Title

Efficacy of enhanced silicate weathering to sequester C in fertile, neutral pH agricultural soils in California

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Efficacy of enhanced silicate weathering to sequester C in fertile, neutral pH agricultural soils in California

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Abstract

Silicate weathering is a primary control on Earth's climate as this process transforms atmospheric CO_2 dissolved in water into solid and aqueous mineral forms. Enhanced silicate weathering (ESW) increases the surface area of this natural reaction by using pulverized silicate rock which increases mineral weathering rates, thus increasing CO_2 consumption associated with mineral dissolution, and increases the reactivity of silicates by applying ground rock to soils or oceans, where H+ enhances dissolution rates. My thesis explores the efficacy of ESW to store CO_2 as inorganic C in soil to decrease radiative forcing caused by anthropogenic greenhouse gas (GHG) emissions. I utilized two silicate minerals, wollastonite and basalt, in a 2-year field study with corn and tomato to ascertain the efficacy of this method to achieve inorganic C storage significant to climate mitigation. I assessed crop yield, soil nutrient content, crop nutrient content, as well as inorganic C formation to draw conclusions about the advantages of enhanced mineral weathering in agriculture. We observed yield and pH increases in both crop types, however only corn showed significant storage of atmospheric carbon (C) as HCO_3^-. Another objective of my research is to determine if ESW will become more effective in future conditions as atmospheric CO_2 and temperature levels continue to rise. We measured yield, alkalinity, pH, and soil and crop nutrient content with soybean amended with basalt alone and basalt in combination with compost in a controlled growth chamber under two climate regimes: ambient CO_2 and temperature and elevated CO_2 and temperature. In ambient conditions, we saw no effect of silicate addition on soybean yield and alkalinity, while in elevated conditions, we observed significant treatment effects in yield, alkalinity, and pH.

Results in these field and pot studies support the use of ESW as a CO_2 drawdown pathway and fertilizer supplement in certain crops. Future studies should continue to assess ESW in fertile, well-buffered soils to determine their efficacy in agricultural environments.

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Introduction

Our global community is faced with the challenge of increasing crop production while reducing the environmental impacts of agriculture, particularly soil health and anthropogenic emissions. Reaching the goals of the Paris Climate Agreement requires rapid establishment of C capture and drawdown technologies, as well as emissions reduction in order to reduce atmospheric C concentration by 2050 (Canadell and Schulze 2013; Ibrahim et al. 2019). In order to incentivize such climate smart technological transformations in agriculture, it will be important to identify technologies that not only increase yields but do so while producing co-benefits for soil health, crop quality, and the environment. The dissolution of silicate minerals acts as a dominant control on Earth's climate on geologic timescales by converting atmospheric CO_2 dissolved in water to mineral forms such as HCO_3^- and $CaCO_3$. Increasing the surface area of this reaction by applying ground silicate rock to soils or ocean is known as enhanced silicate weathering (Schuiling and Krijgsman 2006; Van Straaten 2006; Beerling et al. 2018). This weathering process is accelerated when CO_2 concentrations are high and climate is warm (Kasting 2019), which increases its viability as a climate mitigation strategy. In addition to C sequestration, ESW provides co-benefits to agricultural soils including improving soil nutrient content and rebuilding eroded soil (Van Straaten 2007).

Enhanced weathering aims to offset anthropogenic C emissions by increasing inorganic C sinks both on land and at sea (Schuiling and Krijgsman 2006; Van Straaten 2006; Beerling et al. 2018; Taylor et al. 2017; Kasting 2019; Guntzer et al. 2018). Dissolution occurs when CO_2 in soil pore water reacts with silicate minerals, liberating constituent nutrients, such as Mg^{2+} and Ca^{2+}, and storing CO_2 as aqueous bicarbonate (HCO_3^-) or carbonate mineral precipitates (Schuiling and Krijgsman 2006). Groundwater and rivers transport aqueous products to oceans, where the residence time of dissolved inorganic C is between 100,000–1,000,000 years, making the ocean an essentially permanent C storage reservoir (Van Straaten 2006; Beerling et al. 2018). Enhanced weathering, therefore, utilizes oceans to store atmospheric C as stable inorganic forms, such as calcite ($CaCO_3$), magnesite ($MgCO_3$), and siderite ($FeCO_3$) (Ibrahim et al. 2019). HCO_3^- stores 2 moles of CO_2 per mole cation released from rock (Haque et al. 2019). As CO_2 becomes stabilized as Ca/$MgCO_3$, 1 mole of CO_2 is lost to gaseous CO_2, thus sequestering 1 mole of CO_2 per mole Ca/Mg released from silicates (Haque et al. 2019). CO_3 precipitation typically occurs in arid soils at $pH > 8$ (Manning and Renforth 2013).

In addition to CO_2 removal capacity, ESW offers substantial co-benefits for crops and soils (Van Straaten 2002 and 2007; Beerling et al. 2018). Applying finely ground minerals to agricultural soil as an acidity remediation technique and nutrient supplement dates back to at least the 19th century (Van Straaten 2007). Enhanced weathering has been shown to increase yields (Haque et al. 2018), particularly in nutrient depleted soils when rock-derived nutrients contribute to soil nutrient pools (Anda et. al., 2015; Edwards et al. 2017). Enhanced mineral weathering also buffers pH and increases CEC in highly weathered soil (D'Hotman 1961; Anda et al. 2015; Beerling et al. 2018), can reduce synthetic N fertilizer requirement (Beerling et al. 2018), and improve soil water holding capacity and organic C occlusion by stimulating root and mycorrhizal exudates, which support aggregate stability (Manning 2008; Beerling et al. 2018). Enhanced weathering of silicate minerals supports crop climate resilience by increasing Si^{4+} concentrations to reduce lodging (Haynes et al. 2017) and rebuilds soil by returning mineral volume lost to erosion (Van Straaten 2006).

Although, ESW has been appraised in landscapes including oceans and forests (Peters et al. 2004; Renforth and Henderson 2017), agricultural lands are considered most advantageous for ESW because plant and fungal exudates and organic acids increase rock dissolution rates (Haque et al. 2019; Andrews and Taylor 2019). In addition, agriculture is widely equipped with standard tools and infrastructure to apply large volumes of rock to croplands (Beerling et al. 2018; Andrews and Taylor 2019). ESW may be most effective in tropical climates where high temperature and rainfall increase chemical weathering rates (Edwards et al. 2017; Yan 2018; Andrews and Taylor 2019), but irrigation in arid regions can strongly influence soil moisture and, presumably, weathering rates. This principle could lend itself well to cultivated soils in California due to hot summers and intensive irrigation (Suddick et al. 2010). ESW has been demonstrated as a mineral supplement and C sequestration pathway in forests and watersheds (Peters et al. 2004; Edwards et al. 2017; Beerling et al. 2018), but crop responses and sequestration rates are not well characterized in agriculture systems.

The most apparent incentive to scale ESW is this technology's benefits in CO_2 sequestration, restoration of eroded soil, and rebuilding of soil micronutrient pools depleted by harvest (Van Straaten 2006; Hartmann et al. 2013; Basak et al. 2017; Goll et al. 2021). One other significant advantage to ESW is that it does not require additional land allocation, it can be co-deployed with other land uses and negative emissions technologies (NETs)(Goll et al. 2021). Another prompt is the relative cost effectiveness of ESW of basalt compared to other NETs (IPCC 2019; Goll et al. 2021). The IPCC projects costs of reducing the concentration of atmospheric CO_2, with many scenarios reaching \$1,000/tCO_2 emissions by 2100 (IPCC, 2019). However, Goll et al. (2021) estimates that ESW of basalt can remove up to 2.5 GtCO_2 yr^{-1} for ~\$500/t$CO_{2.}$ Costs may be as low as \$50–200/tCO_2 (Goll et al. 2021) if conditions including land area where basalt is applied, basalt or silicate waste source, and transportation of materials are planned strategically (Beerling et al. 2018).

The objective of this study was to measure the extent of inorganic C storage in field conditions and in a controlled environment chamber under ambient and elevated CO_2 and temperature. I anticipate observing increased C storage as bicarbonate and alkalinity in soils treated with silicate minerals. Plants grown with silicate additions may also exhibit increased yield and elevated soil pH. I also hypothesize that, if limiting, soil nutrients may appear elevated in crop biomass. However, rock-derived soil nutrients will not appear in soils in this study because we utilize fertile, well-buffered soils.

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Chapter 1. Enhanced silicate weathering effects on carbon dioxide removal and soil nutrients across organic vs. conventional agriculture in California

1. Introduction

Modern challenges in agriculture converge around the need to improve food quality and agricultural efficiency, while simultaneously reducing the environmental impacts of agriculture. While advances in crop management have increased crop yield, the overuse of nitrogen (N) fertilizer exacerbates greenhouse gas (GHG) emissions and results in environmental impacts such as soil acidification and groundwater contamination (Cowie and Wood 2004). Standard tillage practices have contributed to rapid erosive soil loss (Busari et al. 2015; FAO 2017). In order to maintain agricultural productivity, growers must employ management practices that counteract these harmful impacts. Given current climate scenario models (IPCC 2019), reaching goals of the Paris Climate Agreement will require not just a reduction of emissions, but carbon (C) capture and drawdown technologies in order to significantly reduce atmospheric C concentration by 2050 (Canadell and Schulze 2013; Ibrahim et al. 2019).

1.1 Enhanced Silicate Weathering

Silicate weathering is one of the main controls on the inorganic carbon (C) cycle and the climate system over Earth's history (Berner, 1983). Silicate weathering transforms atmospheric CO_2 into bicarbonate (HCO_3^-) when CO_2, dissolved in soil pore water as carbonic acid (H_2CO_3), reacts with silicate mineral structures. This reaction liberates constituent nutrients, such as

Mg^{2+} and Ca^{2+}, and stores CO_2 as aqueous HCO_3^- or carbonate mineral precipitates (Schuiling and Krijgsman 2006). Enhanced silicate weathering (ESW) utilizes ground rock to increase reaction surface area, thereby quickening mineral dissolution rates and increasing CO_2 removal rate to timescales relevant to modern climate change mitigation (Schuiling and Krijgsman 2006; Van Straaten 2006; Beerling et al. 2018).

Theory for ESW has been developed from extensive literature on the controls of natural weathering rates (Andrews and Taylor 2019). Laboratory investigations have shown that dissolution rates are a function of temperature and moisture (Edwards et al. 2017), concentration of dissolution products (Renforth et al. 2015), pH (Haque et al. 2018; Pokrovsky and Schott 2000) and mineral surface area (White and Brantley 2003; Renforth et al. 2015). Enhanced weathering increases the dissolution rate of mineral-supplying rock by introducing pulverized rock to soil surface and root zone; this eliminates the rate limiting step in mineral dissolution by substantially increasing the surface area of reactions compared to bedrock and other natural rock fragments. Physical and chemical altering of mineral surfaces, through grinding or acidulation, can enhance dissolution and release of nutrients to the extent of decreasing application rate required for agronomic effects (van Straaten 2006).

Rapid deployment of CO_2 removal technologies is essential to offset carbon emissions and avoid adverse ecological and economic consequences. As croplands occupy about 11% of the terrestrial surface (Beerling et al. 2019), utilizing ESW in agricultural soils may be a pathway to optimize natural carbon sinks, with co-benefits for meeting global nutrient requirements and improving soil quality.

1.2 Benefits and barriers to adoption

Although ESW has been discussed in both marine and terrestrial settings (Peters et al. 2004; Renforth and Henderson 2017), agricultural lands are considered most advantageous for ESW, for several reasons including organic acids from organic matter in soil and plant root exudates contribute to silicate dissolution (Haque et al. 2019; Andrews and Taylor 2019) and because many large-scale agriculture facilities are equipped with tools and infrastructure that can apply large volumes of crushed rock to croplands (Beerling et al. 2018; Andrews and Taylor 2019). ESW may be most effective in tropical climates where high temperature and rainfall increase chemical weathering rates (Edwards et al. 2017; Yan 2018; Andrews and Taylor 2019), but irrigation in arid regions can strongly influence soil moisture and, presumably, weathering rates. This principle could lend itself well to cultivated soils in California due to hot summers and intensive irrigation (Suddick et al. 2010). ESW has been demonstrated as a mineral supplement and C sequestration pathway in forests and watersheds (Peters et al. 2004; Edwards et al. 2017; Beerling et al. 2018), but crop responses and sequestration rates are not well characterized in agriculture systems.

Mineral dissolution may be limited in nutrient-rich soils when cations supplied by rocks or fertilizers are already in abundant supply in soil. However, Schuiling et al. (2011) shows that saturation of silicic acid, an ESW product, is not likely limiting to ESW rate in ecosystems with a significant silicic acid sink. One potential drawback of ESW is the energy cost of mining and grinding rock, as well as transportation to and application in farmland (Van Straaten 2006). These processes could reduce net C drawdown by up to 30%, although many uncertainties remain (Beerling et al. 2018). Research at the Working Lands Innovation Center at UC Davis is exploring sourcing local basalt dust that is a by-product at a mining operation in Ione, CA. Using local and previously mined by-product silicate fines is one strategy to limit costs associated with mining, grinding, and transportation rock for ESW.

There are many unknowns surrounding the science and efficacy of ESW as a C removal technology. Life cycle assessments reveal that grinding silicate mineral and transportation to weathering sites are the dominant factors that may reduce overall C capture (Lefebvre et al. 2019; Eufrasio et al. 2022). Carbonate weathering products increase soil pore water alkalinity, potentially slowing the weathering process as pH rises, which points to questions regarding the long-term efficacy of ESW. Moreover, the rate of ESW differs among plant types because exudates, such as proteins, phenols, sugars, and free amino acids, impact silicate dissolution and vary widely among plant types. Variation of ESW outcomes with soybean and maize have been reported (Krishnapriya & Pandey 2016). This may present opportunities to engineer plant-soil combinations optimized for climate change mitigation through ESW. There are human health risks associated with the application and potential inhalation of silicate fines >10 µm (Eufrasio et al. 2022). Mine and land managers must take precautions including keeping rock dust moist in storage, transit, and during application to minimize dust (Webb 2020).

Furthermore, to be agronomically effective, ESW requires an application rate of several tons per hectare, making it potentially expensive and labor intensive for small-scale farmers. Although land managers can use compost spreaders or tractors that are likely widely available, additional passes with spreaders are needed to apply rock amendments (Van Straaten 2006; Beerling et al. 2018). Questions remain about the practical application rate of rock powder to agricultural soil, effects on soil biota, and the long-term fates of carbonates formed (Beerling et al. 2018; Goll et al. 2021). Further study is required to develop a standard for measuring CO_2 sequestration, ascertain the timeline of complete dissolution of silicate, formation of pedogenic minerals, and soil nutrient benefits which may require several applications and years to decades to be detected (Beerling et al. 2018; Van Straaten 2006).

1.3 Study aim and hypothesis

The aim of this study is to assess the efficacy of ESW as a C sequestration technology in agricultural soil. The hypothesis examined is that it is possible to observe silicate weathering products in soil including increased HCO_3^-, associated pH increases, and an increase in rock-derived cations (Ca, Mg, Fe) in growing season timescales. The pH of the soil is a principal control over which inorganic C species is present; at pH <6, carbonic acid is expected to be the dominant dissolved inorganic C form in natural settings (Manning and Renforth 2013). HCO_3^- will be the dominant weathering product at Russell Ranch because it is the dominant inorganic C species at neutral pH. $CaCO_3^-$ and $MgCO_3^-$ become the dominant inorganic C species as pH exceeds 10 (Manning and Renforth 2013) or when the concentration of CO_3^- and cations is sufficient. However, pH is well buffered at Russell Ranch, so ESW is not anticipated to increase the mean pH above ~8 for the duration of my study. Equations 1-4 describe silicate weathering products and which rock-derived cations I expect to increase in soil.

(Eq. 1) CO_2 dissolution in pore water:

$$2CO_{2(g)} + 2H_2O_{(l)} \leftrightarrow 2H_2CO_{3(aq)} \leftrightarrow 2HCO_3^{-}{}_{(aq)} + 2H^{+}$$

(Eq. 2) Calcium release from wollastonite

$$CaSiO_3 + 2H_2CO_{3(aq)} \rightarrow Ca^{+2} + H_2O + SiO_{2(s)} + 2HCO_3^{-}{}_{(aq)}$$

(Eq. 3) Ca, Al, Fe release from basalt:

$$AlFeCaSiO_{4(s)} + 2H_2CO_{3(aq)} + 2H^{+} \rightarrow Ca^{+2} + Al^{+3} + Fe^{+3} + 2H_2O + SiO_{2(s)} + 2HCO_3^{-}{}_{(aq)}$$

(Eq. 4) Gypsum dissolution:

$$CaSO_4 + 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

2. Methods

2.1 Field site and study design

The Russell Ranch Sustainable Agriculture Facility is a 300-acre UC Davis farm dedicated to elucidating long-term impacts of crop rotation, land management regimes, inputs of water, N, C and other nutrients on agricultural sustainability. Russell ranch has 72 one-acre plots which employ conventional and organic management and various crop rotations. Both management regimes retained crop residue as an organic C source. Conventional management was fertilized with standard fertilizer, UAN32, delivered at a rate of 210 lbs of N/acre throughout the growing season in equal parts urea and ammonium nitrate through drip fertigation. Organic plots received composted poultry manure and underwent winter cover cropping with Lana woolypod vetch (*Vicia villosa*), Magnus peas (*Pisum sativum*), and Montezuma oats (*Avena sativa*), but no synthetic fertilizer was applied. A 2-year field trial was conducted at Russell Ranch Sustainable Agriculture Facility in Davis, CA (USA) from October 2018 to September 2020 to investigate the effects of gypsum and silicate rock dust (wollastonite and basalt). The first year utilized corn and tomato the second year. Both years of this study had 3 replicates each in conventional and organic management. This study utilized a randomized block design. We assessed the impact of silicate application on soil inorganic carbon (SIC) formation, pH, and soil nutrients.

Each block contained a basalt, wollastonite, and gypsum treatment, which were compared to replicated controls without any rock inputs. Two silicate rock treatments, basalt and wollastonite, and a non-silicate mineral, gypsum were selected for this study. These treatments were chosen because basalt is the most dominant silicate in the Earth's crust and is widely suggested as the most important source of rock dust for ESW (Beerling et al. 2018). Wollastonite is less common over Earth's surface but has a more rapid weathering rate than basalt due differences in their chemical composition (Table 1.2, Table 1.4). Gypsum is commonly used in agriculture to supply Ca and S, but does not contain silicate. Gypsum has C drawdown potential based on Zoca and Penn (2017), suggesting that gypsum can elevate Ca concentrations and thereby increase $CaCO_3$ precipitation in the soil.

According to NRCS mapping (Soil Survey Staff), the field blocks in this study are split between two soil series: Rincon and Yolo. Both soil series are deep, well drained soils that formed in alluvium from mixed mineralogy (Soil Survey Staff 2019). There is some variation in clay content, pH, and CEC across these soil classifications (Table 1.1) (Soil Survey Staff 2019), but decades of management have made those differences less distinct. These properties will influence percolation rate, carrying weathering products down the profile. Drip tape is installed at 25 cm. Soil is kept moist through the duration of corn and tomato growing seasons, indicating a high input water regime.

Plots were arranged within larger plots with pulverized rock spread evenly down 9 m length rows. Each treatment, gypsum, wollastonite, and basalt, were applied to 3 adjacent rows, making ~9 m x 4.5 m treatment-plots. There were 3 plots with all treatments replicated within each management regime. Measurements of ESW products were conducted under organic and conventional management to observe differences produced by differences in management regimes such as fertilizer applied in conventional management and cover crop and composted manure applied in organic management.

Image 1.1. Pulverized rock spread evenly down 9m length rows at Russell Ranch. Each rock treatment spans 3 adjacent rows.

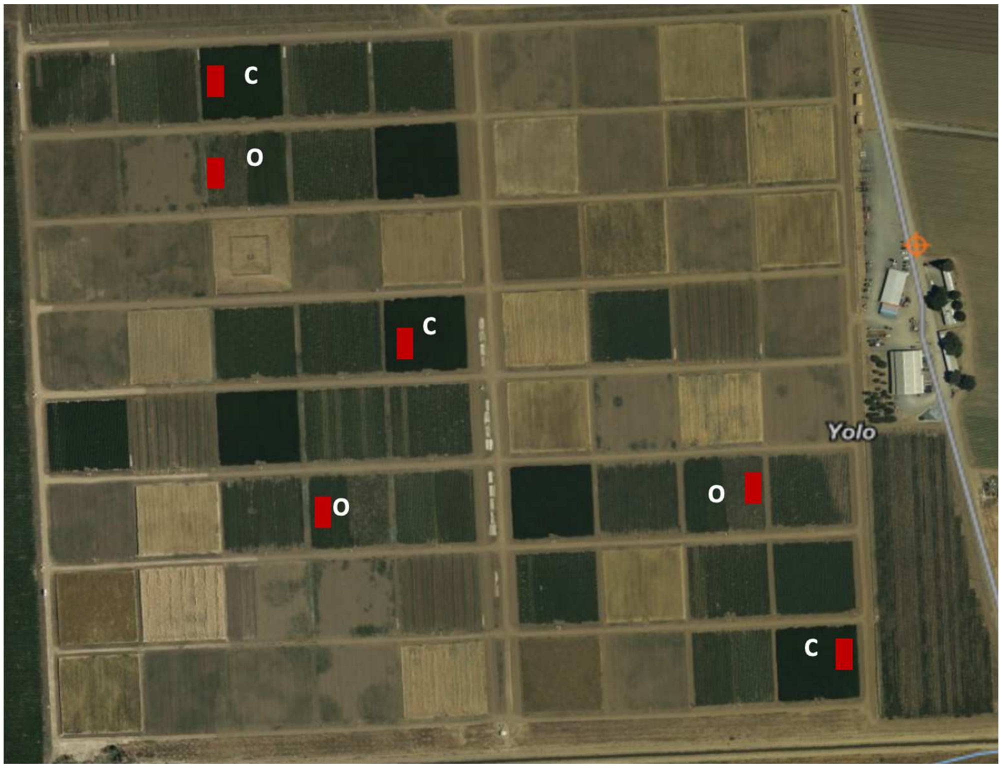

Image 1.2: Conventionally managed plots are represented with a 'C'. Organically managed plots are represented with an 'O'. Red rectangles represent treatment-plots within blocks. Each block was amended with gypsum, wollastonite, and basalt treatments along rows as presented in image 1.1.

Table 1.1 pH, CEC, and clay content in the upper 100 cm of Yolo and Rincon soils based on NRCS soil survey (Soil Survey Staff 2019).

	pH	CEC cmol(+)/kg	Clay %
Rincon	7.9	27	29
Yolo	6.9	18	25

2.2 Rock characteristics and application rate

Gypsum was purchased from Custom Hydro Nutrients (office in Neosho, MO, USA) for application in year 1 and Redi-Gro (office in Sacramento, CA, USA) for application in year 2. Wollastonite was purchased from Vansil (office in Norwalk, CT, USA) in year 1 and NYCO (office in Willsboro, NY, USA) in year 2 of this study. Basalt was purchased from Soil Key (office in Bellingham, WA, USA) for year 1 and Rock Dust Local (office in Bridport, Vermont, USA for year 2. I assessed the particle size distribution of each rock type using a *LS Variable Speed Fluid Module Plus* particle size analyzer. Each had a particle size distribution within 10-100 µm. Mineralogy was described in Vansil brand wollastonite and basalt from Soil Key and Rock Dust Local by quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) bulk mineral analysis (BMA) by Bureau Veritas Metallurgical Division. Bureau Veritas Metallurgical Division also quantified elemental composition of each mineral used in this study by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis (Tables 1.2-1.6).

Rock treatments were applied October 18-22, 2018 and November 8-18, 2019. Rock was incorporated into the soil to 8 cm depth using standard tillage equipment. Conventional plots were left fallow until corn was planted in June. In organic plots, a legume cover crop was planted late November. Gypsum and wollastonite were applied at a lower-end application rate of 8 t/ha (800 g/m^2) in light of ESW literature, and basalt was applied at a suggested application rate of 20 t/ha (2000 g/m^2) for carbon removal (Beerling et al. 2017). These application rates were selected to begin to ascertain C sequestration potential of silicates at a high and low end of the range.

Table 1.2. Vansil (year 1) brand wollastonite mineralogy was measured by BMA.

Wollastonite Mineralogy	**Vansil (%)**
Pyroxene (Augite)	8.2
Quartz	0.9
Wollastonite	84
Epidote	3.58
Calcite	2.44

Table 1.3. Soil Key (year 1) and Rock Dust Local (year 2) brands of basalt mineralogy were measured by BMA.

Basalt Mineralogy	Year 1 - Soil Key (%)	Year 2 - Rock Dust Local (%)
Plagioclase Feldspar	48.1	31.4
K-Feldspar	24.4	>0.1
Pyroxene (Augite)	13	26.4
Ilmenite	4.96	>0.1
Forsterite	4.94	1.98
Quartz	1.01	1.19
Apatite	1.76	>0.1
Chlorite	>0.1	19.0
Epidote	>0.1	9.63
Calcite	>0.1	3.27
Sphene	>0.1	3.41

Table 1.4. Gypsum amount applied (g/m^2) is calculated based on elemental percent composition of gypsum and application rates.

Gypsum Composition	Year 1 (%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Calcium	12.90	103.2	14.12	112.96
Sulfur	9.86	78.88	10.47	83.76
Magnesium	0.02	0.16	0.38	3.04

Table 1.5. Wollastonite amount applied (g/m^2) is calculated based on elemental percent composition of wollastonite and application rates.

Wollastonite Composition	Year 1 (%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Iron	0.13	1.04	0.98	7.84
Calcium	31.89	255.12	33.89	271.12
Phosphorus	0.02	0.16	0.04	0.32
Magnesium	0.88	7.04	0.19	1.52
Aluminum	0.4	3.2	0.68	5.44
Sodium	0.06	0.48	0.09	0.73
Potassium	0.05	0.4	0.03	0.24

Table 1.6. Basalt amount applied (g/m^2) is calculated based on elemental percent composition of basalt and application rates.

Basalt Composition	Year 1 (%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Iron	7.29	145.8	7.69	153.8
Calcium	4.25	85	6.46	129.2
Phosphorus	0.63	12.6	0.05	1
Magnesium	1.75	35	4.14	82.8
Aluminum	7.29	145.8	7.86	157.2
Sodium	2.76	55.2	3.05	61
Potassium	2.59	51.8	0.24	4.8

2.3 Soil sample collection and methods of analysis

Corn was planted in May 2019 and harvested October 2019. Tomato was planted March 2020 and harvested October 2020. Soil samples were collected post-harvest from the upper 30 cm of the soil profile. Three samples per treatment were collected with a trowel and 6 in (15 cm) corer. For control samples, we collected soil 10 m outside of the treated area. Soil samples were air dried and subsampled for analysis. The number of subsamples analyzed varied based on the amount of soil sample collected in the field.

Samples were delivered to the UC Davis analytical lab for quantification of soil HCO_3^- and pH. To quantify soil inorganic carbon as HCO_3^- , the analytical lab extracted soil water from a saturated paste and titrated this sample with 0.025N H_2SO_4 (U.S. Salinity Laboratory Staff). Soil pH was measured by saturated paste and pH probe (U.S. Salinity Laboratory Staff). To measure potential rock-derived, exchangeable cations Ca^{2+} and Mg^{2+}, were extracted from soil samples by displacement from cation exchange complex with an ammonium acetate (NH_4-oAc) solution buffered at pH 7 (Thomas 1982). Soil Fe was measured by diethylenetriaminepentaacetic acid (DTPA) extraction. Ca, Mg, and Fe cations are quantified by ICP-AES.

Results are reported as mean measurements with standard errors. R version 4.1.2 was used for all graphs and statistical analyses. The following packages were used: tidyverse, dplyr, ggplot2, ggpubr, ISLR, and ggstatsplot. A quantile-quantile plot was used to determine the correlation between these data and the normal distribution. The quantile-quantile plot showed that HCO_3^- , pH, and soil cations were not normally distributed, therefore a non-parametric test was required. These data fit the assumptions of Kruskal Wallis test. The Kruskal Wallis test was used to compare across all treatments and control. Significant p-values reflect differences in median measurements in each treatment. $P < 0.05$ was used as the limit for statistical significance. When the Kruskal Wallis test produced a significant result, the Dunn's test with p-values adjusted by the Šidák method was used to determine which treatments significantly differed from one another.

3. Results

3.1 HCO_3^- and pH changes with ESW with corn

Silicate rock (wollastonite and basalt) amendments resulted in increased concentrations of HCO_3^- in the top 30 cm of soil compared to the control and gypsum additions (Figure 1.1; Table 1.7). Soil HCO_3^- is higher in organic management. P-values comparing soil HCO_3^- in all treatments between conventional and organic management display significant results in every treatment except wollastonite (Control, p= 0.038, Gypsum, p = 0.00042, Wollastonite, p = 0.44, Basalt, p = 0.02) (Figure 1.1). This reflects the considerable increase in HCO_3^- in wollastonite compared to other treatments in conventional management. There was no significant treatment effect on HCO_3^- comparing within either management strategy with p-values 0.47 and 0.24 in conventional and organic management, respectively. Mean HCO_3^- measurements are similar among treatments within each management strategy, but wollastonite treated samples had the largest HCO_3^- measurement at 2.7 meq/L in conventional and 2.1 meq/L in organic soil (Figure 1.1). Basalt treated samples had a range larger than control and gypsum with the highest HCO_3^- measurement at 1.8 meq/L in conventional and 1.7 meq/L in organic management. Wollastonite increased HCO_3^- more than basalt in each management strategy. HCO_3^- was higher overall in organic management.

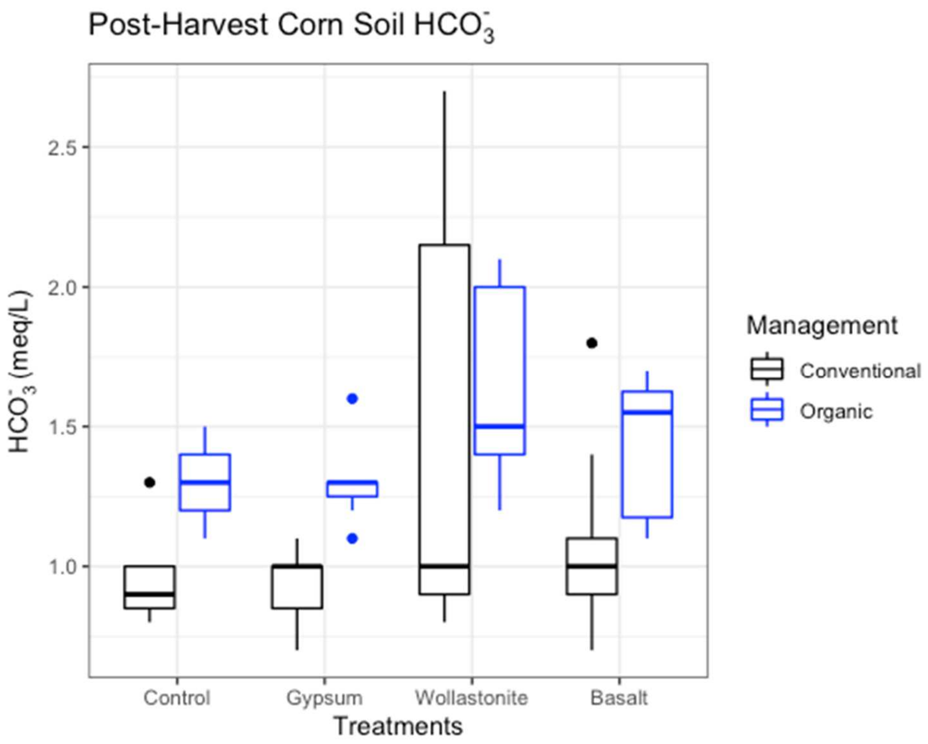

Figure 1.1. Soil HCO_3^- concentration in samples collected post-harvest in conventionally (black) and organically grown corn (blue) with the different treatments studied (control, gypsum, wollastonite, and basalt).

*The lower edge of the box represents the 25th percentile, or quartile 1 (Q1). The upper edge of the box represents the 75th percentile, or quartile 3 (Q3). Q3-Q1 = Interquartile range (IQR). The bold line in the box represents that median value. The upper whisker represents the largest value of Q3 + 1.5 * IQR. The lower whisker represents the smallest value of Q1 – 1.5 * IQR (McGill et al. 1978).

Table 1.7. Soil HCO_3^- concentration (meq/L), pH, and standard errors (SE) and sample size (n) of each from control and treated samples collected post-harvest in conventionally and organically grown corn.

