

The Response of Soil Organic Carbon to Climate Change and Potential to Increase
Carbon Sequestration in Soils through Management

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Abstract

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As the largest terrestrial carbon pool, changes in soil carbon pools in response to climate change or management practices have the potential to significantly impact atmospheric CO₂ concentrations. This dissertation examines the effects of climate change and two management strategies on soil carbon pools in order to understand how soil carbon storage might change under these conditions. Changes in soil carbon concentrations were studied in a Danish heath/grassland exposed to elevated CO₂, summer drought, and warming. Soil carbon was observed to increase significantly over the course of 8 years in the presence of elevated CO₂, regardless of the addition of warming or drought treatments. Soil carbon pools at this site are therefore likely to serve as a negative feedback to increasing atmospheric CO₂ concentrations. To

examine how management strategies could take advantage of the potential for soils to be used as a carbon sequestration tool, this dissertation also investigated the effects of two types of management practices on soil carbon dynamics. In a Pacific Northwest Douglas-fir stand, deep soil carbon storage was shown to increase when competing vegetation was not controlled, presumably due to deeper Douglas-fir rooting in response to competition for more shallow soil moisture reserves. In an incubation study, applying olivine with the goal of increasing soil pH and capturing CO₂ resulted in decreased decomposition of organic matter compared to the application of agricultural lime. There was no difference in CO₂ flux between the olivine amended and control samples, whereas the CO₂ flux from the limed samples was 221% higher than the control. The application of olivine also increased soil pH to a level sufficient to overcome aluminum toxicity. The use of olivine as an alternative to lime would therefore significantly reduce agricultural CO₂ emissions. The results of this dissertation suggest that not only is there potential for increasing soil carbon stocks to serve as a negative feedback to rising atmospheric CO₂ concentrations, but that an opportunity also exists to design management practices that utilize soils as a climate change mitigation tool.

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Chapter 1. INTRODUCTION

Continually increasing anthropogenic CO₂ emissions have elevated atmospheric concentrations far above the level at which it is possible to maintain climatic conditions comparable to those to which human civilization and present day ecosystems are adapted (Hansen et al., 2008). Current atmospheric CO₂ concentrations are predicted to result in drastic changes in climate across the globe, with far reaching implications for vulnerable populations, ecosystems, and food security. Soils comprise the largest terrestrial carbon pool, containing more carbon than both the atmosphere and terrestrial biomass combined (Eswaran et al., 1993; Sundquist, 1993; Jobbagy and Jackson, 2000; Rustad et al., 2000; Scharlemann et al., 2014). As such, the effects of climate change and management practices on soil carbon pools have the potential to significantly impact atmospheric CO₂ concentrations. As concentrations continue to rise, the need to improve our understanding of the role that soil carbon plays in the global carbon cycle and how we can manipulate natural processes to increase soil carbon storage is becoming increasingly urgent. In order to develop accurate predictions of future climatic changes, it will be necessary to determine the direction of soil carbon feedbacks to increasing atmospheric CO₂ concentrations. Such predictions are critical to the development of effective management strategies to improve resilience and mitigate climate change.

Soil organic carbon content is controlled by the balance between the rate of accumulation through plant inputs and microbial decomposition of soil organic matter (Kirschbaum, 2000; Pendall et al., 2004). The effects of climate change and elevated CO₂ are likely to impact both of these processes. The direction of the balance between these two impacts will determine if soils

will serve as a positive or negative feedback to increasing atmospheric CO₂ levels (Kirschbaum, 2000).

Land management, another common driver of changes in soil organic matter, has often been proposed as a mechanism for sequestering carbon (Post and Kwon, 2000). Both agriculture and forestry have been shown to induce changes in soil organic matter (Johnson and Curtis, 2001; Guo and Gifford, 2002), and careful implementation of management practices to maximize soil carbon storage will likely play a key role in counteracting increased atmospheric CO₂ concentrations.

Though management aimed at increasing soil organic matter is the most conventional method of using soils as a tool to sequester carbon, there has recently been increased interest in using soils to enhance mineral weathering, thereby creating a sink for inorganic carbon (Schuiling and Krijgsman, 2006; Köhler et al., 2010; Renforth, 2012; Hartmann et al., 2013). The weathering of silicate minerals naturally consumes CO₂, and the rate at which this process occurs could be enhanced by grinding silicate minerals to increase their surface area then applying them to acidic soils. As the weathering of these minerals in the soil environment may also increase soil pH, silicate minerals could therefore be used as a replacement for agricultural lime (Soldal, 2015). However, proponents of this method have failed to consider that increasing pH can also increase decomposition rates (Neale et al., 1997; Kemmitt et al., 2006), rendering it necessary to evaluate the effects of silicate mineral applications on soil organic matter in addition to assessing the amount of inorganic carbon this process has the potential to sequester.

The purpose of this research is to investigate the role that soil carbon pools and management of them play in the global carbon cycle's response to increasing CO₂ emissions. To address these questions in part, this dissertation examines the effects of a multi-factor climate change

experiment on soil carbon in a Danish heathland and the impacts of two management strategies on soil carbon. This dissertation is divided into three chapters, aimed at investigating the following questions:

1. How have soil carbon pools in a Danish heathland responded to experimental climate change treatments mimicking predicted future conditions at the site over the course of 8 years?
2. How do biomass removal and vegetation control treatments affect deep soil carbon pools in a highly productive Pacific Northwest Douglas-fir forest?
3. How does the application of olivine, an abundant silicate mineral, affect soil organic matter decomposition? What is the net effect of silicate dissolution in the soil environment on carbon storage?

These questions were addressed through analyses of soil carbon concentrations after *in situ* exposure to experimental climate change and forest management treatments and an incubation study to examine the effects of silicate mineral applications on soil carbon flux.

Chapter 2. PROGRESSIVE INCREASES IN SOIL CARBON STORAGE UNDER ELEVATED CO₂ ARE NOT IMPACTED BY DROUGHT OR WARMING IN A TEMPERATE HEATHLAND

Abstract: Changes in soil carbon pools in response to elevated CO₂ or changing climatic conditions have the potential to significantly impact atmospheric CO₂ concentrations. In order to investigate the effects of climate change on soil carbon, we treated a Danish heath/grassland ecosystem with elevated CO₂ (eCO₂), warming, and summer drought, both individually and in combination. The full combination of these treatments represented expected climate conditions in Denmark in 2075. Drought was the only significant main effect, but we suspect that pretreatment differences were responsible for the observed increase in soil carbon with drought. The effect of eCO₂ grew significantly over the course of the experiment- after 8 years soil carbon had increased by 56.2% with the application of eCO₂. The increase in soil carbon in response to CO₂ was not significantly modified by the addition of warming or drought. Warming significantly decreased soil carbon as a single factor effect, but the addition of eCO₂, which will inherently accompany a warming climate, nullified this effect. We therefore do not expect warming to affect soil carbon at this site in the future. We therefore expect that increases in soil carbon storage at this site will serve as a negative feedback to increasing atmospheric CO₂ concentrations under future climate conditions.

2.1 INTRODUCTION

As the largest terrestrial carbon pool (Eswaran et al., 1993; Sundquist, 1993; Jobbagy and Jackson, 2000; Rustad et al., 2000; Scharlemann et al., 2014), changes in soil carbon (C) stocks due to elevated CO₂ and associated changes in climate have the potential to significantly impact atmospheric CO₂ concentrations. The effects of climate change on soil C will depend on the balance between these effects on the rates of C accumulation through plant inputs and microbial decomposition of soil organic matter (SOM) (Kirschbaum, 2000; Pendall et al., 2004). Increased plant inputs combined with lower microbial respiration could induce a negative feedback to increasing atmospheric CO₂ concentrations. Alternatively, reduced plant inputs or enhanced microbial respiration could contribute to a positive feedback cycle, releasing large amounts of C to the atmosphere and exacerbating the effects of climate change. In order to accurately predict future climate impacts, it is critical to understand the role that soil C pools will play in the global C cycle under changing conditions.

In spite of this, soil C has often been neglected in experimental investigations of the effects of climate change as sampling is both expensive and time consuming (Ni et al., 2017). Many of the studies that did investigate soil C have produced inconclusive results due to insufficient power in their experimental design to detect small differences given the large inherent variability in soil C concentrations (Hungate et al., 1996, 2009; Ross et al., 2006; Lichter et al., 2008). Additionally, few of these studies investigated the combined impacts of multiple interacting global change drivers on soil C (Ni et al., 2017; Yue et al., 2017). As the effects of climate drivers such as elevated CO₂, warming, and summer drought are not always additive (Larsen et al., 2011; Dieleman et al., 2012), investigating their interactions is crucial to understanding the role soil organic carbon (SOC) will play in driving atmospheric CO₂ concentrations.

Elevated CO₂ is predicted to “fertilize” plant biomass production by improving plant water use efficiency (Kirschbaum, 2000; Brevik, 2012). There is evidence that much of the additional biomass produced will be allocated belowground in order to access nutrients necessary for increased plant growth (Bassirirad et al., 2001). Stimulation of root biomass by elevated CO₂ (eCO₂) has been observed by a number of studies (Adair et al., 2009; Jackson et al., 2009; Anderson et al., 2010), resulting in additional inputs to soil C pools.

However, these additional inputs of labile organic matter under eCO₂ may stimulate microbial activity, resulting in a priming effect. Priming is the additional mineralization of SOC caused by stimulation of microbial activity in response to the addition of easily decomposable organic substrates (Dalenberg and Jager, 1989; Kuzyakov et al., 2000; Blagodatskaya and Kuzyakov, 2008). The degree to which priming occurs may help explain the contradictory results of studies on soil C response to eCO₂. Soil C losses under eCO₂ may also be induced by increases in soil moisture due to improved plant water use efficiency (Pendall et al., 2003).

Some studies have found that the combination of increased decomposition and plant inputs under eCO₂ results in faster turnover of SOM, but little change in overall soil C storage (Hofmockel et al., 2011). In contrast, several meta-analyses have indicated that eCO₂ is likely to increase soil C, though this impact is greater when high nitrogen availability is maintained, as in fertilized agricultural systems (Jastrow et al., 2005; De Graaff et al., 2006; Luo et al., 2006; van Groenigen et al., 2006; Hungate et al., 2009; Yue et al., 2017). In natural systems, the potential for continual stimulation of plant inputs with eCO₂ may be restricted by progressive N limitation (Luo et al., 2004).

Plant growth and microbial activity are also expected to be stimulated by warming, assuming that increased temperatures do not induce moisture limitation (Kirschbaum, 2000).

Under warmer conditions, increases in the rates of enzyme-mediated reactions allow for accelerated mineralization of SOM (Conant et al., 2011), which can in turn support increased plant growth by making nutrients more available (Melillo et al., 2011). Warming also tends to lengthen the growing season, allowing for increased plant growth to occur over a longer period of time (Rustad et al., 2001; Dieleman et al., 2012). However, though warming may increase plant biomass overall (Rustad et al., 2001), the production of fine roots might decrease in response to increased nutrient availability, thus negatively impacting SOC (Melillo et al., 2011). The results of two meta-analyses indicate that soil C across the globe will decrease with increasing temperatures (Crowther et al., 2016; Yue et al., 2017), suggesting that decomposition of SOM is more sensitive to changes in temperature than net primary productivity.

The impact of warming over the long term will depend on if these changes in microbial processing of SOM remain consistent over time. A number of studies have observed that the enhanced respiration that occurs at the beginning of warming experiments does not continue indefinitely. This reduction in respiration may be due to thermal adaptation of microbes over time (Bradford et al., 2008), the reduction of labile substrates (Tingey et al., 2006; Hartley et al., 2007), or both processes concurrently (Bradford et al., 2008). However, the time frame over which these processes occur is unclear, and will likely vary based on site properties and soil C stabilization mechanisms (Davidson and Janssens, 2006). In one case, respiration was still elevated after 9 years of warming with no evidence of thermal adaptation or substrate depletion (Schindlbacher et al., 2015).

By contrast, lower soil moisture under drought conditions is expected to decrease microbial activity (Jensen et al., 2003), plant growth (Penuelas et al., 2007), and root activity (Borken et al., 2006). Thus far, drought has been observed to reduce turnover of soil C (Prior et

al., 2008; Sardans et al., 2008), but it has not been shown to have a significant effect on the total C pool (Prior et al., 2008; Froberg et al., 2009; Cleveland et al., 2013; Khalili et al., 2016; Yue et al., 2017).

Interactions between the effects of drought, warming, and eCO₂ are hard to predict, as combining treatments may either enhance or dampen their effects compared to single-factor treatments. For example, increased plant water use efficiency under eCO₂ may counteract drying effects of other treatments. In the case of warming combined with eCO₂, this could result in further stimulation of both microbial activity and NPP. This stimulation of microbial activity may counteract N limitations that can develop under eCO₂ by allowing for increased mineralization of SOM (Dieleman et al., 2012). It is unclear how these effects would balance out over a longer growing season, and few studies have investigated the combination of these two treatments (Dieleman et al., 2012). Alternatively, the combination of warming and drought could exacerbate dry conditions, mitigating any stimulating effect of warming on microbial activity or plant growth and further reducing turnover. The effects of the combination of eCO₂, warming, and changes in precipitation are hardest to predict, but will most closely represent the response to future climate conditions.

Though the effects of eCO₂ and warming can vary over time (Luo et al., 2004; Bradford et al., 2008), the majority of studies use only a single measurement point at the end of the experiment to examine differences in soil C under these treatments. Results may therefore be dependent on the duration of the experiment, which on average is less than 4 years (De Graaff et al., 2006; van Groenigen et al., 2006). Longer study periods may be necessary to account for the effects on C pools with slower turnover rates, which may result in more permanent shifts in

SOC. Additionally, the strong interannual variability of rapid cycling C pools may also skew results when single measurements are used (Pendall et al., 2011).

The CLIMAITE experiment was designed to examine the effects of climate change on a mixed heath and grassland ecosystem using a unique, multi-factor approach that allows for the determination of the effects of warming (T), drought (D), and eCO₂, both individually and in combination (Mikkelsen et al., 2008). Previous results from the CLIMAITE experiment indicate significant differences between the effects of combined vs. single factor manipulations on rooting (Arndal et al., 2013, 2014, 2018), aboveground biomass production (Kongstad et al., 2012), photosynthetic activity (Albert et al., 2011a; b), C and N cycling (Nielsen, submitted; Larsen et al., 2011) microbial abundance and growth (Andresen et al., 2010; Haugwitz et al., 2014), and soil respiration (Selsted et al., 2012). As single factor effects are not necessarily additive, it is the full combination of treatments that will give the most accurate representation of future climate scenarios. In order to examine the potential for climate-induced changes in soil C pools to serve as a feedback to increasing atmospheric CO₂ concentrations, we compared treatment effects on soil C concentrations over time.

2.2 METHODS

2.2.1 *Site Description*

This research was conducted at the CLIMAITE experimental site at Brandbjerg, located approximately 50 km NW of Copenhagen, Denmark (55°53' N, 11°58' E). The site is a dry heath/grassland ecosystem dominated by two perennial species, a wavy hair-grass (*Deschampsia flexuosa* (L.), c. 70% cover) and an evergreen dwarf shrub (*Calluna vulgaris* (L.), c. 30% cover). The experimental plots are situated on a hilly, nutrient-poor, sandy moraine from the Weichsel glaciation. Soils at the site are Cambic Arenosols with relatively low cation exchange capacity,

weak signs of podsolization, and a $\text{pH}_{\text{CaCl}_2}$ in the topsoil of 3.3 increasing to 4.5 in the B-horizon. These well-drained soils are 71.5% sand, 20.5% coarse sand, 5.8% silt and 2.2% clay (Nielsen et al., 2009). The well-defined O-horizon above the mineral soil is approximately 2-5 cm thick. The site annually receives 613 mm of rainfall on average, and the mean annual air temperature is 8 °C (Danish Meteorological Institute, 2009, <http://www.dmi.dk>). Bulk atmospheric nitrogen deposition at the site is relatively low; in 2007 the site received $1.35 \pm 0.04 \text{ g N m}^{-2} \text{ y}^{-1}$ (Larsen et al., 2011).

2.2.2 *Experimental Treatments*

The Danish Meteorological Institute has predicted that in the year 2075, Denmark will experience atmospheric CO_2 concentrations elevated to 510 ppm with air temperatures increasing by 2 °C; heavier summer droughts and winter rainfall are expected, resulting in little change in total annual rainfall (Danish Meteorological Institute, 2009, <http://www.dmi.dk>). The experimental treatments implemented at this site were designed to mimic these predicted climatic changes, with the exception that winter rainfall was not modified. This experiment instead focused on the effects of prolonged summer drought in combination with both eCO_2 and warming.

The implementation of the eCO_2 and warming treatments began in October 2005, and the first prolonged summer drought was imposed in July 2006. Free air carbon enrichment (FACE) treatments were used to increase atmospheric CO_2 concentrations to a target value of 510 ppm. The FACE treatments were employed from dawn until dusk and switched off overnight and during periods of complete snow cover.

Passive night-time warming was achieved by the use of curtains that reflected infrared radiation back to the soil surface and vegetation. These were employed from dusk until dawn

throughout the year, but removed during periods of rain, high winds, and severe frost. The warming treatments increased night-time air temperatures by 0.6 and 1.3°C in the summer and winter months respectively. Night-time soil temperatures at a depth of 5 cm were increased by 0.7°C in the summer and 0.3°C in the winter. Averaged across night and day time measurements, the warming treatments increased soil temperatures by 0.4°C in the summer and 0.2°C in the winter. The warming treatment also had the effect of increasing the growing season by two weeks in the spring (Kongstad et al., 2012) and reducing soil moisture relative to the control.

