Finzi et al. 1998a, Zak et al. 1999). For instance, research in the Catskill deciduous forest (NY, US) has shown that increases in sugar maple dominance are partially responsible for a 20-fold increase in nitrate leaching (Lovett et al. 2002). Furthermore, Mitchel et al., (2003) found that soils in the Adirondack forest (NY, US) experienced reduced soil N retention after increases in sugar maple mediated by decreases in beech competition in infected beech scale areas. Similarly, the increase in sugar maple population reported in this study due to decreased ash competition may have led to similar disturbances in the soil nitrogen retention and may have contributed to the detected decrease in total soil N.

The decrease in total soil N could also have been the result of an increase in soil water content. The mean summer rainfall between 2009-2019 increased by 15% when compared to 1988-1998 levels, an increase comparable with the Eastern United States rainfall trends reported by the American Meteorological Society (Peterson et al., 2013), and the 20-year prediction of increasing rainfall made by NASA (Easterling et al., 2017). Moreover, Schumacher and Johnson (2006) reported that 74% of all summer season extreme rainfall events in Easter North America occurred between 1999 and 2003. We also found that soil water content increased in plots with high tree mortality, corroborating the results obtained by Kappler et al. (2018), who observed that increased ash mortality increases the soil water content in deciduous forests due to less root competition and water uptake. Several authors suggest that the increases in soil water content caused by tree mortality are enough to increase nitrate leaching (Bayley et al. 1992; Nieminen 2004; Davis et al. 2019). However, this study's design does not permit the verification of whether the detected decrease in total soil N was due to increased N leaching since we did not measure N in soil solution. Still, there is ample evidence suggesting that significant changes in sugar maple's dominance can modify soil N retention. Hence, we argue that high nitrate concentrations caused by the significant increase in sugar maple and the increases in soil water content detected in this study should be further studied as they could be partially responsible for the detected decreases in total soil N.

5.2.4. Changes in temperature

Like soil BSi, total soil C decreased in the glacial till deposit after 21 years. It is widely acknowledged that many factors can cause a decrease in soil C. Factors like root respiration, leaf detritus, soil fauna and microbial decomposition of organic matter, which were not analyzed in this study, can all affect soil organic matter composition and dynamics (Davidson & Janssens, 2006). It is also known that when soil moisture is not limiting, increases in air/soil temperature can reduce soil C due to an increase in decomposition (D’Orangeville et al., 2015).

I suggest that the increased water availability brought by increases in precipitation and less root competition due to tree mortality would result in soil moisture being less limiting to decomposition in the Arboretum. Furthermore, air temperature for the period of the study showed that mean summer temperature increased 0.9 °C, an increase consistent with temperature increase trends reported by the NOOA for Eastern North America (Menne et al., 2018). Moreover, the increase in ash mortality on the till deposit probably generated several canopy gaps, leading to potentially even higher soil temperatures generated by the additional light reaching the forest floor. With these two factors increasing temperatures on the till deposit and the increase in soil water content, it is plausible that decomposition rates may have increased in the till deposit and resulted in the detected reduction in soil C. Similar reduction in soil C have been detected in Minnesota (Kolka et al., 2018), due to increased decomposition rates in ash forests affected by the emerald ash borer.

5.2.5. Change in soil C:N ratio

Leaf litter of ash tree species is widely acknowledged to be especially high in N compared to other hardwood species (Davis et al., 2019), leading to high litter turnover rates and greater soil N availability. Several authors observed that decreases in ash leaf litter inputs in forests with elevated ash mortality result in increases in soil C:N ratio, given the decrease in soil N (Herms et al., 2014; Kolka et al., 2018).

In contrast, beech and sugar maple trees have been found to have a leaf litter significantly lower in N compared to that of *Fraxinus* species (Vesterdal et al., 2008; Flower et al., 2013). It is therefore plausible that an increase in beech and sugar maple litter and a decrease in ash litter in the forest may have contributed to the increase in soil C:N ratio. Furthermore, as mentioned before, sugar maple increases probably mediated an increase in soil nitrate. Sibley et al. (2011) argue that an increase in non maple tree species in forests with ash mortality increases the vegetation uptake of nitrate and thus reduces the soil N leaching potential. However, the only significant increase in species in our study site was sugar maple. As stated before, despite sugar maple favoring the production of nitrate, it does not readily take up nitrate, promoting its build up and its leaching. An increase in sugar maple is thus related with overall reductions of soil N, which increase soil C:N ratio. Increases in C:N ratio can affect leaf litter decomposition and nutrient release from leaf litterfall. The latter will further impact soil BSi as changes in leaf litterfall decomposition will affect phytolith release into the soil, as previously mentioned.