Post-harvest Corn Soil						
Management	Treatment	HCO_3^-	SE (HCO_3^-)	pH	SE (pH)	n
Conventional	Control	0.96	0.065	6.96	0.046	7
	Gypsum	0.94	0.036	7.0	0.035	11
	Wollastonite	1.47	0.215	7.31	0.101	11
	Basalt	1.07	0.115	7.12	0.0923	9
Organic	Control	1.3	0.115	6.87	0.111	3
	Gypsum	1.3	0.058	6.89	0.033	7
	Wollastonite	1.66	0.141	7.13	0.070	7
	Basalt	1.44	0.092	6.92	0.035	8

Silicate dissolution may buffer, or increase, soil pH. P-values comparing soil pH in all treatments between conventional and organic management only produced significant results in gypsum amended samples, which indicates that gypsum displays the strongest treatment effect (Control p-value = 0.42 , Gypsum p-value = 0.033, Wollastonite p-value = 0.44, Basalt p-value = 0.067) (Figure 1.2; Table 1.7). Wollastonite and basalt addition to the soil revealed a pH increase compared to control in both management strategies with p-values of 0.045 and 0.032 in conventional and organic management, respectively. Comparing soil pH in conventional management via the Dunn's test with the Šidák adjusted p-value reveals a significant treatment effect in wollastonite and control (p-value = 0.0344) where pH in wollastonite was greater than the control. Comparing pH in organic management via the Dunn's test with Šidák adjusted p-value reveals a significant treatment effect in gypsum and wollastonite (p-value = 0.0308) with pH in wollastonite amended samples was higher than gypsum amended samples. Conventional management showed a stronger treatment effect on soil pH than organic management. Wollastonite treated samples had the strongest treatment effect with pH measurements as high as 7.79 in conventional and 7.38 in organic. The mean conventional wollastonite measurement increased 0.35 units compared to control, while the mean organic wollastonite measurement increased 0.26 units compared to control (Figure 1.2). Basalt treated soils in organic management did not perform as well as conventional basalt in buffering pH. The mean organic basalt measurement increased 0.05 units compared to control while the mean conventional basalt measurement increased 0.16 units compared to control (Figure 1.2). Conventional management showed a stronger treatment effect on soil pH than organic management. Wollastonite pH in organic management has a large range with the highest measurement at 7.38.

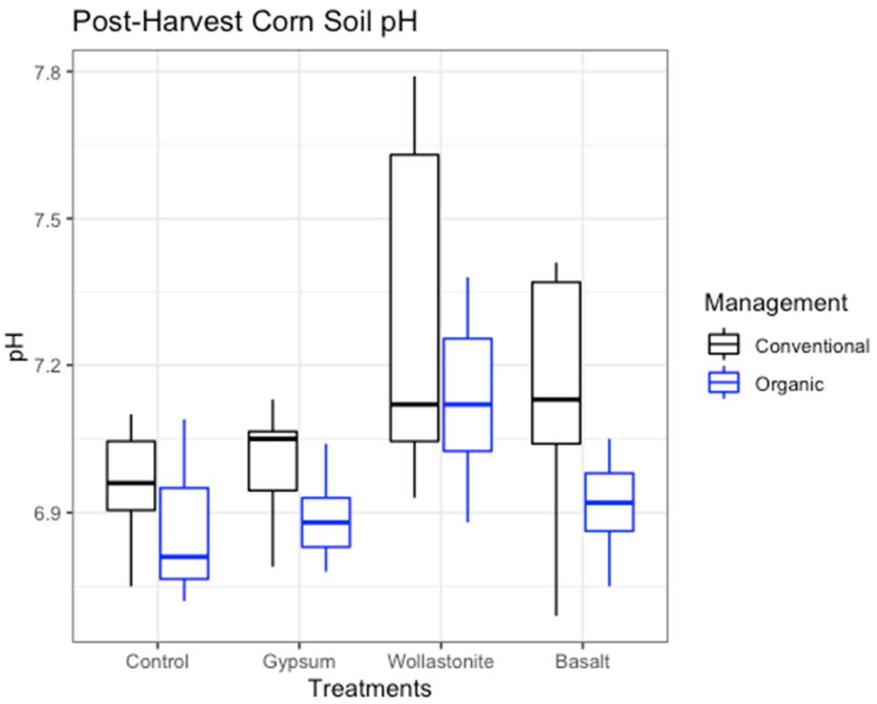

Figure 1.2. Soil pH in samples collected post-harvest in conventionally (black) and organically grown corn (blue) with the different treatments studied (control, gypsum, basalt, and wollastonite).

3.2 HCO_3^- and pH changes with ESW with tomato

Silicate dissolution as measured by concentrations of HCO_3^- in the top 30 cm was not observed in tomato soils (Table 1.8). Soil HCO_3^- in tomato did not increase as much as in corn. The range of HCO_3^- values in conventional and organic management overlap with tomato grown in year 2. However, HCO_3^- in organic management is greater across treated samples and controls than in conventional management. P-values comparing treatments between conventional and organic management are Control, p= 0.025. Gypsum, p = 0.012, Wollastonite, p = 0.39, Basalt, p = 0.0074 (Figure 1.3). HCO_3^- measurements ranged similarly in treated samples and control in conventional management, with all samples measuring between 0.2 and

0.8 meq/L and no significant treatment effect. Soil HCO_3^- measurements in conventionally managed tomato result in an insignificant p-value of 0.42. In organically grown tomato, the mean HCO_3^- measured in wollastonite decreased compared to control but this effect was not statistically significant (p-value = 0.3) (Figure 1.3). Organic basalt has an equivalent mean HCO_3^- measurement as gypsum whose dissolution does not produce HCO_3^-. In tomato, neither silicate mineral yielded a HCO_3^- measurement outside of the range of other treatments.

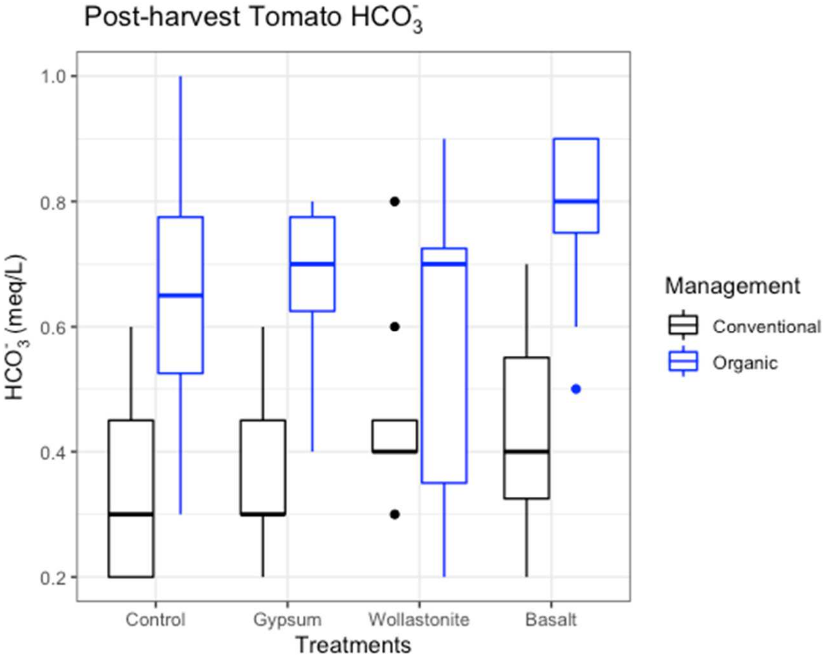

Figure 1.3. Soil HCO_3^- concentration in samples collected post-harvest in conventionally (black) and organically grown tomato (blue) with the different treatments studied (control, gypsum, basalt, and wollastonite).

Table 1.8. Average soil HCO_3^- concentration (meq/L), pH, standard errors (SE), and sample size (n) of each from control and treated samples collected post-harvest in conventionally and organically grown tomato.

Post-harvest Tomato Soil						
Management	Treatment	HCO_3^-	SE (HCO3-)	pH	SE (pH)	(n)
Conventional	Control	0.34	0.065	7.3	0.046	7
	Gypsum	0.37	0.036	7.21	0.035	11
	Wollastonite	0.46	0.215	7.44	0.101	11
	Basalt	0.43	0.115	7.38	0.092	9
Organic	Control	0.65	0.115	7.16	0.111	3
	Gypsum	0.76	0.057	7.11	0.033	7
	Wollastonite	0.58	0.141	7.22	0.070	7
	Basalt	0.76	0.092	7.14	0.035	8

Silicate dissolution was inferred by pH measured in the top 30 cm of soil tomato soils (Table 1.8). Comparing pH in conventional and organic management results in a significant difference in wollastonite and basalt treatments (Control p-value = 0.086 Gypsum p-value = 0.26, Wollastonite p-value = 0.0072, Basalt p-value= 0.0019 (Figure 1.4; Table 1.8). In conventionally managed tomato, wollastonite treated soils showed the largest increase in pH followed by basalt, which showed a minor increase compared to control. Silicate additions in conventional management showed a stronger treatment effect in pH than in organic management. Mean pH in wollastonite increased pH by 0.14 units compared to control in conventional and 0.06 units compared to control in organic management (Figure 1.4).

Conventional wollastonite has the highest pH measurement at 7.69. Mean pH in basalt increased pH by 0.08 units compared to control in conventional management and decreased by 0.02 units compared to control in organic management. Comparing soil pH conventional management results in a significant p-value 0.016. Comparison of pH measurements in conventional management via the Dunn's test with Šidák adjusted p-value reveals significant differences between gypsum and wollastonite (p-value = 0.0247) and gypsum and basalt (p-value = 0.0154) where pH in wollastonite and basalt is greater than pH in gypsum. In organically managed plots, soils amended with wollastonite and basalt showed no significant pH changes compared to control conditions (p=0.27).

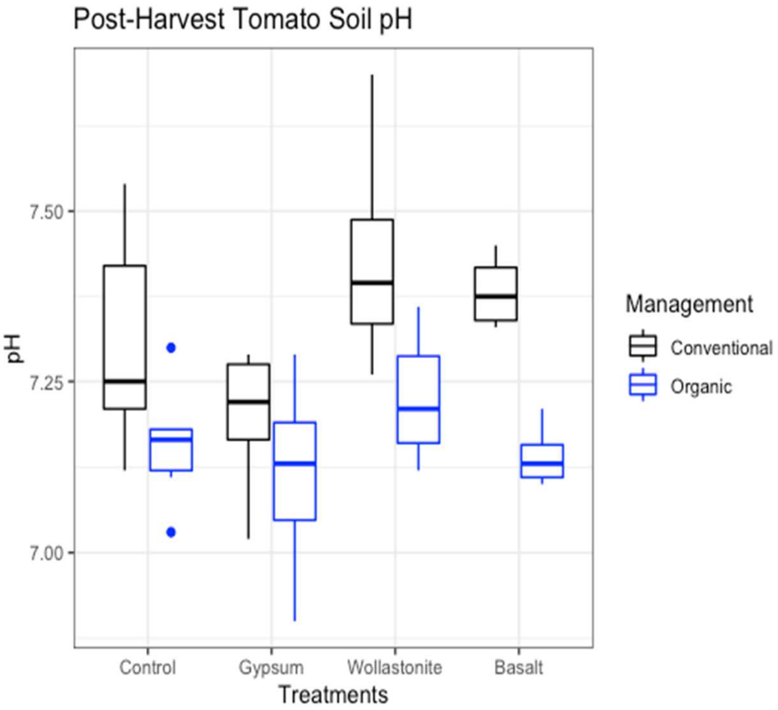

Figure 1.4. Soil pH in samples collected post-harvest in conventionally (black) and organically grown tomato (blue) with the different treatments studied (control, gypsum, basalt, and wollastonite).

3.3 Soil Nutrients with ESW with corn and tomato

Silicate and gypsum dissolution may add constituent cations to the soil. In year 1 where corn was planted, there was no broad change in the soil concentration of Ca, Mg, and Fe, the predominant nutrient cations potentially provided by these amendments (Tables 1.4-1.6, Figures 1.5-1.7). There was a significant increase in exchangeable Ca in corn in organic management (p-value =0.031). Comparing via the Dunn's test with Šidák adjusted p-value results in a significant treatment effect between control and gypsum (p-value = 0.0149), where soil exchangeable Ca is greater in gypsum than control. Organic soil exchangeable Ca in gypsum displayed the largest range with the highest measurement at 15.28 meq/100g. Organic soil exchangeable Ca in wollastonite has the highest value overall at 15.48 meq/100g soil. There was no treatment effect in soil exchangeable Ca in conventional management (Figure 1.5, Table 1.9). There was no treatment effect in soil exchangeable Mg or Fe in corn in either management strategy. The p-values for soil exchangeable Mg and Fe was >0.05 in both management regimes.

Table 1.9. Mean corn soil exchangeable Ca (Ex-Ca) (meq/100 g soil), Mg (Ex-Mg) (meq/100 g soil), and Fe (Ex-Ca) (ppm) samples collected post-harvest from the upper 30 cm, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Management	Treatment	Ex-Ca	SE (Ca)	Ex-Mg	SE(Mg)	Ex Fe	SE (Fe)	n
Conventional	Control	9.66	0.387	14.51	0.65	36.69	3.34	7
	Gypsum	11.44	0.867	13.64	0.349	30.9	1.24	11
	Wollastonite	11.33	0.667	13.58	0.304	27.7	2.45	11
	Basalt	10.01	0.217	14.22	0.437	30.83	2.57	9
Organic	Control	11.58	0.067	12.7	0.404	41.67	4.06	3
	Gypsum	13.58	0.455	11.54	0.464	34.41	1.50	7
	Wollastonite	12.93	0.532	12.49	0.275	31.91	2.51	7
	Basalt	12.24	0.263	12.26	0.355	38.75	1.93	8

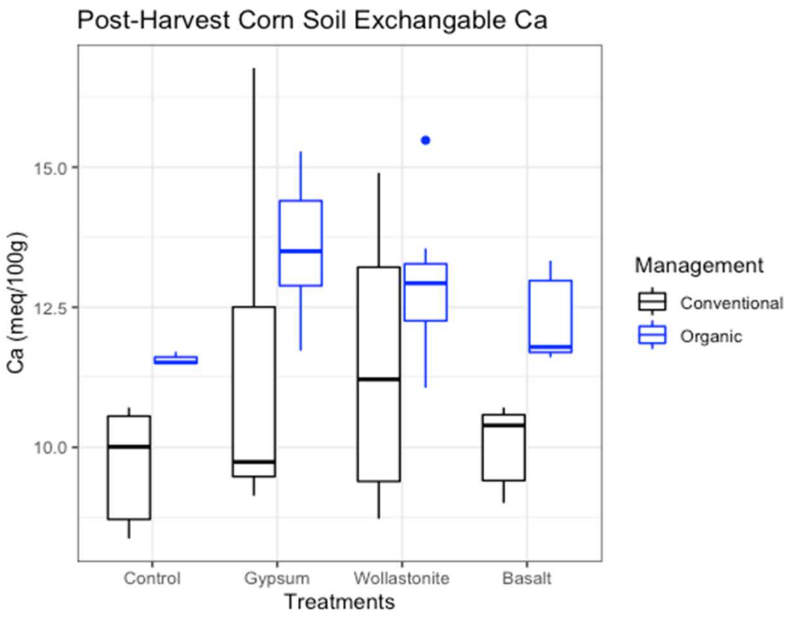

Figure 1.5. Exchangeable Ca (meq/100g) concentration in soil samples collected post-harvest from the upper 30 cm in conventionally (black) and organically grown corn (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

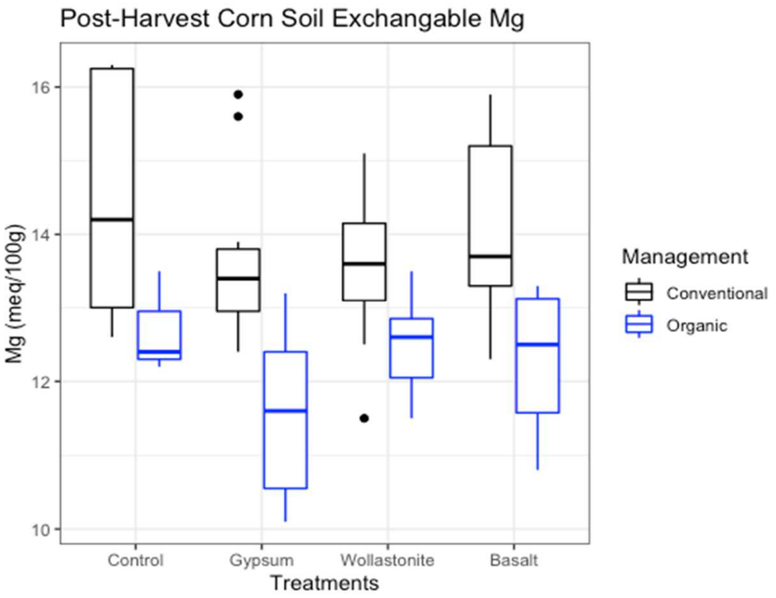

Figure 1.6. Exchangeable Mg (meq/100g) concentration in soil samples collected post-harvest from the upper 30 cm in conventionally (black) and organically grown corn (blue) with the different treatments studied (control, gypsum, basalt, and wollastonite).

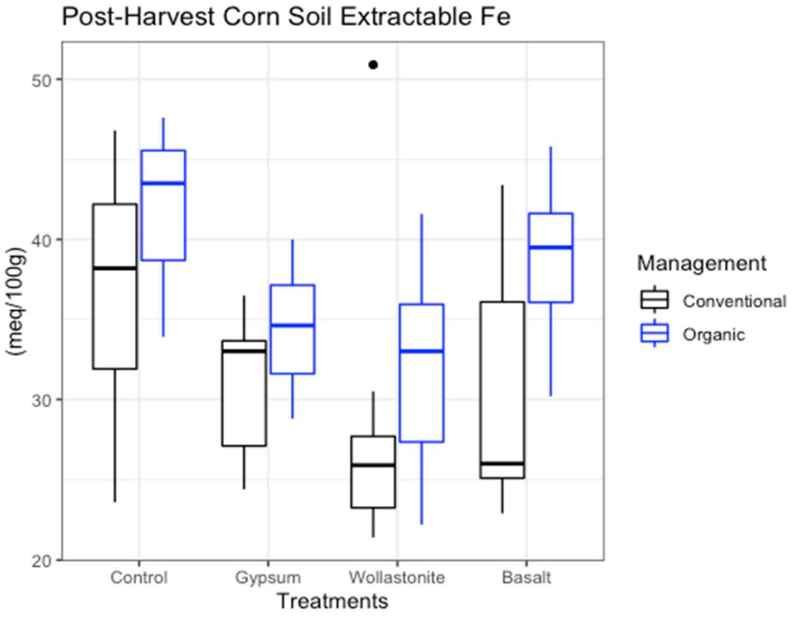

Figure 1.7. Exchangeable Fe (meq/100g) pools from soil samples collected post-harvest from the upper 30 cm in conventionally (black) and organically grown corn (blue) with the different treatments studied (control, gypsum, basalt, and wollastonite).

In the second year with tomato grown with gypsum, wollastonite, and basalt additions, there was no significant change in concentration of rock-related cations, including Ca, Mg, and Fe, in soil-exchangeable pools (Table 1.10; Figure 1.8- 1.10).

Table 1.10. Mean soil exchangeable Ca (Ex-Ca) (meq/100 g soil), Mg (Ex-Mg) (meq/100 g soil), Fe (Ex-Ca) (ppm) pools of soil samples collected post-harvest from the upper 30 cm, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Management	Treatment	Ex-Ca	SE(Ca)	Ex-Mg	SE(Mg)	Ex-Fe	SE(Fe)	n
Conventional	Control	8.49	0.386	13.53	0.692	13.34	1.54	7
	Gypsum	9.9	0.588	13.25	0.437	12.68	0.925	6
	Wollastonite	10.76	0.887	13.54	0.327	11.5	0.813	8
	Basalt	9.09	0.298	13.97	0.591	15.38	2.70	6
Organic	Control	10.88	0.410	13.07	0.212	27.38	2.20	6
	Gypsum	11.51	0.454	13.12	0.398	27.58	4.67	6
	Wollastonite	10.93	0.115	13.34	0.243	41.84	12.91	8
	Basalt	10.76	0.059	13.11	0.245	18.59	1.15	8

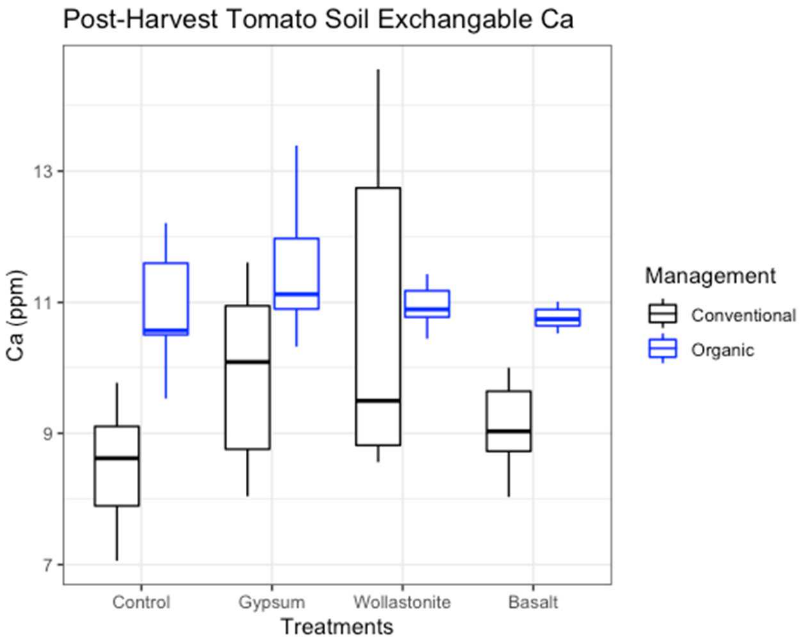

Figure 1.8. Exchangeable Ca (ppm) in soil samples collected post-harvest from the upper 30 cm in conventional (black) and organically grown tomato (blue) amended with the different treatments studied (control, gypsum, basalt, and wollastonite).

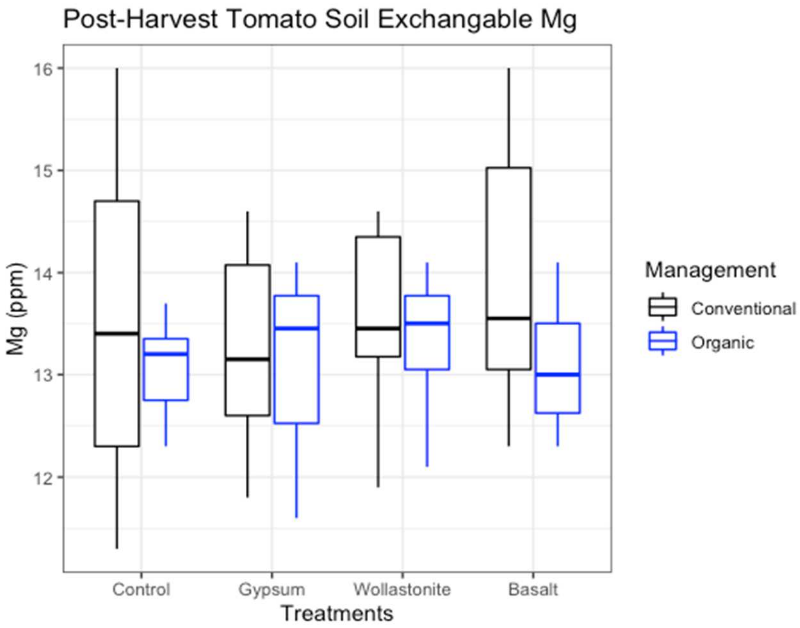

Figure 1.9. Exchangeable Mg (ppm) in soil samples collected post-harvest from the upper 30 cm in conventional (black) and organically grown tomato (blue) amended with the different treatments studied (control, gypsum, basalt, and wollastonite).

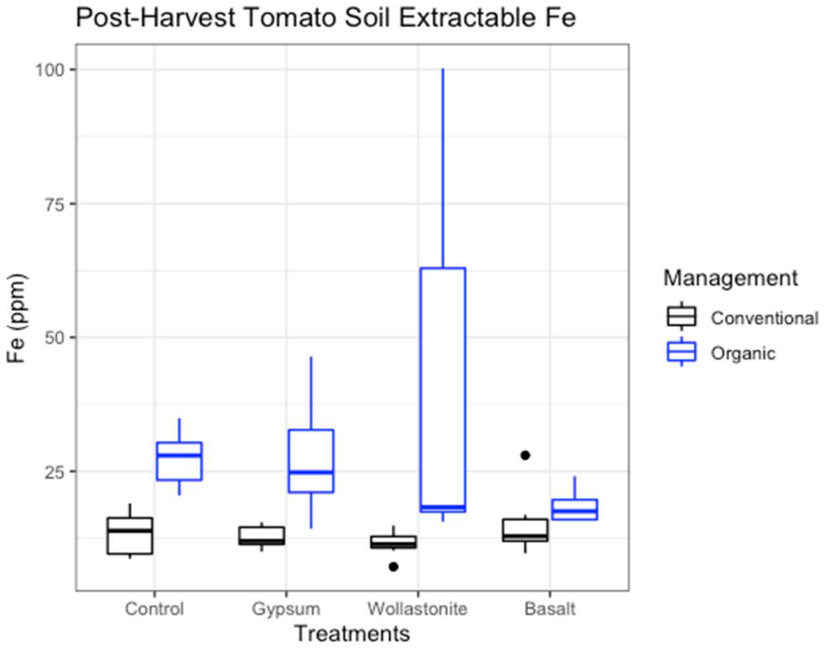

Figure 1.10. Exchangeable Fe (ppm) in soil samples collected post-harvest from the upper 30 cm in conventional (black) and organically grown tomato (blue) amended with the different treatments studied (control, gypsum, basalt, and wollastonite).

4. Discussion

4.1 Effects of ESW on soil HCO_3^-, pH, and plant nutrients

Many studies suggest that silicate rocks can increase soil carbonate concentrations rapidly through ESW; however, few studies have tested the efficacy of different minerals across crops and field conditions. The hypothesis was tested that application of basalt and wollastonite result in inorganic C dissolution formation in the form of HCO_3^- , along with increase in soil. The hypothesis is weathering products would be most pronounced for wollastonite, given the dominant content of a single mineral, $CaSiO_3$, which allows it to break down faster compared to basalt which is composed of several minerals. Gypsum treated soils are not expected to exhibit HCO_3^- effects, given that this mineral dissolves without interacting with carbonic acid, and therefore would not directly form HCO_3^-. Gypsum may buffer pH in soils affected by low pH and aluminum toxicity by binding and reducing soluble Al^{3+} (Kost et al. 2018). However, gypsum is not expected to affect pH in the fertile, well-buffered soil at Russell Ranch. Organic management is expected to show more signs of silicate weathering through more HCO_3^- and increased pH due to increased organic acids from compost and winter cover crop. It was also expected that the second year with tomato may show cumulative effects in HCO_3^- and pH because additional rock treatments were applied the second year. Overall, results of this experiment followed these general predictions, but with important differences observed across crops and management strategies. While HCO_3^- and pH showed general increases with silicate, more prevalent in wollastonite than basalt, the strongest effects were observed in organically managed soils during the corn season. Statistically significant effects were not observed as broadly in silicate amended tomato.

Higher dissolution rates were observed in conventionally and organically grown corn amended with wollastonite as shown by the higher soil pH and content of HCO_3^- , which aligns with my hypothesis regarding its higher dissolution rate and mineralogical composition, which favors CO_2 removal. Although basalt increased HCO_3^- and pH compared to controls, there were several potential reasons for less signs of weathering than wollastonite. Goll et al. (2021) found that C sequestration does not increase with additional basalt added indefinitely, in fact less CO_2 may be removed per amount of additional basalt added in a single application (Goll et al. 2021). This suggests a limit to the extent that CO_2 can be removed by adding greater amounts of weathering material (Dietzen et al. 2018; Goll et al. 2021). Although basalt was applied at a higher application rate than wollastonite, basalt displayed less weathering products through HCO_3^- and pH. The mechanism behind this observation may be that the high application rate saturated soil with weathering material, thereby limiting dissolution.

Changes in HCO_3^- and pH with ESW differ in soils under conventional and organic management. UAN32 N-fertilizer applied in conventional management likely encourages silicate dissolution by adding H^+ to solution (Dietzen et al. 2018). However, cover crop, compost, and manure provide organic acids which may increase silicate dissolution rate (Haque et al. 2019; Andrews and Taylor 2019). Haque (2019) shows improvement in silicate dissolution in soil growing with legume compared to non-leguminous corn. Fortner et al. (2012) observed young, fertile agricultural soils may exhibit accelerated weathering due to fertilizer addition. However, in this study fertilizer application in conventional management did not improve silicate dissolution as much as cover cropping with legumes and manure additions in organic management, as we observed a greater increase in HCO_3^- and pH in silicate treatments in organic management.

Treatments resulted in differences in HCO_3^- and pH in corn and tomato. Corn exhibited an increase in inorganic C pools and pH across management regimes, while tomato showed no increase in HCO_3^- and only significant pH increase in conventional management with silicate addition. Haque (2019) conducted a trial with silicate amended corn and found a similar inorganic carbon (IC) increase compared to controls. Haque et al. (2020) observed that consecutive applications of wollastonite should result in an increase in soil inorganic carbon, however HCO_3^- did not increase in the second year of wollastonite additions with tomato crop. This indicates that factors other than additional silicate applied determine CO_2 removal and storage as HCO_3^- . These factors could include variation in crop exudates and microbial colonization between corn and tomato, as well as variation in temperature and precipitation. Drought and fires in this region of California during tomato trials may have limited silicate weathering by smoke and cloud cover decreasing soil surface temperature and lack of additional moisture from rain that was present during corn trials. Although an increase in HCO_3^- was not detected in tomato soils, the increase in pH reflects silicate dissolution. Li and Dong (2013) conducted a study testing ESW in tomatoes and found a pH increase in soils amended with silicate rock dust. They grew tomatoes in acidic soil amended with an amalgamation of silicate minerals and composted rice straw and found that silicate alone and in combination with compost significantly increased pH (Li and Dong 2013). Collecting soil only post-harvest and from the top 30 cm while rock was applied to the upper >10 cm may be two dominant reasons we did not detect a HCO_3^- increase in tomato soils. However, tomato's more shallow rooting depth compared to corn (Dwyer et al. 1988; Machado and Oliveira 2006) may limit silicate weathering and HCO_3^- detection in tomato soil compared to corn.

Dissolved minerals release constituent cations to soil solution, in fact a number of studies have suggested that rock amendments can rapidly change the nutrient content of soils. However, my results suggest that this is not a predictable outcome of silicate dust amendments in well-buffered soils. Fortifying soils with ground rock has been long practiced as a way of rejuvenating highly weathering soils around the world (de Villiers 1961; Leonardos et al. 1987; Van Straaten 2006; Anda et al. 2013; Jiangang et al. 2021). Swoboda et al. (2022) completed an analysis of 48 crop trials which elucidated the potential of silicates as an alternative K source and multi-nutrient soil amendment in tropical ecosystems. In this analysis, the benefits of silicates as a nutrient supplement in temperate soils were inconclusive (Swoboda et al. 2022).

Based on previous work such as studies cited here, a significant change in soil nutrient pools is not anticipated in the fertile soils like the ones utilized in this study.

5. Uncertainties and future research

Homogenizing soil samples from 0-30 cm and measuring only at the end of the season may have missed the initial weathering pulses as fines dissolve immediately and leave behind more coarse, slow weathering silicate grains. Further research is needed to evaluate the dissolution processes related to grain size. These samples were homogenized from upper 30 cm while mineral was applied to surface and tilled on >10 cm, so weathering product measurements were conservative given the depth of samples. Future studies should take samples in the upper 10 cm where rock is applied for a more precise measurement of soil weathering products. Future research should also compare crop root exudate chemical composition to assess how specific plant derived compounds affect silicate weathering rate.

6. Summary and conclusions

This study was conducted to further elucidate the potential of ESW as C storage strategy in neutral pH soils by amending corn and tomato plots with gypsum, wollastonite, and basalt. Soil pH and HCO_3^- were measured to gauge silicate dissolution and therefore C storage through the weathering process. ESW aims to reduce atmospheric CO_2 on timescales relevant to climate change mitigation. Although we did not observe a significant effect in tomato weathering signals, corn showed promising increases in pH and HCO_3^- which reflect the ability to transform CO_2 dissolved in soil pore water to inorganic C forms. We did not observe a significant change in soil cation pools in either crop. Several research groups have reported increases in inorganic soil carbon and pH when amended with silicate minerals affirming the use of silicates to counteract anthropogenic emissions of CO_2. The findings of this study add breadth to the existing body of knowledge on enhanced silicate weathering by being one of few trials to assess C removal ability in neutral soils in California.

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Chapter 2. Effects of silicate rock dust inputs on crop yield and nutrition: A two-year trial at Russell Ranch

1. Introduction

Decades of intensive cropping and harvesting have mined micronutrients from the soil reducing fruit quality and edible nutrient composition with the depletion of nutrients such as Zinc (Zn) Iron (Fe), Magnesium (Mg), and Sulfur (S) (Tan et al. 2005; Wortmann et al. 2019; Nadeem and Farooq 2019). In 2002, Van Straaten defined “agro-geology” as the use of “rocks for crops” to increase nutrient release rates from rocks that, over time, build the mineral component of soil (Van Straaten 2002). This is especially critical in the 21st century given the role of elevated CO_2 in further diluting the nutrient content of crops for animal and human consumption (Duval et al. 2012; Dietterich et al. 2015). Enhanced silicate weathering (ESW) may have the capacity to change the nutrient content of crops, particularly micro-nutrients, such that rock dust amendments may restore depleted micronutrient pools in soil (2002) and potentially improve food nutrient composition (Beerling et al. 2018). ESW of industrial waste and multi-nutrient minerals has a well-documented history of providing rock-derived nutrients to depleted agricultural soils and increasing yield (Van Straaten 2006; Edwards et al. 2017); but dissolution rates and accessibility of rock-derived nutrients has not been directly assessed in nutrient-rich, neutral pH agriculture soils.