Droughts were induced once or twice a year in the spring or summer by use of a rainfall exclusion curtain during rain events. Drought periods continued until the soil water content fell below 5% in the upper 20 cm of the soil profile as determined by TDR probes, at which point re-wetting was allowed in order to maintain soil moisture slightly above the wilting point of vegetation at the site. Drought periods typically lasted between 1-5 weeks, which is within the range of naturally occurring summer droughts at the site. Mean annual soil moisture was significantly reduced by the drought treatment over the course of the experiment. However, because re-wetting was allowed, the significant drying effect observed when the treatment was applied was not consistent throughout the growing season (Selsted et al., 2012).

2.2.3 *Experimental Design*

Treatments at the site consisted of a full factorial combination of eCO₂, warming, and periodic summer drought (Figure 2.1). Six blocks contained pairwise combinations of 12 octagons. In each block one octagon received eCO₂ (CO₂), whereas the other did not. Each octagon was 7 meters in diameter and divided into four subplots: control, warming (T), summer drought (D), and combined warming and drought (TD). There were therefore 6 replicates of each of the three individual treatments (T, D, CO₂), their combinations (TD, TCO₂, DCO₂, TDCO₂),

and a non-treated control (A) for a total of 48 treatment plots. The full factorial treatment (TDCO₂) simulates the predicted future climate conditions at the site. A full description of the experimental setup can be found in Mikkelsen et al. (2008).

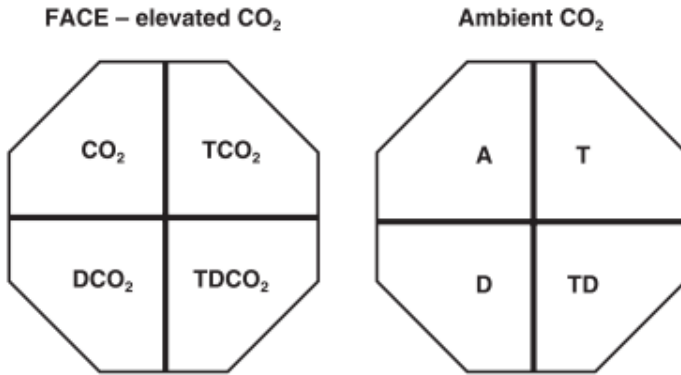


Figure 2.1: Schematic presentation of a block with two separate octagons, receiving elevated CO₂ and ambient CO₂, respectively, and together hosting all eight treatment combinations with elevated CO₂ (CO₂), warming (T), drought (D), and untreated control (A). Reproduced from Mikkelsen et al. (2008).

2.2.4 *Sampling and Analyses*

Soil samples were collected three times over the course of 8 years from the upper 30 cm of the soil profile. Samples were taken in all experimental plots, for a total of 48 samples per depth interval. As these samples were collected for a variety of experimental purposes, soil-sampling intervals varied. A full description of the sampling depth intervals and sampling dates can be found in Table 2.1.

Table 2.1: Sampling depth intervals and dates

Sampling Date	Months after Installation*	Depth intervals (cm)
July, 2007	22	0-5, 5-10, 10-30
Nov., 2011	74	0-10, 10-20, 20-30
June, 2013	93	0-10, 10-30

*Though the eCO₂ and warming treatments were installed in October 2005 (Month 1), the first summer drought treatment was not applied until July 2006 (Month 10).

In July 2007, soil samples were taken during the installation of minirhizotrons (Arndal et al., 2018). These samples were taken by augering at a 45° angle. Fourteen samples were lost from this dataset in the 0-5 cm depth interval, but these missing samples were fairly evenly distributed across treatments. One entire warmed profile was removed from the July 2007 data since plant material was suspected to have contaminated the samples from this plot during the sampling process. In November 2011 soil cores were taken as part of a ¹³C labeling experiment (Nielsen, 2015), and in June 2013, soil samples were taken using a soil column cylinder auger (Eijkelkamp Agrisearch Equipment BV, Giesbeek, The Netherlands) with an inner diameter of 87 mm attached to a gasoline powered percussion hammer (Cobra Combi, Atlas Copco AB, Nacka, Sweden).

All samples were sieved to 2 mm. Fine roots were hand-picked with forceps from the July 2007 samples for comparison in Arndal et al., 2018, but roots that passed through the 2 mm sieve were allowed to remain in the samples from 2011 and 2013. Samples were oven dried at 55° C and homogenized by ball-milling. Carbon concentration of the samples from 2007 and 2013 were determined using an EA Flash 2000 elemental analyzer (Thermo Fisher Scientific) and the samples from 2011 were analyzed using a Eurovector CN elemental analyzer.

2.2.5 *Statistical Analyses*

A linear mixed effects model (“lme” in the “nlme” package in R Version 3.2.3) was used to test the effects of treatments on soil C concentration over time (Pinheiro & Bates, 2000). Treatments, CO₂, T, and D, along with time and depth, were included as fixed effects in a full-factorial statement. Time was represented by the number of months passed since the implementation of the treatments (Table 2.1), and was included in the model as a categorical variable. The midpoint of each depth interval was used to represent the depth of that interval in

the model. For example, the 5-10 cm depth interval was included in the model as a depth of 7.5 cm, whereas the 0-10 cm depth interval was included as a depth of 5 cm. A nested random intercept term, with Plot nested within Octagon nested within Block, was used to account for the experimental design and the repeated measures within each profile.

Prior to analysis, C concentration data were log transformed to decrease heteroscedasticity. This transformation improved the residuals of the model, which were inspected using a residual plot and normal QQ plot. Using a log transformed depth variable also improved residuals and the model as a whole as tested by model comparison using Akaike's Information Criteria. Heterogeneity of variances was further corrected by using the varIdent variance structure (nlme) to allow variances to differ at each depth interval.

Differences of least square means ("lsmeans" in R) were used to interpret significant interactions ($\alpha = .05$). Values were back-transformed from the log scale to give concentration means.

Results are graphed as both concentrations and C pools in order to more clearly present treatment effects, which are somewhat obfuscated by differences in sampling depths from month to month. The differences in sampling depths artificially decrease soil C in Month 74 when concentration data are plotted because there were more measurements in deeper intervals relative to the other months. To better illustrate changes in C with treatment, total C pools were calculated for plotting purposes, but not used for any statistical analyses. Total C pools were calculated for each profile using bulk density values from a pre-experiment description of the soil profile. Missing data points from the upper 0-5 cm interval of Month 22 were point filled for pool calculation by averaging across the other plots from that treatment combination. Though

total pools are plotted, all analysis and results are based on soil C concentration. Results are presented as concentration means \pm standard error of the mean.

2.3 RESULTS

Drought, which was the only treatment that was significant as a main effect, increased soil C concentration from 16.31 ± 0.85 %C to 19.04 ± 1.14 %C ($p = 0.0012$) (Figure 2.2, Table 2.2). The effect of drought did not change over time: both the drought and non-drought plots increased at the same rate throughout the experiment, and the initial increase with drought is suspected to be due to pretreatment differences. As a single factor effect, drought was not significant and did not increase soil C over the control plots.

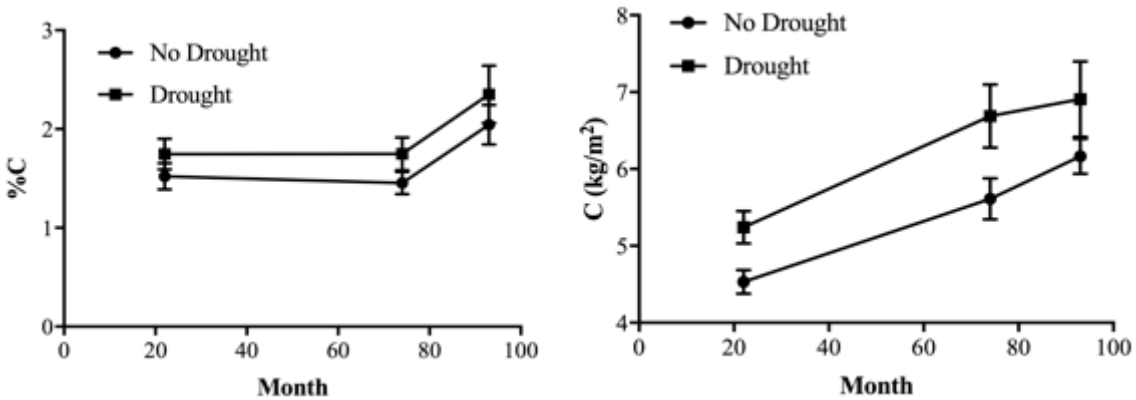


Figure 2.2: Mean soil C concentration (left) and soil C pools (right) with and without drought over time. Error bars indicate standard error.

Table 2.2: Treatment means and standard errors of the means along with main, single factor, and interactive effects.

Treatment	Mean \pm SEM %C	Main Treatment Effects	Single Treatment Effects	Interactions	Interactions with Time
A	1.736 \pm 0.175				
D	1.752 \pm 0.179	0.0012			
T	1.439 \pm 0.158		0.0097		
CO ₂	1.641 \pm 0.168				<0.0001
DT	1.631 \pm 0.177				
DCO ₂	2.018 \pm 0.231				
TCO ₂	1.699 \pm 0.176			0.0051	
DTCO ₂	2.203 \pm 0.302				

Plots treated with eCO₂ significantly increased in soil C concentration over time compared to ambient plots ($p < 0.001$) (Table 2.2). By the end of the study, the addition of eCO₂ had resulted in a significant increase in soil C from 18.61 ± 1.74 %C under ambient CO₂ to 25.35 ± 3.01 %C under eCO₂ ($p = 0.0341$) (Figure 2.3, Table 2.3). Though soil C increased in both ambient and eCO₂ plots over the course of the experiment, the 56.2% increase in the eCO₂ plots was much greater than in the 11.7% increase in the ambient plots.

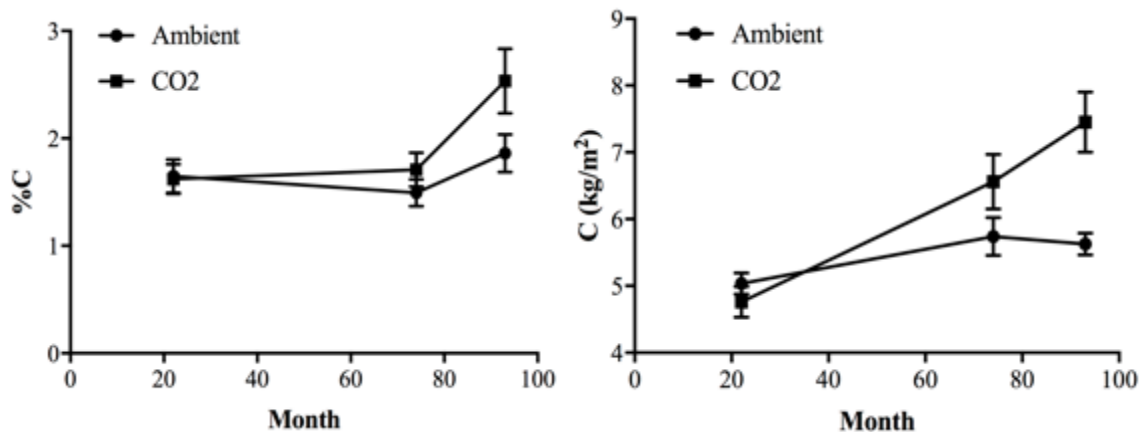


Figure 2.3: Mean soil C concentration (left) and soil C pools (right) with and without elevated CO₂ over time. Error bars indicate standard error.

Table 2.3: Effects of CO₂ by Month

	Ambient %C	CO ₂ %C	P value
Month 22	1.648 ± 0.156	1.622 ± 0.138	
Month 74	1.493 ± 0.125	1.709 ± 0.158	
Month 93	1.861 ± 0.174	2.535 ± 0.301	0.0341

Warming was not significant as a main factor, nor did it interact with time (Figure 2.4).

As a single factor warming significantly decreased soil C ($p = 0.0097$) (Table 2.2).

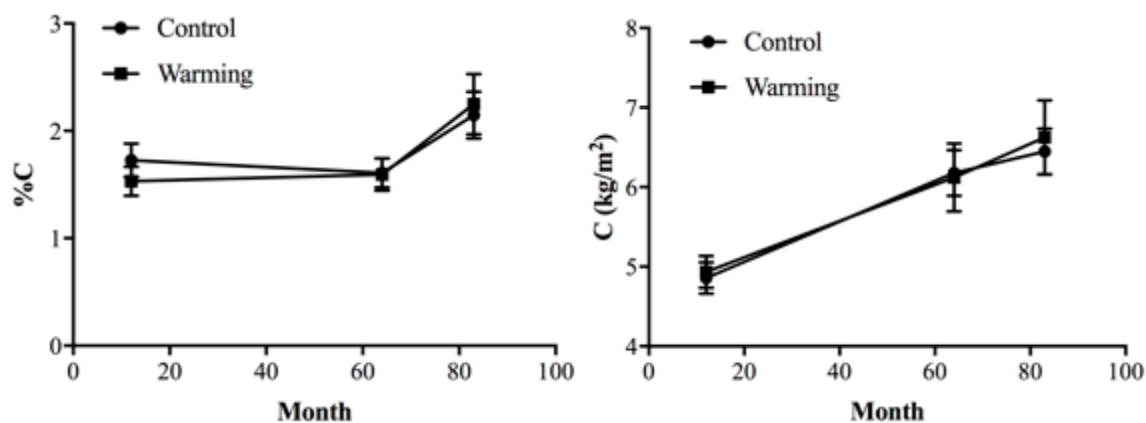


Figure 2.4: Mean soil C concentration (left) and soil C pools (right) with and without warming over time. Error bars indicate standard error.

However, there was a significant interaction between the warming and eCO₂ treatments ($p = 0.0051$), which had contrasting effects on soil C (Figure 2.5, Table 2.3). Warming significantly decreased soil C under ambient CO₂ from 17.44 ± 1.24 %C in non-warmed plots to 15.22 ± 1.16 %C in warmed plots ($p = 0.0471$). However, the addition of eCO₂ dampened this effect.

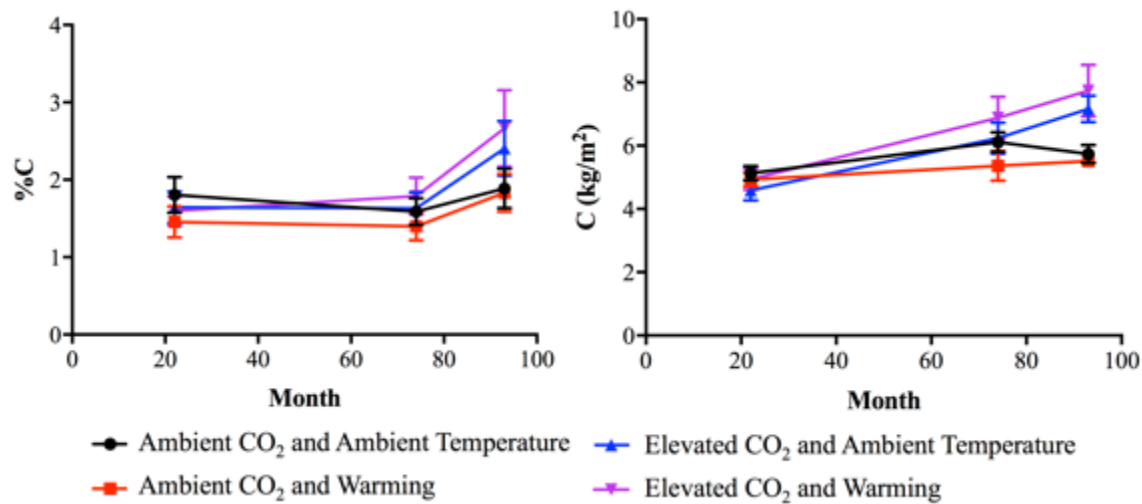


Figure 2.5: Mean soil C concentration (left) and soil C pools (right) with and without elevated CO₂ and warming over time. Error bars indicate standard error.

Table 2.4: Interactive Effects of CO₂ and Warming

Treatment	Mean %C	P value
A	1.744 ± 0.124	
T	1.522 ± 0.116	0.0471
CO ₂	1.834 ± 0.144	
TCO ₂	1.951 ± 0.176	

Though there was no significant three-way interaction between drought, warming, and eCO₂, the combination of all three treatments typically resulted in the highest soil C of all

treatments (Figure 2.6). At the last measurement point, the full combination of treatments had increased the soil C concentration over the control by 58.3%.