6. Conclusions and summary

Understanding the processes that contribute to changes in soil BSi is of utmost importance due to BSi's role in promoting marine photosynthesis and regulating global carbon dioxide levels. Although thoroughly investigated in agricultural systems, few studies have evaluated the factors influencing the biogeochemical cycle of Si in a natural forest. The results obtained in this thesis pertain specifically to these factors influencing soil BSi and can be potentially incorporated into forest and land management plans, where different tree species, soil types, and soil properties can be considered to optimize soil BSi levels and cycling for the benefits of ecosystems.

6.1. Evaluating the effects of tree species and soil properties on soil biogenic Si

Active Si accumulating tree species are expected to uptake high amounts of dissolved Si. However, whether soil BSi is mostly influenced by tree species or by soil parameters is still not well understood. I hypothesized that soil BSi would be high under beech and sugar maple in a natural forest since they are active Si accumulating species, and that clay textured soils would have high BSi. Our results indicate that although beech and red maple had relatively high soil BSi, sugar maple was associated with low soil BSi. Furthermore, despite BSi being higher in the lacustrine clay deposit, soil texture was not the best BSi predicting factor. Finally, although we found that soil pH, Al, and tree species composition were all significant predictors of soil BSi, these variables are not independent and, in turn, depend on other factors like the soil deposit and parent material. Thus, the results obtained in this study suggest that to correctly estimate the amount of soil BSi at a given time of the year, the several interrelationships between pH, Al, tree species composition, and season sampling must be considered. Due to these interacting factors, sugar maple, despite being an active Si accumulating species, had the lowest soil BSi.

Given the various interacting factors that influence soil BSi, it is best to analyze it as an emergent property of the ecosystem. Thus, soil BSi is not necessarily high under active Si accumulating species in a natural ecosystem.

6.2. Temporal changes in soil biogenic Si, total nitrogen and total carbon after 21 years of tree species composition change

To my knowledge, this is the first study to estimate the effects of changes in the composition of tree species in a temperate forest on soil BSi. In this study, I measured changes in soil BSi, total C and N over a twenty-one-year period to assess the effect of climate change and increased tree mortality associated with novel insects and diseases on these key soil constituents.

I found evidence supporting my initial hypothesis, as soil BSi and C decreased on the till deposit, which was the only deposit where species composition changed. Changes in soil BSi were not significant in the clay or sand deposits, which also had smaller tree basal area changes. Thus, I attributed the changes in soil BSi to an increase in BSi uptake by sugar maple. Although not measured in this study, I suspected an increase in BSi leaching in plots with increased ash mortality and no sugar maple replacement, since this phenomenon has been reported extensively in forests with extended aboveground mortality. Similarly, I argue that soil C decreased due to canopy gaps left by dying or dead ash trees, increases in mean summer temperatures, and the higher soil water content in the till deposit. These factors probably enhanced decomposition rates and generated the detected decrease of soil carbon in the till deposit. Finally, I observed a generalized decrease in soil N for the entire study area. These decreases in soil N were attributed to an increase in sugar maple, which has reiteratively been shown to decrease the soil's N retention by increasing nitrate production, the form of inorganic nitrogen most susceptible to leaching. This study's results corroborate other studies that have reported that large forest cover changes reduce soil BSi and soil total N levels. However, my results suggest that changes in only two tree species can also generate significant effects on the terrestrial Si cycle, with twenty-one years being sufficient to detect significant decreases in soil BSi. Hence, tree mortality associated with invasive pest species that target specific tree species can have a stronger effect than previously thought. It is essential to explore these effects further since modifications to the terrestrial Si cycle will impact exports of Si to water bodies, with repercussions to global carbon dioxide levels. With atmospheric carbon levels far from being in decline, monitoring factors that increase selective tree mortality and its repercussion on soil N, C, and BSi will be needed.

Annex

1. Regression coefficients of the regression of the change of soil BSi between 1998 and 2019.

	Coefficient	p value
Intercept	1.14	0.019
Ca	0.426	0.56
K	4.4	0.51
Mg	-3.8	0.22
P	0.25	0.10
pH	-0.202	0.63
C	0.14	0.42
N	0.202	0.109
sugar maple	-0.131	0.005
white ash	0.171	0.006
$r^2 = 0.24$ p value=0.002		

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