1.1 Silicate mineral properties

The mineralogical composition of rock dust amendments in agronomic settings determines weathering rates, potential nutrients supplied to soils, microbes, and plants, and metal accumulation and secondary mineral formation (Andrews and Taylor 2019), among other factors, akin to how parent material imparts substantial control over soil and plant properties in natural ecosystems (Van Straaten 2007). Therefore, the agronomic effectiveness of minerals for fertilizer and carbon dioxide removal is principally affected by the mineral content of rock dust inputs, all else being equal.

Past studies have explored an array of mineral and rock-based fertilizers including multi-nutrient silicate rock fertilizer (ex. fine-grained volcanic rocks such as basalt and other silicates), single-nutrient rock fertilizer (ex: phosphate rock fertilizers), and mineral “waste” (ex: steel slag and coal waste) (Van Straaten 2006; Beerling et al. 2018). Fine-grained minerals that contain large amounts of olivine, amphiboles, and Ca-rich plagioclase feldspars, as well as low concentrations of free quartz, generally exhibit highest natural weathering rates (Goldich 1938; Van Straaten 2006). Olivine is one of the fastest weathering silicate minerals at $pH < 6$, owing to the high temperature of olivine formation and the thermodynamic instability of this mineral in Earth’s surface environment (Schuiling and Krijgsman 2006; Kohler et al. 2010; Renforth et al. 2015). This suggests exceedingly high capacity for CO_2 removal via silicate dissolution reaction when crushed olivine is applied to agricultural soil (Beerling et al. 2018). However, olivine, and certain silicates, contain high concentrations of potentially harmful trace metals such as

Chromium (Cr) and/or Nickel (Ni) (Schuiling and Krijgsman 2006; Kohler et al. 2010). These elements present in minerals and corresponding mafic to ultramafic rocks, can accumulate in soil and either enter a bioavailable cycle directly or block availability of plant essential nutrients, for example, in the case of Ni and its inhibitory effect on plant Mg uptake (Beerling et al. 2018). Renforth (2015) demonstrated the accumulation of Cr and Ni in a soil profile in North Oxfordshire, UK in response to crushed olivine applications for ESW. It is imperative to select rock types that do not impose a risk of toxic metal accumulation and match rock types (potential rock-nutrient supply) with plant and soil needs (Van Straaten 2006).

Silicate minerals have relatively low solubility and thus slowly release nutrients to plants (Van Straaten 2006), making them comparable to slow-release fertilizers. Beerling et al. (2018) estimates 17 Pg of reactive silicates are mined each year, implying a significant global pool of available rock dust as a byproduct of normal quarry operations that could be repurposed for ESW. This study uses wollastonite and basalt rock dust amendments, because these minerals/rocks are the predominant candidates for widespread ESW applications, based on the low concentration of toxic metals and high proportion of plant-relevant nutrients in these substrates. According to Van Straaten (2006), advantages of multi-nutrient silicates such as basalts/meta-basalts include:

- Source of micro and macronutrients (Ca, Mg, K, Mn, Zn, Fe)
- Liming effects can buffer soil pH
- Act as slow-release fertilizers in nutrient depleted soils

- Often locally available as quarry and mine wastes
- Relatively inexpensive
- Low environmental impacts compared to other rock types

While all these benefits hold merit, and some have been evaluated, there remains a lack of substantial field testing of different mineral amendments in agronomic settings, particularly in cropping systems under common practices used by farmers and growers.

1.2 Crop nutrition and ESW

Many silicates that are suitable for ESW contain essential plant nutrients, including P, Mg, Ca, K, Fe, Zn, and Si. As a result, ESW can stimulate plant growth and increase crop yields through direct nutrient inputs (Haque et al. 2019; Kelland et al. 2020; Swoboda et al. 2021; Taylor et al. 2021; Van Straaten 2006; Haque et al. 2018), particularly in micro-nutrient depleted soils when rock-derived nutrients contribute to soil nutrient pools and support crop yield (Anda et. al. 2015; Edwards et al. 2017). Still there are cases when ESW does not improve crop yield, depending on silicate type deployed, baseline soil conditions, and crop varieties and systems (Haque et al. 2020; Swoboda et al. 2021; Wang et al. 2018). Buffered pH associated with HCO_3^- and $CaCO_3^-$, which form as silicate dissolution products, may alleviate the limitation of soil acidification on plant productivity, which could also lead to increased yields in acidified soils, such as those in sub-tropical and tropical areas where soils are naturally highly weathered and acidic.

Although Si is not *sensu stricto* considered an essential plant nutrient, all plants use Si in some form or another, including metabolically (Haynes 2017). 200 Mt of Si are removed from cultivated soils around the world each year during harvest (Matichenkov and Bocharnikova 2001). ESW has been shown to support crop resilience to abiotic stressors such as drought and extreme wind by increasing soil silicon (Si) concentrations (Haynes et al. 2017). There is mounting evidence that Si can induce a broad range of beneficial responses to biotic and abiotic stressors (Epstein 1999; Guntzer et al. 2012; Haynes 2014). Si can improve water-use efficiency, for example, by lowering leaf transpiration rates, thereby increasing resilience to drought (Hartmann et al. 2013; Haynes 2017). Such abiotic stresses are predicted to worsen with climate change making Si fertilization a potential climate change mitigator. Phytoliths, deposition of silicon within tissues, fortifies stems, leaves, and roots by mechanically reinforcing the cell wall (Haynes 2017). Si-fertilization activates specialized Si transporter proteins that improve N, P, and Zn uptake and use (Guntzer et al. 2010; Haynes 2017). Yield increases in wheat, rice, and sugarcane in response to Si fertilization have also been observed (Korndörfer & Lepsch 2001; Liang et al. 2015; Neu et al. 2017). Several studies document the benefits of applying Si slag on productivity in crops including wheat, rice, corn and sugarcane with some yield improvements greater than 40% with this Si-rich waste product (Tubana et al. 2016; Das et al. 2019). Several of the most important crops globally are considered Si-accumulators (Table 2.1) (FAOSTAT 2018; Guntzer et al. 2010, Edwards et al. 2017). The demand for Si in agriculture is therefore expected to increase in the future (Haynes 2014).

Table 2.1. Crop assimilation of silica by % dry mass in above ground biomass of silica hyper-accumulators (Guntzer et al. 2010; Edwards et al. 2017; Beerling et al. 2018).

Crop	Silica concentration (%)
Rice	4.1%
Sugar Beet	3%
Wheat	2.45%
Barley	1.8%
Soybeans	1.4%
Tomato	1.5%
Sugar Cane	1.5%
Maize	0.8%

1.3 Soil health and ESW

ESW has been postulated to improve several facets of soil health: rebuilding the soil mineral composition lost to erosion (Van Straaten 2006); acting as a slow-release fertilizer (Hartmann et al. 2013; Basak et al. 2017); buffering soil acidity and increasing CEC in highly weathered soil (D'Hotman 1961; Anda et al. 2015; Beerling et al. 2018); and improving soil water holding capacity and organic C occlusion by stimulating root and mycorrhizal exudates thereby supporting aggregate stability (Manning 2008; Beerling et al. 2018). Although agricultural soil is ideally approximately neutral to slightly acidic in pH, soil acidity is common in agriculture (Guo et al. 2010). ESW of silicate rocks reduces soil acidity by generating cations and HCO_3^- which increases soil pore water alkalinity. The gradual liming effect of ESW reduces metal toxicity and can act to increase phosphorus (P) availability in acidic soils (Beerling et al. 2018).

ESW has the potential to increase soil pore water alkalinity beyond a range optimal for crop growth, although this concept is more theoretical than empirical (Beerling et al. 2018). However, by releasing protons and CO_2, roots reduce soil pH and increase the CO_2

concentration in the rhizosphere (Lenzewski et al. 2018; Vicca 2021), both of which stimulate mineral weathering (Harley & Gilkes 2000). Sources of soil acidity such as organic acids and root exudates (lichen acid, uronic acid, malate and citrate), microbial decay of plants/animals, carbonic acid (product of root and microbial respiration), and protons released during N-fixation, may balance the liming effect of ESW (Beerling et al. 2018; Vicca 2021). Generally, organic acids in the soil can serve to chelate Al and solubilize nutrients like Fe (Haque et al. 2019), but they can also serve to dissolve silicate minerals at near-neutral pH, where abiotic dissolution rates are limited (Harley & Gilkes 2000). Roots take up elements that are released during weathering reactions, such as Si, Mg, Ca, and Fe, thereby avoiding pore water saturation of reaction products which slows down weathering rates (Vicca et al. 2021; Harley & Gilkes 2000; Hinsinger 1998). Long-term application of ESW may produce secondary carbonates in soil if pH and other factors permit, though this is a relatively slow process compared to the rapid production of HCO_3^- (Beerling et al. 2018).

Soil biota can also reinforce ESW through bioturbation and digestion (Vicca 2021). Large shifts in soil microbial communities have been associated with the addition of silicates (Carson et al. 2007; Gwon et al. 2019; Zhou et al. 2018). For example, Zhou et al. (2018) observed changes in bacterial and fungal community composition with silicate rock additions. Soil pH is one of the main determinants of microbial community composition (Fierer 2017), and pH changes following silicate addition will thus directly influence which microbial taxa flourish (Gwon et al. 2019; Fierer 2017). The enzymes and proteins that play an important role in weathering of silicates are often excreted by microbes experiencing a nutritional deficiency. Microbial extracellular enzymes are activated both by nutrient limitation and the proximity to the nutrient-carrying mineral (Xiao et al. 2015; Zaharescu et al. 2020). Some enzymes, such as carbonic anhydrases (CA) which are found within all domains of life and play a fundamental role in respiration, CO_2 transport, and photosynthesis, have a combined effect of both increasing silicate weathering and carbonate precipitation (Vicca 2021). The impact of ESW on the microbial community will likely create new equilibrium and impact various soil processes related to soil C and GHG emissions (Gwon, et al. 2019; Vicca 2021).

ESW alters soil physical properties such as texture, structure, and porosity by the addition of silt-sized particles (Beerling et al. 2018). Soil structure may be improved as rocks stimulate root and mycorrhizae to produce exudates that can accelerate and strengthen the formation of soil aggregates. It may prevent cation leaching, increase soil nutrient availability and reduce elemental toxicities, particularly in highly weathered soils (Anda et al. 2014).

1.4 Study aim and Hypothesis

ESW of industrial waste and multi-nutrient minerals has a well-documented history of providing rock-derived nutrients to depleted agricultural soils and increasing yield (Van Straaten 2006; Edwards et al. 2017); but dissolution rates and accessibility of rock-derived nutrients has not been directly assessed in nutrient-rich, neutral pH agriculture soils. Field studies involving rock amendments and their effect on plant nutrients, yield and soil health parameters are lacking. This study aims to address this research gap by measuring the impact of ESW on corn and tomato yield in fertile, neutral pH soils. The study also measures the elemental composition of corn and tomato with a focus on elements potentially supplied to the soil by silicate dissolution to determine ESW's ability to alter elemental composition of these crops. My hypothesis is that rock amendments may improve crop yield. The hypothesis was tested by growing corn and tomato with gypsum, wollastonite, and basalt additions in conventional and organic management at Russell Ranch. We measure yield of above ground biomass and crop elemental composition by acid digestion and ICP-AES. My hypothesis regarding the elemental composition of corn and tomato is that ESW will not change the elemental composition because Russell Ranch soils are not limiting in essential plant nutrients.

2. Methods

2.1 Field site and study design

A 2-year field trial was conducted at Russell Ranch Sustainable Agriculture Facility in Davis, CA (USA) from October 2018 to September 2020 to investigate the effects of gypsum and silicate rock dust (wollastonite and basalt). The Russell Ranch Sustainable Agriculture Facility is a 300-acre UC Davis farm dedicated to elucidating long-term impacts of crop rotation, land management regimes, inputs of water, nitrogen, C and other nutrients on agricultural sustainability. Russell ranch has 72 one-acre plots which employ conventional and organic management and various crop rotations. Both management regimes retained crop residue as an organic C source. Conventional management is fertilized with standard fertilizer, UAN32, delivered at a rate of 210 lbs of N/acre throughout the growing season in equal parts urea and ammonium nitrate through drip fertigation. Organic plots receive composted poultry manure and winter cover cropping with Lana woolypod vetch (*Vicia villosa*), Magnus peas (*Pisum sativum*), and Montezuma oats (*Avena sativa*), but no synthetic fertilizer was applied.

In this study, corn was grown the first year and tomato was grown the second year. Corn was planted May 2018 and harvested October 2018. Tomato was planted March 2020 and harvested October 2020. Two silicate rock treatments, basalt and wollastonite, and a non-silicate mineral, gypsum were selected for this study. These treatments were chosen because basalt is the most dominant silicate in the Earth's crust and is widely suggested as the most important source of rock dust for ESW (Beerling et al. 2018). Wollastonite is less common over Earth's surface, but has a more rapid weathering rate than basalt due differences in their chemical composition (Table 1.2, Table 1.4). Gypsum is commonly used in agriculture to supply Ca and S, but does not contain silicate. Gypsum has C drawdown potential based on Zoca and Penn (2017), suggesting that gypsum can elevate Ca concentrations and thereby increase $CaCO_3$ precipitation in the soil. Mineralogy and elemental composition of these materials are shown in tables 2.2 - 2.8. Treatments were randomized in each block. There were 3 blocks for each management system. Each treatment had 3 replicates within each management system, making ~9 m x 4.5 m treatment-plots. We assessed the impact of silicate application on corn and tomato yield and the elemental composition of these crops, particularly elements potentially released to soil by silicate mineral dissolution.

According to NRCS mapping (Soil Survey Staff), the field plots in this study are split between two soil series: Rincon and Yolo. Both soil series are deep, well drained soils that formed in alluvium from mixed mineralogy (Soil Survey Staff, 2019). There is some variation in clay content, pH, and CEC across these soil classifications (Table 2.2) (Soil Survey Staff, 2019), but decades of management have made those differences less distinct. These properties will influence percolation rate, carrying weathering products down the profile. This site is located in a Mediterranean climate and uses irrigation. Drip tape is installed 25 cm into soil profile.

2.2 Rock characteristics and application rate

Gypsum was purchased from Custom Hydro Nutrients (office in Neosho, MO, USA) for application in year 1 and Redi-Gro (office in Sacramento, CA, USA) for application in year 2. Wollastonite was purchased from Vansil (office in Norwalk, CT, USA) in year 1 and NYCO (office in Willsboro, NY, USA) in year 2 of this study. Basalt was purchased from Soil Key (office in Bellingham, WA, USA) for year 1 and Rock Dust Local (office in Bridport, Vermont, USA for year 2. I assessed the particle size distribution of each rock type using a *LS Variable Speed Fluid Module Plus* particle size analyzer. Each had a particle size distribution within 10-100 µm. Mineralogy was described in Vansil brand wollastonite and basalt from Soil Key and Rock Dust Local by quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) bulk mineral analysis (BMA) by Bureau Veritas Metallurgical Division. Bureau Veritas Metallurgical

Division also quantified elemental composition of each mineral used in this study by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis (Tables 1.2-1.8).

Rock treatments were applied October 18-22, 2018 and November 8-18, 2019. Rock was incorporated into the soil to 8 cm depth using standard tillage equipment. Conventional plots were left fallow until corn was planted in June. In organic plots, a legume cover crop is planted late November. Gypsum and wollastonite were applied at a lower-end application rate of 8 t/ha (800 g/m^2) based on ESW literature, and basalt was applied at a suggested application rate of 20 t/ha (2000 g/m^2) for carbon removal (Beerling et al. 2017). These application rates were selected to begin to ascertain C sequestration potential of silicates at a high and low end of the range.

Table 2.2. Soil pH, CEC, and clay content in the upper 100 cm based on NRCS soil survey (Soil Survey Staff 2019).

Soil series	**pH**	**CEC** cmol(+)/kg	**Clay %**
Rincon	7.9	27	29
Yolo	6.8	18	25

Table 2.3. Mineralogy of wollastonite from Year 1 (Vansil) as percent composition.

Wollastonite Mineralogy	**Vansil (%)**
Pyroxene (Augite)	8.2
Quartz	0.9
Wollastonite	84
Epidote	3.58
Calcite	2.44

Table 2.4. Basalt mineralogy as percent composition in year 1 (Soil Key) and year 2 (Rock Dust Local).

Basalt Mineralogy	**Soil Key (%)**	**Rock Dust Local (%)**
Plagioclase Feldspar	48.1	31.4
K-Feldspar	24.4	>0.1
Pyroxene (Augite)	13	26.4
Ilmenite	4.96	>0.1
Forsterite	4.94	1.98
Quartz	1.01	1.19
Apatite	1.76	>0.1
Chlorite	>0.1	19.0
Epidote	>0.1	9.63
Calcite	>0.1	3.27
Sphene	>0.1	3.41

Table 2.5. Elements applied via gypsum in year 1 (Custom Hydro Nutrients) and year 2 (Redi-Gro).

Gypsum Composition	Year 1 (%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Calcium	12.90	103.2	14.12	112.96
Sulfur	9.86	78.88	10.47	83.76
Magnesium	0.02	0.16	0.38	3.04

Table 2.6. Elements applied via wollastonite from Vansil (year 1) and NYCO (year 2) brands.

Wollastonite Composition	Year 1(%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Iron	0.13	1.04	0.98	7.84
Calcium	31.89	255.12	33.89	271.12
Phosphorus	0.02	0.16	0.04	0.32
Magnesium	0.88	7.04	0.19	1.52
Aluminum	0.4	3.2	0.68	5.44
Sodium	0.06	0.48	0.09	0.73
Potassium	0.05	0.4	0.03	0.24

Table 2.7. Elements applied via basalt from Soil Key (year 1) and Rock Dust Local (year 2) brands.

Basalt Composition	Year 1 (%)	Year 1 (g/m^2) Applied	Year 2 (%)	Year 2 (g/m^2) Applied
Iron	7.29	145.8	7.69	153.8
Calcium	4.25	85	6.46	129.2
Phosphorus	0.63	12.6	0.05	1
Magnesium	1.75	35	4.14	82.8
Aluminum	7.29	145.8	7.86	157.2
Sodium	2.76	55.2	3.05	61
Potassium	2.59	51.8	0.24	4.8

2.3 Plant sample collection and methods of analysis

The Russell Ranch team completed a hand harvest in 2 randomly selected rows along a 1 m length. Hand harvest involved shearing to cut corn stalks at their base. Ears were immediately separated from stalks. Ears and stalks were oven dried at 60 °C for 8 weeks. Oven dried samples were weighed and recorded for total yield data. Yield data was measured as lb/m and scaled to t/ha in order to be relevant for growers. Grains were removed from cobs before analysis. Dried biomass was ground to 2 mm using a Wiley mill.

Hand harvested tomato fruit and vines were completed for nutrient composition. Fruit was frozen, pureed and freeze dried in preparation for analysis. Vine samples were oven dried at 60 °C for 8 weeks and ground to 2 mm by Wiley mill. Tomato was harvested mechanically for yield data. The center 6 m length within blocks were mechanically harvested to limit edge effect. Two randomly selected rows of each treatment-plot were mechanically harvested. For controls, yield data from 4 rows for each of the 3 plots was used.

Crop biomass was analyzed by acid digestion to measure nutrient content and potential rock-derived nutrients in corn and tomato. A 1:3 ratio of nitric acid and hydrochloric acid coupled with microwave digestion was used to analyze samples for chemical constituents via Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Results are reported as mean measurements with standard errors. R version 4.1.2 was used for all graphs and statistical analyses. The following packages were used: tidyverse, dplyr, ggplot2, ggpubr, ISLR, and ggstatsplot. A quantile-quantile plot was used to determine the normality of the variables analyzed. The quantile-quantile plot showed that yield and biomass nutrients were not normally distributed, therefore a non-parametric test was required. These data fit the assumptions of Kruskal Wallis test. The Kruskal Wallis test was used to compare across all treatments and control. Significant p-values reflect differences in median measurements in each treatment. $P < 0.05$ was used as the limit for statistical significance. When the Kruskal Wallis test produced a significant result, the Dunn's test with Šidák adjusted p-values was used to determine which treatments were significantly different.

3. Results

3.1 Corn Yield

There was no significant treatment effect in stover yield of corn plants grown in conventionally managed plots (p-value = 0.97) (Table 2.8; Figure 2.1). Treatments in organically managed blocks, by contrast, showed a set of significant treatment effects (p-value = 0.032). To determine which treatments were significantly different, the Dunn's test with Šidák adjusted p-value for adjusting p-value was used and indicated a significant difference in stover yield between control and gypsum in organic management (p= 0.0127), where stover yield was greater in gypsum compared to control. In organic management, gypsum treated soil showed the highest stover yield with a maximum yield measurement of 11.93 t/ha. Gypsum amended stover biomass increased 30.8% on average compared to control. Basalt and wollastonite additions improved crop yields in organic management by 21.4% and 19.9% on average compared to the control, respectively.

Figure 2.1. Corn stover yield (t/ha) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Although all treatments showed grain yield increase compared to the controls in both conventional and organic management, this increase was not statistically significant in either management regime (Table 2.8; Figure 2.2). Conventional basalt showed the greatest improvement in grain yield with 17.81% increase compared to control. Gypsum and wollastonite treated soils displayed improved grain yields at 14.57% and 11.13%, respectively, in conventional management. Despite these increases, grain in conventional management in response to treatments did not show a statistically significant effect (p-value = 0.27). Gypsum increased the most in organic management by 31.3% compared to the control. Wollastonite and basalt increase 30.8% and 23.6% respectively. All treatments showed grain increase compared to controls, but treatment effect in organic management was not significant (p-value = 0.46).

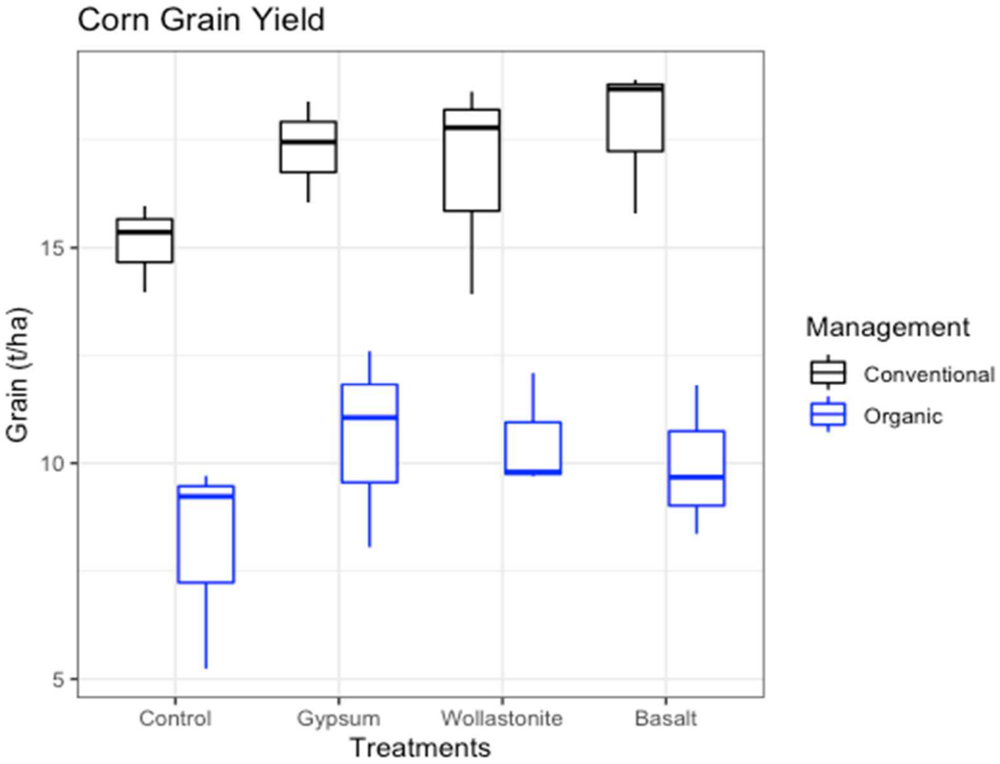

Figure 2.2. Corn grain yield (t/ha) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Similarly, despite discernible treatment increases compared to the control, there was no statistically significant treatment effect in cob yield (Table 2.8; Figure 2.3). Conventional cob responses were close to significant, with a treatment effect at a p-value equal to 0.063 and organic treatment effects were not significant (p-value = 0.13). Gypsum amended organic cob yield increased the most, 31.57%, compared to the control. Wollastonite and basalt amendments increased cob yield 22.5% and 21%, respectively.

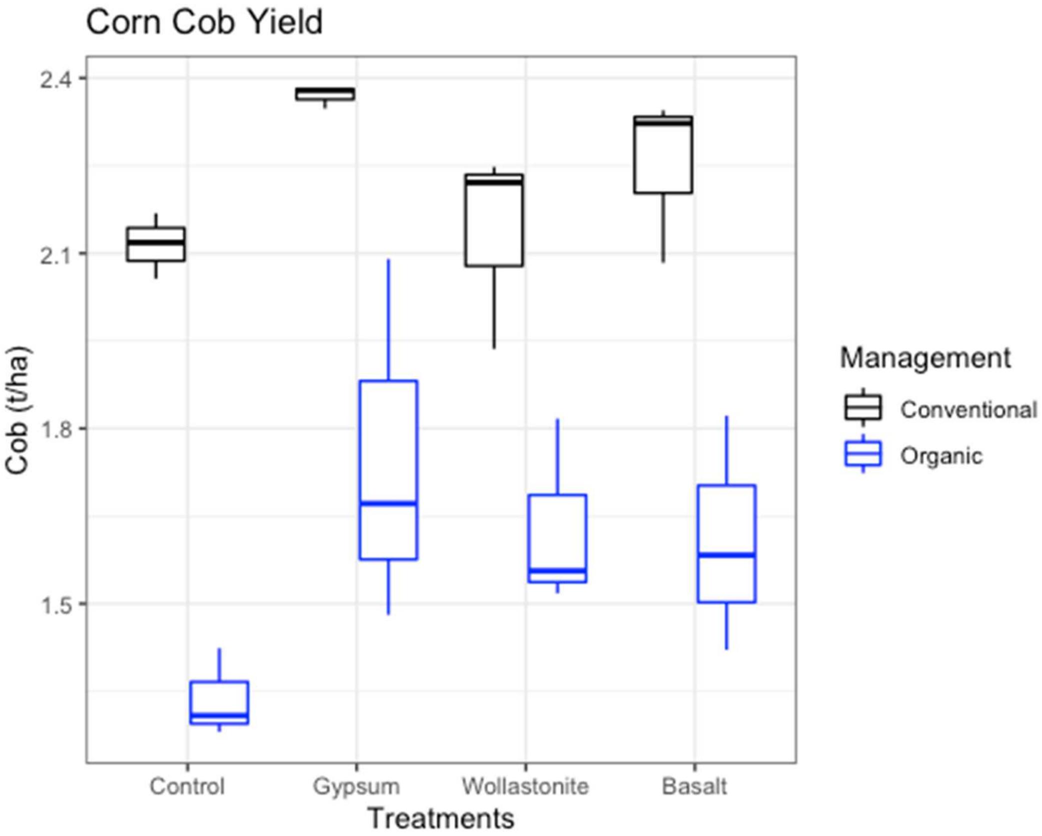

Figure 2.3. Corn cob yield (t/ha) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Table 2.8. Corn stover, grain, and cob yields (t/ha) and standard errors (SE). Stover sample size n=6, grain and cob sample size n=3.

Russell Ranch Corn Yield							
Management	Treatment	Stover (t/ha)	SE (Stover)	Grain (t/ha)	SE (Grain)	Cob (t/ha)	SE (Cob)
Conventional	Control	11.01	0.345	15.1	0.59	2.11	0.033
	Gypsum	10.76	0.361	17.3	0.68	2.37	0.011
	Wollastonite	10.93	0.739	16.98	1.44	2.13	0.100
	Basalt	10.77	0.313	17.79	0.10	2.25	0.083
Organic	Control	7.81	0.371	8.05	1.42	1.34	0.044
	Gypsum	10.20	0.619	10.57	1.34	1.75	0.18
	Wollastonite	9.47	0.565	9.47	0.78	1.63	0.094
	Basalt	9.35	0.385	9.35	1.00	1.61	0.116

3.2 Corn nutrient composition

Although it would be ideal to have control samples to compare with the treatments, sampling constraints did not permit the collection of plant and soil samples for nutrient contents in control plots, in contrast to yield estimates above. Consequently, I compared gypsum, a non-silicate and highly soluble mineral composed of only calcium (Ca) and sulfur (S), to silicate amended plots to evaluate for nutrient changes in response to ESW. Silicates contain many elements, including Ca, magnesium (Mg), iron (Fe), silicon (Si), sodium (Na), and potassium (K), particularly in the case of basalt, which has a cosmopolitan array of minerals. Wollastonite is dominated by Ca and Si, and weathers in the presence of carbonic acid. Carbon

(C) and nitrogen (N) composition in corn is also measured to evaluate for indirect nutrient effects of ESW.

Although there was no significant treatment effect in corn nutrient composition between either management regime, both conventional and organic management showed marked and non-systematic variation in nutrient composition among treatments. P-value for stover Ca composition was 0.95 and 0.67 in conventional and organic management respectively (Table 2.9; Figure 2.4). P-value for kernel Ca composition was 0.9 and 0.44 in conventional and organic management respectively (Table 2.10; Figure 2.5).

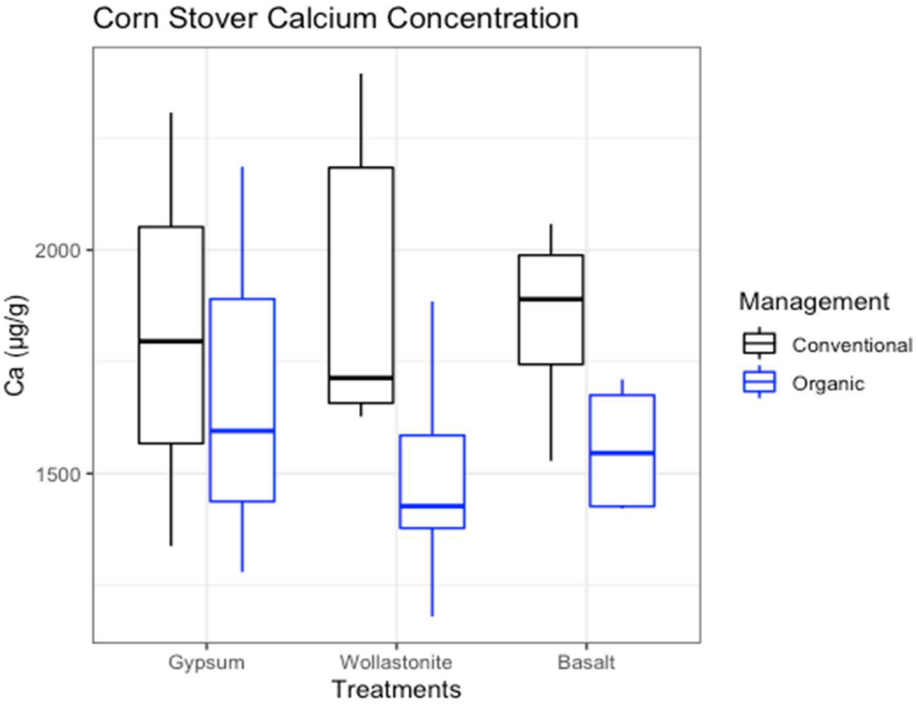

Figure 2.4. Corn stover Ca concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

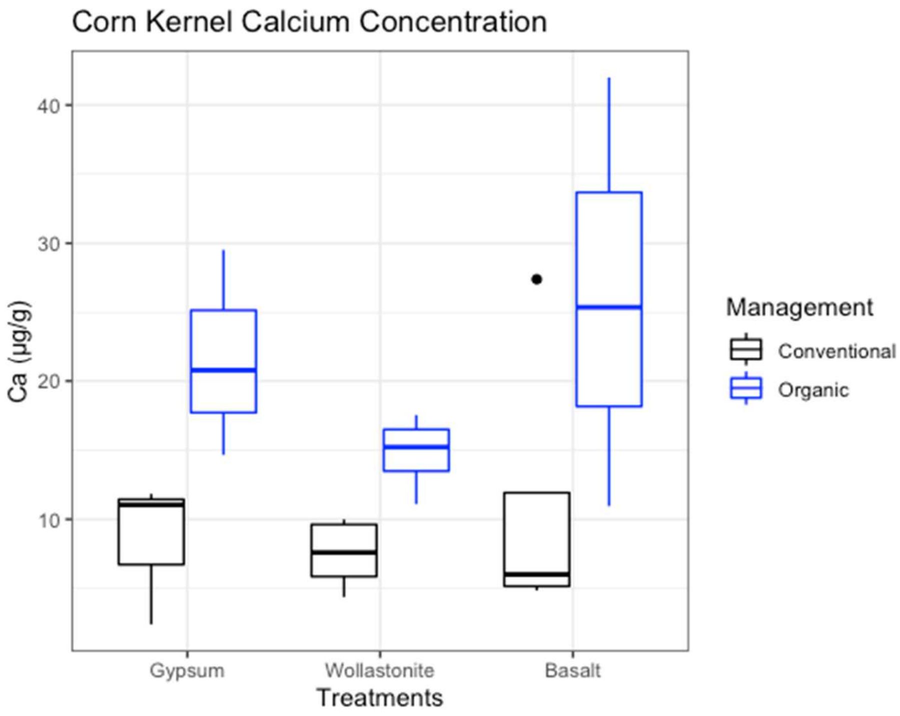

Figure 2.5. Corn kernel Ca concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

There was no consistent effect of wollastonite and basalt compared to gypsum on corn in stover and kernel concentration of Mg. The p-value for stover Mg composition was 0.46 and 0.51 in conventional and organic management respectively (Table 2.9; Figure 2.6). P-value for kernel Mg composition 0.38 and 0.64 in conventional and organic management respectively (Table 2.10; Figure 2.7).