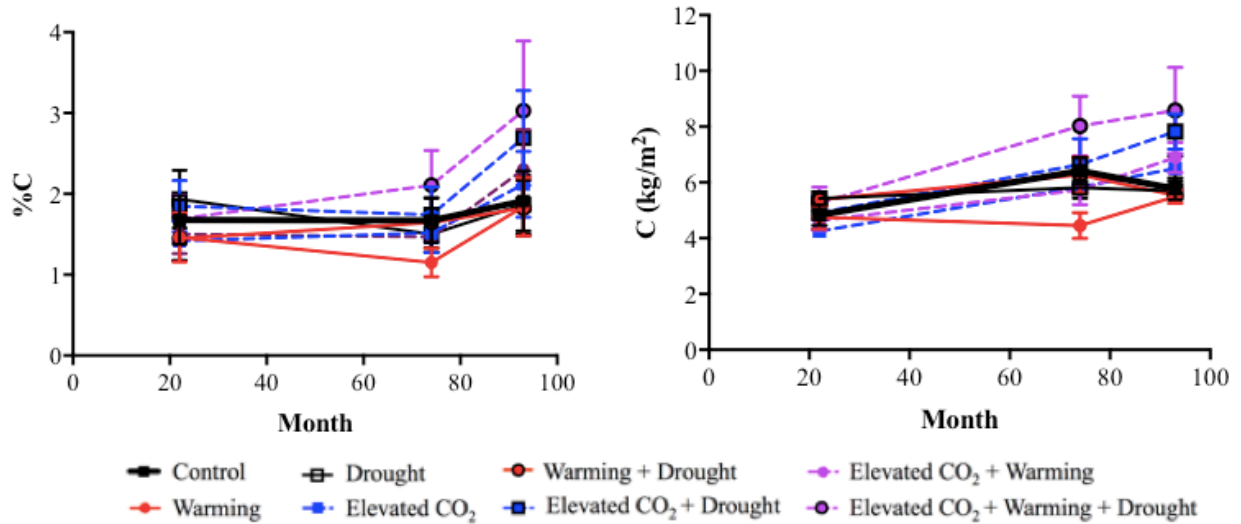


Figure 2.6: Mean soil C concentration (left) and soil C pools (right) for each treatment combination over time. Error bars indicate standard error.

2.4 DISCUSSION

2.4.1 *Drought*

We suspect that the observed increase in soil C with drought may have actually been the product of pretreatment differences in soil C caused by differences in plant community composition. Previous research at the site indicated that there is more SOM under *Calluna* than *Deschampsia* (Nielsen et al., 2009), and through random chance the majority of drought treatment plots had a greater proportion of *Calluna* than their non-drought counterparts (Table 2.5).

Table 2.5: Pretreatment Ratio of *Calluna* to *Deschampsia* by Treatment

Treatment	Pretreatment Ratio of <i>Calluna</i> to <i>Deschampsia</i>
TCO2	0.335
CO2	0.362
DCO2	0.431
A	0.515
TD	0.528
D	0.569
TDCO2	0.572
T	0.592

Previous research at the site also indicates that the drought treatment had negative effects on plant photosynthesis (Albert et al., 2011c), aboveground biomass (Kongstad et al., 2012), and rooting (Arndal et al., 2014), but that the turnover rate of newly assimilated C was lower under drought conditions (Nielsen, submitted). Despite indications of lower turnover rates, in light of the evidence for a pretreatment effect we cannot confidently claim that the decreased respiration under drought conditions (Selsted et al., 2012) compensated for the observed reduction in plant inputs and resulted in net C storage. However, a recent meta-analysis found that drought induced small increases in soil C pools, which would agree with our results (Zhou et al., 2016).

The exception to this uncertainty is the effect of drought on the warmed plots in the absence of eCO₂. Though the pretreatment biomass ratio suggests that the plots that received both warming and drought may have initially had a lower soil C than the plots that only received warming, we observed soil C in the warmed plots to increase with the application of drought. The combination of drought and warming resulted in the driest conditions of any treatment. These dry conditions in these plots counteracted the increase in respiration that typically accompanies warming and rendered losses of soil C due to respiration the lowest of any treatment combination (Selsted et al., 2012).

SOC progressively increased with the application of eCO₂ over the course of the experiment, resulting in significantly elevated soil C concentrations compared to the ambient plots at the end of the study. Pretreatment measurements indicated that soil C in the eCO₂ plots was initially 15.6% lower than in the ambient plots in the upper 10 cm of the soil profile, presumably due to the higher prevalence of *Calluna* in the ambient plots. These pretreatment differences imply that the effect of eCO₂ on soil C was even stronger than measured as the increase with eCO₂ also compensated for the initially lower soil C concentration in these plots.

CO₂ fertilization of plant growth is likely the driving factor for this increase in soil C. Elevated CO₂ increased photosynthetic activity in both *Calluna* and *Deschampsia* (Albert et al., 2011a; b) and resulted in some seasonal increases in aboveground *Deschampsia* biomass production (Kongstad et al., 2012). Most notably, belowground biomass production increased in response to the greater demand for nutrients to accommodate increased plant growth (Arndal et al., 2013). The eCO₂ treatment induced the greatest increase in root growth (Arndal et al., 2014, 2018), particularly in the deeper soil horizons (Arndal et al., 2018), where allocation of newly assimilated C to roots was three times greater than in ambient plots (Nielsen, submitted). The observed increase in respiration in these plots (Selsted et al., 2012) suggests that the increased allocation of C belowground resulted in some priming of SOC. Though some studies observed that soil C was diminished by the effect of priming (Hoosbeek et al., 2004; Trueman and Gonzalez-Meler, 2005; Carney et al., 2007; Langley et al., 2009; Butterly et al., 2016), at our site the increase in belowground inputs outweighed losses due to increased respiration under eCO₂.

Though our results are in agreement with several meta-analyses that indicate that soil C tends to increase with eCO₂ (Jastrow et al., 2005; De Graaff et al., 2006; Luo et al., 2006; van

Groenigen et al., 2006; Hungate et al., 2009; Yue et al., 2017), the majority of individual experiments testing the effects of eCO₂ on soil C found no significant difference (Torbert et al., 1997; Cardon et al., 2001; Allard et al., 2005; Dijkstra et al., 2005; Ross et al., 2006; van Kessel et al., 2006; Gill et al., 2006; Pendall and King, 2007; Lichter et al., 2008; Talhelm et al., 2009; Garten et al., 2009; Hoosbeek et al., 2011; Dorodnikov et al., 2011; Drake et al., 2011; Hofmockel et al., 2011; Reid et al., 2012; Chen et al., 2012; Dieleman et al., 2012; Procter et al., 2015). The fact that we did observe a significant increase at the end of our study may speak more to differences in experimental and statistical design between our study and others rather than strongly differing impacts (Hungate et al., 1996, 2009; Ross et al., 2006; Lichter et al., 2008). As soil C concentration varies widely with depth, the use of larger sampling intervals in many other studies may have masked any change in C concentration that developed in smaller segments of the profile (Jastrow et al., 2005). Our use of both a relatively high number of replicates and repeated measurements over time and depth increased our power to detect a difference despite the large inherent variability in soil C concentrations.

In comparison to other studies that did observe a significant increase with the application of eCO₂, the increase in soil C at our site was among the greatest. By the final measurement point, soil C in the upper 10 cm of the eCO₂ plots was 40.2% higher than the ambient plots, averaging out to an increase of 5.2% over ambient conditions per year. This average does not account for the fact that the CO₂ plots initially had lower soil C than the ambient plots, yet is still a stronger response than the 4% and 1.5% annual increases observed with eCO₂ in two spruce/beechn model ecosystems with differing soil types (Hagedorn et al., 2001). It is also greater than the 1.2% increase per year observed in the last 5 years of a 9 year FACE experiment on a dry pasture in New Zealand (Ross et al., 2013) and the even smaller annual increase of

0.67% observed in a Kansas grassland (Jastrow et al., 2005). In contrast, a greater annual increase of 6.2% under eCO₂ was observed in a grain sorghum field under water-limited conditions in Arizona (Prior et al., 2008). This strong response may be in part due to changes in rooting with plant succession, as the site was managed as a heathland until the beginning of the experiment. In fact, the annual increase in soil C in the ambient plots was comparable to the increase in C under eCO₂ in a number of other studies. The species composition of the site may also play a role. The association between *Calluna* and ericoid mycorrhizal fungi, whose ability to scavenge organic N enables them to reduce N limitations to plant growth (Orwin et al., 2011) be an important factor driving the relatively high rate of increase in soil C at this site compared to other ecosystems.

Studies that used repeated measurements similarly observed that the magnitude of the effect of eCO₂ on soil C increased over time (Jastrow et al., 2005; Hoosbeek et al., 2006; Ross et al., 2013). The fact that we see a consistent increase in soil C over the course of the experiment may indicate that though nutrient availability was never high enough to result in significant increases in aboveground biomass (Kongstad et al., 2012), plant growth at this site is not yet so nitrogen limited as to reduce root production. Further, some degree of further accumulation is expected, as the increase in soil C under eCO₂ had not slowed after 8 years. However, it is possible that progressive nitrogen limitation may eventually limit plant growth and the potential for increases in soil C under eCO₂ (Hungate et al., 2006).

2.4.3 *Interaction between Warming and Elevated CO₂*

Warming significantly decreased soil C at ambient CO₂ at our study site, though this effect was nullified by the application of eCO₂. Our results agree with the conclusions of two meta-analyses which predict soil C across the globe to decrease with increasing temperatures

(Crowther et al., 2016; Yue et al., 2017). This loss of soil C in the warmed plots was likely driven by the stimulation of microbial abundance and growth (Andresen et al., 2010; Haugwitz et al., 2014). A slight yet consistent increase in soil respiration was observed with warming, but this effect was only periodically significant (Selsted et al., 2012). However, since warming treatments were applied at night and flux measurements were taken during the day, the full magnitude of changes due to warming may not have been captured.

Decreased belowground biomass allocation may have also played a role in reducing soil C under warming at our site, as standing root biomass was observed to be lower in the warmed plots (Arndal et al., 2014, 2018). This decrease in allocation of C belowground may be a response to more easily accessible N in the warmed plots as a result of increased turnover (Larsen et al., 2011).

A number of studies have observed the effect of warming to be transient as microbes undergo some form of thermal acclimation or labile substrates are depleted (Knorr et al., 2005; Hartley et al., 2007; Bradford et al., 2008; Tucker et al., 2013). We did not observe a significant change in the effect of warming over the 8 years of our study, though the much smaller difference between the warmed and control plots at the last measurement point may suggest that the warming effect was beginning to decline.

However, the effect of eCO₂ nullified that of warming; warming + eCO₂ treatment plots had SOC concentrations that were comparable to plots that only received eCO₂. As increased temperatures are caused by increased atmospheric CO₂ concentrations, future warming will be inherently accompanied by elevated CO₂. The decrease in soil C observed with the warming treatment alone is therefore not a response we would expect to see in response to similar increases in temperature at this site. However, as our warming treatments were fairly mild and

did not achieve the 2°C increase that would correspond with predictions of future conditions, it is possible that in the future a stronger response may occur than observed in this study.

These results agree with a meta-analysis which found eCO₂ to have a stronger effect on soil C than warming (Dieleman et al., 2012). Unlike the plots which only received warming, there was no decrease in standing root biomass when eCO₂ was added (Arndal et al., 2013, 2018). In fact, the increase in root growth and biomass observed with the application of eCO₂ was typically greatest when CO₂ was elevated in the warmed plots (Arndal et al., 2013, 2018). In these combined treatment plots, the increased N availability due to increased microbial activity with warming may have contributed to plant growth by reducing nitrogen limitations under eCO₂ (Larsen et al., 2011), which is in line with the results of Dieleman et al.'s (2012) meta-analysis. As the warming treatment also lengthened the growing season, the combination of warming and eCO₂ allowed for increased plant inputs (Arndal et al., 2013, 2018) over a longer period of time (Albert et al., 2011b).

2.4.4 *Interactions between Temperature, Elevated CO₂, and Drought*

Like the other eCO₂ treatments, the soil C concentration in the plots that received a combination of drought, warming, and eCO₂ increased over the course of the study. Though there was no significant three-way interaction between the three treatments, by the second measurement point, the plots that received all three treatments had the greatest soil C concentration. After 8 years of treatment, this future climate scenario induced an increase in soil C on the order of 28 tonnes C ha⁻¹. As this is the only eCO₂ treatment that was any drier than ambient, the combination of drought and warming seems to have had a sufficiently strong drying effect to counteract the typical increase in soil moisture associated with eCO₂, resulting in reduced respiration compared to the other eCO₂ treatments (Selsted et al., 2012). It is therefore

possible that the future climate scenario induced sufficiently dry conditions to result in greater retention of carbon compared to the other eCO₂ treatments, strengthening the negative feedback to eCO₂. However, the observed increase was not significant, and pretreatment differences may play a role here as well. Plots that received all three treatments had the highest proportion of *Calluna* and were among the highest in terms of C concentration at the first measurement point. Given the lack of significant interaction and potential pretreatment differences, it seems that warming and drought are not likely to significantly affect the rate of increase in soil C concentrations under eCO₂ in the future at this site. Though our study did not account for impacts of expected increases in winter precipitation, the fact that the effects of drought, warming, and CO₂ on soil moisture did not seem to play a strong role in determining their effects on SOC suggests that increased precipitation may have a minimal effect, though further experimentation is necessary to confirm this.

2.5 CONCLUSION

The effects of climate change on soil C pools have the potential to either exacerbate or alleviate the detrimental effects of rising atmospheric CO₂ concentrations. A number of studies have raised concerns that climate change may reduce soil C stocks via increased decomposition under warmer temperatures (Crowther et al., 2016; Yue et al., 2017) or a priming effect caused by elevated CO₂ (Carney et al., 2007; Langley et al., 2009). However, at this site soil C losses with warming were nullified by the increase in plant growth with eCO₂ concentrations, which will inherently be present in a warming world. Over the 8 years of our study, we observed that the stimulating effect of elevated CO₂ on belowground plant growth had a stronger impact on soil C than the effects of either drought or warming. This site is therefore expected to store more

C under future climate conditions, serving as a negative feedback to elevated atmospheric CO₂ concentrations.

Chapter 3. RESPONSE OF DEEP SOIL CARBON POOLS TO FOREST MANAGEMENT IN A HIGHLY PRODUCTIVE ANDISOL

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Abstract: Soil contains more carbon than the atmosphere and plant biomass combined.

Consequently, it is the most important long-term sink for carbon within terrestrial ecosystems.

An understanding of the potential to induce carbon sequestration in soils through management is crucial in light of increasing anthropogenic CO₂ emissions. Nevertheless, soil has historically been under-represented in carbon cycling research, especially in regards to subsurface (>30 cm) layers and processes. Research on the effects of forest management practices on deep soil carbon has been particularly lacking. To test the effects of biomass removal and vegetation control treatments on deep soil carbon, soils were sampled to a depth of 3 meters at the Fall River Long-term Soil Productivity Site in western Washington, USA. Treatments were installed 15 years previously in a complete, randomized block design. No difference was found in total soil carbon between treatments, but there was significantly less ($\alpha=0.10$) carbon stored at the deepest interval measured (250-300 cm) in the plots with vegetation control (8.9 Mg C ha⁻¹) than in those without (16.6 Mg C ha⁻¹). These results suggest the stability of soil carbon pools at Fall River and indicate that more intensive management practices may not deplete carbon pools at this site, but imply that these deep soil pools may be more sensitive to change than shallow pools. 58.1% of the soil carbon pool is located below 30 cm, which demonstrates that shallow sampling

significantly underestimates soil carbon pools and highlights the importance of understanding processes that control deep soil carbon.

3.1 INTRODUCTION

Soils play a key, yet often overlooked, role in global carbon cycling. They comprise the largest terrestrial carbon pool, containing approximately 1500 Pg (Eswaran et al., 1993; Sundquist, 1993; Jobbagy and Jackson, 2000; Rustad et al., 2000; Scharlemann et al., 2014). However, this estimate only accounts for the upper 1 m of the soil profile. Jobbagy & Jackson (2000) concluded that incorporating the 2nd and 3rd meters of the soil profile would increase the estimated soil carbon pool by 842 Pg, and Köchy et al. (2015) more recently estimated that including all soil layers deeper than 1 meter would increase the global soil carbon pool to almost 3000 Pg.

This amount exceeds the pool of carbon contained in both terrestrial biomass and the atmosphere, which contain 750 and 560 Pg of carbon, respectively (Rustad et al., 2000). In spite of the large amount of carbon stored in deep soils, there has been a paucity of research investigating how changing conditions induced by management or environmental change may affect deep soil carbon stocks. Further, the scarcity of deep soil studies makes an accurate estimation of these deep carbon pools difficult (Lorenz and Lal, 2005), which in turn limits the accuracy of carbon cycle and climate models.

Most coupled carbon-climate models, including the CMIP5 models, consistently underestimate soil carbon by only including the upper meter of the profile (Todd-Brown et al., 2013). This oversight is primarily due to the lack of sufficient data below 1 m. The default sampling depth recommended by the IPCC's Guidelines for National Greenhouse Gas Inventories is only 30 cm (Paustian et al., 2006), and the majority of studies on soil carbon

change do not even sample that deeply: a sampling depth of 20 cm is much more common (Post and Kwon, 2000; West and Post, 2002). The long residence times of subsurface soil carbon have been used to justify shallow sampling practices and support the assumption that these deeper pools were either negligible or resistant to change (Kaiser et al., 2002; Chabbi et al., 2009). However, recent research has shown that not only is there a significant amount of carbon at depth (Jobbagy and Jackson, 2000; Harrison et al., 2011; Harper and Tibbett, 2013; James et al., 2014), but that the environmental conditions under which this carbon is stabilized are, in fact, the primary cause of these long residence times, rather than inherent chemical recalcitrance of the material (Mikutta et al., 2006; Marschner et al., 2008; Schmidt et al., 2011). Climatic or management changes can alter soil conditions such that seemingly recalcitrant organic matter becomes bioavailable and vulnerable to decomposition (Trumbore et al., 1995; Kuzyakov et al., 2000; Fontaine et al., 2007). In spite of this new paradigm for understanding the stabilization of soil organic matter, deep soil studies are still uncommon due to the expense and time associated with deep sampling. However, without more data on subsurface carbon pools, it will be impossible to accurately estimate the amount of carbon that is stored in deep soils or how vulnerable this carbon may be to changing conditions induced by management or climate change.