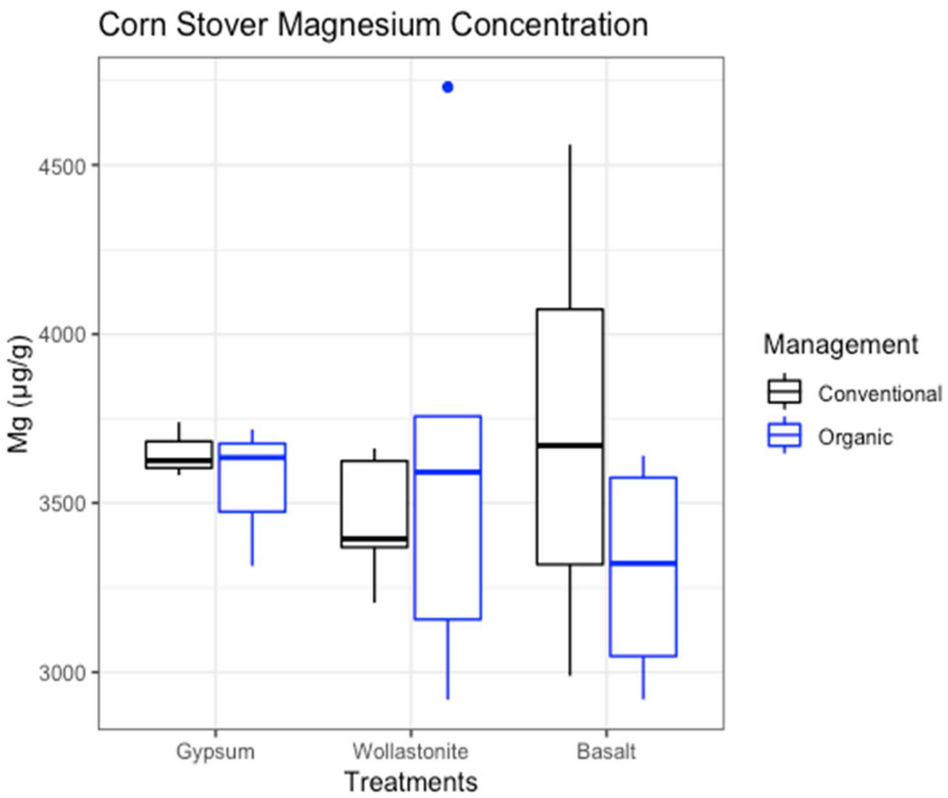

Figure 2.6. Corn stover Mg concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

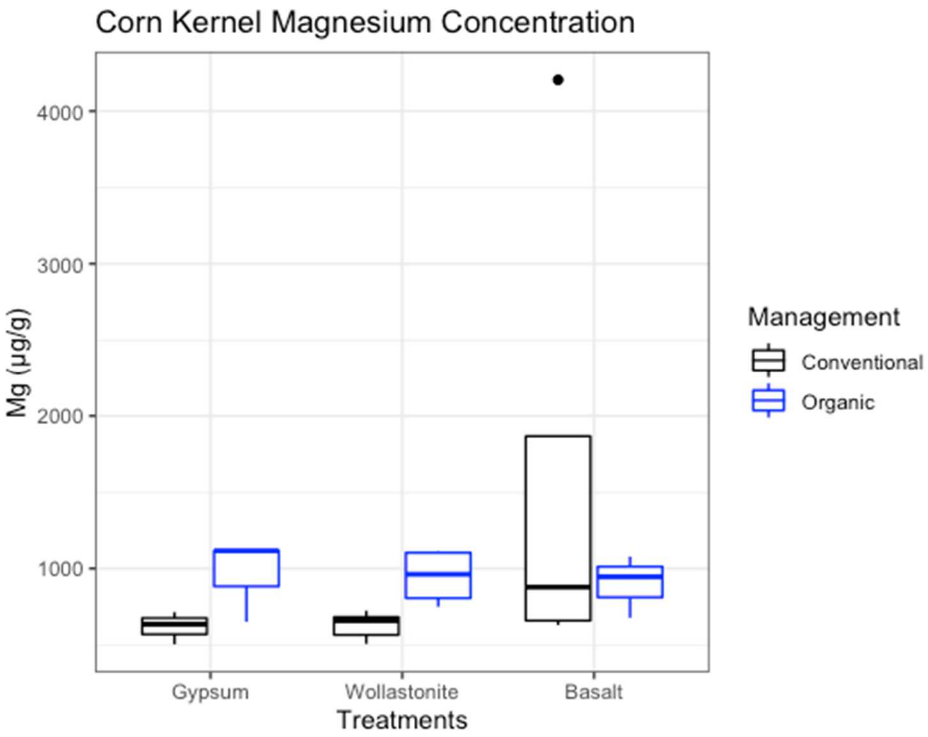

Figure 2.7. Corn kernel Mg concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

Although there was no consistent treatment effect in corn Fe concentration, wollastonite showed elevated Fe concentration in corn stover in organic management and corn kernel in conventional management. The p-value for stover Fe composition was 0.89 and 0.57 in conventional and organic management respectively (Table 2.9; Figure 2.8). The p-value for kernel Fe composition was 0.12 and 0.28 in conventional and organic management respectively (Table 2.10; Figure 2.9).

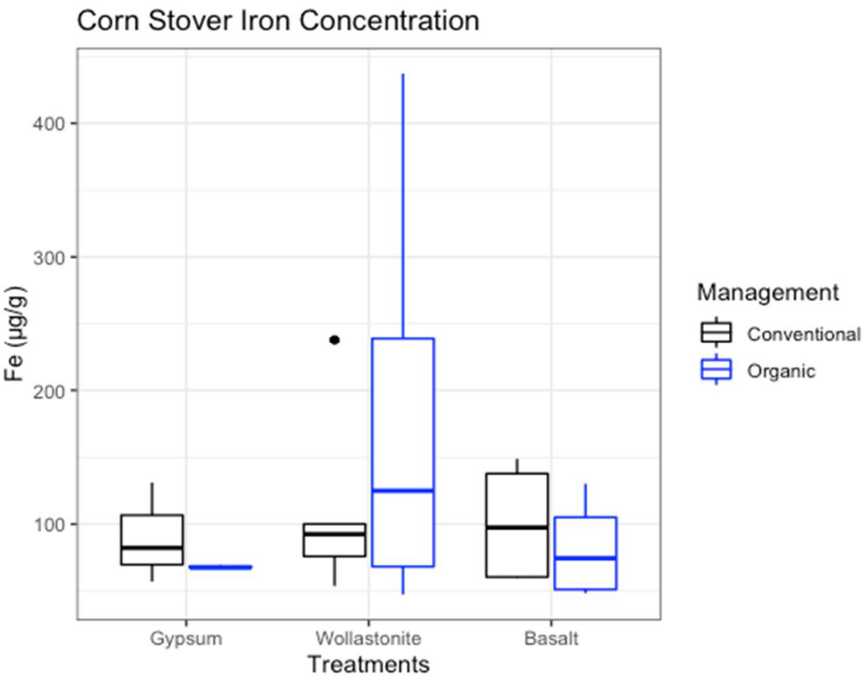

Figure 2.8. Corn stover Fe concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

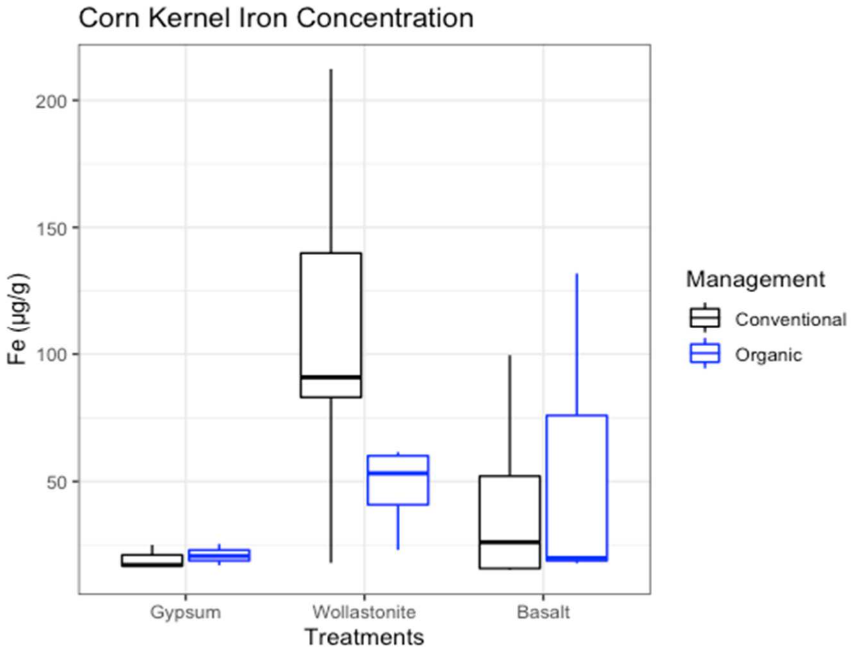

Figure 2.9. Corn kernel Fe concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

Table 2.9. Mean corn stover concentration of Ca, Mg, and Fe (µg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch Corn stover nutrients								
Management	Treatment	Ca	SE (Ca)	Mg	SE (Mg)	Fe	SE (Fe)	n
Conventional	Gypsum	1813.7	279.87	3648.67	46.84	90.18	21.71	3
	Wollastonite	1915.0	156.86	3450.6	85.01	112.02	32.43	5
	Basalt	1841.5	115.87	3722.0	336.86	100.83	23.64	4
Organic	Gypsum	1687.0	265.55	3555.0	122.86	68.21	0.66	3
	Wollastonite	1491.2	117.7	3630.4	312.86	183.35	71.63	5
	Basalt	1555.75	76.11	3300.75	175.14	81.87	19.51	4

Table 2.10. Mean corn kernel concentration of Ca, Mg, and Fe (µg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch Corn kernel nutrients								
Management	Treatment	Ca	SE (Ca)	Mg	SE (Mg)	Fe	SE (Fe)	n
Conventional	Gypsum	8.43	3.02	618.13	61.73	19.6	2.76	3
	Wollastonite	7.49	1.08	627.32	40.03	108.83	32.33	5
	Basalt	11.07	5.46	1647.87	858.66	41.79	19.86	4
Organic	Gypsum	21.65	4.31	961.2	155.3	47.75	8.85	3
	Wollastonite	14.77	1.40	947.33	93.81	21.07	2.43	5
	Basalt	26.1	N/A	900.800	N/A	56.56	N/A	4

There was no consistent effect of wollastonite and basalt compared to gypsum on corn stover and kernel concentration of S (Table 2.11 and 2.12). P-value for stover S composition was

0.1 and 0.21 in conventional and organic management respectively (Figure 2.10). P-value for kernel S composition was 0.87 and 0.39 in conventional and organic management respectively (Figure 2.11).

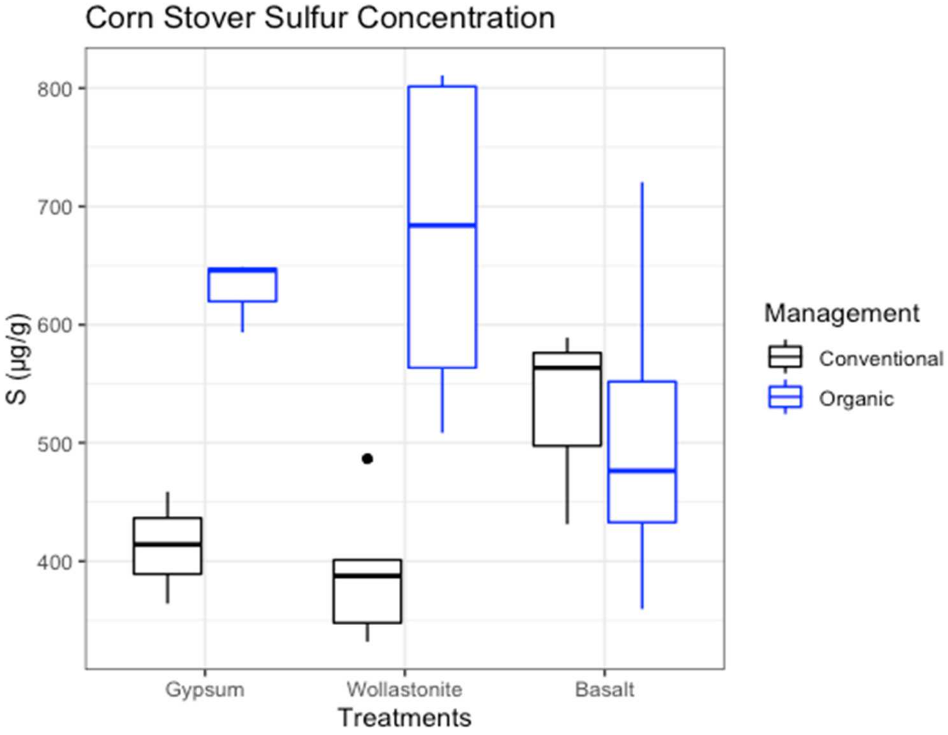

Figure 2.10. Corn stover S concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

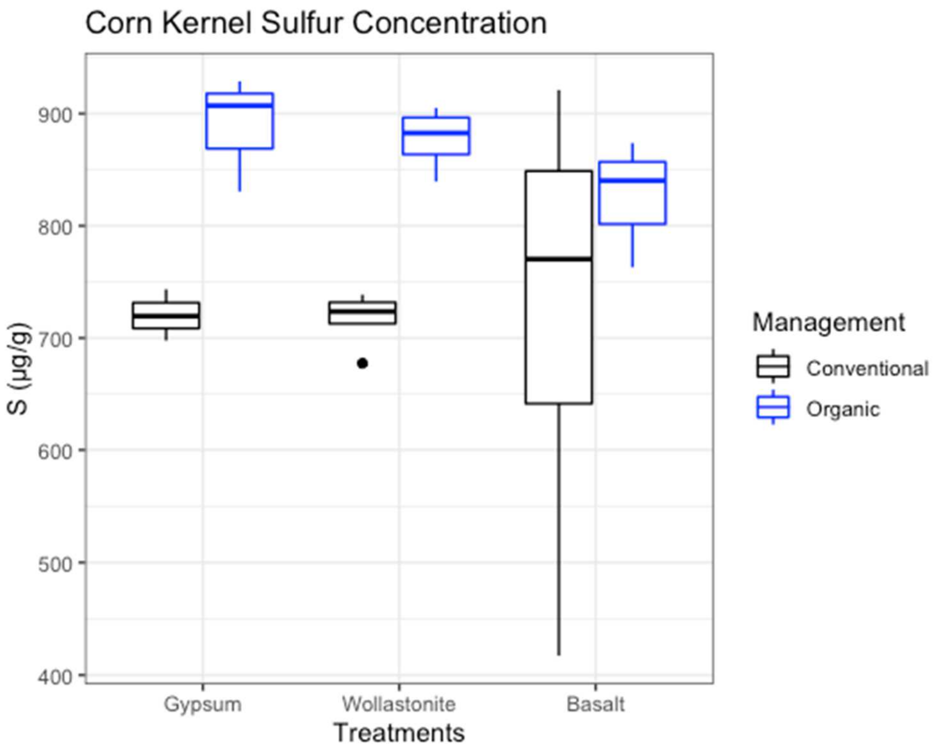

Figure 2.11. Corn kernel S concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

There was no consistent effect of wollastonite and basalt compared to gypsum on corn stover and kernel concentration of Al (Table 2.11 and 2.12). P-value for stover Al composition was 0.23 and 0.066 in conventional and organic management respectively (Figure 2.12). P-value for kernel Al composition was 0.59 and 0.99 in conventional and organic management respectively (Figure 2.13).

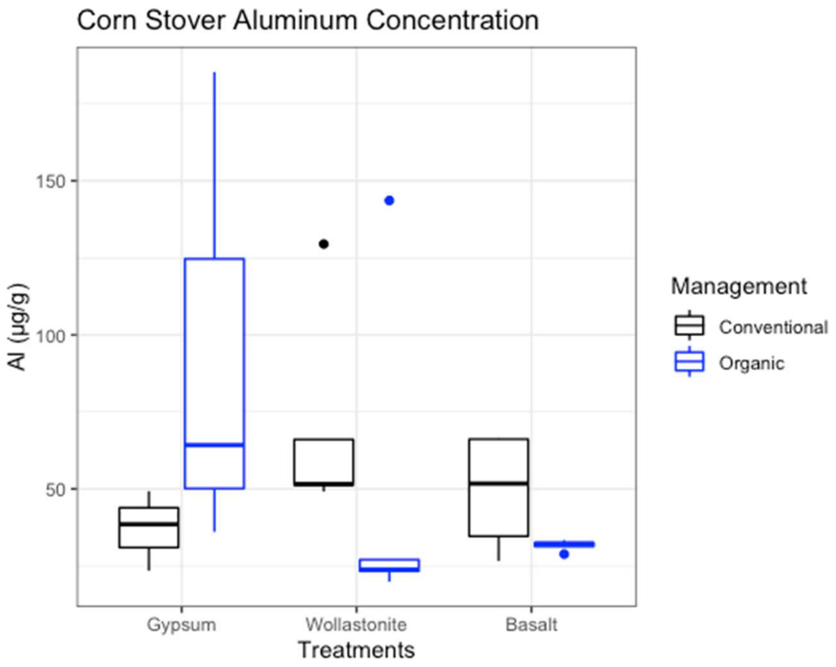

Figure 2.12. Corn stover Al concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

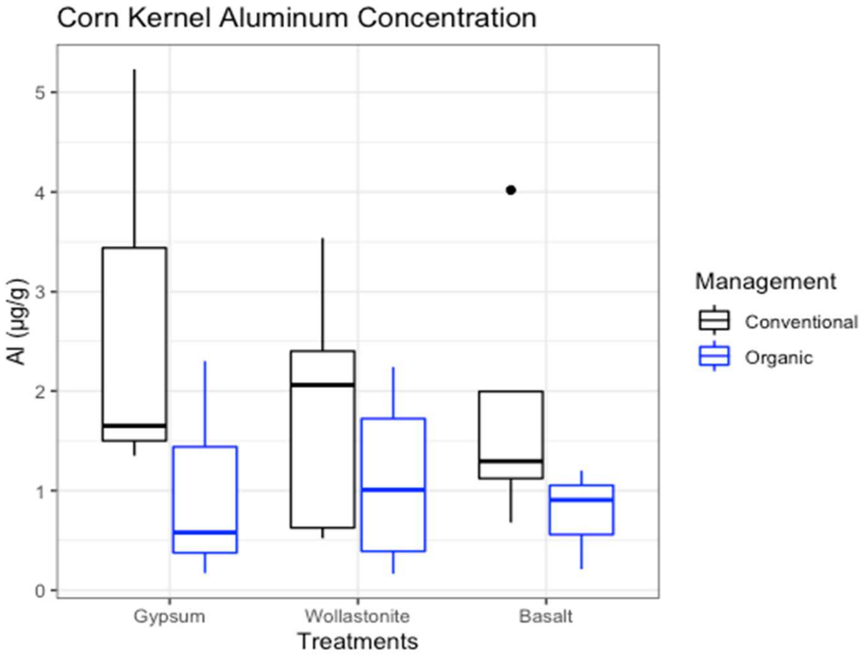

Figure 2.13. Corn kernel Al concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

There was no consistent effect of wollastonite and basalt compared to gypsum on corn stover and kernel concentration of Na (Table 2.11 and 2.12). P-value for stover Na composition was 0.98 and 0.61 in conventional and organic management respectively (Figure 2.14). Kernel Na is not shown because samples were below detection levels.

Figure 2.14. Corn stover Na concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

Table 2.11. Corn stover concentration of Na, Al, and S (μg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch corn stover nutrients								
Management	Treatment	Na	SE (Na)	Al	SE (Al)	S	SE (S)	n
Conventional	Gypsum	16.88	10.33	37.09	7.48	412.33	27.29	3
	Wollastonite	11.36	N/A	69.50	15.3	391.06	26.97	5
	Basalt	10.87	3.27	49.07	10.09	527.9	N/A	4
Organic	Gypsum	6.18	0.37	95.15	45.75	629.47	17.95	3
	Wollastonite	7.6	1.13	47.57	24.03	673.58	61.11	5
	Basalt	6.74	0.744	31.69	0.98	508.18	76.36	4

Table 2.12. Corn kernel concentration of Al and S (μg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch corn kernel nutrients						
Management	Treatment	Al	SE (Al)	S	SE (S)	n
Conventional	Gypsum	2.74	1.25	720.23	13.23	3
	Wollastonite	1.83	0.57	716.88	10.75	5
	Basalt	1.82	0.75	719.73	109.17	4
Organic	Gypsum	1.02	0.65	888.77	29.75	3
	Wollastonite	1.11	0.48	877.45	14.45	5
	Basalt	0.773	N/A	825.67	N/A	4

There was no consistent pattern in %C of stover and kernel amended with wollastonite and basalt compared to gypsum in conventional or organic management (Table 2.13 and 2.14). P-value for stover C composition was 0.59 and 0.48 in conventional and organic management (Figure 2.15). P-value for kernel C composition was 0.36 and 0.1 in conventional and organic management (Figure 2.16).

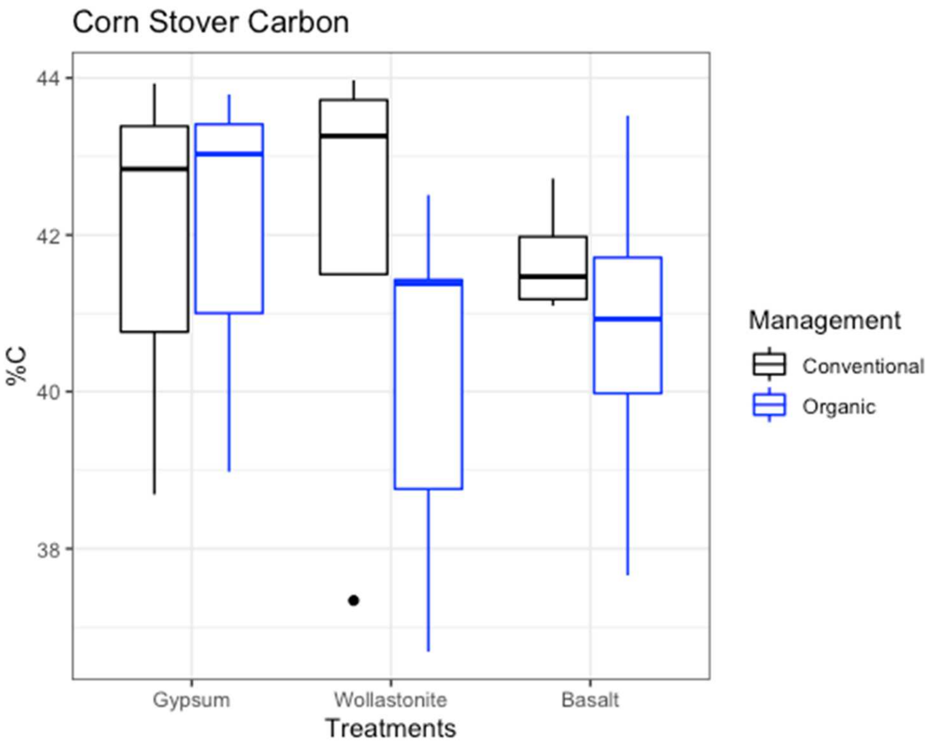

Figure 2.15. Corn stover %C concentration in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

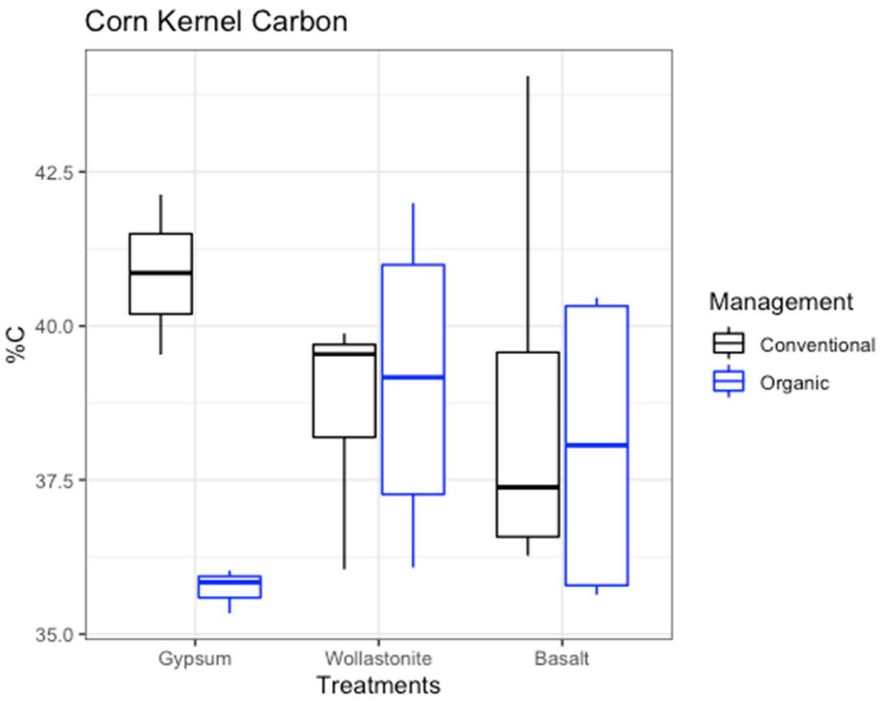

Figure 2.16. Corn kernel %C concentration in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

There was no consistent pattern in %N of stover and kernel amended with wollastonite and basalt compared to gypsum in conventional or organic management (Table 2.13 and 2.14). P-value for stover N composition was 0.88 and 0.15 in conventional and organic management (Figure 2.17). P-value for kernel N composition was 0.55 and 0.74 in conventional and organic management (Figure 2.18).

Figure 2.17. Corn stover %N concentration in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

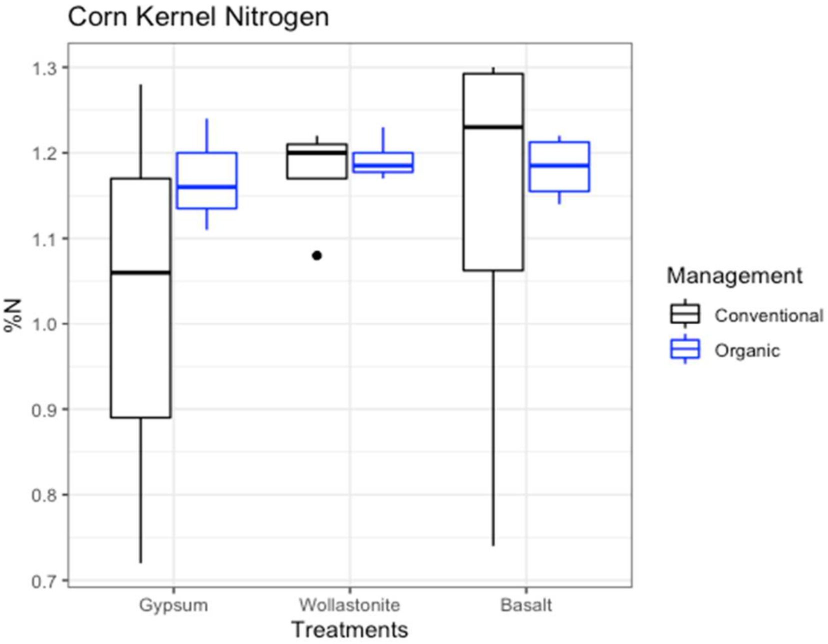

Figure 2.18. Corn kernel %N concentration in conventional (black) and organic (blue) management with the different treatments studied (gypsum, basalt, and wollastonite).

Table 2.13. Mean corn stover % C and N, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch Corn stover nutrients						
Management	Treatment	C	SE (C)	N	SE (N)	n
Conventional	Gypsum	41.82	1.60	0.9	0.282	3
	Wollastonite	41.96	1.23	0.694	0.04	5
	Basalt	41.69	0.37	0.8125	0.144	4
Organic	Gypsum	41.93	1.49	0.7	0.027	3
	Wollastonite	40.15	1.06	0.628	0.015	5
	Basalt	40.76	1.20	0.6	0.046	4

Table 2.14. Mean corn kernel %C and N, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch Corn kernel nutrients						
Management	Treatment	C	SE (C)	N	SE (N)	n
Conventional	Gypsum	40.84	0.75	1.02	0.163	3
	Wollastonite	38.67	0.72	0.025	0.025	5
	Basalt	38.77	1.80	1.125	0.132	4
Organic	Gypsum	35.74	0.21	1.17	0.038	3
	Wollastonite	93.10	1.35	1.193	0.013	5
	Basalt	38.06	1.34	1.183	0.019	4

3.3 Tomato Fruit Yield

Tomato fruit yield was measured using mechanical harvest. There was a significant treatment effect observed in conventional tomato fruit yield (p-value= 0.02) amendments underperformed compared to the control (Table 2.15; Figure 2.19). Dunn's test with Šidák adjusted p-value indicates that there was significant difference in tomato fruit yield control and basalt (p-value = 0.0100). Conventionally grown tomatoes amended with gypsum, wollastonite, and basalt resulted in reduced yield on average, by 11.6%, 20.1%, and 31.7% respectively compared to unamended controls. The organically grown tomato yields did not result in a significant treatment effect (p-value= 0.25). Organically grown tomatoes amended with gypsum, wollastonite, and basalt resulted in reduced yield on average, by 14.2%, 25.1%, and 16.5% respectively compared to unamended controls (Table 2.15; Figure 2.19).

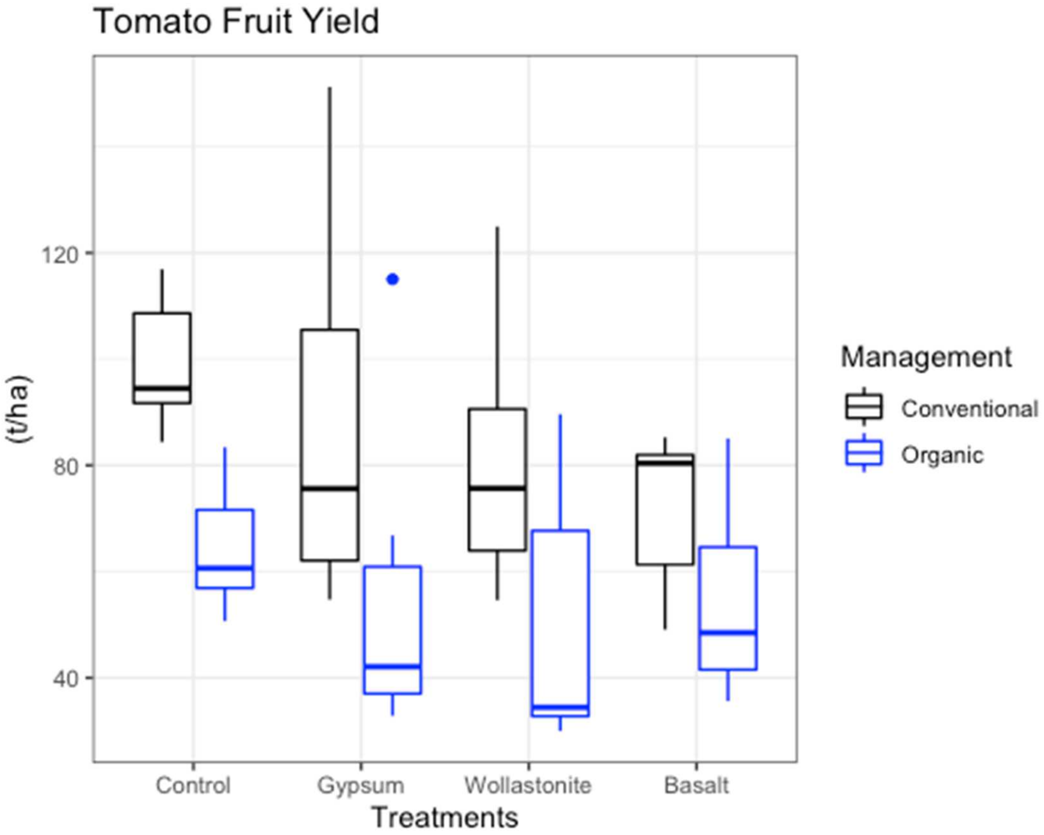

Figure 2.19. Tomato fruit yield (t/ha) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Table 2.15. Mean tomato fruit yield (y/ha), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown corn.

Russell Ranch Tomato Yield				
Conventional	Treatment	Fruit (t/ha)	SE (Fruit)	n
	Control	99.29	3.18	12
	Gypsum	88.35	15.19	6
	Wollastonite	81.08	10.46	6
	Basalt	72.08	6.44	6
Organic	Control	64.28	2.95	12
	Gypsum	55.75	12.82	6
	Wollastonite	49.94	10.88	6
	Basalt	54.47	7.76	6

3.4 Tomato nutrient composition

Silicates potentially provide Ca, Al, Mg, Fe, and Na. Although there was no significant treatment effect in tomato nutrient composition in either management regime, both conventional and organic management show marked variance in nutrient composition within and among treatments.