Management is one of the most common drivers of changes in soil carbon, and it has often been proposed as a mechanism for sequestering carbon in order to combat rising atmospheric CO₂ levels (Post and Kwon, 2000). Both agriculture and forestry have been shown to induce change in the upper layers of soil (Johnson and Curtis, 2001; Guo and Gifford, 2002). However, there is evidence that the results of analyses of change in total soil carbon pools may be dependent on sampling depth, as various soil horizons may respond to change differently

(Liebig et al., 2005; Baker et al., 2007; Gál et al., 2007). Improved understanding of deep soil processes is crucial in order to predict which environmental changes may induce the mineralization of previously stable deep soil carbon or increase carbon storage in deep layers. Deep soils are particularly important in forest ecosystems, as many tree species root very deeply (Nepstad et al., 1994; Canadell et al., 1996; Jackson et al., 1996; Schenk and Jackson, 2002). The maximum depth of Douglas-fir rooting is often over 3 m (Stone and Kalisz, 1991). This deep rooting provides biogeochemical interactions with deep soil through nutrient uptake as well as root exudates and turnover (Maeght et al., 2013).

It has been estimated that 70% of soil organic carbon is stored in forest ecosystems (Jandl et al., 2007), making the study of deep soil carbon in these systems particularly crucial to the understanding of global carbon cycling. Additionally, forest soil carbon has been shown to respond more strongly to management change than soils influenced by other forms of land use (Jandl et al., 2007). Over 200 million hectares of forest land are managed for timber production in the U.S. alone (USDA Forest Service, 2001), and the effects of this management could include the release or storage of large amounts of soil carbon, with effects on climate that are not currently being incorporated into carbon and climate models. Control of competing vegetation (Shan et al., 2002; Miller et al., 2006) and increased biomass removal (Mendham et al., 2002, 2003) are two common forest management practices that have been shown to affect soil carbon stores in surface horizons.

Increased biomass removal has become progressively more common as the market value of the logging residues left behind by conventional harvesting has escalated due the rising demand for biofuel feedstock (White, 2010). These biofuels would serve as a renewable, carbon neutral alternative to fossil fuels (Caputo et al., 2005). However, removal of this material could

impair forest sustainability, as whole tree harvesting removes an important source of organic matter and nutrients to the soil (Ares et al., 2007b). Increasing the amount of organic material removed from a site can lead to changes in carbon dynamics and, in some locations, has been shown to decrease soil organic matter in surface horizons (Olsson et al., 1996; Mendham et al., 2002, 2003; Laclau et al., 2010)..

Control of competing vegetation has also produced varied results but has been shown to decrease shallow soil organic matter in some instances (Shan et al., 2002; Powers et al., 2013). After forest harvest, early successional vegetation will typically flourish. However, if left unchecked, this vegetation can lead to significant mortality of young seedlings, especially if invasive species predominate. Thus, herbicides are frequently used to control competing vegetation in early-rotation forests. A side effect of this treatment may be reduction in soil carbon (Slesak *et al.*, 2011). In untreated forest, the competing vegetation will die back once crown closure is reached, leading to a flux of fresh organic matter onto the soil, which would not be present if herbicide were used to control understory vegetation. Additionally, increased irradiance due to a lack of shading from early successional species could result in greater decomposition and loss of soil organic matter due to increased temperature throughout the profile. Given how widely used vegetation control practices have become, improved understanding of their effects on soil carbon pools is necessary for accurate evaluation of the long-term impacts of forest management.

The effects of management on soil carbon may determine the sustainability of these practices in the long term. Soil organic matter provides nutrients, structure, and water holding capacity, all of which are driving factors of site productivity (Powers et al., 1990).

Understanding the effects of management practices on soil carbon at depth is therefore important

both in light of its effects on atmospheric CO₂ concentrations and for maintaining sustainable forestry practices. Though it has been recommended that soil sampling be conducted to a depth of at least one meter in order to accurately assess change in forest soil carbon pools (Hamburg, 2000), deep soil is often neglected in forest management studies. Our study is unique in that we sampled to a depth of 3 m.

In order to understand the potential for changes in deep soil carbon pools as a result of forest management practices, the effects of increased biomass removal and vegetation control on soil carbon were examined throughout the profile to a depth of 3 m. Treatments were applied to an intensively managed Douglas-fir stand in western Washington. Soils at this site are representative of some of the most productive and carbon rich soils in the Pacific Northwest (Ares et al., 2007b). Previous sampling at the site to a depth of 1 meter indicated that difference between treatments was greatest in the deepest measured interval (60-100 cm). However, even at that interval, the difference in total carbon content was not statistically significant (Knight et al., 2014). Our study aimed to investigate if the trend of increasing difference in carbon content between treatments with depth continued, and if the difference in total carbon content between treatments became significant with the inclusion of deep soil carbon pools.

3.2 METHODS

3.2.1 *Site Description*

The Fall River research area is an affiliate site of the North American Long-Term Soil Productivity Network, a collaborative program led by the U.S. Forest Service and aimed at understanding the effects of forest management on soil organic matter and pore space, which are hypothesized to be determining factors for site productivity (Powers et al., 2005; Ares et al., 2007b). This network includes more than 40 sites across the U.S. and Canada. The research goals

of the Fall River site include the investigation of the effects of various forest management practices, including control of competing vegetation and removal of excess biomass for use as biofuels, on soil processes and long-term productivity. Our study supports these goals by assessing the effects of these forest management practices on deep soil carbon. Knowledge generated by research at this site will allow for the improvement of forest management practices aimed at sustaining site productivity.

Understanding deep soils is particularly important at sites like Fall River, where soils are many meters deep. Fall River is located in the Willappa Hills in the Coast Range of Washington (46° 43'N, 123° 25'W) (Ares et al., 2007b). The site is located on a plateau formed by the Pomona basalt flow, and slopes average from 10-15% with a westerly exposure at an elevation of 300-375 m. Soils and topography are fairly uniform, and therefore limit any confounding effects of variability due to these two factors. The area has a maritime climate with a mean annual air temperature of 9.2 °C and mean annual precipitation of 2260 mm. Winters are mild and wet and summers are warm and dry. Site history has been well documented, and includes previous harvesting of the initial old growth Douglas-fir (*Pseudotsuga menziesii*) and western hemlock (*Tsuga heterophylla*) stand in 1952-1953. A full description of the site is available in Ares et al. (2007a).

The soil at this site is classified as a medial over clayey, ferrihydritic over parasesquic, mesic Typic Fulvudand of the Boistfort series (Soil Survey Staff, 2010). The Boistfort Series includes some of the most productive and carbon-rich soils in the Pacific Northwest (Ares et al., 2007b). Pre-harvest soil analysis estimated the top 80 cm of soil at the site to contain 248 Mg C ha⁻¹. This Andisol is well-drained with a medium to moderately fine texture and few rocks (Terry et al., 2001; Ares et al., 2007b). It has a low bulk density which increases with depth and a high

water holding capacity (Ares et al., 2007b). This soil developed on Miocene basalt, though the upper horizons have been considerably influenced by volcanic ash, some of which was likely deposited after the Mt. Mazama eruption approximately 6,850 years ago (Steinbrenner and Gehrke, 1973; Ares et al., 2007b). Soils at Fall River are rich in iron and aluminum oxides, which contribute to a significant capacity for anion sorption that increases with depth (Strahm and Harrison, 2007). Selective dissolutions of iron, aluminum, and silica indicated that allophane and imogolite concentrations also increase with depth, although they are low compared to other Andisols in the region (Ares et al., 2007b). Previous research has indicated that Andisols with large quantities of similar noncrystalline, variable-charge minerals, contain more carbon both in total and at depth than other soil types in the Pacific Northwest (James et al., 2014). It is therefore likely that these mineralogical properties are driving factors for the high carbon content of soils at Fall River.

This site was chosen because it is representative of soils developed on basic igneous parent material with volcanic tephra influence which are found throughout the Coast Range and Western Cascades of Washington and Oregon (Terry et al., 2001). These types of soils are among the most productive in the Pacific Northwest, and are commonly intensively managed as Douglas-Fir plantations (Ares et al., 2007b).

3.2.2 *Experimental Design*

This study focused on three of the treatments implemented at the Fall River site: commercial bole only removal with vegetation control by annual herbicide application (BO+VC), commercial bole only removal without vegetation control (BO-VC), and total-tree plus removal with vegetation control (TTP+VC). These treatments differ the most in terms of organic matter retention (BO and TTP) and vegetation control (+VC and -VC). They were

selected because these treatments best represented management extremes, with BO-VC as the least managed and TTP+VC as the most intensely managed. The largest measurable difference between treatments was therefore expected to be represented by the comparison of these extremes.

In the BO+VC and BO-VC treatments, remaining tops, broken logs less than 3 meters in length, and all remnant coarse woody debris were left in place (Ares et al., 2007b). In the TTP+VC treatment, harvesting removed the entire aboveground tree including branches and foliage. Most remaining coarse woody debris was removed and herbicide was used to control competing vegetation. The TTP treatment was estimated to have removed 69 Mg C ha⁻¹ more carbon than BO treatments, with 244 Mg C ha⁻¹ and 175 Mg C ha⁻¹ removed respectively. Vegetation control did not mimic conventional vegetation control methods, but was strictly administered with the intention of eliminating all competing vegetation; it was therefore applied more frequently than standard commercial practices would dictate. These treatments are described in further detail by Ares et al. (2007a).

Installation of the experiment began in 1999 with the harvesting of the previous stand and implementation of biomass removal treatments (Ares et al., 2007b). The current Douglas-fir stand was planted in 2000 with a stand density of 1,600 trees per hectare. Vegetation control treatments were initiated the following year, and continued for the following five years. Four replicates of 12 treatments were administered in a complete, randomized block design. Arrangement of experimental blocks was based on slope position and composition of original stand (percentage Douglas-fir and western hemlock). Each of four blocks contains two 30 x 85 m plots for each treatment, each containing a 15 x 70 m (0.10 ha) measurement plot. For this study,

one sampling location was randomly selected per treatment, per block, for a total of 12 plots sampled (Ares et al., 2007b).

3.2.3 *Sampling Methodology*

To assess soil carbon throughout the profile, samples were taken to a depth of 3 meters from the center of 8 depth intervals: 0-15 cm, 15-30 cm, 30-50 cm, 50-100 cm, 100-150 cm, 150-200 cm, 200-250 cm, and 250-300 cm. Sampling intervals are smaller in the upper 50 cm of the soil profile to account for the higher expected rate of change in carbon concentration with depth in the upper soil horizons. The forest floor was also sampled at each plot. Sampling took place between June and November, 2014.

This experiment employed a novel vertical coring method to take samples to a depth of 3 meters. This method eliminated the need to dig soil pits, making the sampling process much more efficient and less destructive. It is, however, still a difficult and time-consuming process, which limited the number of plots we were able to sample to one per treatment, per block, rather than using the full set of two plots that were available for each treatment in each block. An AMS Signature Series Split-Core Sampling Kit was used to auger to the desired depth and then to extract samples of a known volume suitable for both chemical analysis and measurement of bulk density. Before beginning our sampling, we verified the accuracy of the bulk density values produced by this method compared to the more common punch core method. To do this, we took punch core samples horizontally from the face of a pit at 20 cm intervals to a depth of 140 cm for comparison with samples taken using the vertical core directly behind the face of the pit at the same depths. The 0-20 cm interval was excluded from the analysis due to the intermittent presence of red rot causing large variability. To calculate bulk density, samples were air dried at room temperature for one week and then weighed. Though there was some variability, as is

expected in any bulk density measurements (Raper and Erbach, 1987), values produced by the two methods were not significantly different ($p = 0.509$, F-test). The difference between bulk density values produced by the vertical core as compared to the punch core ranged from 0.21 g cm^{-3} to -0.01 g cm^{-3} . The bulk density values of the vertical core samples were, on average, 0.09 g cm^{-3} higher than the punch core samples. This vertical coring method works well when not impeded by rocky soils or an impermeable layer. We successfully reached 3 meters in all but one plot (Block 4: TTP+VC), in which an impermeable layer at 2 meters prevented further sampling. Increased use of this method has the potential to expand the study of deep soil horizons.

In preparation for determination of soil carbon concentrations using a Perkin-Elmer 2400 CHN analyzer, dry samples were passed through a 4.75 mm sieve. Though the $<2 \text{ mm}$ fraction is typically used in soil carbon analysis, Zabowski et al. (2004) demonstrated that a significant portion of soil carbon is found in the coarse fraction of some Pacific Northwest Andisols, thus we elected to use a larger mesh size. Subsamples were then ground using a porcelain mortar and pestle.

The total carbon content (C_t) for each depth interval was calculated from the layer thickness (h), the bulk density (D_b) and the carbon concentration ($C_{\%}$). For calculation purposes, $C_{\%}$ is assumed to be constant throughout each depth interval.

$$C_t = D_b h C_{\%}$$

Mean total carbon content per treatment was calculated by averaging the content at each depth interval and summing these to the desired depth.

3.2.4 *Statistical Analyses*

A two-way (randomized block) ANOVA ($\alpha=0.10$) was used to test the effect of treatments on cumulative carbon content from the surface to the bottom of each depth interval to determine if sampling depth affected the results of analysis. Treatment effects on carbon content and concentration within each depth interval were also tested using a two-way ANOVA ($\alpha=0.1$) (IBM SPSS Statistics, Version 19.0.0). Because there was an impermeable layer at 200 cm in the TTP+VC treatment in Block 4, the TTP+VC treatment had a sample size (n) of 3 instead of 4 at the deepest two intervals. Post hoc comparisons were performed using Tukey's tests at $\alpha=0.1$ when statistical differences were detected by the ANOVA analysis. To ensure that any differences in carbon content between treatments were not primarily driven by differences in bulk density, differences in bulk density were likewise assessed and any correlation between carbon concentration and bulk density was determined using Pearson correlation analysis.

To assess the effect of deep sampling on estimates of total carbon content across all profiles, a linear mixed effects model was used to determine the depth at which deeper sampling no longer statistically influenced the total carbon content of the profile. This analysis was conducted in R (R Core Team, 2014) using the nlme package (Pinheiro et al., 2015), with depth as a fixed effect and plot as a random effect. A logarithmic transformation of the data was used as it improved normality as assessed by visually inspecting residual and Q-Q plots and lowered the AIC and BIC of the model. Multiple comparisons between sampling depths were calculated using Tukey's Honestly Significant Difference, part of the multcomp package in R (Hothorn, 2008).

3.3 RESULTS

Across all treatments, the mean total carbon stock to a depth of 300 cm was 351 ± 18 Mg C ha⁻¹. On average, $76 \pm 1\%$ of the soil carbon pool was located below 15 cm, $58 \pm 2\%$ was located below 30 cm, and $27 \pm 2\%$ was located below one meter (Figure 3.1). The upper 1 m contained 259 ± 18 Mg C ha⁻¹ on average, the 1-2 meter interval contained 64 ± 4 Mg C ha⁻¹, and the 2-3 meter interval contained 29 ± 5 Mg C ha⁻¹. The forest floor, on average, contained 12.6 ± 1.2 Mg C ha⁻¹, excluding two plots for which measurements were missing (Blocks 1 & 3: BO+VC).

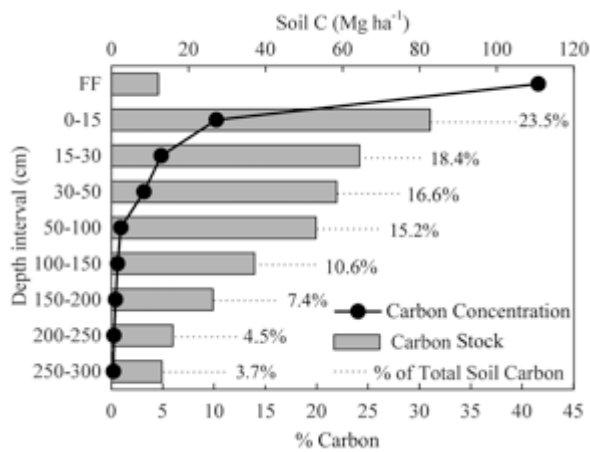


Figure 3.1 Mean soil carbon content and carbon concentration across all measured soil profiles and the forest floor.

We found no statistically significant difference in cumulative soil carbon content between treatments 15 years after their installation, regardless of sampling depth (Figure 3.2). Average total soil carbon to a depth of 3 meters was 343 ± 26 Mg C ha⁻¹ for the BO+VC treatments, 352 ± 44 Mg C ha⁻¹ for the TTP+VC treatments, and 359 ± 35 Mg C ha⁻¹ for the BO-VC treatments (Table 3.1).