There was no consistent effect on the concentration of Ca in tomato vine and fruit with gypsum and silicate amendment. P-value for vine Ca composition was 0.77 and 0.3 in conventional and organic management respectively (Table 2.16; Figure 2.20). P-value for fruit

Ca composition was 0.83 and 0.46 in conventional and organic management respectively (Table 2.17; Figure 2.21).

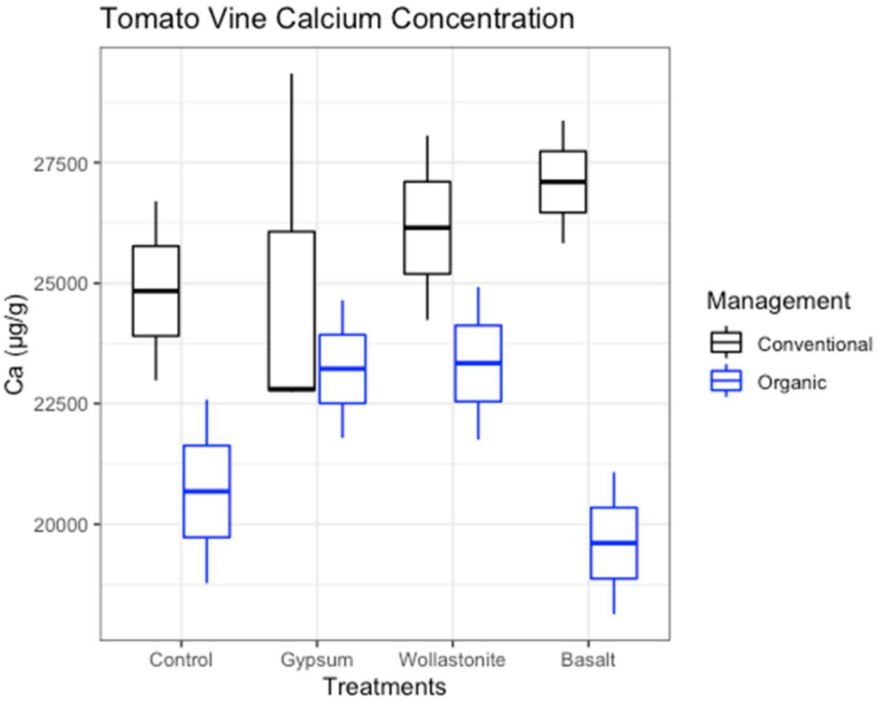

Figure 2.20. Tomato vine Ca concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

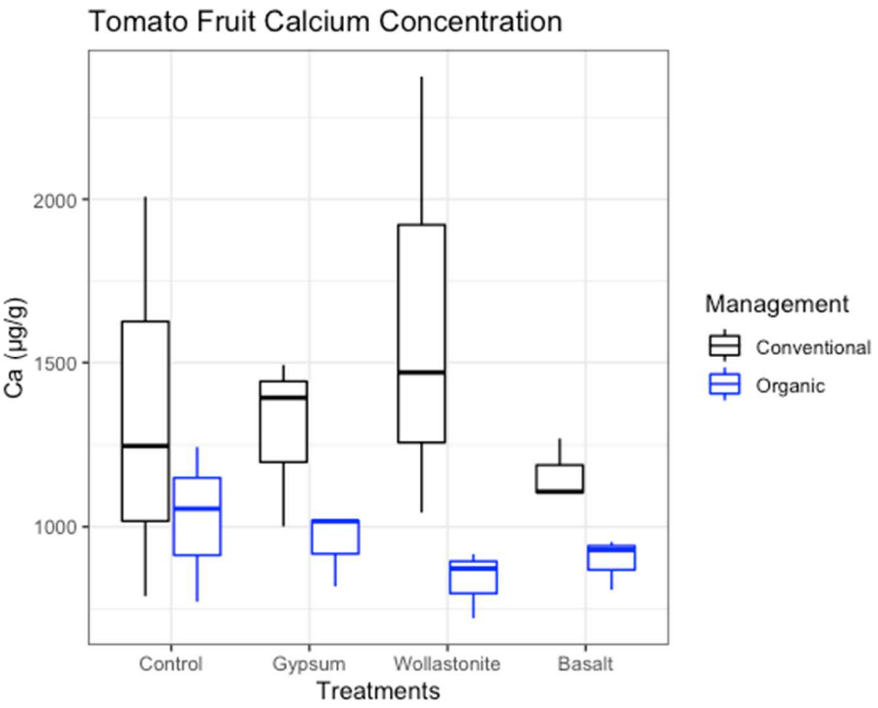

Figure 2.21. Tomato fruit Ca concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

There was no consistent effect on the concentration of Al in tomato vine and fruit with gypsum and silicate amendment. P-value for vine Al composition was 0.9 and 0.32 in conventional and organic management respectively (Table 2.16; Figure 2.22). P-value for fruit Al composition was 0.15 and 0.54 in conventional and organic management respectively (Table 2.17; Figure 2.23).

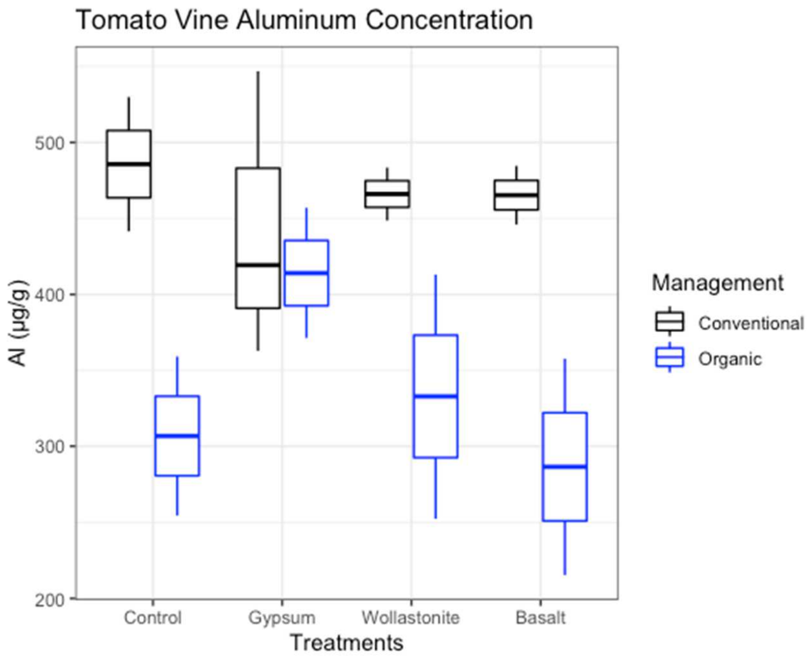

Figure 2.22. Tomato vine Al concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

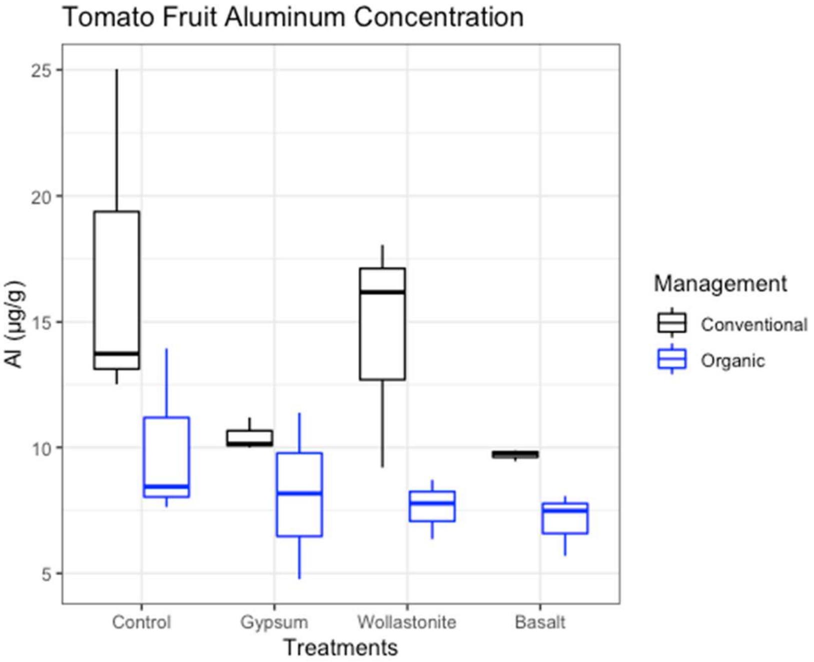

Figure 2.23. Tomato fruit Al concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

There was no consistent effect on the concentration of Fe in tomato vine and fruit with gypsum and silicate amendment. P-value for vine Fe composition was 0.99 and 0.68 in conventional and organic management respectively (Table 2.16; Figure 2.24). P-value for fruit Fe composition was 0.12 and 0.075 in conventional and organic management respectively (Table 2.17; Figure 2.25).

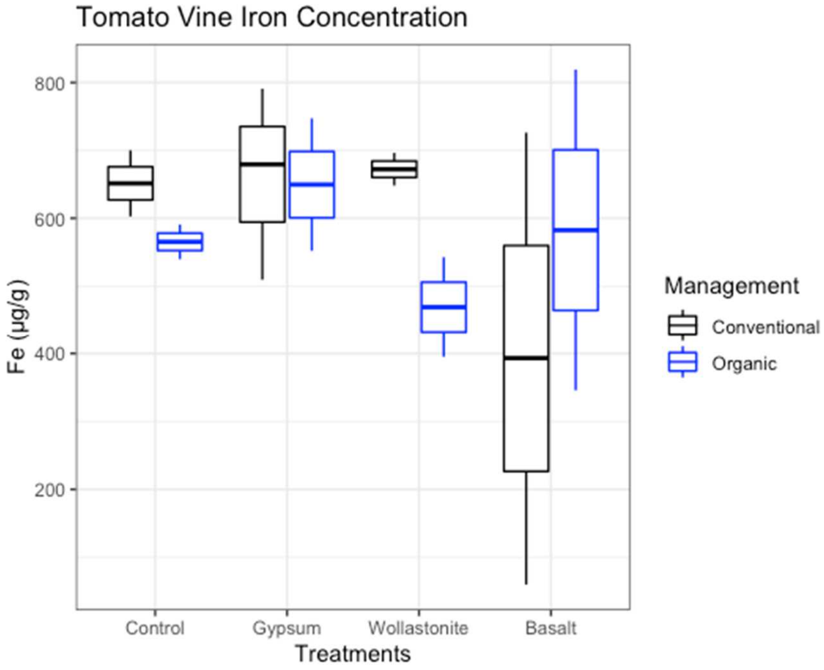

Figure 2.24. Tomato Vine Fe concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

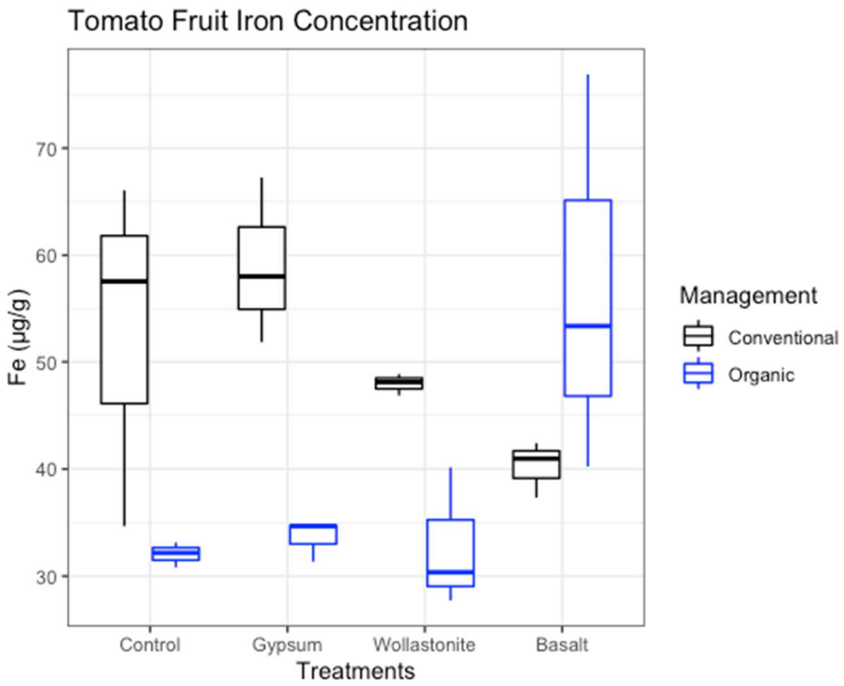

Figure 2.25. Tomato fruit Fe concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Table. 2.16. Mean tomato vine concentration of Ca, Al, and Fe (µg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch Tomato vine nutrients								
Management	Treatment	Ca	SE (Ca)	Al	SE (Al)	Fe	SE (Fe)	n
Conventional	Control	24,840	1860	485	44.2	651	48.8	2
	Gypsum	24,963	2188	442	54.46	659	81.9	3
	Wollastonite	25,150	1910	466	17.45	672	24.15	2
	Basalt	27,100	1270	465	19.3	393	333.1	2
Organic	Control	20,680	1900	306	52.2	651	25.6	2
	Gypsum	23,220	1430	414	42.95	659	97.7	2
	Wollastonite	23,335	1585	332	80.4	672	73.7	2
	Basalt	19,610	1470	286	71.05	393	236.6	2

Table. 2.17. Mean tomato fruit concentration of Ca, Al, and Fe (µg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch tomato fruit nutrients								
Management	Treatment	Ca	SE (Ca)	Al	SE (Al)	Fe	SE (Fe)	n
Conventional	Control	1347	355.6	17.09	3.98	52	9.37	2
	Gypsum	1295	150.1	10.44	0.375	59	4.46	3
	Wollastonite	1629	392.3	14.48	2.69	47	0.58	2
	Basalt	1,159	54.85	9.7	0.129	40	1.52	2
Organic	Control	1023	136.9	10.0	1.98	32	0.67	2
	Gypsum	951	66.77	8.11	1.90	33	1.13	2
	Wollastonite	837	59.06	7.62	0.683	32	3.77	2
	Basalt	897	45.18	7.08	0.715	56	10.71	2

There was no consistent effect on the concentration of Na in tomato vine and fruit with gypsum and silicate amendment. P-value for vine Na composition was 0.65 and 0.68 in conventional and organic management respectively (Table 2.18; Figure 2.26). P-value for fruit Na composition was 0.21 and 0.22 in conventional and organic management respectively (Table 2.19; Figure 2.27).

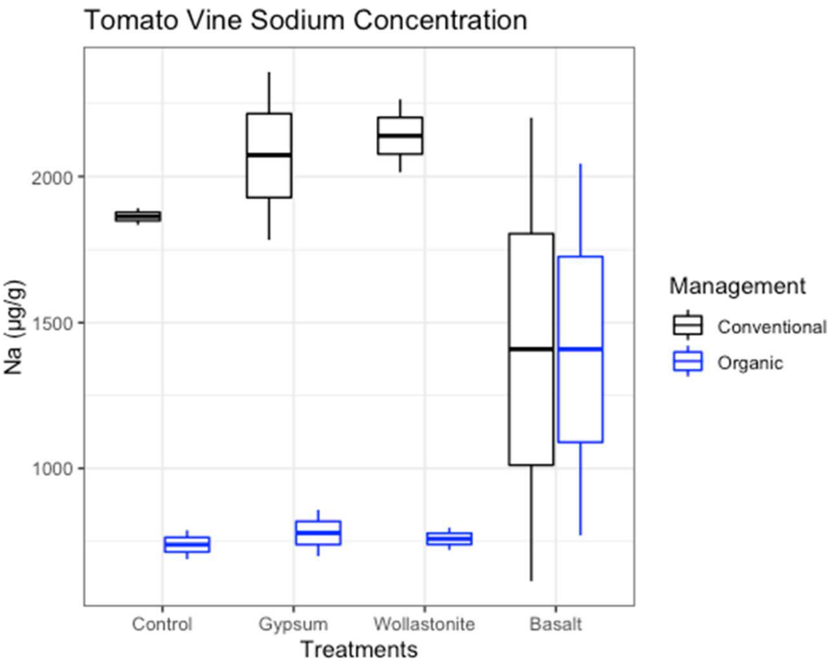

Figure 2.26. Tomato vine Na concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

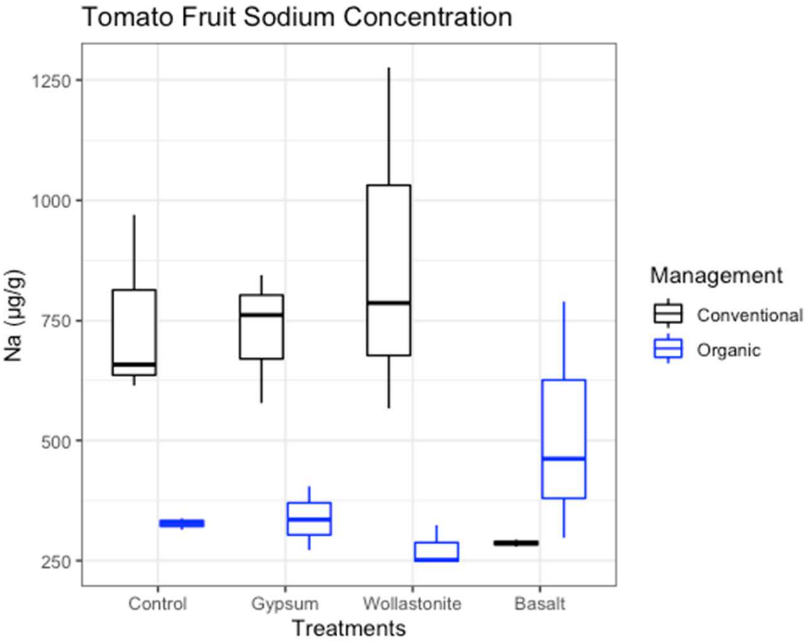

Figure 2.27. Tomato fruit Na concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

There was no consistent effect on the concentration of Mg in tomato vine and fruit with gypsum and silicate amendment. P-value for vine Mg composition was 0.87 and 0.61 in conventional and organic management respectively (Table 2.18; Figure 2.28). P-value for fruit Mg composition was 0.25 and 0.39 in conventional and organic management respectively (Table 2.19; Figure 2.29).

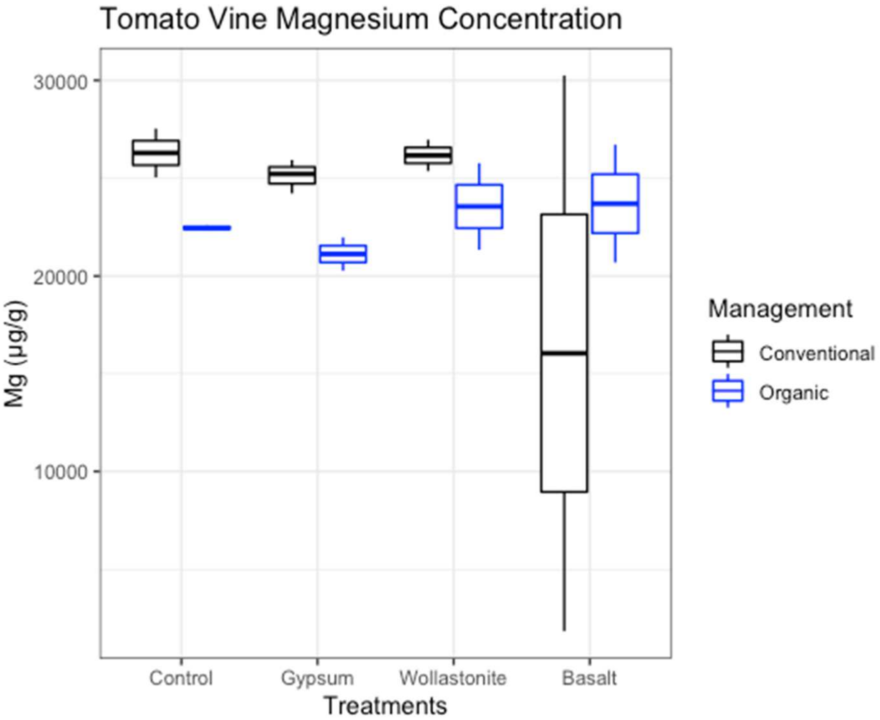

Figure 2.28. Tomato vine Mg concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

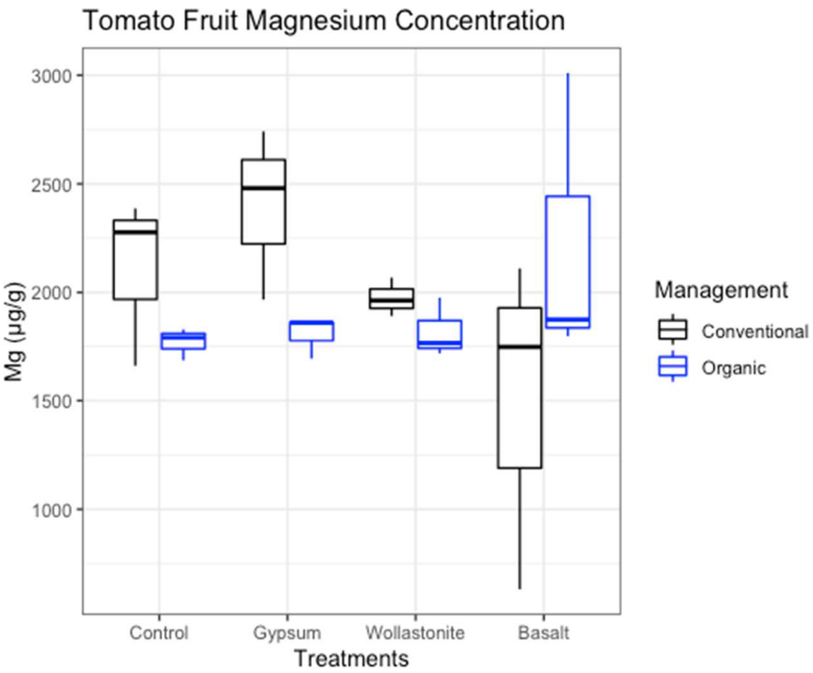

Figure 2.29. Tomato fruit Mg concentration (µg/g) in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

There was no consistent pattern in %C of tomato vines and fruit amended with gypsum or silicate compared to control in conventional or organic management. P-value for vine C composition was 0.7 and 0.29 in conventional and organic management respectively (Table 2.18; Figure 2.30). P-value for fruit C composition was 0.11 and 0.4 in conventional and organic management respectively (Table 2.19; Figure 2.31).

Table. 2.18. Mean tomato vine concentration of Na and Mg (μg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch tomato vine nutrients						
Management	Treatment	Na	SE (Na)	Mg	SE (Mg)	n
Conventional	Control	1863.0	29	26,290	1250	2
	Gypsum	2071	165	25123	495	3
	Wollastonite	2139	125	26165	805	2
	Basalt	1407	793	16052	14197	2
Organic	Control	739	49.7	22,460	130	2
	Gypsum	718	79.4	21125	855	2
	Wollastonite	758	38.2	23555	2215	2
	Basalt	1407	636	23700	3010	2

Table. 2.19. Mean tomato fruit concentration of Na and Mg (µg/g), and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch tomato fruit nutrients						
Management	Treatment	Na	SE (Na)	Mg	SE (Mg)	n
Conventional	Control	747	112	2108	226	3
	Gypsum	728	78.9	2396	227	3
	Wollastonite	876	209	1974	51.7	3
	Basalt	286	N/A	1496	444	3
Organic	Control	326	6.97	1769	43.4	3
	Gypsum	337	38.4	1805	56.3	3
	Wollastonite	274	24.8	1819	79.5	3
	Basalt	516	144	2228	391	3

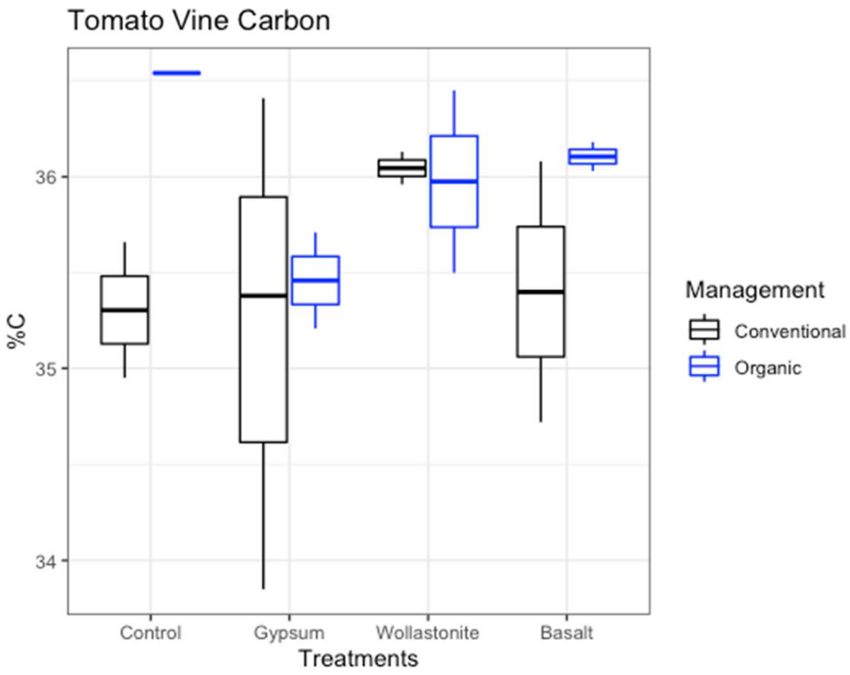

Figure 2.30. Tomato vine %C concentration in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

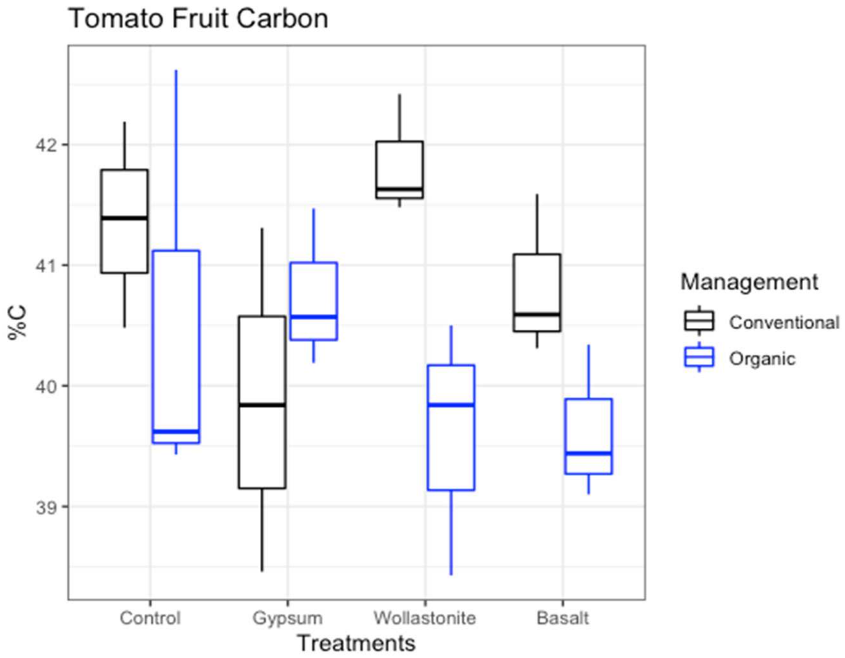

Figure 2.31. Tomato fruit %C concentration in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

There was no consistent pattern in %N of tomato vines and fruit amended with gypsum or silicate compared to control in conventional or organic management. P-value for vine N composition was 0.26 and 0.19 in conventional and organic management respectively. Fruit N composition was 2.48, 2.4, 2.52, and 2.57 % in control, gypsum, wollastonite, and basalt treatments respectively for conventional management (Figure 2.32). P-value for fruit N composition was 0.92 and 0.17 in conventional and organic management respectively (Figure 2.33).

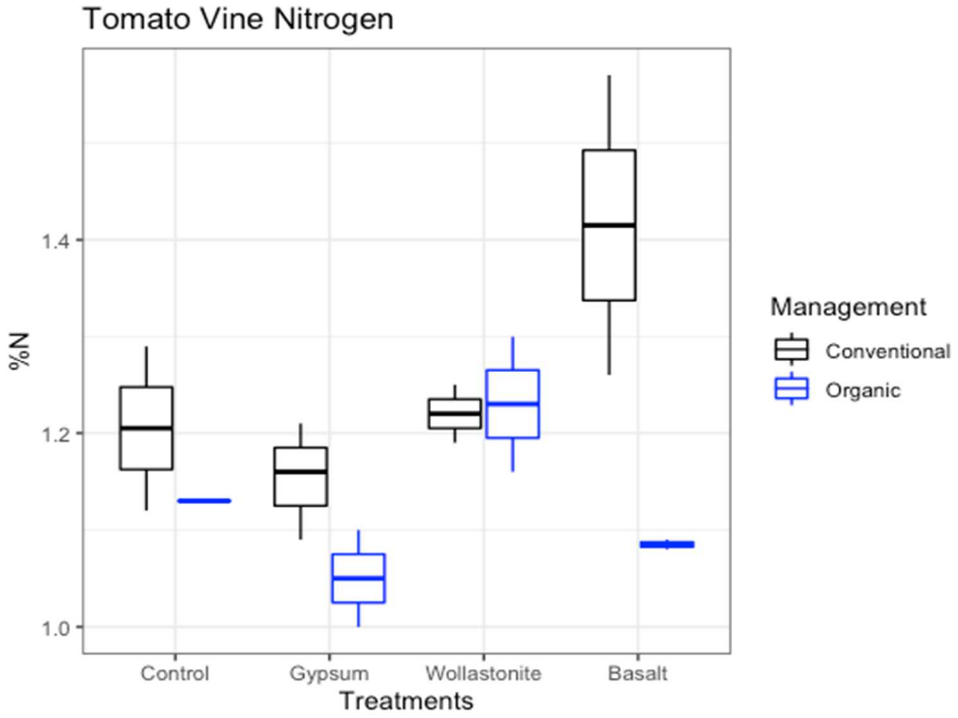

Figure 2.32. Tomato vine %N concentration in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

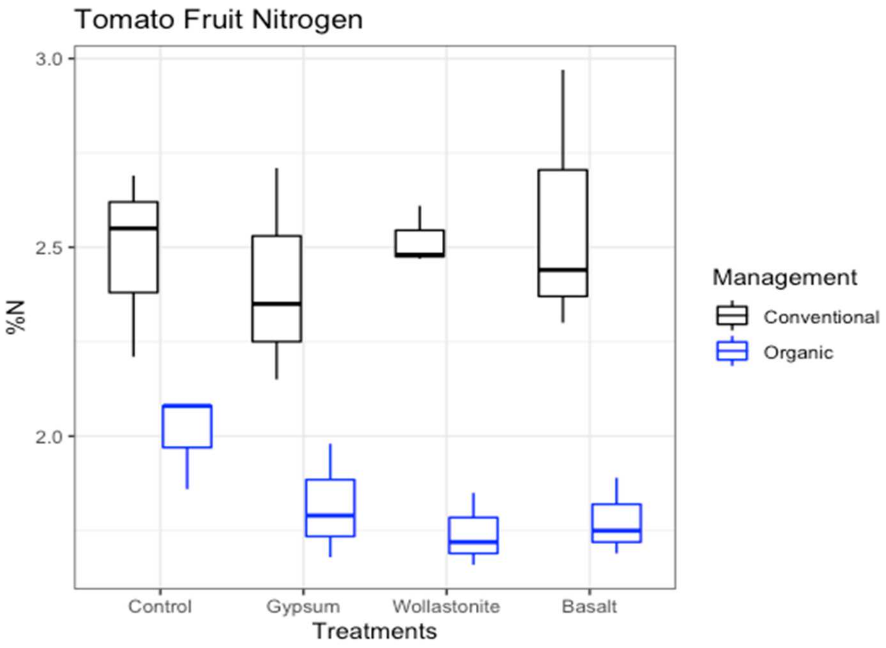

Figure 2.33. Tomato fruit %N concentration in conventional (black) and organic (blue) management with the different treatments studied (control, gypsum, basalt, and wollastonite).

Table. 2.20. Mean tomato fruit concentration of % C and N, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch tomato vine nutrients						
Management	Treatment	C	SE (C)	N	SE (N)	n
Conventional	Control	35.31	0.355	1.21	0.085	2
	Gypsum	35.21	0.743	1.15	0.034	3
	Wollastonite	36.05	0.085	1.22	0.03	2
	Basalt	35.4	0.68	1.42	0.155	2
Organic	Control	36.54	N/A	1.13	N/A	2
	Gypsum	35.46	0.25	1.05	0.05	2
	Wollastonite	35.98	0.475	1.23	0.07	2
	Basalt	36.11	0.075	1.09	0.005	2

Table. 2.21. Mean tomato fruit concentration of % C and N, and standard errors (SE) and sample size (n) of each from control and treated samples in conventionally and organically grown tomato.