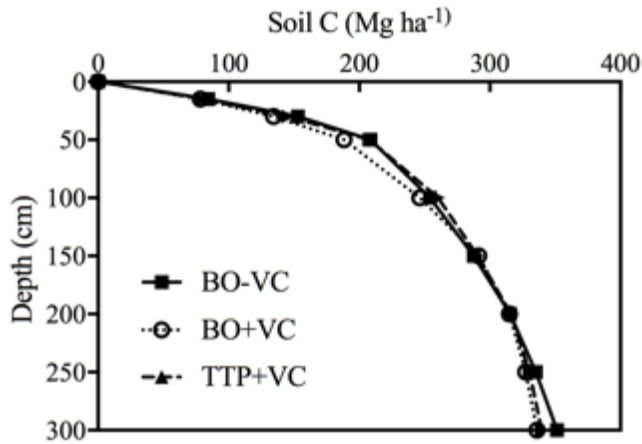


Figure 3.2 Cumulative soil carbon content by depth to 300 cm. BO+VC: Bole only removal plus vegetation control; BO-VC: Bole only removal without vegetation control; TTP+VC: Total tree plus coarse woody debris removal with vegetation control. Each point indicates the treatment average for cumulative carbon content as measured at that depth interval. Statistical difference in cumulative carbon content between treatments was not found at any depth interval measured ($\alpha = 0.10$).

Table 3.1 Estimated treatment averages for soil carbon concentration, carbon content, and total accumulated carbon by depth from ANOVA. BO+VC: Bole only removal plus vegetation control; BO-VC: Bole only removal without vegetation control; TTP+VC: Total tree plus coarse woody debris removal with vegetation control. Standard error shown in parentheses; * indicates $n = 3$ due to the presence of an impermeable layer at 200 cm (TTP+VC, Block 4), for all other tests $n = 4$.

Depth	Treatment	Bulk Density (g cm ⁻³)	Concentration (%)	Content (g cm ⁻³)	Total Accumulated (Mg C ha ⁻¹)
0-15	BO-VC	0.59 (0.13)	14.27 (6.99)	0.057 (0.006)	86.2 (9.2)
	BO+VC	0.81 (0.07)	6.86 (1.03)	0.053 (0.005)	80.0 (7.9)
	TTP+VC	0.64 (0.10)	9.59 (3.16)	0.055 (0.008)	82.1 (12.3)
15-30	BO-VC	0.85 (0.07)	5.57 (0.73)	0.046 (0.005)	156.0 (17.0)
	BO+VC	1.00 (0.09)	3.94 (0.86)	0.038 (0.008)	136.7 (18.7)
	TTP+VC	0.93 (0.09)	5.07 (1.33)	0.045 (0.010)	148.9 (26.5)
30-50	BO-VC	0.84 (0.04)	3.51 (1.01)	0.028 (0.008)	212.9 (29.6)
	BO+VC	1.07 (0.06)	2.64 (0.52)	0.027 (0.004)	191.6 (26.9)
	TTP+VC	0.96 (0.07)	3.44 (1.08)	0.032 (0.008)	212.5 (39.0)
50-100	BO-VC	1.11 (0.07)	0.82 (0.08)	0.009 (0.001)	259.3 (34.1)
	BO+VC	1.17 (0.03)	1.01 (0.18)	0.012 (0.002)	251.0 (26.2)
	TTP+VC	1.13 (0.06)	0.96 (0.28)	0.011 (0.003)	265.9 (39.5)
100-150	BO-VC	1.16 (0.04)	0.59 (0.05)	0.007 (0.001)	293.7 (37.4)
	BO+VC	1.30 (0.03)	0.71 (0.08)	0.009 (0.001)	297.1 (27.4)
	TTP+VC	1.10 (0.06)	0.56 (0.07)	0.006 (0.001)	296.9 (38.8)
150-200	BO-VC	1.37 (0.10)	0.42 (0.03)	0.006 (0.000)	322.3 (38.0)
	BO+VC	1.30 (0.06)	0.39 (0.12)	0.005 (0.001)	321.3 (27.0)
	TTP+VC	1.32 (0.09)	0.47 (0.12)	0.005 (0.002)	323.1 (39.7)
200-250	BO-VC	1.13 (0.07)	0.37 (0.13)	0.004 (0.001)	342.4 (35.6)
	BO+VC	1.23 (0.05)	0.21 (0.03)	0.003 (0.000)	334.1 (26.3)
	TTP+VC	1.32 (0.07)*	0.21 (0.06)*	0.003 (0.001)*	337.6 (39.0)
250-300	BO-VC	1.07 (0.04)	0.32 (0.10)	0.003 (0.001)	359.0 (35.4)
	BO+VC	1.23 (0.04)	0.14 (0.03)	0.002 (0.000)	343.0 (26.4)
	TTP+VC	1.07 (0.12)*	0.21 (0.04)*	0.003 (0.001)*	351.6 (40.0)

However, the effect of treatment on the carbon content of individual depth intervals was found to be significant at the 250-300 cm depth interval ($p = .081$, F-test) (Figure 3.3). At this interval, the BO-VC treatment had a significantly higher average carbon content than the BO+VC treatment ($p = .07$, Tukey HSD), which contained 16.6 ± 4.4 Mg C ha⁻¹ and 8.9 ± 2.0 Mg C ha⁻¹, respectively. TTP+VC was intermediate containing 14.0 ± 2.5 Mg C ha⁻¹.

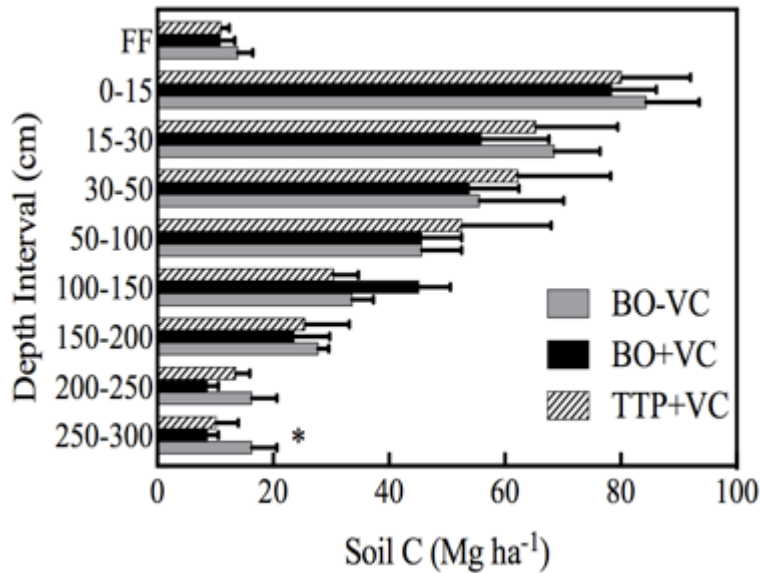


Figure 3.3 Mean soil carbon content by treatment at each depth interval. BO+VC: Bole only removal plus vegetation control; BO-VC: Bole only removal without vegetation control; TTP+VC: Total tree plus coarse woody debris removal with vegetation control. Error bars indicate standard error. Significant difference between treatments ($\alpha = 0.10$) is indicated by an asterisk (*).

The effect of treatment on carbon concentration was also significant in the 250-300 cm interval at $p = .097$ (F-test) (Figure 3.4), as BO-VC had a significantly higher mean of $0.32 \pm 0.10\%$ carbon than the BO+VC treatment, which had a mean carbon concentration of $0.14 \pm 0.03\%$ ($p = .094$, Tukey HSD). TTP+VC was not significantly different from either of the other two treatments, with a concentration of $0.21 \pm 0.04\%$.

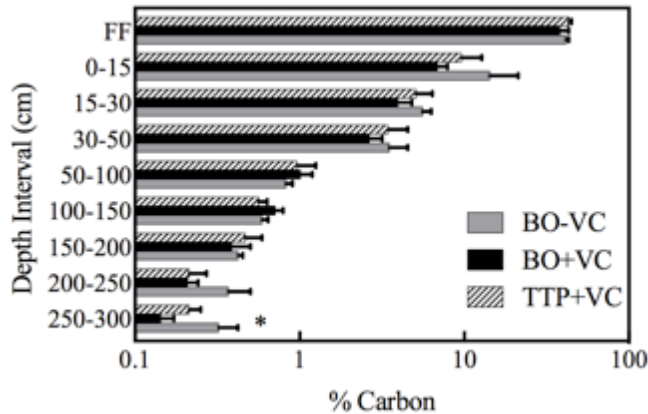


Figure 3.4 Mean soil carbon concentration by treatment at each depth interval. BO+VC: Bole only removal plus vegetation control; BO-VC: Bole only removal without vegetation control; TTP+VC: Total tree plus coarse woody debris removal with vegetation control. Error bars indicate standard error. Significant difference between treatments ($\alpha = 0.10$) is indicated by an asterisk (*). Carbon concentration is plotted on a log scale to better illustrate the difference between treatments at the low concentrations found deeper in the profile.

Though BO-VC is only significantly greater in carbon concentration and content than BO+VC in the deepest interval, throughout all depths, with the exception of 50-100 cm and 100-150 cm, there is a trend such that the mean carbon concentration and content of BO-VC is consistently greater than the mean of BO+VC (Figure 3.3, Figure 3.4). The carbon content and concentration of TTP+VC tends to fall in the middle, though this treatment is somewhat more variable in regards to its relation to the other two.

A pattern opposite to that found in carbon concentration appears between treatment means for bulk density such that in all intervals, with the exception of 150-200 cm, the bulk density of BO-VC is lower than BO+VC (Figure 3.5). This treatment effect is significant in the 30-50 cm interval ($p = .096$, F test), in which the mean bulk density of BO+VC ($1.07 \pm 0.06 \text{ g cm}^{-3}$) is significantly greater than the mean bulk density of the BO-VC treatment ($0.84 \pm 0.04 \text{ g cm}^{-3}$) ($p = .087$, Tukey HSD). The bulk density of TTP+VC also tends to fall between the other two treatments. Treatment had a significant effect on bulk density in the 100-150 cm interval ($p = .082$, F test), as TTP+VC displayed significantly lower bulk density ($1.10 \pm 0.06 \text{ g cm}^{-3}$) than

BO+VC ($1.30 \pm 0.03 \text{ g cm}^{-3}$) ($p = .076$, Tukey HSD). In the 200-250 cm interval, treatment was also significant ($p = .086$, F test), but in that interval the bulk density of TTP+VC ($1.32 \pm 0.07 \text{ g cm}^{-3}$) was significantly higher than BO-VC ($1.13 \pm 0.07 \text{ g cm}^{-3}$) ($p = .04$, Tukey HSD).

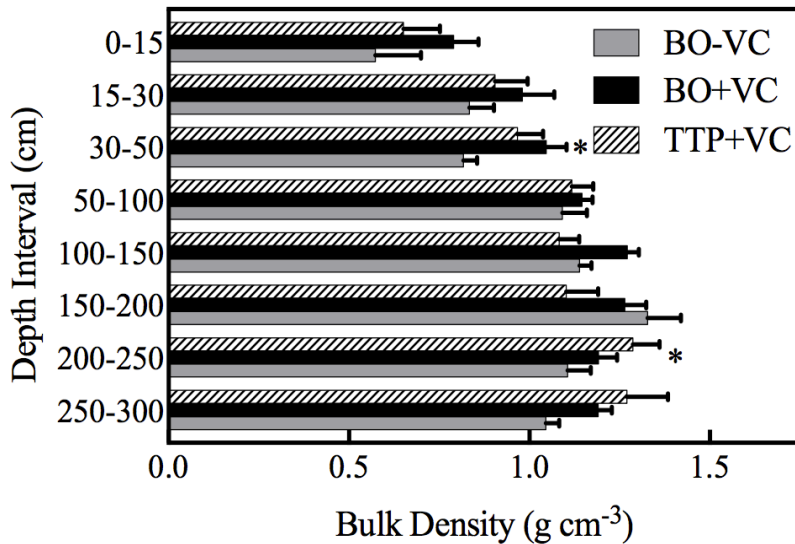


Figure 3.5 Mean bulk density by treatment at each depth interval. BO+VC: Bole only removal plus vegetation control; BO-VC: Bole only removal without vegetation control; TTP+VC: Total tree plus coarse woody debris removal with vegetation control. Error bars indicate standard error. Significant difference between treatments ($\alpha = 0.10$) is indicated by an asterisk (*).

Throughout the profile, the expected increase in bulk density with depth is apparent to a depth of 100 cm, after which bulk density values level off but become more variable (Figure 3.5). Results of Pearson correlation analysis across all samples indicated that there is a statistically significant correlation between bulk density and carbon concentration such that bulk density decreases as carbon concentration increases ($r = -0.777$, $n = 94$, $p < .01$, two-tailed) (Figure 3.6). This correlation is particularly evident at higher carbon concentrations in the upper part of the profile; at carbon concentrations below approximately 1%, which predominantly occur below 100 cm, bulk density values become much more variable. It is possible that this increased variability is an artifact of the difficulties of sampling the deepest layers of the profile.

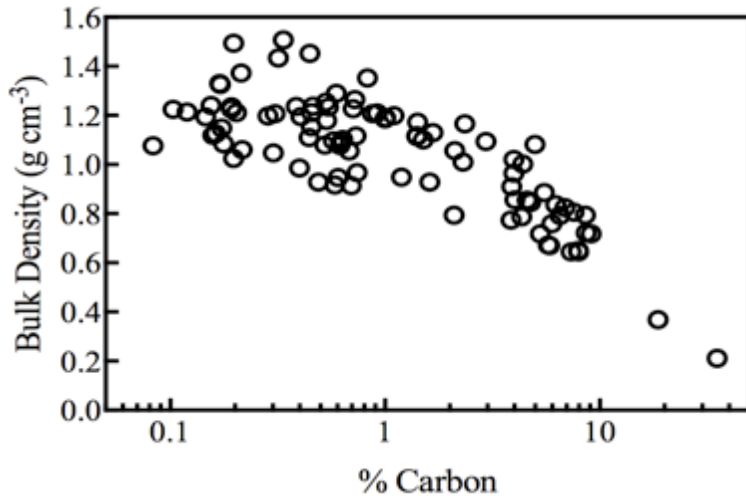


Figure 3.6 Bulk density values for all samples analyzed plotted as a function of carbon concentration. Note the log scale on the x-axis.

Multiple comparisons between sampling depths indicated that each sampling interval to a depth of 150 cm significantly increased the total measured carbon content of the profile ($p \leq .001$, Tukey HSD) (Figure 3.7). Further, cumulative carbon content significantly increased from 150 cm to 250 cm ($p = .003$, Tukey HSD), and from 150 cm to 300 cm ($p < .001$, Tukey HSD).

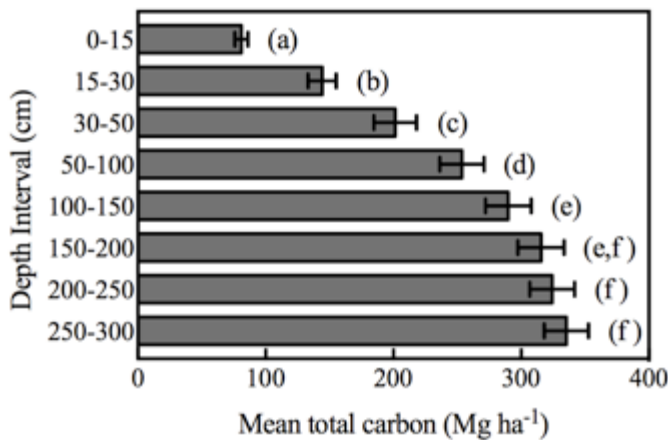


Figure 3.7 Mean total carbon at each depth interval. Error bars indicate standard error of the mean. Mean carbon is not significantly different between intervals followed by the same letter, as indicated by Tukey's Honestly Significant Difference ($p < .10$).

3.4 DISCUSSION

The lack of significant difference in cumulative soil carbon between treatments is indicative of the stability of soil carbon pools in this Andisol. The use of more intensive management practices, including removing extra biomass for use as biofuels, may not deplete carbon pools at this site or at similar deep, highly productive soils. This indicates that these practices may be sustainable over the long term. Though vegetation control resulted in a significant difference in carbon content at the lowest depth, the relative content of that depth interval was quite small, and there was no difference in the total soil carbon pool. Therefore, the effects of vegetation control on soil carbon may also be sustainable in the long term. However, as there was a non-significant trend such that mean soil carbon tended to be lower in the BO+VC treatment than the BO-VC treatment, special attention to changes in soil carbon when vegetation control treatments are applied may be necessary to ensure continued sustainability.

Soil characteristics, particularly mineralogy and texture, may play an important role in determining how much carbon is stored at depth and if soil organic matter at a particular site is resistant to change. Soils similar to Fall River have some of the highest carbon contents across the region, both in total and at depth (James et al., 2014). An abundance of iron and aluminum oxides, which have been shown to stabilize carbon by adsorbing organic matter onto reactive mineral surfaces and forming organo-mineral complexes (Torn et al., 2002; Mikutta et al., 2006; Jandl et al., 2007), contributes to this soil's considerable ability to adsorb organic acids (Strahm and Harrison, 2008).

Soils with different mineralogical characteristics may have a lower proportion of carbon stored deep in the profile, but may be more responsive to the same treatments.