Russell Ranch tomato fruit nutrients						
Management	Treatment	C	SE (C)	N	SE (N)	n
Conventional	Control	41.35	0.493	2.48	0.142	3
	Gypsum	39.87	0.822	2.5	0.163	3
	Wollastonite	41.84	0.291	2.52	0.045	3
	Basalt	40.83	0.388	2.57	0.204	3
Organic	Control	40.56	1.03	2.01	0.073	3
	Gypsum	40.74	0.379	1.82	0.087	3
	Wollastonite	39.59	0.61	1.74	0.056	3
	Basalt	39.63	0.369	1.78	0.059	3

4. Discussion:

Previous studies examining rock and mineral amendments for ESW have reported various degrees of crop yield increases in response to treatments, although primarily in highly weathered, acidic soil (Haque et al. 2019, Kelland et al. 2020). The hypothesis was tested that silicate amendments can improve yield in fertile, neutral soil conditions. The findings of this study suggest that yields were generally enhanced with rock and mineral amendments, with notable differences across conventional and organic management strategies, plant biomass allocations (i.e., stover, grain, etc.), and amendment types. While it has been suggested that nutrients delivered by ESW could supplement crop elemental composition, especially in vital micronutrients for humans and animals, the corn and tomato biomass nutrients results in this study did not support this hypothesis. Rather, elemental composition measurements were highly variable and non-systematic. Below are the findings and their implications for understanding the benefits of rock and mineral amendments for supporting improved crop yields, plant nutrient contents, and changes in soil nutrients.

4.1 Corn and Tomato Yield

Corn and tomato yields increased in response to rock amendments, but with both significant and non-significant effects depending on management, amendment, and plant biomass allocation. Stover yield did not significantly increase in conventional management. However, stover yield in organic management did increase significantly. In organic management, each treatment improved yield. The unfertilized organic system maintained a significantly lower grain yield than conventional by 37.3%, which is expected for systems without standard fertilizer (Suddick et al. 2010). Average tomato fruit yield did increase with amendments in both management strategies, but not significantly. Gypsum and silicate amendments were able to improve yield in corn and tomato even in the fertilized conventional system, which suggests that by some mechanism, nutrient addition or soil pH change, amendments made growing conditions more favorable.

Gypsum increased yield on par with silicates across crop type and management regime. This suggests that yield improvements were not strictly due to micronutrients in wollastonite and basalt. Sulfur in gypsum may have supported yield in each portion of corn biomass. Alternatively, yield may be improved due to pH increases. Each amendment contains significant portions of Ca, however high baseline Ca at Russell Ranch makes it unlikely that Ca in any of the amendments boosted yield. Future studies should assess the impact of ESW on crop yield in neutral pH, nutrient-rich soils. This may give silicates a better opportunity to supplement crop yield via nutrient release (Haque et al. 2019; Kelland et al. 2020; Swoboda et al. 2021). ESW studies are also needed to assess the impact of silicate amendment in fertile, agricultural soils. Studies show no consistent effect of gypsum on crop yield, particularly in fertile, neutral pH soils (Kost et al. 2018). Gypsum improved corn yield in acidic soil by alleviating Al toxicity (Pias et al. 2018).

In corn trials, the larger treatment effect was observed in organic management, whereas with tomato the more significant treatment effect was in conventional management. Microorganism populations vary between management regimes and across plant types. Certain microbes can improve weathering rates, and consequently nutrient availability (Khan et al. 2007; Garcia et al. 2020). Moreover, high-input agriculture in nutrient dense soils with high base saturation have pushed yields to their upper limits of global production. So, silicate additions in these soils should only be expected to show marginal improvement if any.

Soils where tomatoes are grown are frequently amended to increase calcium (Taylor and Locascio 2004) and Russell Ranch field soils typically have a low Ca:Mg ratio. So the treatment effect observed in tomato may be partially attributed to Ca additions from gypsum and silicates. The effect of ESW in corn and tomato in field conditions has seldom been measured thus far, particularly in fertile soils. Many ESW studies utilize highly weathered or acidic soils. Haque (2019) assessed corn growth amended with wollastonite in a low-pH soil and observed significant yield improvement. Sugarcane was amended with crushed basalt at 20 t/ha in combination with conventional NPK fertilizers in Mauritius and increased yields by up to 30% on the highly weathered soils (de Villiers 1961). Swoboda et al. (2021) conducted a meta-analysis to assess crop yield in low fertility soils amended with K-Feldspar. Corn and cherry tomatoes were among the crops in this study and demonstrated significant yield increases. These results differ from my results in terms of the soil type and silicate applied, however they reinforce the observation that ESW can be a suitable fertilizer supplement, particularly in highly weathered and acidic soils (Berge et al. 2012; Silva et al. 2015; Haque 2019; Swoboda et al. 2021).

4.2 Crop nutrient composition

These results suggest that elements potentially derived from silicate and gypsum did not present as increased in biomass under either management system in corn or tomato. A measurable increase in elements contained in silicate and gypsum would be expected in crop biomass if they were initially limited in soil, however they likely were not. We also assessed C and N to measure any potential changes in these key elements. There were no significant changes in C and N composition. In fact, the standard error in many nutrients is large which suggests that there were other factors driving crop composition than treatment alone.

5. Summary and conclusions

ESW aims to reduce atmospheric CO_2, but it must also provide co-benefits to crops or soil in order to be a viable climate change mitigation pathway. This study was conducted to better understand the potential for ESW as a fertilizer supplement in various crop types and in a robust, well-buffered soil. Although we did not observe a significant, systematic change in corn or tomato yield, there was improvement in yields on average that may be relevant for growers. We did not observe a significant change in crop elemental composition with silicate addition in agricultural soil.

Our findings add to the existing body of knowledge on enhanced silicate weathering as a CO_2 removal strategy and provide additional support for the application of ESW in field crop soils to synergistically promote plant growth. We observed that silicates can even improve yield in conventional, high-intensity agricultural systems and that silicates and gypsum can be an effective mineral supplement in systems without mineral NPK fertilizers.

Future studies should continue to assess the efficacy of silicates as a fertilizer supplement across crop and soil types. As well as pair silicates with crops that are limited by elements present in that silicate rock. Future studies should also assess crop properties such as rigidity in windy environments or resilience to herbivory as silica additions has been shown to improve these properties, but the mechanism and magnitude of these effects are not well characterized (Guntzer et al. 2011; Bocharnikova & Matichenkov 2012).

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Chapter 3. Robustness of CO_2 removal via enhanced weathering in response to elevated CO_2 concentrations and warming temperatures

1. Introduction

As climate change risks continue to grow worldwide, global nations are committing to limiting planetary warming to less than 2°C over pre-industrial levels. However, meeting a 2 °C or 1.5 °C target is increasingly unlikely since the global mean temperature has already risen about 1 °C over the 20th century. Reaching goals of the Paris Climate Agreement will require not just a reduction of emissions, but carbon (C) capture and drawdown technologies (Canadell and Schulze 2013; IPCC 2019; Ibrahim et al. 2019). In order to achieve negative emissions in agriculture, it is imperative to identify technologies that remove CO_2 from the atmosphere, and simultaneously support crop biomass increase and produce co-benefits for soil health, crop quality, and the environment. This chapter focuses on the robustness of CO_2 removal via enhanced weathering in response to future changes in CO_2 and temperature in a growth chamber experiment, thereby complementing and advancing findings from my field-based studies in Chapters 1 and 2.

1.1 Chemical Weathering of Silicate Minerals

Silicate weathering occurs when CO_2 in soil pore water reacts with water and silicate minerals, liberating constituent nutrients, such as Mg^{2+} and Ca^{2+}, and storing CO_2 as aqueous bicarbonate (HCO_3^-) or carbonate mineral precipitates in soils, freshwater and the ocean

(Schuiling and Krijgsman 2006). Grinding minerals increases the surface area for reactions and thereby enhances dissolution kinetics, carbonate formation, and the release of rock-derived nutrients (Van Straaten 2006). When finely crushed Ca/Mg-silicate rock dust is applied to soil, typically cropland soil, the series of reactions are greatly accelerated via a process referred to as enhanced silicate weathering (ESW). ESW utilizes ground rock from mining operations to increase reaction surface area, quickening mineral dissolution rates and increasing CO_2 removal rate to timescales relevant to modern climate change mitigation (Schuiling and Krijgsman 2006; Van Straaten 2006; Beerling et al. 2018).

Laboratory investigations have shown that silicate dissolution rates are a function of temperature (Edwards et al. 2017), concentration of dissolution products (Renforth et al. 2015), pH (Haque et al. 2018; Pokrovsky and Schott 2000) and mineral surface area (White and Brantley 2003; Renforth et al. 2015). A review study conducted by Goll et al. (2021) found that plants and other soil biota can increase silicate dissolution rate by as much as 80%, although their impact varies depending on ecosystem type and soil conditions.

1.2 Enhanced weathering potential in future climate

Increasing atmospheric CO_2 and global temperature are predicted to increase natural and enhanced silicate weathering rates through both the direct effect of temperature on reaction kinetics and the role of CO_2 as a reactant (Lenton and Britton 2006). Models predict that hot and wet climates optimize ESW (Taylor et al. 2016; Edwards et al. 2017). Taylor et al. (2016) estimates that applying basalt in the tropics and subtropics could reduce global temperatures by 0.2 °C to 1.6 °C by 2100. Models and bench studies that utilize present-day climate and CO_2 concentration suggest that the large-scale deployment of basalt to croplands in temperate and tropical regions could counter up to 40% of current fossil fuel emissions by 2100 (Gomez-Casanovas et al. 2021). These assessments suggest that ESW may be more productive as temperatures increase due to GHG concentration. However, direct assessments of ESW under future conditions have not been conducted to empirically examine whether this technology results are more effective under rising CO_2 concentrations and global warming.

1.3 Study aim and hypothesis

To stabilize the concentration of GHGs in Earth's atmosphere, both emissions reductions through reduction in fossil fuel combustion and land use change and scalable negative emissions technologies will need to play a role. The National Academies of Sciences, Engineering, and Medicine (2019) estimates that we will need to remove ~10 Gt/y CO_2 by midcentury and ~20 Gt/y CO_2 by the end of the century to avoid the most dangerous climate impacts in the future. The goal of this study is to determine if ESW will be more efficient in the climate of 2050 by exercising this negative emissions technology with soybean grown with basalt and compost in ambient CO_2 and temperature and elevated CO_2 and temperature. To explore whether ESW can play a significant role in consuming CO_2 under present and simulated future conditions, soybean was grown in a set of controlled growth chamber experiments under ambient temperature and CO_2 conditions and 5 °C of additional warming and an increase of 300 ppm CO_2 above ambient conditions. The hypothesis is that higher temperatures and elevated CO_2, as dominant controls over mineral dissolution, will accelerate alkalinity generation in basalt amended mesocosms compared to ambient conditions. Compost paired with basalt (compost+basalt) will further improve ESW rate as organic acids from compost further encourage mineral dissolution.

2. Methods:

2.1 Experimental design

This experiment presents measurements of HCO_3^-, alkalinity, change in pH, changes in soil cations, and plant biomass in response to ESW in current climate and the projected future climate conditions this century. Soybean (*Glycine max* L.) was used in this study partly because N-fixers may improve silicate dissolution rate as they release H^+ during nitrification (Beerling et al. 2018), and because this is a crop of global significance. Soil was amended with basalt, as its mineralogical nutrient profile contains Ca and Mg, which can restore soil fertility and buffer pH, while lacking the potentially harmful metals such as Ni or Cr, which are associated with fast-weathering silicates like olivine (Beerling et al. 2018). Basalt is considered the most abundant source of rock dust that is produced as a by-product of mining operations (Beerling et al. 2018), so focusing on this rock-type makes sense within the context of ESW supplies and potential scalable deployment.

In this study at the UC Davis Controlled Environment Facility, temperature and CO_2 were manipulated in a growth chamber to experimentally determine ESW and plant responses to potential future conditions. First, soybean was grown in a chamber set to ambient temperature and CO_2. For the ambient conditions, soybean seeds were inoculated and planted on 4/6/21 and transplanted to begin the experiment on 4/28/21. Soybean grew for 9 weeks and was harvested on 6/25/21. Second, soybean was grown under elevated CO_2 and temperature in precisely the same manner as the ambient case except for the simulated future climate conditions. Seeds were inoculated and planted on 6/18/21 and transplanted to begin the experiment on 7/9/21. Soybean grew amended for 9 weeks and was harvested on 9/10/21.

In the ambient climate simulation, light intensity was increased from 8am to 9am, and temperature from a low of 10 °C to a daily high temperature of 30 °C from 12pm to 5pm. CO_2 concentrations fluctuated around 425-450 ppm, equivalent to outdoor air. The chamber settings for future conditions were as follows: light intensity increased from 8am to 9am, temperatures were increased gradually from low of 15 °C to a daily high temperature of 35 °C from noon to 5pm, and CO_2 was set to 600 ppm. Temperature is increased by 5 °C because total atmospheric warming is expected to surpass 1.5°C above pre-industrial levels by 2050 and could exceed this global rate of temperature increase by the end of the century.

N-Dure brand soybean seeds and inoculum (*Bradyrhizobium japonicum*) were purchased from SeedWorldUSA. Soybean was inoculated by adding 0.5 g inoculum to 20 g water purified by reverse osmosis (RO) to create a slurry. Inoculum slurry was added to seeds, and they were allowed to dry covered lightly by aluminum foil. Inoculated seeds were planted in Miracle Gro Seedling Starter potting soil blend. A mixture of agricultural soil which was collected from the upper 30 cm of a conventionally managed plot at Campbell Tract, a UC Davis agriculture facility, was combined with Lapis Lustre sand size #2-/16 to ensure sufficient soil water leaching. Each pot contained a mixture of 2 parts soil and 1 part sand. After 3 weeks, 4 seedlings were transplanted into each 2-gallon pot with this sand-soil mixture and exposed to a set of soil amendment treatments and growth chamber conditions.

Treatments for this study were compost, basalt, basalt in combination with compost (basalt+compost), and control. Basalt+compost may improve silicate dissolution by supplying additional organic acids to the soil matrix. Compost was purchased from Marin compost company. We selected the Marchino blend which has a low N/P ratio. We chose basalt because of its nutrient profile. Its availability as mine waste makes it a particularly good option to maximize potential C sequestration. Basalt was purchased from Nature's Footprint. Each treated pot has 120 g basalt and 25 g compost mixed into the upper half of the sand-soil mixture. The basalt application rate was equivalent to 15 t/ha and the compost application rate is equivalent to 3 t/ha. Treatments were arrayed in a three-block design with each treatment replicated four times per block. Soybean was watered daily weeks 1-4 with 150 ml unfertilized, RO water. Water was increased to 300 ml per pot the remaining 5 weeks.

2.2 Sample collection

Soil leachate was collected to assess for changes in alkalinity and carbon removal via ESW, recognizing that this approach reflects a lower bound on total carbon removal: it does not consider the formation of carbonates, which are difficult to detect over short-term experiments. In contrast, dissolved alkalinity enables the rapid detection of ESW in response to treatments. Leachate collections were conducted by drilling circular holes in the table beneath each pot, which was placed on top of plastic containers where drainage water was collected. Leachate collection was administered by slowly pouring 150 mL RO water over the soil, allowing water to percolate through the soil at a moderate pace. After collection, all samples were immediately refrigerated and stored for analysis. Leachate was collected on week 7 and 9 of the ambient climate run and weeks 4, 6, and 8 of the future climate run. In preparation for alkalinity titrations, we used a syringe with a 60 µm filter attached to remove any soil particles. We diluted soil leachate samples by 30% before alkalinity titration. A Hanna HI932 Automatic Potentiometric Titrator was used for alkalinity titrations.

2.3 Methods of Analysis

At harvest, the entire plant was removed and immediately separated into roots and shoots. Ultimately, we mailed soil samples to the Ohio State University analytical lab for soil Ca, Mg, and Na quantification analyses. Shoots were weighed, and dried in a 65 °C oven for 5 days, then weighed again for dry biomass. Subsequently, soybean biomass was analyzed to measure potential rock-derived nutrients assimilated during this trial. Plant biomass was ground to 2 mm using a Wiley mill and sent to Ohio State University (OSU) analytical lab for Al, Mg, Ca, Si, Cu, Fe, Na, Mo, Zn, K, P, Ba, C and N composition analyses. The lab utilizes a 1:3 ratio of nitric acid and hydrochloric acid for a microwave digestion, then elemental quantification by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Sah and Miller 1992; Meyer and Keliher 1992).

Soil pH was measured by saturated paste and pH probe. To measure soil nutrients, the OSU analytical lab used a semi-quantitative method to measure potential rock-derived, exchangeable cation, where cations on soil exchange sites were displaced with an ammonium acetate (NH_4-oAc) solution buffered at pH 7. Cations were then quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES). We run filtered and diluted soil leachate samples on the Hanna autotitrator with 0.025N H_2SO_4. Then alkalinity is determined by the endpoint method.

Data on elemental composition of soybean was examined as both contents on a per gram basis and as total content per plant by diving by the number of plants per pot. Total elemental content per plant was calculated by multiplying element per gram by dry weight biomass per plant. Given that total plant biomass can change in response to treatments, with plants potentially increasing nutrient use-efficiency by increasing carbon gains per unit of biomass gain, especially under elevated CO_2, this approach allowed for an assessment of total nutrient changes and how this may be affected by rock dust and compost across ambient vs. elevated climate conditions.

Results are reported as mean measurements with standard errors. R version 4.1.2 was used for all graphs and statistical analyses. The following packages were used: tidyverse, dplyr, ggplot2, ggpubr, ISLR, and ggstatsplot. A quantile-quantile plot was used to determine the correlation between these data and the normal distribution. The quantile-quantile plot showed that HCO_3^- , pH, yield, elemental composition of biomass, and soil cations was not normally distributed, therefore a non-parametric test was required. These data fit the assumptions of Kruskal Wallis test. The Kruskal Wallis test was used to compare across all treatments and control. Significant p-values reflect differences in median measurements in each treatment. $P < 0.05$ was used as the limit for statistical significance. When the Kruskal Wallis test produced a significant result, the Dunn's test with Šidák adjusted p-value was used to determine which treatments were significantly different.

Results

3.1 Soybean biomass

Soybean biomass significantly increased in elevated temperature and CO_2 compared to ambient in every treatment except compost (control p-value = 0.039, compost p-value = 0.079, basalt p-value = 9e-05, basalt+compost p-value = 0.0003). There was no treatment effect observed for soybean biomass (g/plant) under ambient conditions (p-value = 0.24) (Table 3.1; Figure 3.1). In contrast, mean soybean biomass changed in elevated temperature and CO_2 conditions and revealed significant treatment effects where basalt and basalt+compost increased yield compared to control and compost treatments (p-value = 1.6e-05) (Table 3.1; Figure 3.1). Biomass of plants grown with basalt and basalt+compost was increased by 20.39% and 24.9% compared to control in elevated temperature and CO_2 conditions. Comparing between treatments in elevated temperature and CO_2 using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in basalt+compost and control (p-value = 0.0003), basalt and control (p-value = 0.0049), basalt and compost (p-value = 0.0055), and basalt+compost and compost (p-value = 0.0004).

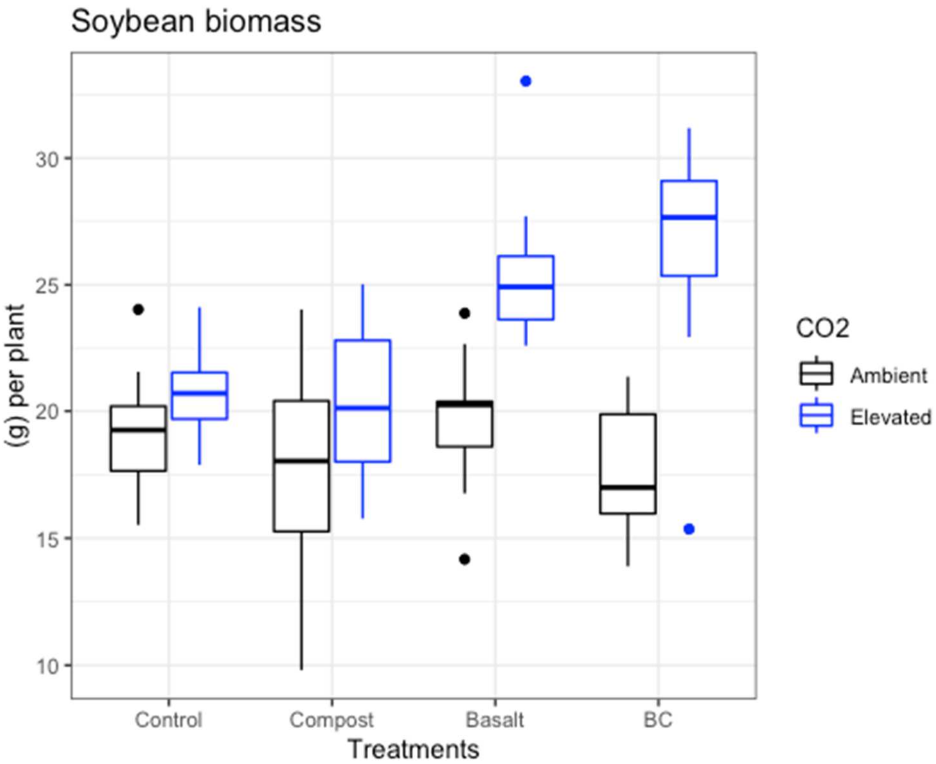

Figure 3.1. Soybean biomass (g/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.1. Mean soybean biomass per plant (g) and standard error (SE) of each from control and treated samples in soybean in ambient and elevated CO_2 and temperature. Sample size (n)= 12.

Soybean biomass			
Climate	Treatment	(g)	(SE)
Ambient	Control	19.04	0.704
	Compost	17.88	1.16
	Basalt	19.65	0.729
	Basalt+Compost	17.58	0.703
Elevated	Control	20.74	0.462
	Compost	20.34	0.890
	Basalt	25.45	0.781
	Basalt+Compost	26.64	1.20

3.2 Soybean biomass nutrients

There was no discernable pattern in plant nutrient content across treatments and conditions. In contrast, a set of statistically significant responses were observed on a total plant content basis in many nutrients based on total biomass increase. There was no significant treatment effect (p-value = 0.59) observed for mean soybean Al concentration in ambient conditions (Table 3.2; Figure 3.2). There was no significant treatment effect observed for total soybean shoot Al content in ambient CO_2 and temperature (p-value = 0.56) (Table 3.3; Figure 3.3). Under elevated CO_2 and temperatures, soybean shoot Al concentration increased in compost amended samples compared to basalt and resulted in a significant p-value of 0.019 (Table 3.2; Figure 3.2). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in compost and basalt (p-value = 0.0063). There was no significant treatment effect observed in total soybean shoot Al content (p-value 0.1) (Table 3.3; Figure 3.3).

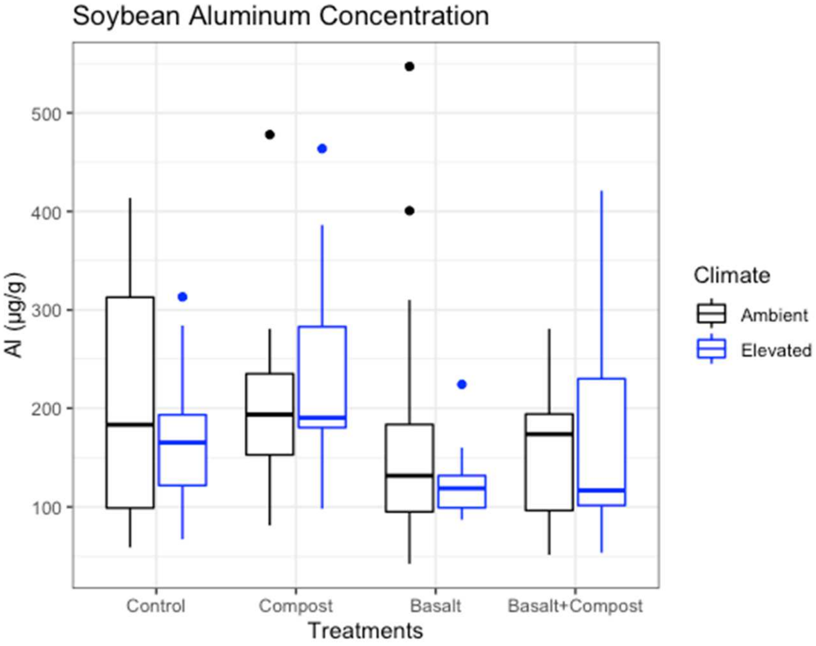

Figure 3.2. Soybean Al concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

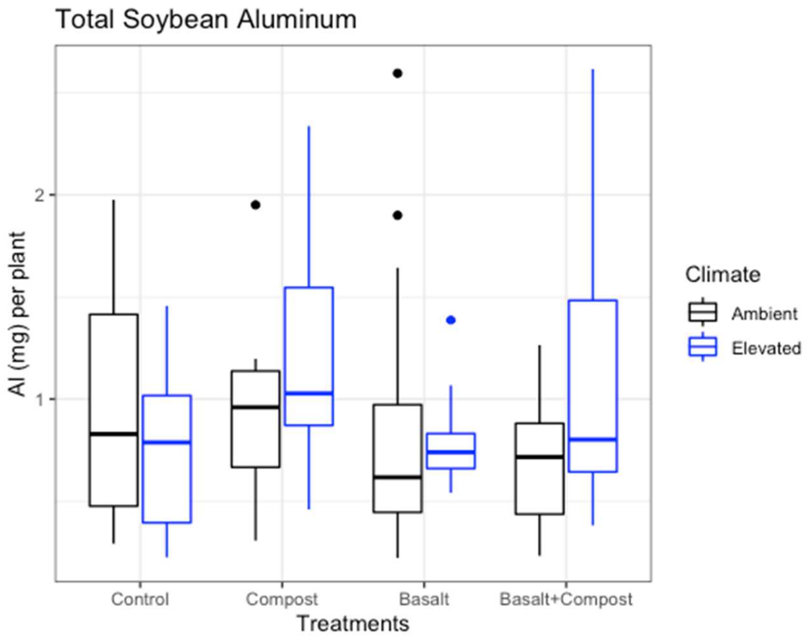

Figure 3.3. Total soybean Al content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was no significant treatment effect in soybean shoot Mg concentration under ambient temperature and CO_2 (p=0.334) (Table 3.2; Figure 3.4). There was no significant treatment effect in soybean total Mg content grown in ambient temperature and CO_2 (p=0.566) (Table 3.3; Figure 3.5). There was no treatment effect in soybean Mg concentration under elevated CO_2 and temperature (p-value = 0.4) (Table 3.2; Figure 3.4). Mean total soybean shoot content demonstrated a significant increase in total Mg content when amended with basalt and basalt+compost compared to control and compost under elevated CO_2 and temperatures (p-value = 2e-04) (Table 3.3; Figure 3.5). Comparing between treatments using Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value =

0.0014), compost and basalt (p-value = 0.0053), compost and basalt+compost (p-value = 0.0193), and basalt+compost and control (p-value = 0.0061).

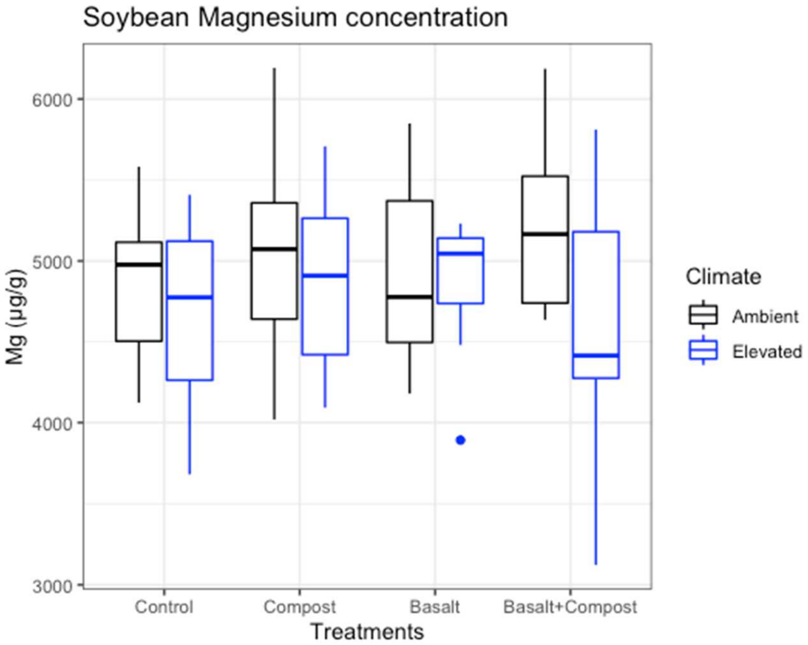

Figure 3.4. Soybean Mg concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

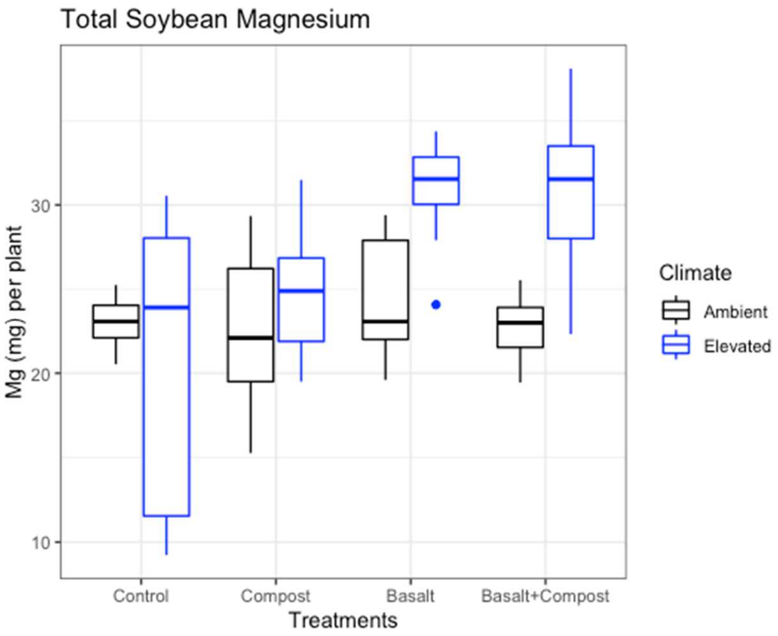

Figure 3.5. Total soybean Mg content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was a treatment effect in soybean shoot Ca concentration in ambient CO_2 and temperature (p-value = 0.0023) where basalt and basalt+compost increased soybean Ca concentration compared to the control (Table 3.2; Figure 3.6). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0439) and control and basalt+compost (p-value = 0.0008). Total soybean shoot Ca content produced a significant result in ambient CO_2 and temperature (p-value = 0.022) (Table 3.3; Figure 3.7) with basalt increasing total Ca content compared to compost and control treatments. Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0237) and compost and basalt (p-value = 0.0439). There was no significant treatment effect in soybean Ca concentration in elevated CO_2 and temperature (p= 0.499) (Table 3.2; Figure 3.6). There was a significant treatment effect in total soybean shoot Ca content (p-value 2.31e-06) under elevated CO_2 and temperature where basalt and basalt+compost increase total Ca content compared to control and compost treatments (Figure 3.7). Comparing between treatments using the Dunn's test with Šidák adjusted p-value revealed significant treatments effects in control and basalt (p-value = 0.0016), compost and basalt (p-value = 0.0029), compost and basalt+compost (p-value = 0.0011), and control and basalt+compost (p-value = 0.0006).

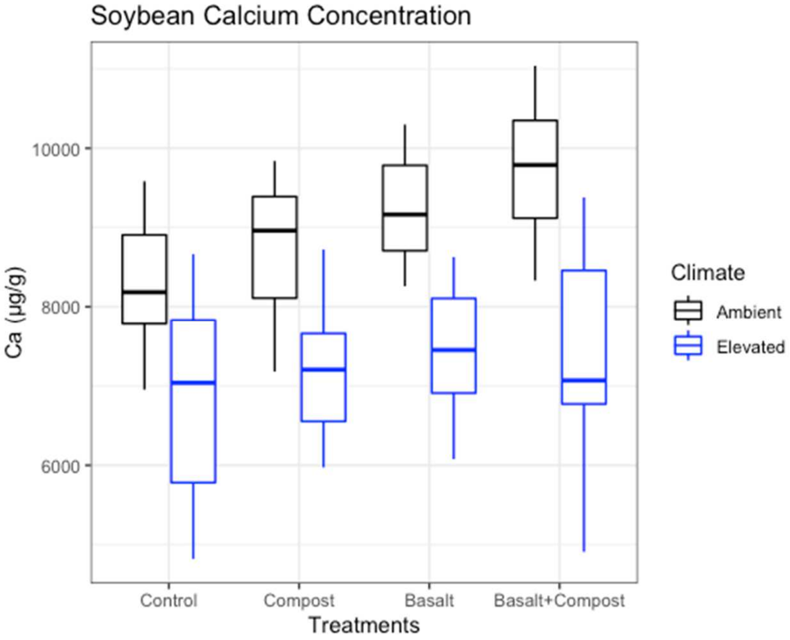

Figure 3.6. Soybean Ca concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

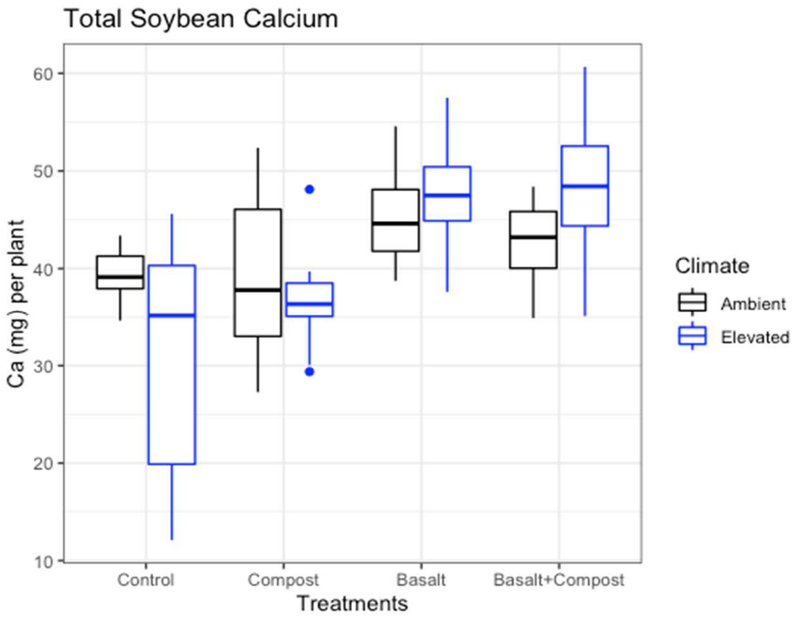

Figure 3.7. Total soybean Ca content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.2. Mean soybean shoot Al, Mg, and Ca concentrations as µg/g and standard error (SE) of each from control and treated samples in soybean in ambient and elevated CO_2 and temperature. Sample size (n) = 12.