Further research into the effects of mineralogy on the sensitivity of deep soil carbon to treatments may provide insight into the drivers of carbon stabilization, as results from studies on the effects of biomass removal treatments have thus far been inconclusive. Mendham et al. (2002) found that excess biomass removal treatments resulted in differences in soil organic carbon in sandy soils but not in clayey soils, although the sampling depth of this analysis was limited to 20 cm. However, Olsson et al. (1996) and Laclau et al. (2010) found no significant change as result of excess biomass removal on soils with very low clay contents, though Olsson's analysis was restricted to the upper 20 cm and Laclau analyzed only the upper 1 m of the profile.

Though vegetation control was not found to have a significant effect on total soil carbon at Fall River, previous studies on its effects have also produced differing results. Some studies produced results similar to ours, indicating that vegetation control has no effect on total soil carbon when assessed at depths ranging from 20 cm to 1 m (McFarlane et al., 2009, 2010; Powers et al., 2013). However, a number of studies, with sampling depths ranging from 30 cm to 1 m, have shown that the presence of competing vegetation results in higher levels of soil carbon compared to vegetation control treatment plots in similarly aged stands (Shan et al., 2002; Miller et al., 2006; Hoepting et al., 2011). These studies have suggested that higher levels of soil carbon in the treatments that allow the growth of competing vegetation are due to the input of fine roots and detritus from understory plants in the early years of tree growth. These results are in line with the observed, but non-significant, trend of lower soil carbon in vegetation control plots throughout the majority of the soil profile at Fall River.

Though we did not detect a change in total carbon between vegetation control treatments, our analysis did indicate a difference in carbon concentration and content at the deepest sampling

interval: plots with vegetation control contained significantly less carbon than the plots without vegetation control. We did not study potential mechanisms for this difference in carbon in the deepest layers, but it is possible that the difference is due to differences in rooting depth between treatments in the early years of stand development. It is not uncommon for some species, including Douglas-fir, to increase biomass allocation to roots under dry conditions in order to access a larger volume of soil and reach deeper sources of moisture (Chan et al., 2003; Hutchings and John, 2003). Though there have been no studies of root density at this site, measurements of soil moisture in years 2-5 indicated that conditions were significantly moister in the BO+VC treatment than the BO-VC treatment, with TTP+VC falling in the middle (Devine and Harrington, 2006; Ares et al., 2007a). The drier conditions observed in the BO-VC plots are presumed to be due to the depletion of soil moisture by competing vegetation, though the shading effect of biomass left on-site in the BO treatments may reduce evaporation from the soil surface. Monitoring through year 5 of the study indicated that this difference in available soil water resulted in corresponding differences in tree growth (Devine and Harrington, 2006; Ares et al., 2007a). Trees in the BO+VC plots were significantly larger than the trees in the BO-VC plots, with TTP+VC once again falling between the other two treatments. This difference in aboveground biomass suggests that the trees in the drier plots may have allocated more biomass to their root systems in order to attain sufficient moisture. This additional allocation of carbon belowground could explain the significant difference in carbon between treatments in the deepest interval measured, and the corresponding pattern of treatment means appearing in shallower intervals.

Analyses of differences in bulk density, which are not statistically significant between treatments in the 250-300 cm interval, indicate that carbon concentration, rather than bulk

density, is the primary driver of the significant difference in carbon content in that interval. Rather, carbon concentration appears to be a driver for bulk density; complementary trends in carbon concentration and bulk density were apparent in most depth intervals. As increased organic matter is known to decrease bulk density, this trend and the significant correlation between the two is not surprising (Ruehlmann, 2009). However, the complementary trend between these two independently measured variables may serve as further evidence for a treatment effect on soil carbon such that the BO-VC treatment results in higher, though not statistically significant, carbon concentrations than the BO+VC treatment throughout the majority of the profile.

Our results indicated that there was a significant pool of carbon below depths typically measured. Multiple comparisons of cumulative carbon between sampling depths indicated that there is a significant difference in total carbon between the 150 cm and 300 cm sampling depth, justifying the benefit of deep sampling in this soil in order to accurately assess soil carbon pools. The majority of soil organic carbon was located below 30 cm (58.1%). Including the 1-3 m interval in analysis increases the carbon pool by 35.8% as compared to only including the upper 1 m. Standard sampling practices would therefore significantly underestimate carbon pools at this site. In fact, there was slightly more carbon stored on average in the deepest interval measured ($13.1 \pm 2.0 \text{ Mg C ha}^{-1}$) than in the forest floor ($12.6 \pm 1.2 \text{ Mg C ha}^{-1}$), indicating that though concentrations may be low, the sheer volume of deep soils results in a large pool of carbon, which is often overlooked.

As soils are the largest pool of terrestrial carbon (Eswaran et al., 1993; Sundquist, 1993; Jobbagy and Jackson, 2000; Rustad et al., 2000; Scharlemann et al., 2014), underestimation of the amount of carbon stored in soil profiles due to shallow sampling may limit the accuracy of

coupled carbon-climate models. The amount of carbon stored at depth at this site and the increased sensitivity of the deepest layers to change highlights the importance of quantifying deep soil carbon pools and understanding the processes that control them. Increased sampling of deep soil carbon pools across a variety of soil types and environments will be necessary in order to fully understand the implications of the effects of changing environments and management on soil carbon pools for global carbon cycling.

Chapter 4. EFFECTIVENESS OF ENHANCED MINERAL WEATHERING AS A CARBON SEQUESTRATION TOOL AND ALTERNATIVE TO AGRICULTURAL LIME: AN INCUBATION EXPERIMENT

Published as: Dietzen, C., R. Harrison, and S. Michelsen-Correa. 2018. Effectiveness of enhanced mineral weathering as a carbon sequestration tool and alternative to agricultural lime : An incubation experiment. *Int. J. Greenh. Gas Control* 74: 251–258. doi: 10.1016/j.ijggc.2018.05.007

Abstract: Applying finely ground silicate minerals to soils could mitigate CO₂ emissions by enhancing the rate of carbon sequestration via silicate weathering. Using these minerals instead of agricultural lime to increase soil pH would also eliminate the dissolution of lime as a major source of agricultural CO₂ emissions. However, dissolution rates of silicate minerals in the soil environment are uncertain and impacts of their application on the decomposition of soil organic matter have yet to be determined. A 3-month soil incubation was performed to investigate the effects of olivine, a highly weatherable silicate mineral, at two application rates (OLIV_{low}, OLIV_{high}) on soil CO₂ flux, available Mg and Al, and pH in comparison to control and lime-amended soils. There was no difference in cumulative net CO₂ flux between the olivine-amended soils and the control though total flux from the limed soils was 221% higher than the control. Heterotrophic respiration was also greatest in the lime-amended soils. The weathering rate of OLIV_{low} (26.7%) was higher than of OLIV_{high} (7.1%), but both treatments increased soil pH to a level sufficient to overcome aluminum toxicity. Our results suggest that olivine amendments are an effective tool for carbon sequestration and a suitable replacement for lime.

4.1 INTRODUCTION

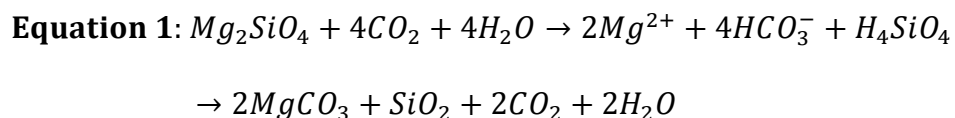
Global agricultural productivity is limited by soil acidity, which impacts over 50% of the world's potentially arable land (von Uexküll and Mutert, 1995). The use of agricultural lime (CaCO_3) to raise soil pH has therefore increased the amount of land available for cultivation and greatly improved crop yields (Sumner and Noble, 2003; Yamada, 2005). However, the dissolution of agricultural lime is a major source of atmospheric CO_2 (West and McBride, 2005). Alternative methods of increasing soil pH that do not result in high rates of CO_2 production would be preferable from the standpoint of reducing global warming. Continually rising atmospheric CO_2 concentrations have rendered agricultural practices that result in CO_2 sequestration rather than production particularly desirable. Replacing agricultural lime with silicate minerals could be a viable strategy for raising soil pH while simultaneously sequestering carbon.

Silicate minerals have long been applied to both agricultural soils in the tropics and forest soils in Europe as a mineral fertilizer that has the added benefit of increasing soil pH (Gillman et al., 2002; Van Straaten, 2006; Anda et al., 2009, 2015). Uptake of CO_2 through the weathering of silicate minerals is the primary regulator of atmospheric CO_2 concentrations on geologic time scales (Gislason and Oelkers, 2008). However, the natural rate of uptake by weathering is not sufficient to negate anthropogenic CO_2 emissions, which are produced at a rate over 35 times higher than the natural rate of carbon sequestration via weathering (Amiotte Suchet et al., 2003; Olivier et al., 2016).

Using finely ground silicate minerals as a replacement for agricultural lime would expose these minerals to soil acidity, enhancing their weathering rate to expedite CO_2 consumption and serve as a low-risk method of mitigating anthropogenic CO_2 emissions (Schuiling and

Krijgsman, 2006; Hangx and Spiers, 2009; Beerling et al., 2018). The consumption of protons during the weathering of applied silicate minerals would also increase soil pH, though few studies have quantified the magnitude of this effect (ten Berge et al., 2012; Renforth et al., 2015). Model results indicate that sufficient application of such minerals to weathering hotspots could draw atmospheric CO₂ concentrations back down to 350-390 ppm by 2100 (Taylor et al., 2015). However, due to the paucity of experimental data, it is unclear how the application of silicate minerals may affect soil properties, including soil pH and the decomposition rate of soil organic carbon.

The weathering of silicate minerals consumes dissolved CO₂ by neutralizing carbonic acid (H₂CO₃) to produce bicarbonate (HCO₃⁻), silicic acid (H₄SiO₄), and base cations in solution (i.e Ca²⁺, Mg²⁺, Na⁺, and K⁺) (Equation 1). These reaction products may then be leached out of the soil and transported to the ocean. The resulting influx of bicarbonate contributes to ocean alkalinity, thus counteracting ocean acidification. If the additional bicarbonate precipitates as biogenic carbonates, a portion of this carbon can then be permanently sequestered in geologic formations by forming limestone or dolomite seabeds. (Wallmann and Aloisi, 2012)



Equation 1: Weathering reaction of Mg-olivine (forsterite), an abundant silicate mineral, and ensuing precipitation of magnesium carbonate. The weathering reaction results in 4 moles of CO₂ consumed per mole of olivine weathered. The precipitation of carbonate minerals results in more permanent sequestration but reduces the amount of CO₂ sequestered by 50%.

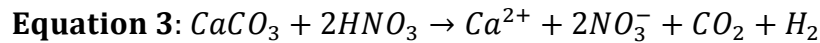
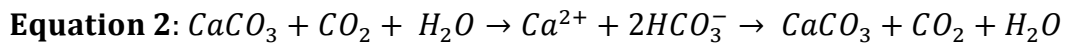
For the consumption of CO₂ by weathering of applied minerals to occur on useful time scales, it would be necessary to select silicate minerals that are easily weatherable. Volcanic rocks with low silica content and poor or glassy crystal structure weather the most quickly

(Gislason and Oelkers, 2011). Of the major silicate minerals, olivine, which is common in basic igneous rocks, is the most rapidly weathered (Schuiling and Krijgsman, 2006).

Exposure to soil acidity enhances mineral weathering rates; soil organic acids in particular are dominant drivers of mineral dissolution in the soil (Berner and Berner, 2012). The presence of oxalic acid, for example, has been observed to increase forsterite (Mg-olivine) dissolution rates by as much as 600% (Olsen and Rimstidt, 2008). Additionally, the decomposition of soil organic matter renders the $p\text{CO}_2$ of the soil pore space 10 to 100 times higher than the $p\text{CO}_2$ of the atmosphere (Bohn et al., 1985). This elevated $p\text{CO}_2$ increases the concentration of carbonic acid in the soil solution and further enhances weathering rates. However, very acidic soils may neutralize a portion of the bicarbonate produced to re-emit CO_2 , reducing net carbon sequestration.

On the other hand, the standard practice of neutralizing soil acidity with agricultural lime adds to agricultural greenhouse gas emissions (West & McBride, 2005), which are the second largest source of greenhouse gasses globally (IPCC, 2014). The United States alone emits between 4.4 and 13.4 Tg CO_2 per year from the dissolution of agricultural lime (West and McBride, 2005). This large range in estimates is due in part to the challenge of determining the relative amounts of weathering carried out by carbonic acid and other, stronger acids. The relative importance of carbonic acid in the weathering process can vary with soil pH and agricultural practices (Semhi et al., 2000; Hamilton et al., 2007; Perrin et al., 2008). Strong mineral acids, such as nitric acid (HNO_3), which is derived from the dissolution of nitrogen fertilizers or from inputs by acid rain, can also play an important role in carbonate weathering (Semhi et al., 2000; Hamilton et al., 2007; Perrin et al., 2008). Though the dissolution of lime by

carbonic acid effectively converts CO₂ to bicarbonate (Equation 2), its dissolution by strong acids like nitric acid produces CO₂ (Equation 3).



There is therefore some debate as to whether the dissolution of lime is in fact a source or sink of CO₂. The IPCC assumes that all carbon applied as lime becomes CO₂ upon dissolution (Houghton et al., 1997), but some studies indicate that the net effect of the dissolution of applied lime is to consume CO₂ (Oh and Raymond, 2006; Hamilton et al., 2007). Though the bicarbonate produced when lime is dissolved by carbonic acid serves as a temporary carbon sink, the release of CO₂ during the eventual reprecipitation of carbonate minerals renders this reaction a carbon neutral process in the long term (Equation 2). This temporary sink may be relevant to addressing elevated atmospheric CO₂ concentrations in the short term, but more research defining its residence time is needed (Hamilton et al., 2007).

Alternatively, the weathering of olivine by carbonic acid consumes twice as much CO₂ as the dissolution of lime, making it a more effective soil amendment with respect to carbon sequestration (Figure 4.1). However, the weathering effect of strong acids also needs consideration when assessing the carbon sequestration potential of silicate minerals, particularly when soil pH is below 5 (Plummer et al., 1979). The dissolution of silicate minerals by nitric acid, for example, does not produce carbonate alkalinity, and would therefore reduce the carbon sequestration efficiency of the process. Nonetheless, given that dissolution of agricultural lime by nitric acid is a source of CO₂, the replacement of lime with an alternative soil amendment would be still more critical in terms of preventing CO₂ emissions if such acids play a strong role in mineral dissolution in a particular environment.

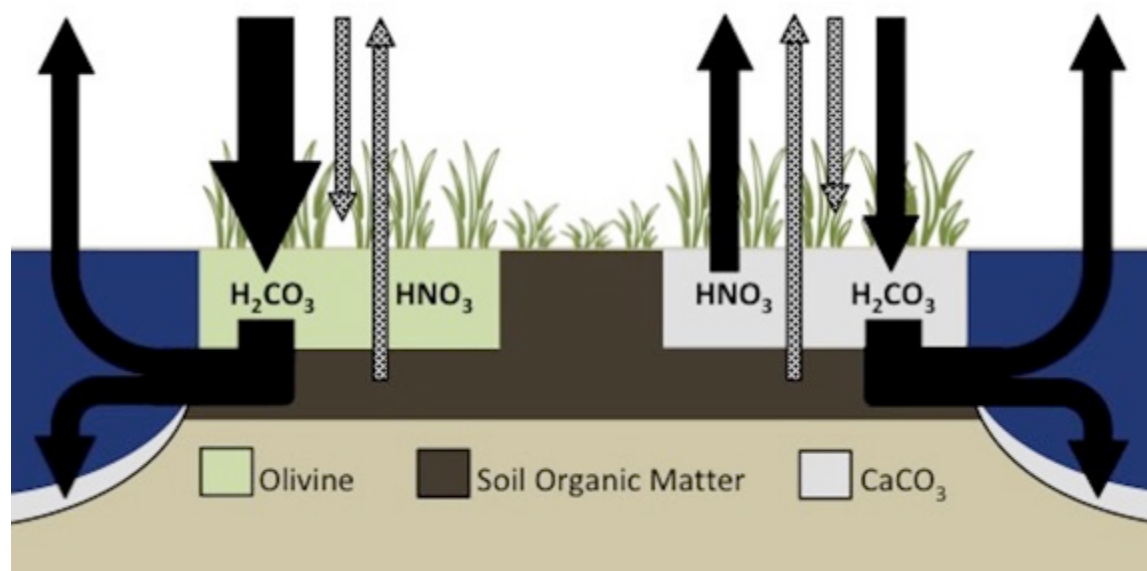


Figure 4.1 Carbon fluxes induced by the application of olivine and agricultural lime (CaCO_3) to soils. Black arrows indicate known CO_2 fluxes and are scaled based on the magnitude of flux in moles of carbon per mole of applied soil amendment. Shaded arrows represent unknown CO_2 fluxes that would result if the amendments increase soil organic matter decomposition, which this experiment aims to assess, or net primary productivity. The size of these shaded arrows is not representative of expected flux sizes. Green represents olivine, gray represents CaCO_3 , and brown represents soil organic matter. The reacting acid is indicated within the treatment box, with nitric acid (HNO_3) representing strong acids that may weather applied minerals instead of carbonic acid (H_2CO_3).

However, the potential effects of applied silicate minerals on soil organic carbon (SOC) have yet to be addressed by those promoting the use of enhanced mineral weathering as a carbon sequestration technique. It is well established that microbial activity increases with increasing pH, which can result in faster turnover of soil organic matter (Fuentes et al., 2006; Paradelo et al., 2015). Therefore, raising soil pH by the addition of olivine has the potential to increase SOC loss by decomposition, reducing the efficiency of carbon uptake by enhanced mineral weathering.