Soybean biomass nutrients							
Climate	Treatment	Al	Al (SE)	Mg	Mg (SE)	Ca	Ca(SE)
Ambient	Control	208.38	37.47	4836.67	130.48	8291.58	230.5
	Compost	211.81	N/A	5027.75	174.18	8763.17	251.4
	Basalt	183.06	44.5	4926.25	154.06	9219.75	195.1
	Basalt+Compost	161.16	21.35	5215.67	140.65	9720.83	252.2
Elevated	Control	170.61	21.13	4681.92	164.48	6864.25	351.6
	Compost	242.15	31.07	4860.33	155.16	7200.42	228.1
	Basalt	124.85	10.99	4881.42	114.96	7451.33	228.7
	Basalt+Compost	175.8	33.97	4236.93	N/A	7390.58	346.3

Table 3.3. Total soybean content of Al, Mg, and Ca given as mg/plant per plant and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	Al	Al (SE)	Mg	Mg (SE)	Ca	Ca(SE)
Ambient	Control	3.92	0.17	22.95	0.416	157.48	0.84
	Compost	3.82	N/A	22.51	1.36	157.12	2.39
	Basalt	3.58	0.213	24.24	0.997	181.43	1.52
	Basalt+Compost	2.84	0.097	22.88	0.527	170.93	1.23
Elevated	Control	3.03	0.11	21.28	2.43	124.67	3.63
	Compost	4.96	0.16	24.79	1.12	146.44	1.4
	Basalt	3.17	0.069	31.06	0.823	189.62	1.54
	Basalt+Compost	4.6	0.22	30.72	N/A	195.2	2.01

There was no treatment effect in soybean shoot Si concentration in ambient temperature and CO_2 (p-value = 0.27) (Table 3.4; Figure 3.8). Total soybean shoot Si content in ambient temperature and CO_2 did not show a treatment effect (p-value = 0.14) (Table 3.5; Figure 3.9). There was no treatment effect in soybean Si concentration in elevated temperature and CO_2 (p-value = 0.24) (Table 3.4; Figure 3.8). Total soybean shoot Si content in elevated temperature and CO_2 indicates a treatment effect (p-value = 0.014) with basalt and basalt+compost increased compared to control (Table 3.5; Figure 3.9). Comparing between treatments using Dunn’s test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0182) and control and basalt+compost (p-value = 0.0139).

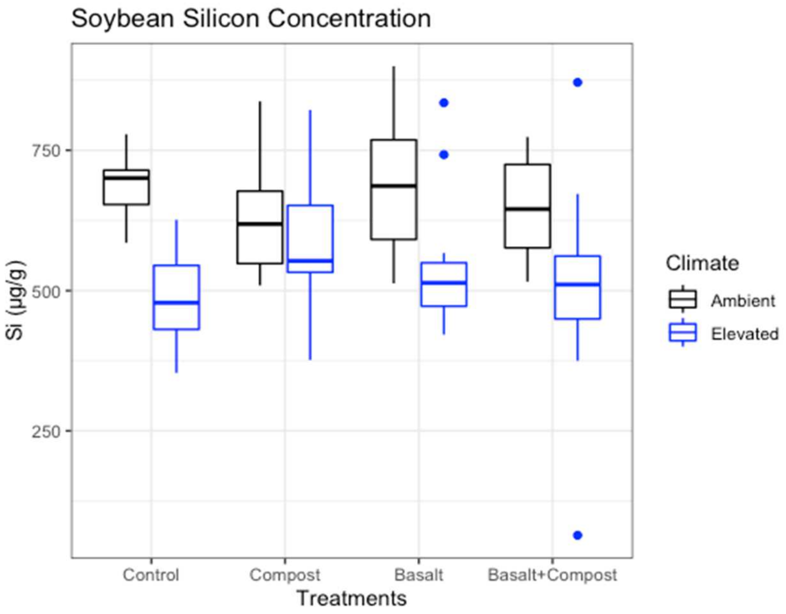

Figure 3.8. Soybean Si concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

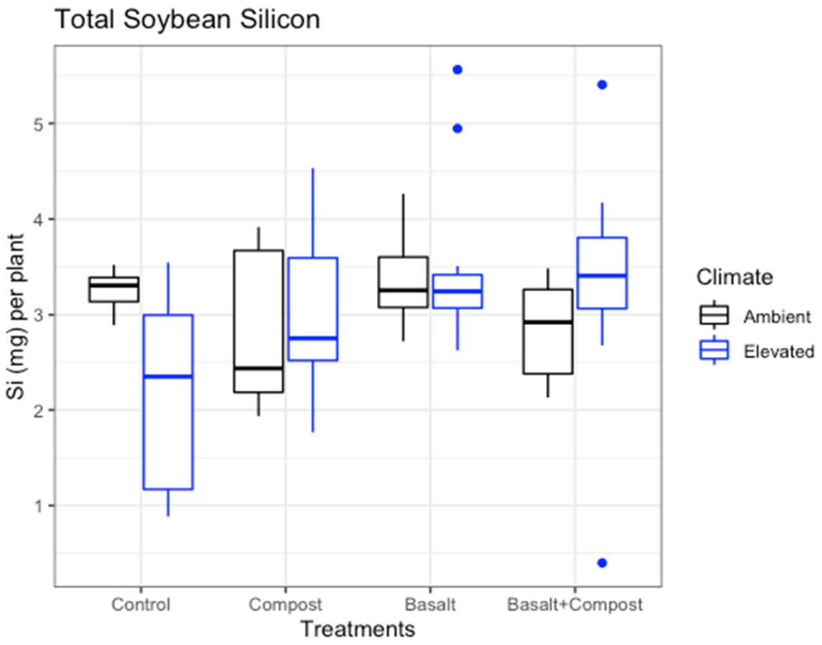

Figure 3.9. Total soybean Si content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was no treatment effect in soybean shoot Cu concentration in ambient temperature and CO_2 (p-value = 0.29) (Table 3.4; Figure 3.10). Total soybean shoot Cu content did not show a treatment effect in ambient temperature and CO_2 (p-value = 0.86) (Table 3.5; Figure 3.11). Soybean shoot Cu concentration did not have a treatment effect in elevated temperature and CO_2 (p-value = 0.32) (Table 3.4; Figure 3.10). Total soybean shoot Cu content did reflect a significant treatment effect in elevated temperature and CO_2 (p-value = 0.00064) with basalt and basalt+compost increased compared to control. Comparing between treatments using Dunn's test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0039) and control and basalt+compost (p-value = 0.0021) (Table 3.5; Figure 3.11).

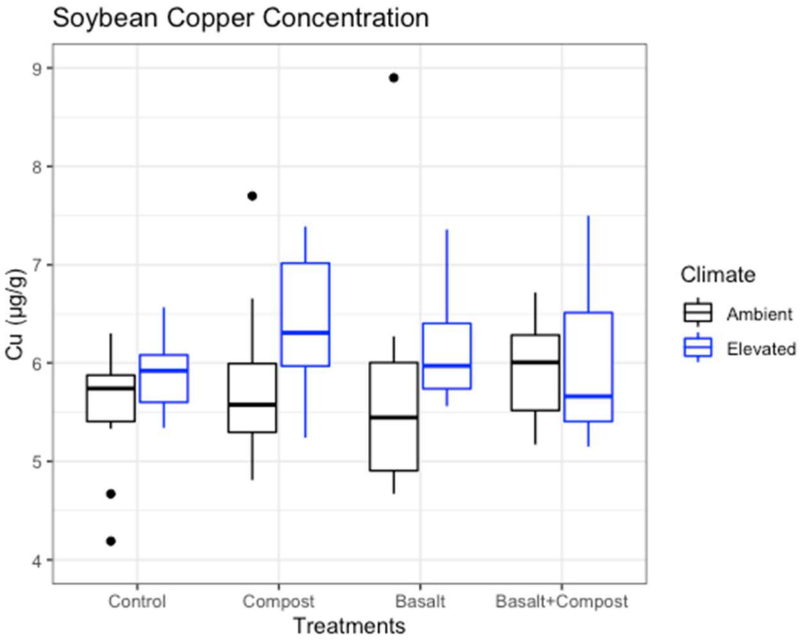

Figure 3.10. Soybean Cu concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

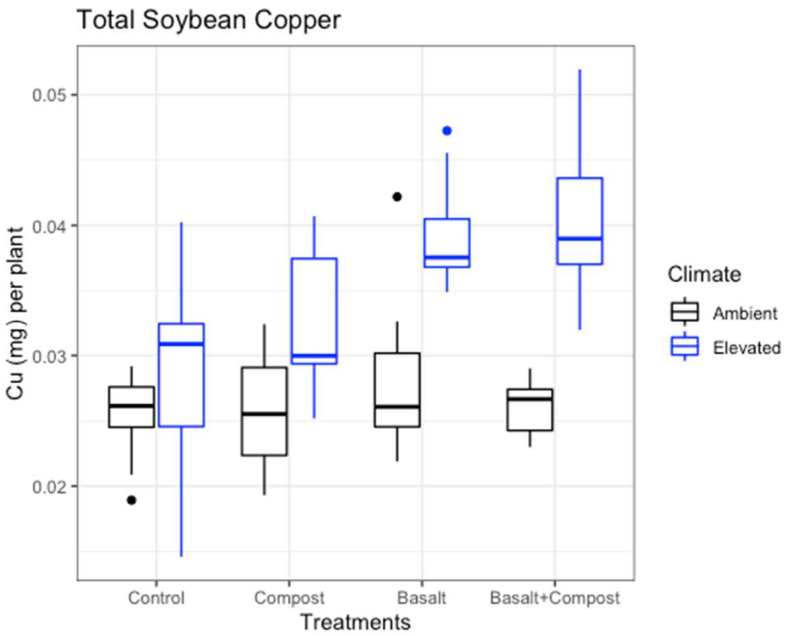

Figure 3.11. Total soybean Cu content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Soybean shoot Fe concentration did not show a treatment effect (p-value = 0.86) (Table 3.4; Figure 3.12). Total soybean shoot Fe content did not have a treatment effect (p-value = 0.85) in ambient temperature and CO_2 (Table 3.5; Figure 3.13). Soybean shoot Fe concentration in elevated temperature and CO_2 did not show a treatment effect (p-value = 0.15) (Table 3.4; Figure 3.12). Total soybean shoot Fe content did not show a treatment effect (p-value = 0.22) in elevated temperature and CO_2 (Table 3.5; Figure 3.13).

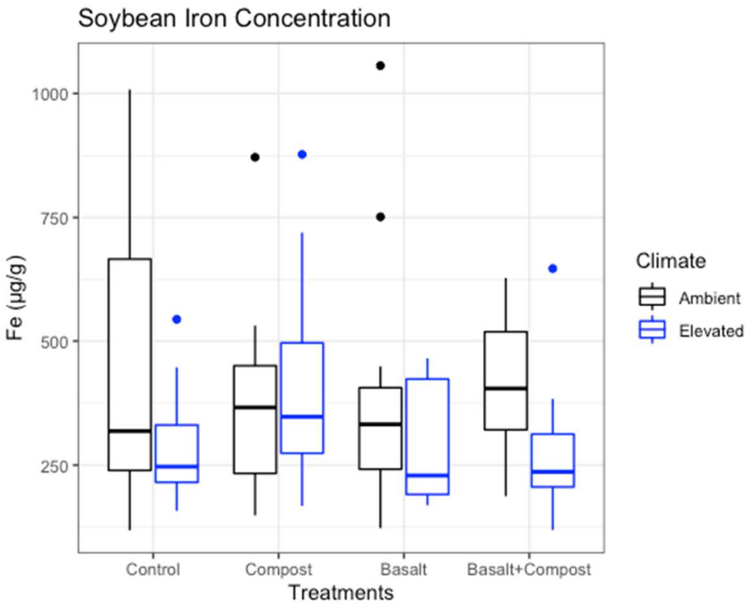

Figure 3.12. Soybean Fe concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

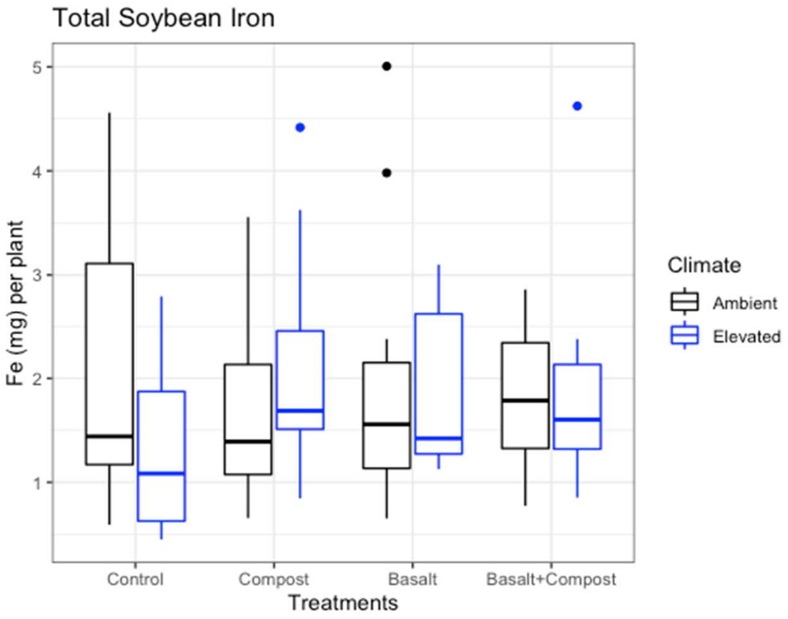

Figure 3.13. Total soybean Fe content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.4. Soybean shoot biomass concentration of Si, Cu, and Fe as µg/g and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	Si	Si (SE)	Cu	Cu (SE)	Fe	Fe (SE)
Ambient	Control	686.37	16.61	686.37	0.21	464.19	N/A
	Compost	627.0	27.26	627.0	0.23	378.75	N/A
	Basalt	683.1	33.63	683.1	0.33	397.64	N/A
	Basalt+Compost	645.02	26.22	645.02	0.14	408.36	40.78
Elevated	Control	486.41	24.41	486.41	0.851	287.1	32.98
	Compost	584.37	37.5	584.37	0.214	417.45	61.50
	Basalt	547.73	34.84	547.73	0.178	283.92	33.10
	Basalt+Compost	504.3	54.44	504.3	N/A	280.82	N/A

Table 3.5. Soybean shoot biomass content of Si, Cu, and Fe as mg/plant and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	Si	Si (SE)	Cu	Cu (SE)	Fe	Fe (SE)
Ambient	Control	3.26	0.060	0.0254	0.00089	1.34	N/A
	Compost	2.83	0.229	0.0256	0.0012	2.12	N/A
	Basalt	3.32	0.126	0.0278	0.0016	1.80	N/A
	Basalt+Compost	2.84	0.144	0.0260	0.00056	1.88	0.193
Elevated	Control	2.22	0.278	0.0281	0.0024	1.34	0.232
	Compost	3.0	0.244	0.0327	0.0015	2.12	0.316
	Basalt	3.49	0.249	0.0391	0.0011	1.80	0.209
	Basalt+Compost	3.33	0.336	0.0403	N/A	1.88	N/A

There was a treatment effect in above ground soybean Na concentration in ambient temperature and CO_2 (p-value = 0.016), with compost increased compared to control and basalt (Table 3.6; Figure 3.14). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and compost (p-value = 0.0317) and compost and basalt (p-value = 0.0389). There was no treatment effect in total soybean shoot Na content in ambient conditions (p-value = 0.89) (Table 3.7; Figure 3.15). There was a treatment effect in soybean shoot Na concentration in elevated temperature and CO_2 where Na in treated samples decreased compared to the control (p-value = 0.0317) (Table 3.6; Figure 3.14). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and compost (p-value = 0.0317) and compost and basalt (p-value = 0.0389). Total soybean shoot Na content did not show a treatment effect (p-value = 0.19) in elevated temperature and CO_2 (Table 3.7; Figure 3.15).

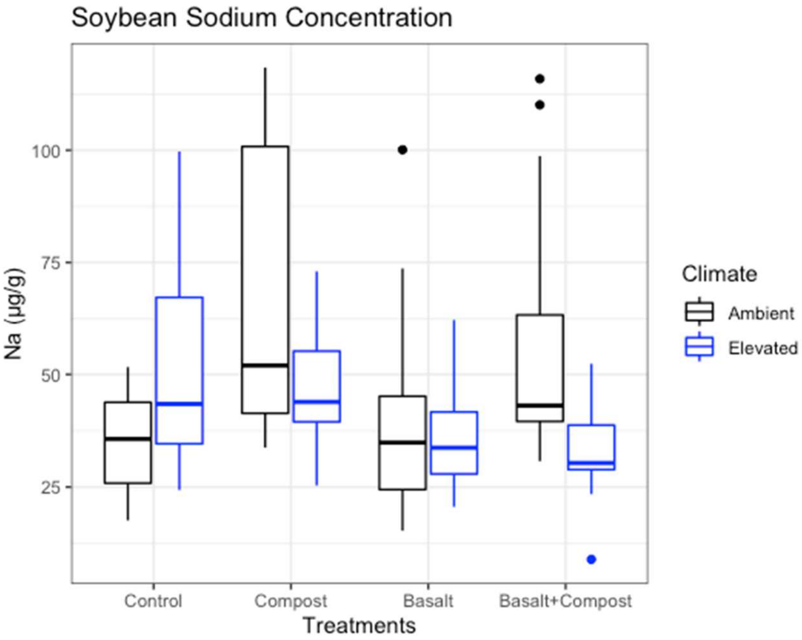

Figure 3.14. Soybean Na concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

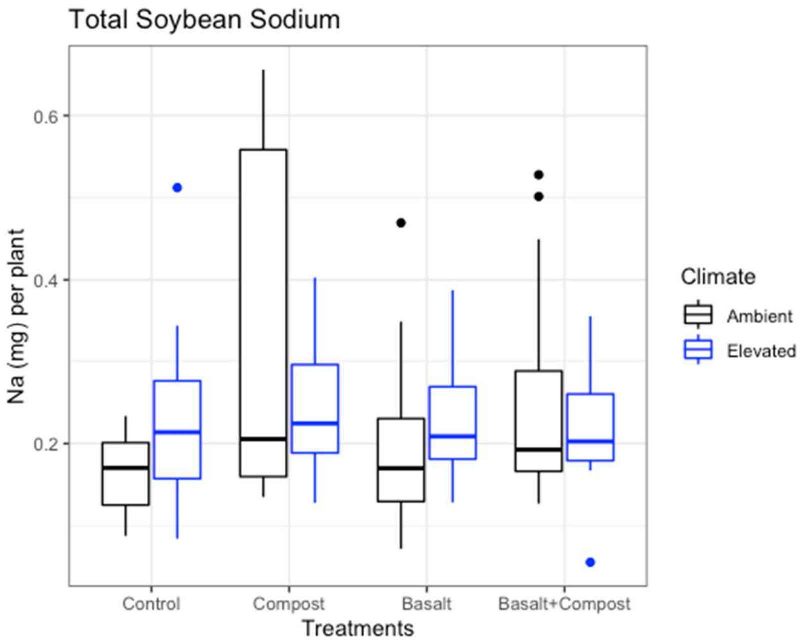

Figure 3.15. Total soybean Na content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was a treatment effect in soybean shoot Mo concentration in ambient temperature and CO_2 where Mo in compost and basalt+compost treatments increased compared to the control (p-value = 0.011) (Table 3.6; Figure 3.16). Comparing between treatments using the Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and basalt+compost (p-value = 0.0292) and control and compost (p-value = 0.0080). There was no treatment effect observed in total soybean shoot Mo content in ambient conditions (p-value = 0.05) (Table 3.7; Figure 3.17). Soybean shoot Mo concentration in elevated conditions reflects a significant treatment effect where Mo in basalt treated soybean increased compared to compost and control (p-value = 0.0067) (Table 3.6; Figure 3.16). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and basalt (p-value = 0.0085) and compost and basalt (p-value = 0.0219). Total soybean shoot Mo content in elevated temperature and CO_2 reflects a significant treatment effect where Mo in compost and basalt+compost treatments increased compared to the control (p-value = 0.00019) (Table 3.7; Figure 3.17). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatments effects in control and basalt (p-value = 0.0005), control and basalt+compost (p-value = 0.0063), and compost and basalt (p-value = 0.0071).

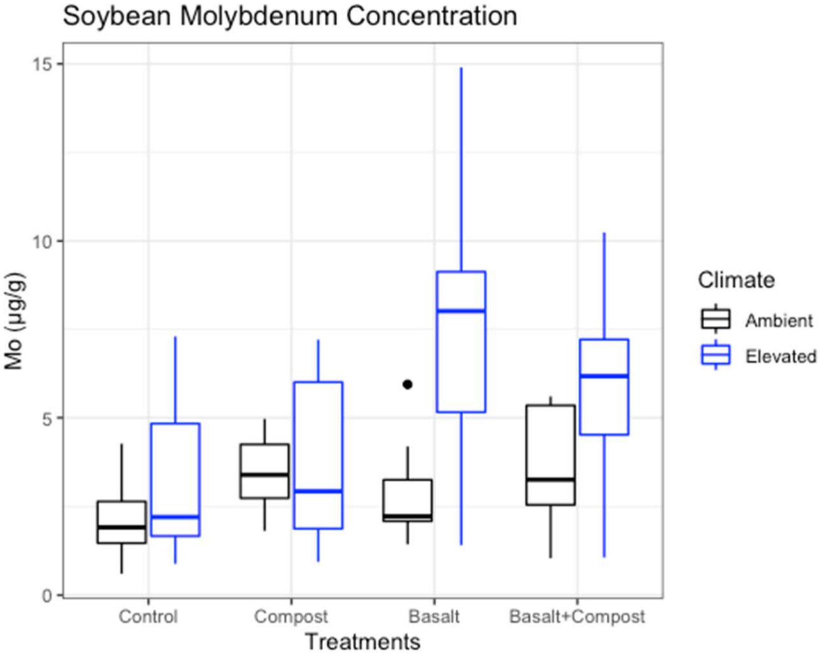

Figure 3.16. Soybean Mo concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

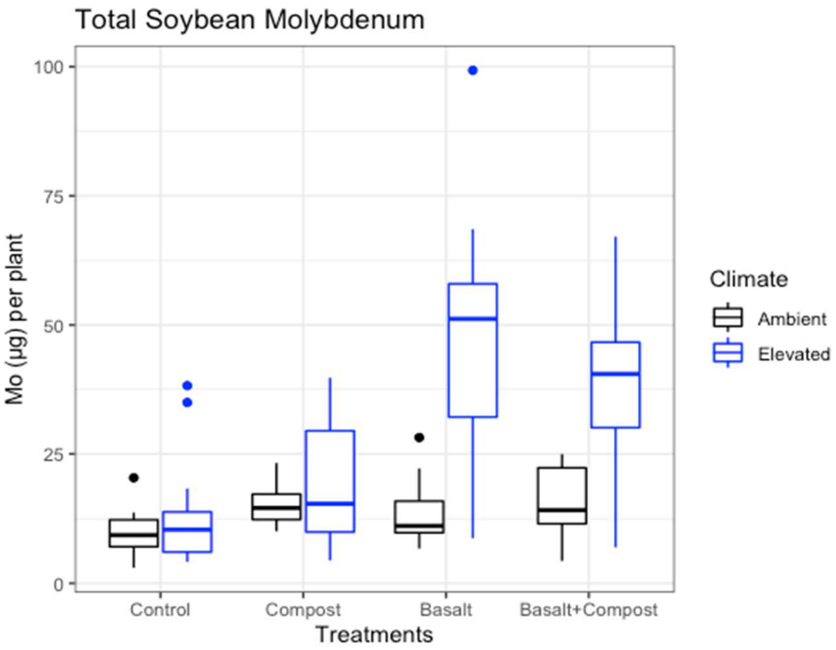

Figure 3.17. Total soybean Mo content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There is no treatment effect in soybean shoot Zn concentration in ambient temperature and CO_2 (p-value = 0.25) (Table 3.6; Figure 3.18). Total soybean shoot Zn content in ambient temperature and CO_2 did not indicate a treatment effect (p-value = 0.65) (Table 3.7; Figure 3.19). There is a treatment effect in soybean shoot Zn concentration in elevated temperature and CO_2 where Zn in basalt and basalt+compost treated soybean decreased compared to compost treated soybean (p-value = 0.0044) (Table 3.6; Figure 3.18). Comparing between treatments using Dunn's test with Šidák adjusted p-value significant treatment effects in compost and basalt (p-value = 0.0027) and compost and basalt+compost (p-value = 0.0338). There is no treatment effect in total soybean shoot Zn content in elevated temperature and CO_2 (p-value = 0.17) (Table 3.7; Figure 3.19).

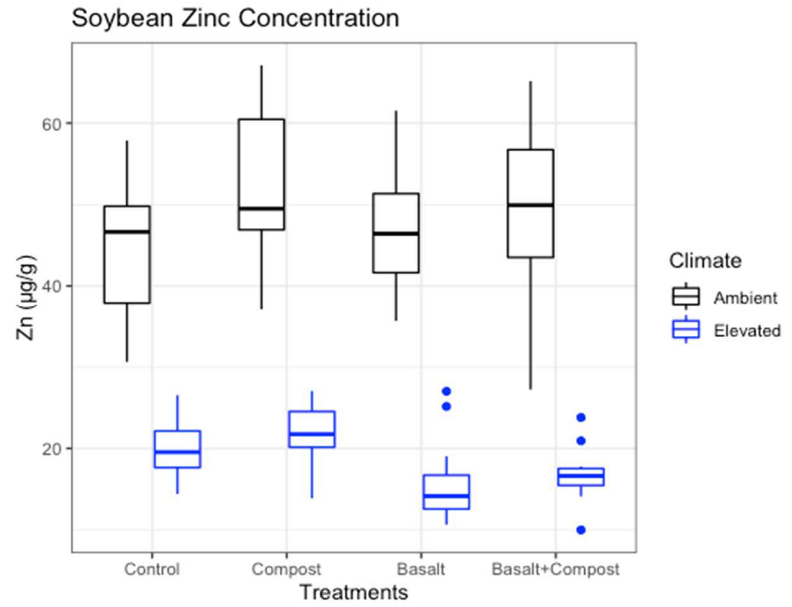

Figure 3.18. Soybean Zn concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

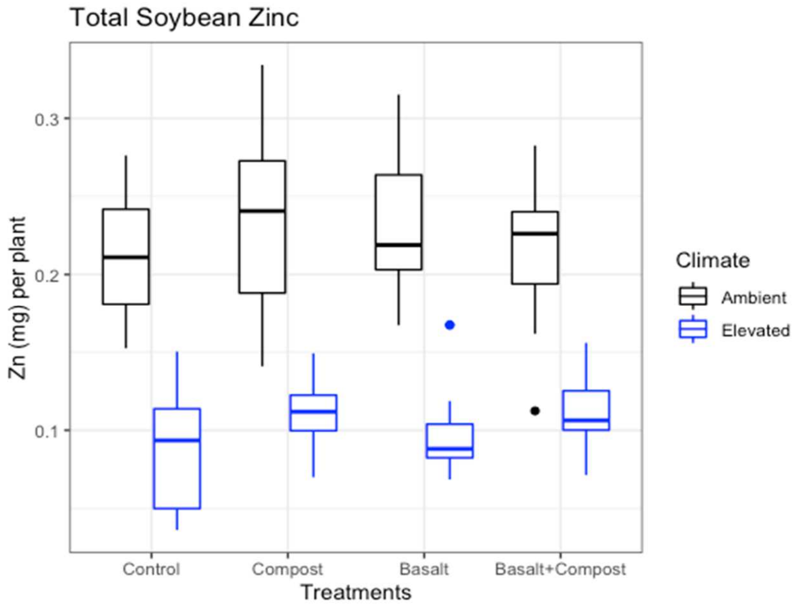

Figure 3.19. Total soybean Zn content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.6. Concentration of soybean shoot biomass nutrients Na, Mo, and Zn by ug/g and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n= 12).

Soybean biomass nutrients							
Climate	Treatment	Na	Na (se)	Mo	Mo (se)	Zn	Zn (se)
Ambient	Control	34.78	3.61	34.78	0.286	44.74	2.66
	Compost	68.22	9.71	68.22	0.272	52.05	2.49
	Basalt	40.6	7.04	40.6	0.362	47.62	2.41
	Basalt+Compost	58.32	8.89	58.32	0.449	48.92	3.14
Elevated	Control	53.74	7.62	53.74	0.687	19.73	1.12
	Compost	47.88	4.32	47.88	0.654	21.99	1.02
	Basalt	36.3	3.30	36.3	1.11	15.93	1.51
	Basalt+Compost	33.17	3.40	33.17	N/A	16.79	N/A

Table 3.7. Soybean biomass nutrients Na, Mo, and Zn by mg/plant of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	Na	Na (se)	Mo	Mo (se)	Zn	Zn (se)
Ambient	Control	0.163	0.0155	0.65	1.35	0.211	0.0114
	Compost	0.328	0.0624	1.31	1.20	0.233	0.0166
	Basalt	0.259	0.0326	0.79	1.81	0.234	0.0129
	Basalt+Compost	0.197	0.0417	1.04	1.92	0.215	0.0139
Elevated	Control	0.92	0.0343	0.229	3.27	0.0891	0.0110
	Compost	0.98	0.0241	0.244	3.49	0.1118	0.0058
	Basalt	0.92	0.0214	0.231	7.31	0.1012	0.0097
	Basalt+Compost	0.89	0.0242	0.221	N/A	0.1115	N/A

Soybean shoot K concentration in ambient conditions results in a significant treatment effect, where K control and basalt treated soybean biomass are decreased compared to compost (p-value = 0.00067) (Table 3.8; Figure 3.20). Comparing between treatments using the Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and compost (p-value = 0.0011) and compost and basalt (p-value = 0.0040). There was no treatment effect total soybean shoot K content in ambient temperature and CO_2 (p-value = 0.49) in ambient temperature and CO_2 (Table 3.9; Figure 3.21). Soybean shoot K concentration in elevated conditions resulted in a significant treatment effect where K in control and basalt are decreased compared to K concentration in compost treated soybean biomass (p-value = 0.01) (Table 3.8; Figure 3.20). Comparing between treatments using the Dunn's test with Šidák adjusted p-value revealed significant treatment effects in control and compost (p-value = 0.0167) and compost and basalt (p-value = 0.0079). There was a significant treatment effect in total soybean shoot K content in elevated temperature and CO_2 where total K content in treatments were increased compared to the control (p-value = 4e-05) (Table 3.9; Figure 3.21). Comparing between treatments using the Šidák method reveals significant treatments effects in control and basalt (p-value = 0.0026), compost and basalt+compost (p-value = 0.0197), and control and basalt+compost (p-value < 0.0001).