Before the application of silicate mineral amendments can be considered as a management tool for carbon sequestration, it is critical that any effects on SOC are assessed. This study aimed to determine if increases in decomposition with the application of olivine

outweighed the uptake of carbon by enhanced weathering. To do this, we examined the effects of these amendments on heterotrophic respiration and estimated the consumption of CO₂ associated with mineral weathering. As silicate minerals may replace lime, it is also necessary to compare the effects of olivine amendments with the effects of agricultural lime applications and assess differences in net soil CO₂ flux between the two treatments. A liming treatment was included in the study for this purpose.

We also endeavored to assess the effectiveness of olivine as an alternative to agricultural lime. To this end, we compared the effects of these amendments on soil pH. As high levels of exchangeable aluminum at low pH are often the limiting factor for plant productivity in acidic soils (Adams, 1984), we also tested the effects of olivine on aluminum availability.

Though it is known that olivine dissolution proceeds most quickly in warm, moist, low-pH environments (Hangx and Spiers, 2009) and there is general consensus that organic anions and high molecular weight organic acids act to increase the rate of olivine dissolution (Wogelius and Walther, 1991; Olsen and Rimstidt, 2008), only two studies have attempted to quantify weathering rates of applied olivine in the soil environment (ten Berge et al., 2012; Renforth et al., 2015). Uncertainty surrounding dissolution rates has therefore resulted in a wide range of predicted values for the amount of CO₂ the weathering of applied olivine has the potential to sequester (Renforth, 2012). The extent to which olivine application rates may influence dissolution is also unclear, though such information is critical to maximizing the efficiency of this process. Our study therefore included two application rates with the goal of quantifying olivine dissolution as a function of the amount applied.

4.2 METHODS

4.2.1 *Sampling and Analyses*

Soil samples were taken from Nørholm Hede, a heathland in southwestern Denmark. This site was chosen for its organic-rich, acidic soils and because it had not been managed as an agricultural field since the 1890's, eliminating any risk of the presence of residual applied lime which could impact our results. Though these highly acidic soils are not reflective of typical agricultural soils, the soil properties at this site increased the probability of detecting any effects of olivine applications within the short time frame of our incubation. The low pH of these soils was expected to increase the rate of mineral dissolution, whereas the high carbon content was likely to magnify the effect size of any impacts on the decomposition of soil organic matter. The results of this study therefore represent an approximate upper limit to the impacts of mineral applications.

Soils at the site were developed on glacial sand and are classified as sandy podzols. The undisturbed portion of the heathland has a typical podzol profile, but in the previously cultivated area from which our samples were taken the A horizon has been mixed with the E horizon in a plough layer. Our samples were taken from the organic-rich top 0-10 cm of the soil in an area dominated by the perennial grass *Deschampsia flexuosa* (L.). The initial pH was 3.55, and the soil carbon concentration was 5.49%. (Evelien, 2012)

The moist-weight equivalent of 20 g of dry soil was placed into each of forty 110 ml bottles after being sieved to 2 mm. Any roots that passed through the 2 mm sieve remained in the samples. These samples were then divided into four treatment groups: control, lime, high olivine (OLIV_{high}), and low olivine (OLIV_{low}). For our treatments we used a finely ground olivine and a finely ground lime, both of which had a d50 grain size of 20 microns. This lime was determined

to be 97% CaCO₃ based on acid digestion according to EPA Method 3050 followed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Our olivine powder was primarily composed of forsterite, containing 22.3% Mg and only 3.62% Fe by mass as determined by ICP-AES following acid digestion according to AOAC Method 957.02. The chemical composition of the applied olivine is shown in Table 4.1.

Table 4.1 Chemical Composition of Olivine

	Content (%)
Mg	22.30
Fe	3.62
Al	0.70
Ni	0.232
Ca	0.31
Cr	0.157
K	0.065
Na	0.043
S	0.022

To the ten lime-amended samples, 0.16 g of lime ($.008 \text{ g}_{\text{lime}} \text{ g}_{\text{soil}}^{-1}$) was added and thoroughly mixed into the soil (Table 4.2). Similarly, 0.16 g of olivine was added to the OLIV_{low} treatment, and 0.80 g of olivine ($.04 \text{ g}_{\text{oliv}} \text{ g}_{\text{soil}}^{-1}$) was added to the OLIV_{high} treatment. All samples, including the controls, were mixed for the same amount of time in order to ensure similar amounts of disturbance. Soils were then packed down in the chambers to a bulk density of approximately 1.245 g cm^{-3} .

Table 4.2 Treatment application rates.

Treatment	Amount applied ($\text{g g}_{\text{soil}}^{-1}$)
Control	-
Lime	0.008
OLIV _{low}	0.008
OLIV _{high}	0.04

The higher olivine application rate was chosen to match the $5 \text{ kg m}^{-2} \text{ yr}^{-1}$ of harzburgite, an olivine rich rock, that Taylor et al. (2015) estimated would result in a drawdown of CO_2 sufficient to return atmospheric CO_2 concentrations to approximately 350 ppm by 2100 if applied to weathering hotspots, assuming a 10 cm mixing depth. Without this harzburgite application, atmospheric CO_2 concentrations are otherwise predicted to reach 540 ppm by 2100 under the IPCC's RCP 4.5 medium-level mitigation scenario (Taylor et al., 2015). $\text{OLIV}_{\text{high}}$ was therefore intended to represent an application rate large enough to substantially impact atmospheric pCO_2 . The application rate for OLIV_{low} and lime was selected with several factors in mind. This application rate matched Taylor et al.'s $1 \text{ kg m}^{-2} \text{ yr}^{-1}$ application rate, which under the same conditions as previously described is expected to decrease CO_2 concentrations by ~ 140 ppm compared to the standard RCP4.5 scenario. It was also not considerably higher than the approximately $0.006 \text{ g}_{\text{lime}} \text{ g}_{\text{soil}}^{-1}$ recommended to raise soil pH from 3.5 to 6.5 according to the manufacturer's instructions (Columbia River Carbonates). These application rates also fall within the range of olivine application rates used as treatments by ten Berge et al. (2012) ($0.000727, 0.00364, 0.0182, \text{ and } 0.105 \text{ g}_{\text{oliv}} \text{ g}_{\text{soil}}^{-1}$), allowing for comparison with their results.

$$\textbf{Equation 4: } F_{\text{net}} = F_{\text{resp}} + F_{\text{diss}} - F_{\text{weathering}}$$

The net flux of CO_2 between the incubated soil and the atmosphere (F_{net}) reflects the combination of heterotrophic soil respiration (F_{resp}) and CO_2 produced by the dissolution of lime (F_{diss}), if applicable, less any consumption of CO_2 due to mineral weathering ($F_{\text{weathering}}$) (Equation 4). F_{net} was determined by measuring the CO_2 concentration in the headspace of the closed chamber with an SBA-5 infrared gas analyzer (PP Systems, Amesbury, MA), connected via a closed loop. As the CO_2 flux from the soil decreases as the headspace pCO_2 increases, linearly determining the flux rate based on the first and last measurement would underestimate

the rate of CO₂ accumulation in the chamber. Therefore, the Hutchinson-Mosier non-linear exponential regression model was used to calculate the initial F_{net} in μmol CO₂ day⁻¹ g-soil⁻¹ from a continuous time series of headspace CO₂ measurements (Hutchinson and Mosier, 1981; Pihlatie et al., 2013). Measurements started from standard initial concentration of 425 ppm. The length of the sampling period ranged from 1 to 3 minutes over the course of the experiment based on the rate of CO₂ production, but the same measurement period was used for all samples at each time point.

Initial measurements were taken after two days of pre-incubation following the addition of treatments to the samples. Measurements were taken over the course of three months on days 3, 5, 7, 10, 13, 20, 27, 41, 69, and 97 after the addition of treatments. Throughout the experiment, de-ionized water was added after flux measurements to maintain soil moisture approximating field conditions. Samples were stored at room temperature (20-25° C) and left uncovered between measurements to prevent the buildup of CO₂ from inhibiting microbial activity.

After the 3-month incubation period, samples were oven dried at 60° C for 48 hours, re-homogenized, and split into three sets of subsamples for additional analyses. Soil pH was measured in a 1:1 mixture of soil and deionized water (Burt, 1996). Subsamples of the control and olivine treated soils were subjected to 1 M NH₄NO₃ extraction. 30 ml of 1 M NH₄NO₃ were added to 3 g of soil, which was shaken over night. After centrifuging for 10 minutes, the supernatant was retained. This process was repeated two more times with 10 ml 1 M NH₄NO₃ and 10 minutes of shaking before centrifuging. The resulting solution was then vacuum-filtered through a 0.22 μm Millex-GP filter (Millipore) and analyzed for exchangeable cations, including Mg and Al, by ICP-AES.

The fraction of olivine weathered (%O_w) was calculated by subtracting the amount of exchangeable Mg in the control samples (Mg_{control}) from the amount of exchangeable Mg in the olivine-treated samples (Mg_{OLIV}), and dividing by the total amount of Mg applied as olivine (Mg_{applied}) (Equation 5) (ten Berge et al., 2012).

$$\text{Equation 5: } \%O_w = (Mg_{OLIV} - Mg_{control}) / Mg_{applied}$$

In making this calculation, we assumed stoichiometric dissolution. This is a reasonable assumption as magnesium from weathering olivine has been shown to dissolve congruently with silica in conditions comparable to the soil environment after an initial period in which preferential removal of cations by organic acids results in an silica rich phase developed on the surface (Barman et al., 1992; Olsen and Rimstidt, 2008). However, there is evidence that some organic acids may preferentially remove iron over magnesium, which could result in an underestimation of the amount of olivine weathered when using magnesium as a proxy (Barman et al., 1992). The theoretical upper limit for CO₂ consumption by olivine weathering is 4 moles of CO₂ per mole of olivine to produce 4 moles of bicarbonate (Equation 1). This 4:1 ratio was used to estimate the amount of CO₂ that was converted to bicarbonate by weathering of the applied olivine, assuming that carbonic acid was the driver of all weathering.

4.2.2 *Statistical Analyses*

Differences in F_{net} over time between treatments were compared using a linear mixed effects model (“lme” in R Version 3.2.3) with sample number as a random intercept term to account for repeated measures and treatment and day as categorical fixed effects (α=0.05) (Pinheiro et al., 2017). Heterogeneity of variances was corrected for by allowing variances to differ for each treatment and day. The first four measurements from day 69, one from each treatment, were suspected to be influenced by measurement errors and were therefore removed. Post hoc

comparisons using Tukey's tests ("lsmeans" in R) were used to interpret significant interactions ($\alpha=0.05$).

The cumulative F_{net} over the course of the experiment ($F_{\text{net, tot}}$) for each sample was determined by calculating the area under the curve of F_{net} rates over time (Prism 7, La Jolla, CA). We calculated the cumulative soil respiration ($F_{\text{resp.tot}}$) of the olivine-amended samples by adding the amount of CO_2 consumed by olivine weathering ($F_{\text{weathering}}$) to $F_{\text{net, tot}}$. As our methods did not allow us to separate out lime-derived CO_2 from microbially respired CO_2 , we were only able to calculate a minimum value for $F_{\text{resp.tot}}$ for our lime-amended samples. To do this we subtracted the amount of CO_2 that would be produced if all of the added lime-C were converted to CO_2 from $F_{\text{net, tot}}$. Though there is significant uncertainty in this estimate, any deviations from our assumed conditions would result in a larger value for $F_{\text{resp.tot}}$ of the limed samples. We are therefore confident in this calculated minimum, which allows for comparison with other treatments. In the control samples, $F_{\text{resp.tot}}$ was equivalent to $F_{\text{net, tot}}$.

Differences in $F_{\text{net, tot}}$, $F_{\text{resp.tot}}$, exchangeable Mg and Al, and pH were tested across treatments by one-way ANOVA followed by Tukey's tests for multiple comparisons ($\alpha=0.05$) (Prism 7, La Jolla, CA). We also tested for any correlation between $F_{\text{resp.tot}}$ and sample pH using Pearson's correlation coefficient (Prism 7, La Jolla, CA) to determine if changes in pH with treatment were responsible for any observed differences in respiration. Straight lines and quadratic curves were fit to the data in order to assess the form of the relationship.

4.3 RESULTS

We found a significant interaction between the effects of treatment and time on F_{net} ($p < .001$, F-test). Lime had a significantly higher F_{net} than all other treatments until day 97 ($p < .001$, Tukey's HSD), at which point there was no significant difference between lime and the other

treatments (Figure 4.2, Table 4.3). F_{net} of OLIV_{high} was initially significantly higher than the control and OLIV_{low} ($p < .05$, Tukey's HSD). However, by day 10, OLIV_{high} was no longer elevated relative to OLIV_{low} and the control. Beginning on day 20, there was a trend such that F_{net} from the control was higher than F_{net} from the olivine treatments, but the only significant difference was between OLIV_{high} and the control on day 97, at which point OLIV_{high} was 17.5% lower than the control ($p = .0421$, Tukey's HSD). At no point was there a significant difference between OLIV_{low} and the control.

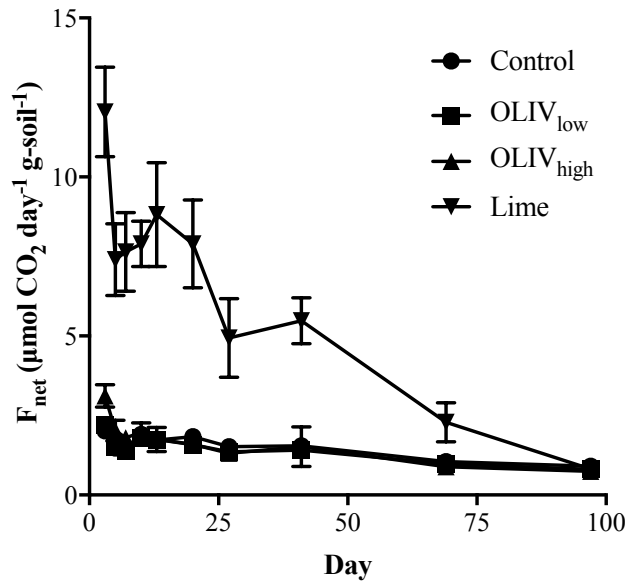


Figure 4.2 Net CO₂ flux (F_{net}) by treatment over the course of the incubation. Error bars indicate SD.

Table 4.3 Mean net CO₂ flux (F_{net}) for each treatment by day (SD). Treatment means from the same day followed by the same letter are not significantly different ($\alpha=0.05$), as assessed by Tukey's HSD.

Day	Control	Oliv-Low	Oliv-High	Lime
3	2.02 (0.12)a	2.22 (0.23)a	3.12 (0.35)b	12.04 (1.41)c
5	1.47 (0.22)a	1.51 (0.18)a	2.03 (0.33)b	7.40 (1.13)c
7	1.45 (0.26)a	1.39 (0.10)a	1.80 (0.14)b	7.64 (1.24)c
10	1.91 (0.23)a	1.80 (0.24)a	1.97 (0.30)a	7.89 (0.72)b
13	1.73 (0.19)a	1.75 (0.38)a	1.76 (0.17)a	8.82 (1.63)b
20	1.83 (0.17)a	1.59 (0.13)a	1.59 (0.21)a	7.89 (1.38)b
27	1.52 (0.09)a	1.35 (0.16)a	1.32 (0.18)a	4.94 (1.24)b
41	1.55 (0.17)a	1.41 (0.17)a	1.52 (0.62)a	5.48 (0.73)b
69	1.05 (0.17)a	0.98 (0.18)a	0.89 (0.19)a	2.28 (0.62)b
97	0.91 (0.04)a	0.81 (0.12)a,b	0.75 (0.13)b	0.82 (0.20)a,b

Treatment had a significant effect on available magnesium ($p < .001$, F-test). The amount available in the control (52.5 mg kg^{-1} , $SD = 3$) was significantly lower than OLIV_{low} (529 mg kg^{-1} , $SD = 88$) ($p < .001$, Tukey HSD), which was in turn significantly lower than OLIV_{high} (685 mg kg^{-1} , $SD = 131$) ($p = .0022$, Tukey HSD) (Figure 4.3). From these values we estimate that 26.7% ($SD = 4.9$) of the applied olivine was dissolved in OLIV_{low}, whereas only 7.1% ($SD = 1.8$) of the applied olivine was weathered in OLIV_{high}.

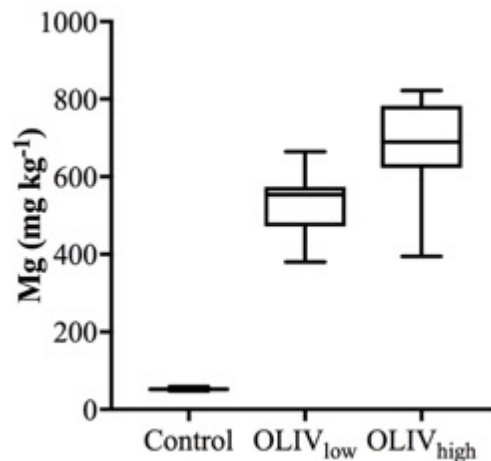


Figure 4.3 Distribution of exchangeable Mg values as a function of treatment at the end of the experiment. The central line indicates the median value, the boxes extend from the 25th to 75th percentiles, and the whiskers indicate the minimum and maximum values. All treatments were significantly different from one another ($p < .005$, Tukey HSD).

Based on the amount of olivine dissolved in each treatment, we calculate that gross carbon sequestration was on average 0.050 g CO₂ (*SD* = 0.009) per chamber for OLIV_{low} and 0.067 g CO₂ (*SD* = 0.017) for OLIV_{high}. Scaling these values up with an assumed 10 cm mixing depth, OLIV_{high} application rates would have consumed 4.16 metric tons CO₂ ha⁻¹ (*SD* = 1.04), and OLIV_{low} application rates would have consumed 3.13 t CO₂ ha⁻¹ (*SD* = 0.58) over the course of three months.

Treatment had a significant effect on both $F_{\text{net, tot}}$ and $F_{\text{resp, tot}}$ ($p < .001$, *F*-test) (Figure 4.4). Only the $F_{\text{net, tot}}$ of lime (405 $\mu\text{mol CO}_2 \text{ g}^{-1}$, *SD* = 55) was significantly higher than the other treatments (OLIV_{low}, OLIV_{high}, and control) ($p < .001$, Tukey's HSD). Lime increased $F_{\text{net, tot}}$ by a factor of 3.21 over the control, 3.49 over OLIV_{low}, and 3.58 over OLIV_{high}. There was no significant difference in $F_{\text{net, tot}}$ between the control (126 $\mu\text{mol CO}_2 \text{ g}^{-1}$, *SD* = 8), OLIV_{low} (116 $\mu\text{mol CO}_2 \text{ g}^{-1}$, *SD* = 11), and OLIV_{high} (113 $\mu\text{mol CO}_2 \text{ g}^{-1}$, *SD* = 21).

OLIV_{low} and OLIV_{high} both had significantly higher $F_{\text{resp, tot}}$ than the control ($p < .05$, Tukey's HSD). However, at 174 (*SD* = 18) and 188 (*SD* = 29) $\mu\text{mol CO}_2 \text{ g}^{-1}$, respectively, OLIV_{low} and OLIV_{high} were not significantly different from one another. $F_{\text{resp, tot}}$ from the lime-amended samples (325 $\mu\text{mol CO}_2 \text{ g}^{-1}$, *SD* = 55) was significantly higher than all other treatments ($p < .001$, Tukey's HSD): $F_{\text{resp, tot}}$ with lime was 2.6 times higher than the control, 1.9 times higher than OLIV_{low}, and 1.7 times higher than OLIV_{high}.

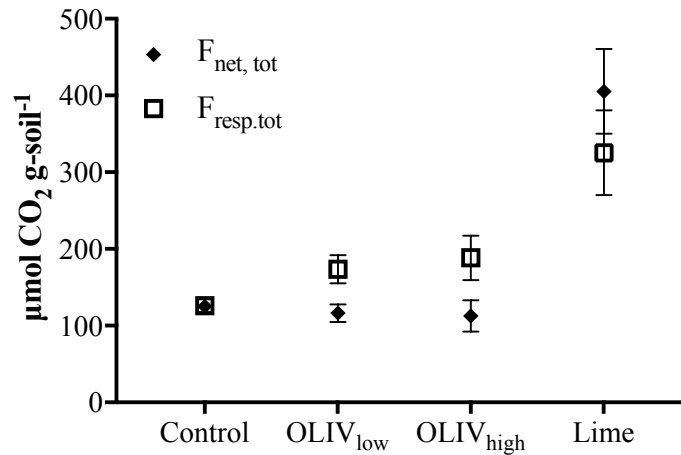


Figure 4.4 Mean cumulative net CO₂ flux ($F_{\text{net,tot}}$) and mean cumulative soil respiration ($F_{\text{resp,tot}}$) by treatment. Error bars indicate SD, but are not shown when shorter than the height of the symbol. Lime is significantly higher than all other treatments with respect to both variables ($p < .001$, Tukey HSD). $F_{\text{resp,tot}}$ of OLIV_{high} ($p = .0008$, Tukey HSD) and OLIV_{low} ($p = .0129$, Tukey HSD) are significantly higher than the control.

Soil pH was significantly affected by treatment ($p < .001$, F-test); the mean pH of all treatments were significantly different from one another ($p < 0.001$, Tukey's HSD) (Figure 4.5). The final pH of the control was 3.56 ($SD = 0.04$), OLIV_{low} was 4.69 ($SD = 0.05$), OLIV_{high} was 5.18 ($SD = 0.06$), and lime was 6.06 ($SD = 0.4$). Lime increased soil pH by 2.51 points compared to the control, whereas the OLIV_{high} and OLIV_{low} increased pH by 1.63 and 1.13 points respectively.

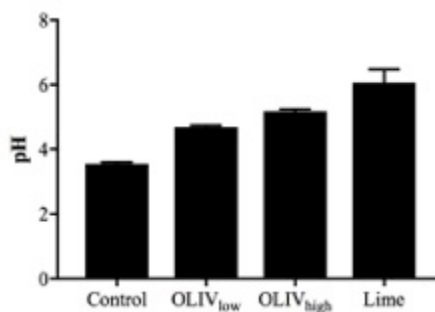


Figure 4.5 Treatment effects on soil pH. All treatments are significantly different from one another ($p < .05$). Error bars indicate SD.

The increase in pH decreased the availability of aluminum ($p < .001$, F-test), which was available in significantly lower concentrations in both OLIV_{high} (2.8 mg kg⁻¹, $SD = 0.6$) and OLIV_{low} (7.7 mg kg⁻¹, $SD = 1.1$) compared to the control (134 mg kg⁻¹, $SD = 9.7$), ($p < .001$, Tukey HSD).

$F_{\text{resp.tot}}$ was positively correlated with soil pH as assessed by Pearson's r ($r = .88$, $n = 40$, $p < .001$). This correlation was characterized by a quadratic relationship ($r^2 = .85$, Figure 4.6).

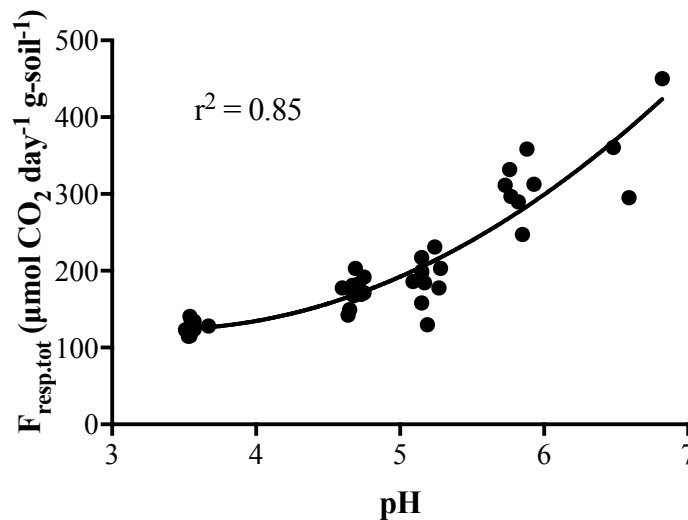


Figure 4.6 Relationship of cumulative soil respiration ($F_{\text{resp.tot}}$) to soil pH, fit with a quadratic curve. Each point represents an individual sample.

4.4 DISCUSSION

Results suggest that the application of olivine to agricultural soils reduces agricultural CO₂ emissions compared to the use of agricultural lime and has the potential to be an effective tool for carbon sequestration. The lime-amended soils were a source of CO₂ compared to the control, but the olivine-amended samples were not. The cumulative net flux ($F_{\text{net,tot}}$) of the olivine treatments was not lower than the control due to the increase in respiration accompanying the application of olivine. However, this does not necessarily imply that olivine amendments are ineffective at sequestering carbon as our experiment did not account for potential changes in

plant inputs to soil carbon with treatments. Long term studies on the effects of applying agricultural lime on soil organic carbon often indicate that improved plant productivity associated with higher soil pH results in greater inputs of organic matter to the soil, resulting in increased SOC (Paradelo et al., 2015). It is therefore likely that the improved soil conditions due to the effects of olivine application would likewise result in increased inputs to the SOM pool, negating losses due to increased decomposition rates, and rendering the application of olivine a net carbon sink. However, long-term field studies are needed to assess any differences in effects between lime and olivine on plant inputs to the soil, which would affect the overall carbon balance.

Though we observed a significantly greater increase in total soil respiration in the lime-amended soils, the olivine treatments also increased $F_{\text{resp.tot}}$ over the control. However, as we are unable to parse out any changes in the effects of olivine amendments on respiration or in the rate of weathering over the course of the experiment, it is unclear whether the increase in $F_{\text{resp.tot}}$ with the application of olivine was due to a larger initial increase in respiration, or if soil respiration remained consistently elevated compared to the control throughout the experiment. The small initial increase in the F_{net} of the OLIV_{high} treatments compared to the control was followed by a decrease on the final day. Though our methods did not allow us to determine if this decrease was primarily due a decrease in respiration or increase in consumption of CO₂ by weathering, there was a non-significant trend in which the olivine-amended treatments had lower F_{net} than the control beginning on day 20. We can therefore presume that around this time the amount of CO₂ consumption in these treatments began to outweigh any effects on soil respiration. Had our incubation period been longer and this trend continued, we might have eventually seen a net sink in OLIV_{high} compared to the control, even without changes in plant inputs playing a role.

Though the exact effects of changes in soil pH on soil carbon mineralization can be hard to predict, the increase in pH with the application of our treatments is likely driving the increase in respiration in this experiment. Soil respiration has generally been shown to increase with pH (Kemmitt et al., 2006; Paradelo et al., 2015), and indeed we observed a strong positive correlation between these two variables, but other studies on the effects of liming on soil respiration have produced varied results. Some, like ours, have found soil respiration to increase with the application of agricultural lime (Dumale et al., 2011; Ahmad et al., 2014), while others observed no effect (Bertrand et al., 2007; Biasi et al., 2008), or even reduced decomposition (Wachendorf, 2015). Yet another study found that agricultural lime induced increases in soil respiration for the first three days, likely resulting from increased solubility of SOC, but reduced SOC mineralization after that point, presumably due to greater microbial C-use efficiency under more favorable pH conditions (Grover et al., 2017). Similar mechanisms may be responsible for the changes in $F_{\text{net,resp}}$ of OLIV_{high} over the course of our experiment.

Olivine proved to be effective at increasing soil pH in a relatively short time, though its effect was not as strong as lime. However, a number of studies have indicated that lime requirements should be determined with the goal of correcting the underlying problems associated with low pH, such as toxic levels of aluminum, rather than achieving the near-neutral pH that is typically recommended (Farina et al., 1980; Adams, 1984; Hoyt and Nyborg, 1987; Farina and Channon, 1991). Aluminum toxicity, which develops below a pH of approximately 5.2 (Sumner and Noble, 2003), is often the most limiting factor affecting plant growth in acid soils (Adams, 1984; Sumner and Yamada, 2002). Raising soil pH above the level required to eliminate exchangeable aluminum has not been shown to provide additional benefits, and in some cases may even decrease yields (Farina et al., 1980). The application of olivine decreased

aluminum availability from levels that were high enough to be toxic to plants to levels that fall within a suitable range for crop growth (Kochian et al., 2005). These results indicate that olivine is a suitable replacement for lime in regards to its ability to correct problems of soil acidity, providing an additional use for this product that would aid in its adoption for carbon sequestration purposes. As existing infrastructure for applying lime to croplands could be repurposed to apply silicate minerals, the cost of applying olivine-rich rock would be comparable to current liming practices (Schuiling and Krijgsman, 2006), and may be further offset by the sale of carbon credits or increases in crop productivity (Beerling et al., 2018), increasing the economic viability of this method of sequestering carbon.

When assessing the suitability of olivine as a soil amendment and determining application rates, it is also necessary to take into account its heavy metal content. Nickel toxicity in particular may pose a problem. However, other forms of silicate minerals, such as olivine-rich basalt, may work well as a more widely available alternative. Though the carbon capture potential of basalt is lower, it tends to have lower concentrations of nickel than olivine and also contains additional plant nutrients. Mining wastes or calcium silicate by-products of cement and steel production are also potential sources of silicate minerals that may be suitable for agricultural applications. (Beerling et al., 2018)

Determining ideal application rates will be necessary to maximize efficiency and cost-effectiveness. A significant amount of Mg was weathered from both OLIV_{high} and OLIV_{low}, which would be of substantial benefit to Mg-limited agricultural soils. However, the %O_w was dependent on the rate of application. The percentage of olivine weathered was higher at the lower application rate: 26.7% of the applied Mg in the OLIV_{low} treatment was released into solution, whereas only 7.1% of the applied Mg was released in the OLIV_{high} treatment. Though

the olivine application rate of OLIV_{low} was only 20% of OLIV_{high}, OLIV_{low} released 75.4% of the amount of Mg released by OLIV_{high}.

A similar trend in the fraction of olivine weathered was observed by ten Berge et al. (2012). In a pot study, they also found that higher application rates resulted in a lower percentage of olivine dissolved over the course of 32 weeks (ten Berge et al., 2012). However, the proportion of applied olivine dissolved observed in our experiment was markedly higher. The %O_w in OLIV_{low} was 80% higher than observed in ten Berge et al.'s (2012) lowest application rate. Only 14.8% of the applied olivine dissolved at their lowest application rate, compared to the %O_w of 26.7% in OLIV_{low}, despite the fact that our application rate was almost 50 times theirs and their incubation period was almost three times longer. Renforth et al. (2015) did not calculate the fraction weathered, but found dissolution rates in their column leaching study that were comparable to or slightly lower than those found by ten Berge et al. (2012). The discrepancy between our results and the results of these other experiments is likely due to our use of a highly acidic soil for the incubations.

At the dissolution rates we observed, the annual application rates proposed by Taylor et al. (2015) are too high. Only 28.4% of the applied olivine at the 5 kg m⁻² yr⁻¹ application rate would have dissolved before the following years application, and the 1 kg m⁻² yr⁻¹ application would have just completed dissolution within one year. However, as pH increases and the soil approaches saturation with respect to olivine, dissolution rates should decrease. It is therefore unlikely that quick dissolution observed in the three months of our experiment would remain constant throughout the year. Further, additional applications would not be likely to weather as rapidly, rendering such high annual application rates an inefficient use of resources.

The fact that %O_w decreased at higher application rates suggests that further work is needed to optimize this process and determine the most cost-effective application rate. It may be preferable to apply smaller amounts of olivine over a larger area to maximize CO₂ consumption, rather than using high application rates on smaller areas. Optimizing the spatial distribution and application rates of silicate minerals with respect to carbon sequestration will require more data across the range of typical site conditions in agroecosystems. Such information will also be critical in order to accurately quantify the amount of CO₂ this process consumes. Accurate accounting of sequestered carbon will be necessary if this process is to be certified for carbon credits, which may offset some of the cost and increase its adoption by farmers.

4.5 CONCLUSION

Our results illustrate the potential utility of enhanced mineral weathering as a carbon sequestration tool. Over the course of only three months, on an areal basis the dissolution of olivine at the lower application rate would have sequestered 3.13 t CO₂ ha⁻¹. This amount is within the range of expected sequestration rates over the course of an entire year for a number of common land management practices aimed at carbon storage, including conservation tillage, changes in grazing management, reforestation, or the conversion of cropland to permanent grassland (Murray et al., 2005). The use of olivine or other easily weatherable silicate minerals instead of lime to increase the pH of agricultural soils would also prevent the emission of lime-derived CO₂ and may decrease the amount of soil respiration induced by the addition of soil amendments. By consuming anthropogenic CO₂ and reducing agricultural CO₂ emissions, enhanced mineral weathering has the potential to serve as an important part of the solution to the problem of elevated atmospheric CO₂ concentrations.

Chapter 5. CONCLUSION

This research highlights the potential for soil carbon storage to play an important role in controlling atmospheric CO₂ concentrations. Though there has been some concern that climate change may reduce soil carbon stocks due to increased decomposition under warmer temperatures or a priming effect caused by elevated CO₂, these results showed a significant increase in soil carbon in a Danish grass/heathland under future climate conditions due to the effect of elevated CO₂ on plant rooting.

These findings also suggest that there is an opportunity to mitigate anthropogenic CO₂ emissions by managing soils to increase carbon storage through reduced decomposition of existing organic matter and increased plant inputs. The use of less intensive forest management strategies that allow for the growth of competing vegetation resulted in a shift towards deeper rooting by Pacific Northwest Douglas fir trees in an effort to access soil moisture reserves. As deep soil carbon typically has long residence times, increasing inputs to these deep pools is likely to result in long-term storage.

Even more promising in terms of net carbon sequestered is the impact of changing management strategies for controlling soil pH in agricultural soils. Not only was decomposition of soil organic matter reduced by replacing lime with olivine, but the emission of CO₂ via the dissolution of lime was also prevented. Instead, the dissolution of olivine resulted in the consumption of CO₂ and concurrently raised soil pH to a high enough level to correct aluminum toxicity.

The significant amount of carbon that soils have the potential to sequester has often been overlooked in the development of climate change mitigation strategies. These results provide evidence for the necessity of including soil carbon cycling processes in carbon-climate models in

order to make accurate predictions of future climate changes, which are critical to the development of successful adaptation plans. Further, these results highlight the importance of incorporating land management practices into strategies for addressing the problem of increasing atmospheric CO₂ concentrations.

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