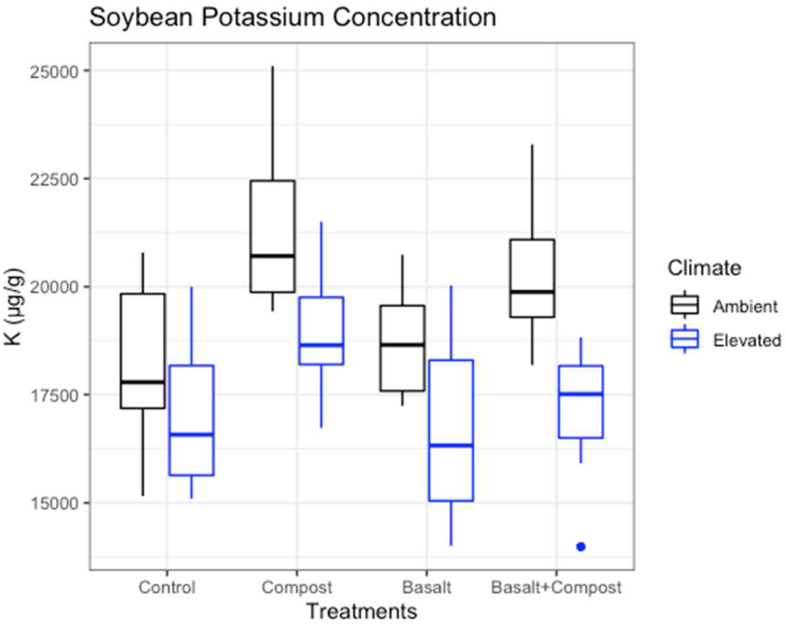

Figure 3.20. Soybean K concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

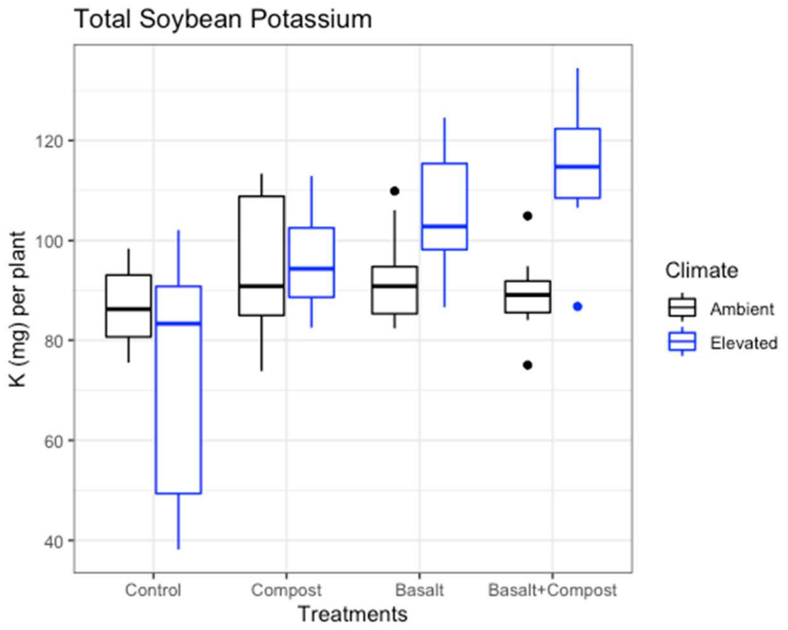

Figure 3.21. Total soybean K content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was a treatment effect in soybean shoot P concentration in ambient temperature and CO_2 where P in compost treated soybean biomass increased compared to control and basalt (p-value = 0.0053) (Table 3.8; Figure 3.22). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatments effects in control and basalt (p-value = 0.0026), compost and basalt+compost (p-value = 0.0197), and control and basalt+compost (p-value < 0.0001). There was no treatment effect in total soybean shoot P content in ambient temperature and CO_2 (p-value = 0.68) (Table 3.9; Figure 3.23). There was a treatment effect in soybean shoot P concentration in elevated temperature and CO_2 where P in control, basalt, and baslt+compost treated soybean biomass was decreased compared to P in compost treated soybean biomass (p-value = 0.0015) (Table 3.8; Figure 3.22). Comparing between treatments using the Dunn's test with Šidák adjusted p-value revealed significant treatments effects in control and basalt (p-value = 0.0026), control and compost (p-value = 0.0075), compost and basalt (p-value = 0.0008), and compost and basalt+compost (p-value = 0.0285). Total soybean shoot P content in elevated temperature and CO_2 represent a significant treatment effect where P in treated samples increased compared to the control (p-value = 3.7e-05) (Table 3.9; Figure 3.23). Comparing between treatments using Dunn's test with Šidák adjusted p-value revealed significant treatments effects in control and basalt (p-value = 0.0083), control and basalt+compost (p-value < 0.0001), and compost and basalt+compost (p-value = 0.0065).

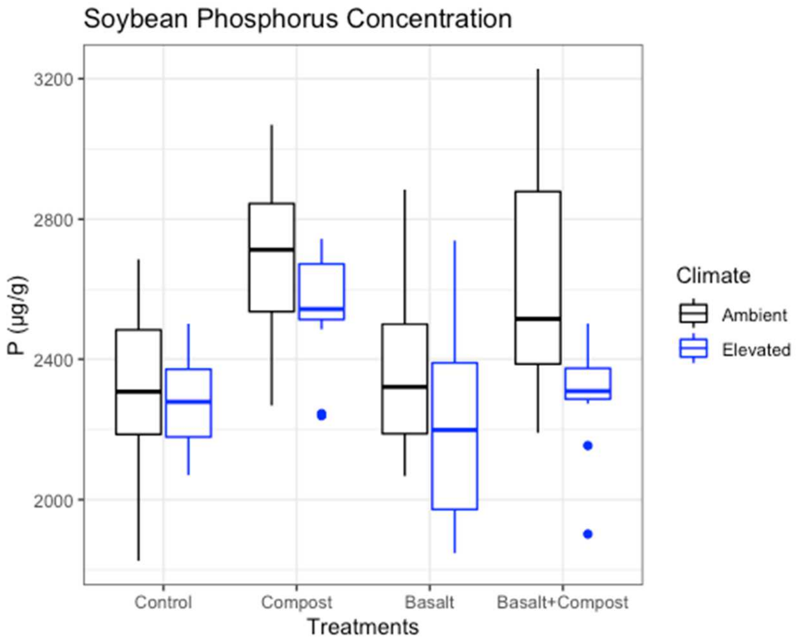

Figure 3.22. Soybean P concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

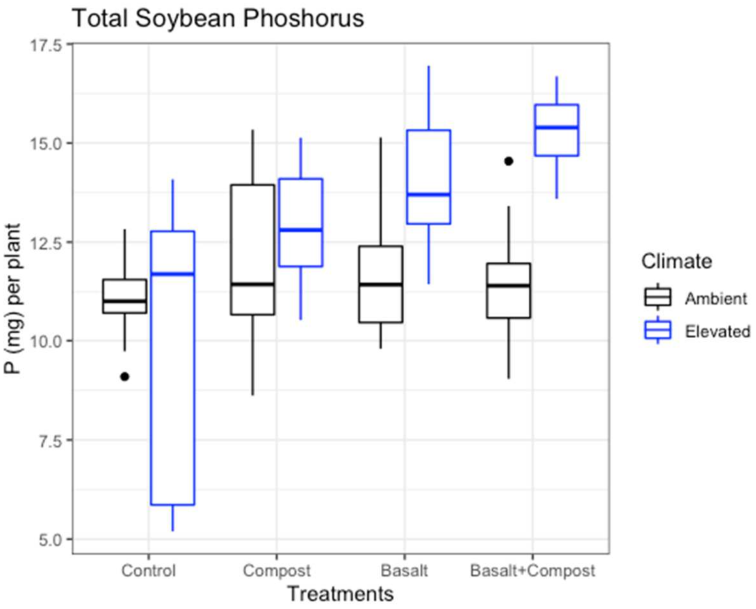

Figure 3.23. Total soybean P content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Soybean shoot Ba concentration results indicate a significant treatment effect where Ba in basalt and basalt+compost decreased in soybean biomass compared to the control (p-value = 1.8e-06) (Table 3.8; Figure 3.24). Comparing between treatments the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value < 0.0001), basalt and compost (p-value < 0.0001), and compost and basalt+compost (p-value = 0.0088). There is a treatment effect in total soybean shoot Ba content in ambient temperature and CO_2 where Ba in basalt and basalt+compost is decreased in soybean biomass compared to the control (p-value = 1.1e-05) (Table 3.9; Figure 3.25). Comparing between treatments using Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value = 0.0005), basalt and compost (p-value = 0.0004), control and basalt+compost (p-value = 0.0028), and compost and basalt+compost (p-value = 0.0022). Soybean shoot Ba concentration in elevated temperature and CO_2 results indicate a significant treatment effect where Ba concentration in basalt amended soybean biomass decreased compared to compost and control (p-value = 7e-06) (Table 3.8; Figure 3.24). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and compost (p-value = 0.0108), basalt and compost (p-value < 0.0001), and compost and basalt+compost (p-value = 0.0086). Total soybean shoot Ba content suggests a significant treatment effect where basalt and basalt+compost are decreased compared to the control (p-value = 0.0011) (Table 3.9; Figure 3.25). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt+compost (p-value = 0.0012), basalt and basalt+compost (p-value = 0.0069).

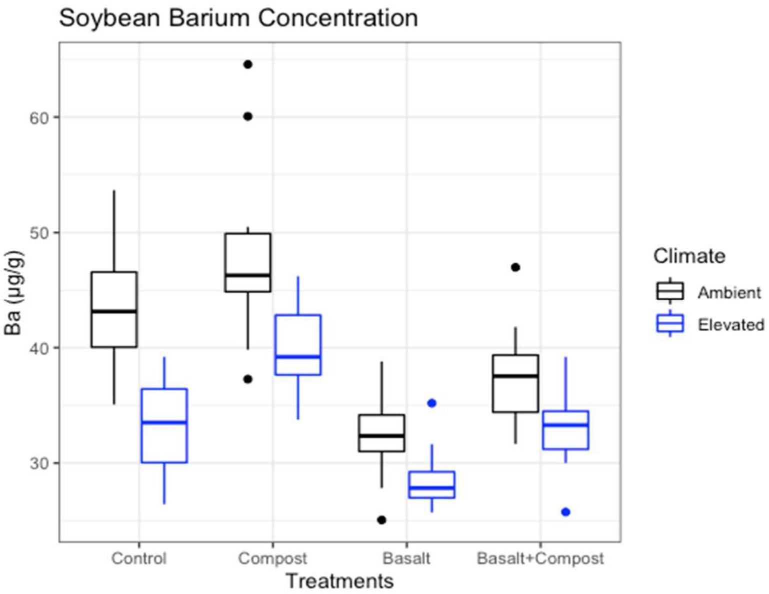

Figure 3.24. Soybean Ba concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

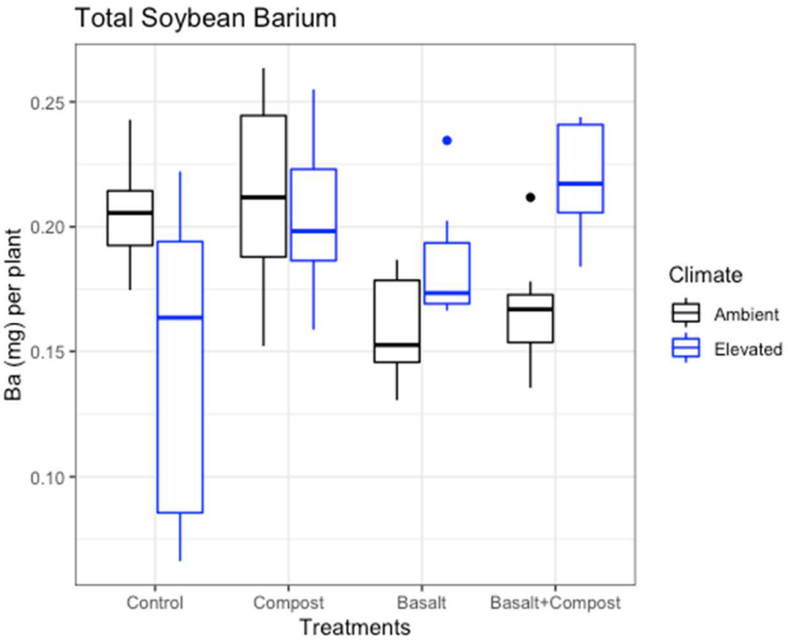

Figure 3.25. Total soybean Ba content (mg/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.8. Soybean biomass nutrients K, P, and Ba as ug/g and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	K	K (se)	P	P (se)	Ba	Ba (se)
Ambient	Control	18266.6	513.4	2316.1	73.10	43.52	1.53
	Compost	21310.0	532.0	2693.6	66.23	48.16	2.21
	Basalt	18750.0	368.3	2383.3	79.96	32.17	1.04
	Basalt+Compost	20315.8	473.8	2606.8	93.31	37.5	1.24
Elevated	Control	16911.6	465.5	2282.0	42.99	33.20	1.20
	Compost	18920.8	383.2	2552.9	49.42	39.94	1.07
	Basalt	16625.0	562.2	2207.5	76.54	28.67	0.75
	Basalt+Compost	17203.6	N/A	2298.4	N/A	33.09	0.99

Table 3.9. Soybean biomass nutrients as mg/plant and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients							
Climate	Treatment	K	K (se)	P	P (se)	Ba	Ba (se)
Ambient	Control	86.81	2.20	10.99	0.281	0.206	0.0058
	Compost	94.56	3.80	12.01	0.616	0.213	0.0102
	Basalt	92.09	2.55	11.70	0.449	0.157	0.0058
	Basalt+Compost	89.23	2.08	11.45	0.431	0.165	0.0056
Elevated	Control	74.27	6.65	10.16	0.999	0.150	0.0169
	Compost	96.22	2.84	13.00	0.439	0.203	0.0089
	Basalt	105.77	3.76	14.03	0.467	0.182	0.0059
	Basalt+Compost	114.91	N/A	15.30	N/A	0.218	0.0058

There was no treatment effect in soybean shoot %C in ambient temperature and CO_2 (p-value = 0.22) (Table 3.10; Figure 3.26). Total soybean shoot C content in ambient conditions reflects a significant treatment effect where total C in basalt+compost treated soybean decreased compared to basalt alone (p-value = 3.8e-05) (Table 3.11; Figure 3.27). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in basalt and basalt+compost (p-value = 0.0236). There is no treatment effect in soybean shoot %C in elevated temperature and CO_2 (p-value = 0.83) (Table 3.10; Figure 3.26). There is a significant treatment effect in total soybean shoot C content in elevated temperature and CO_2 where basalt and basalt+compost increased compared to the control (p-value = 3.4e-08) (Table 3.11; Figure 3.27). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value = 0.0010), basalt and compost (p-value = 0.0006), control and basalt+compost (p-value > 0.0000), and compost and basalt+compost (p-value < 0.0001).

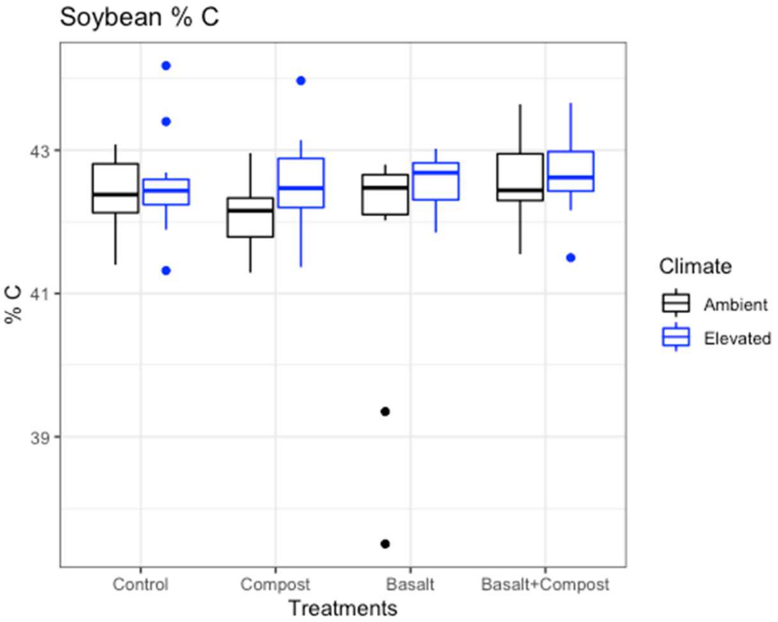

Figure 3.26. Soybean %C in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

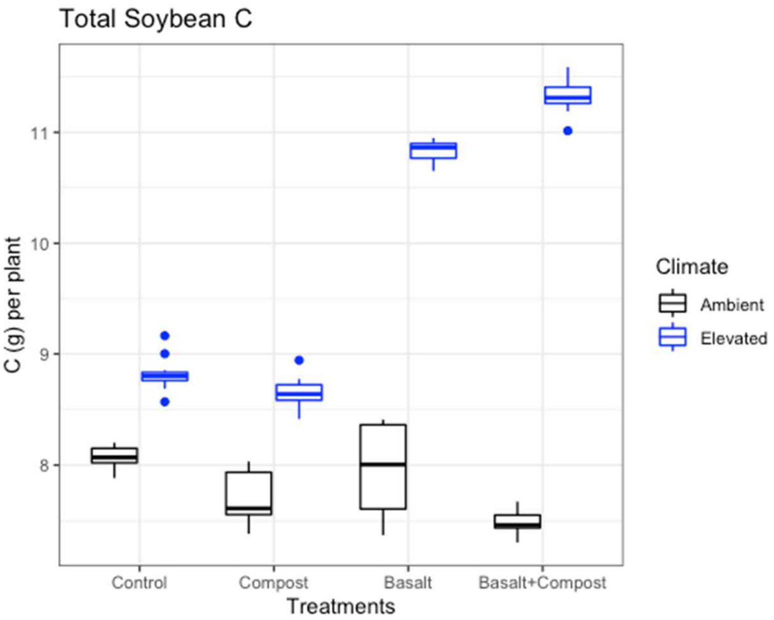

Figure 2.27. Total soybean C content (g/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There is no treatment effect in soybean shoot %N in ambient temperature and CO_2 (p-value = 0.48) (Table 3.10; Figure 3.28). Total soybean shoot N content in ambient temperature and CO_2 does not reflect a treatment effect (p-value = 0.97) (Table 3.11; Figure 3.59). There is no treatment effect in soybean shoot %N in elevated temperature and CO_2 in elevated temperature and CO_2 (p-value = 0.64) (Table 3.10; Figure 3.58). There is a treatment effect in total soybean shoot N content in elevated temperature and CO_2 with N in basalt and basalt+compost amended soybean increased compared to the control (p-value = 0.00037) (Table 3.11; Figure 3.60). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0023) and control and basalt+compost (p-value = 0.0016).

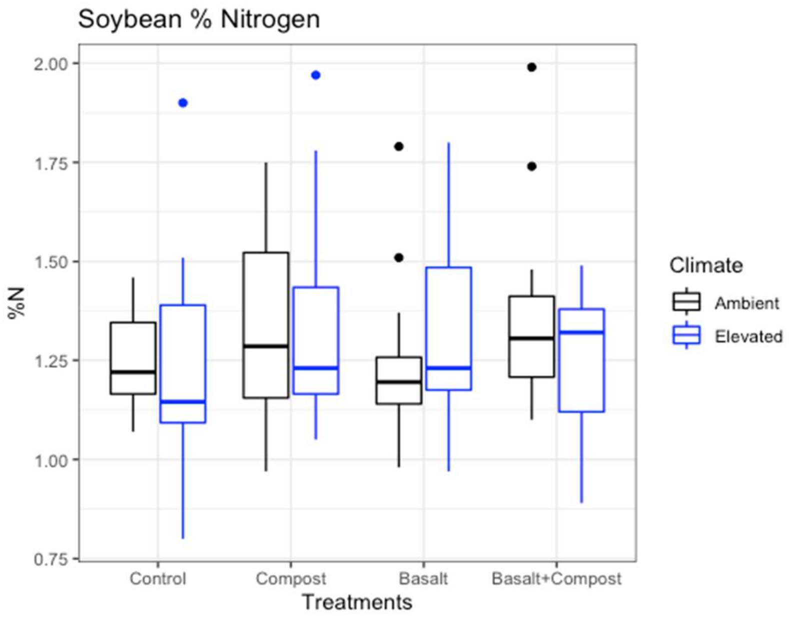

Figure 3.28. Soybean %N in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

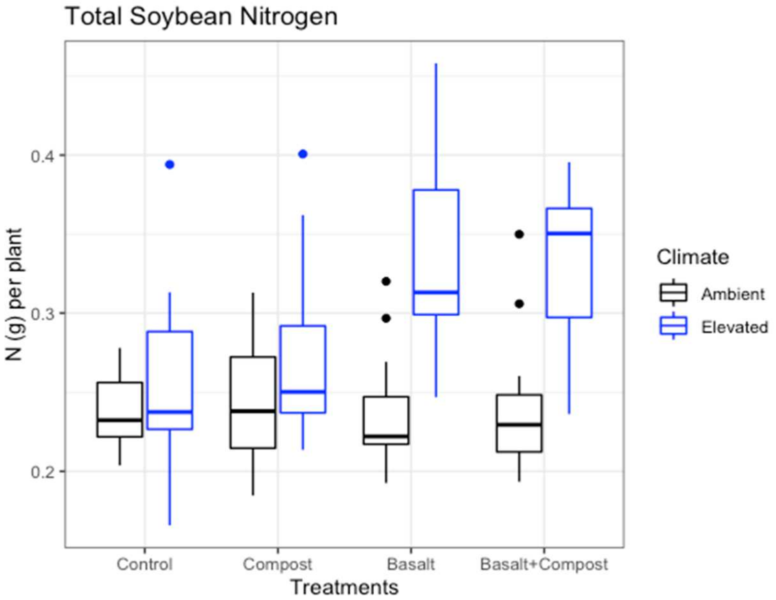

Figure 3.29. Total soybean N content (g/plant) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.10. %C and %N and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients					
Climate	Treatment	C	C (se)	N	N (se)
Ambient	Control	42.4	0.148	1.24	0.0356
	Compost	42.14	0.135	1.34	0.0690
	Basalt	41.81	0.474	1.25	0.0626
	Basalt+Compost	42.57	0.180	1.36	0.0768
Elevated	Control	42.51	0.207	1.22	0.0844
	Compost	42.55	N/A	1.33	N/A
	Basalt	42.56	0.112	1.32	0.0735
	Basalt+Compost	42.61	N/A	1.26	N/A

Table 3.11. Total C and N as g/plant and standard error (SE) of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean biomass nutrients					
Climate	Treatment	C	C (se)	N	N (se)
Ambient	Control	8.07	0.028	0.236	0.0067
	Compost	7.69	0.062	0.243	0.0114
	Basalt	7.96	0.120	0.237	0.011
	Basalt+Compost	7.48	0.031	0.239	0.013
Elevated	Control	8.81	0.042	0.254	0.0175
	Compost	8.65	N/A	0.272	N/A
	Basalt	10.83	0.028	0.336	0.0187
	Basalt+Compost	11.30	N/A	0.334	N/A

3.3 Soybean weathering products

Although basalt does show elevated alkalinity compared to control in ambient temperature and CO_2, there is not a significant treatment effect in ambient soybean alkalinity (p-value = 0.68) (Table 3.12; Figure 3.30). Basalt and basalt+compost increase 10.72% and 24.63% in ambient conditions. Alkalinity in elevated temperature and CO_2 did show a significant treatment effect (p-value = 1.6e-11)(Table 3.12; Figure 3.30). Comparing between treatments using the Dunn’s test with Šidák adjusted p-value reveals significant treatment effects in control and basalt (p-value = 0.0004), compost and basalt (p-value = 0.0004), control and basalt+compost (p-value > 0.0000), and compost and basalt+compost (p-value > 0.0000). In elevated temperature and CO_2 basalt and basalt+compost treatments increase 55.1% and 57.7% compared to controls.

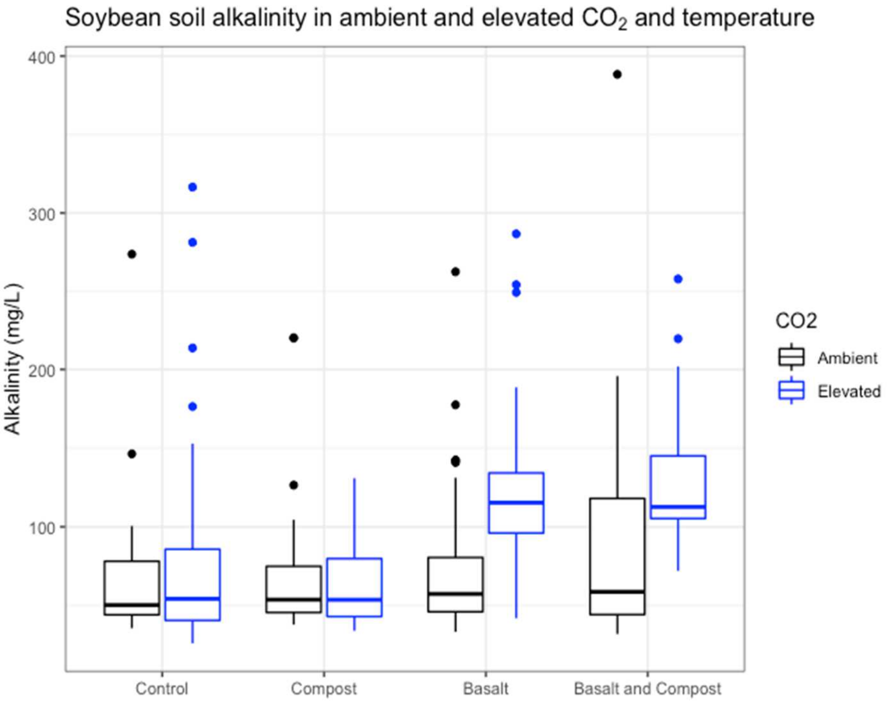

Figure 3.30. Soybean soil alkalinity (mg/L) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

We measured soybean soil pH to measure the extent of basalt dissolution. There was a significant treatment effect in pH in ambient CO_2+temperature where basalt and basalt+compost amended soil samples had a higher pH than control and compost (p-value = 2.5e-05) (Table 3.12; Figure 3.31). Comparing between treatments using the Šidák method reveals significant treatments effects in control and basalt (p-value = 0.0010, compost and basalt (p-value = 0.0054), control and basalt+compost (p-value = 0.0005), and compost and basalt+compost (p-value = 0.0029). There was a significant treatment effect in pH in elevated CO_2+temperature (p-value = 4.5e-07) (Table 3.12; Figure 3.31). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value = 0.0003, compost and basalt (p-value = 0.0002), control and basalt+compost (p-value = 0.0002), and compost and basalt+compost (p-value = 0.0001).

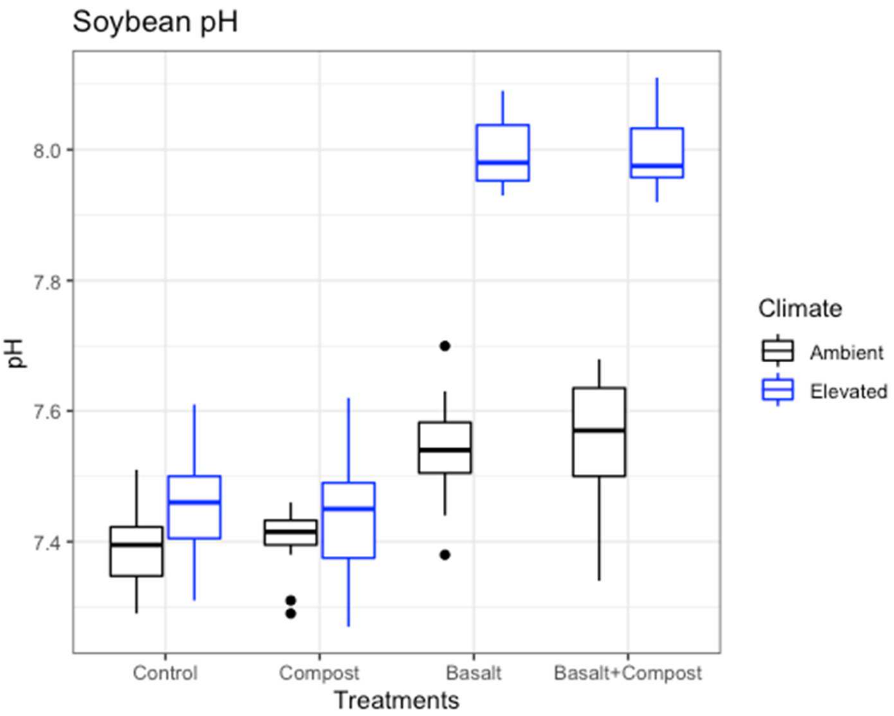

Figure 3.31. Soybean soil pH in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.12. Soybean biomass, alkalinity (mg/L), and pH of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Climate	Treatment	Biomass (g)	Alkalinity	pH
Ambient	Control	19.04	69.55	7.39
	Compost	17.88	72.17	7.40
	Basalt	19.65	77.43	7.54
	Basalt+Compost	17.58	86.09	7.55
Elevated	Control	20.74	81.36	7.45
	Compost	20.34	63.39	7.44
	Basalt	25.45	126.2	7.995
	Basalt+Compost	26.64	128.3	7.993

3.4 Soil nutrients

We measured potentially rock-derived plant relevant nutrients in soil after harvest. There was no treatment effect in exchangeable Ca in ambient CO_2 and temperature (p-value = 0.71) (Table 3.13; Figure 3.32). There was a treatment effect in exchangeable Ca in elevated CO_2 and temperature (p-value = 6e-05) where soil exchangeable Ca decreased in basalt and basalt+compost compared to compost and control (Table 3.13; Figure 3.32). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in compost and basalt (p-value = 0.0047), control and basalt+compost (p-value = 0.0214), and compost and basalt+compost (p-value > 0.000).

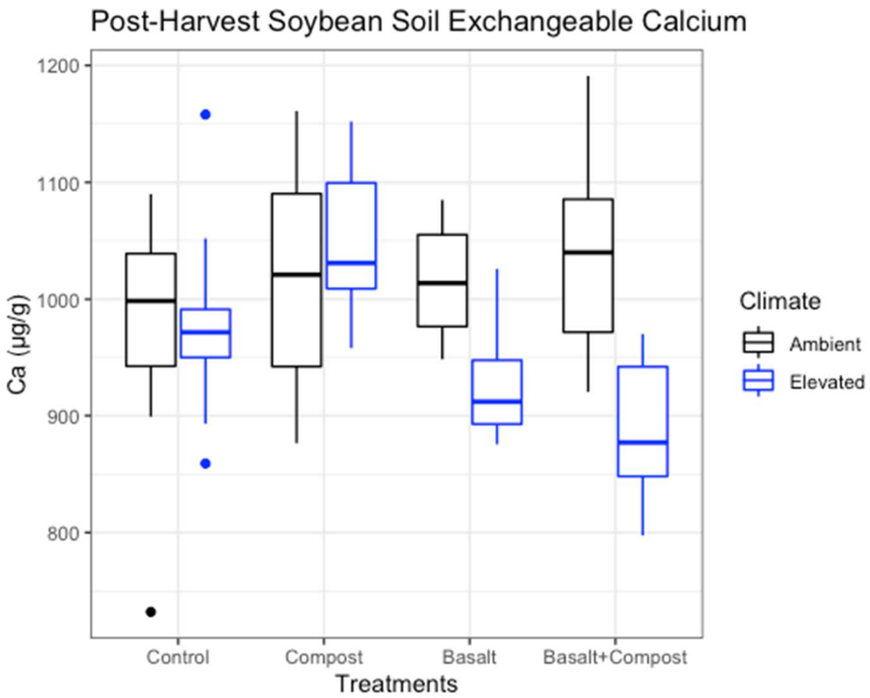

Figure 3.32. Soybean soil Ca concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was a treatment effect in exchangeable Mg in ambient CO_2 and temperature (p-value = 0.00012) where soil exchangeable Mg decreased in basalt and basalt+compost compared to compost and control (Table 3.13; Figure 3.33). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value = 0.0017), compost and basalt (p-value = 0.0054), control and basalt+compost (p-value = 0.0029), and compost and basalt+compost (p-value = 0.0088). There was a treatment effect in exchangeable Ca in elevated CO_2 and temperature (p-value = 5.4e-06) where soil exchangeable Mg decreased in basalt and basalt+compost compared to compost and control (Table 3.13; Figure 3.33). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in compost and basalt (p-value = 0.0058), control and basalt+compost (p-value = 0.0015), and compost and basalt+compost (p-value > 0.0001).

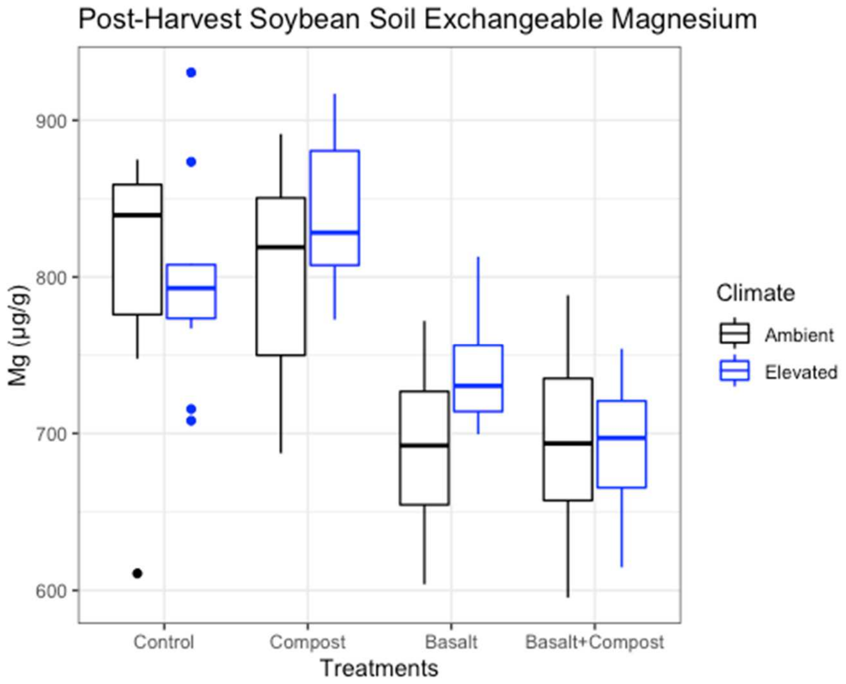

Figure 3.33. Soybean soil Mg concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

There was a treatment effect in average exchangeable Na in ambient CO_2 and temperature (p-value = 0.0071) (Table 3.13; Figure 3.34). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatment effects in control and compost (p-value = 0.0026). There was a treatment effect in average exchangeable Na in elevated CO_2 and temperature (p-value = 2.5e-06) (Table 3.13; Figure 3.34). Comparing between treatments using the Dunn's test with Šidák adjusted p-value reveals significant treatments effects in control and basalt (p-value = 0.0088), basalt and basalt+compost (p-value = 0.0066), and compost and basalt (p-value > 0.0001).

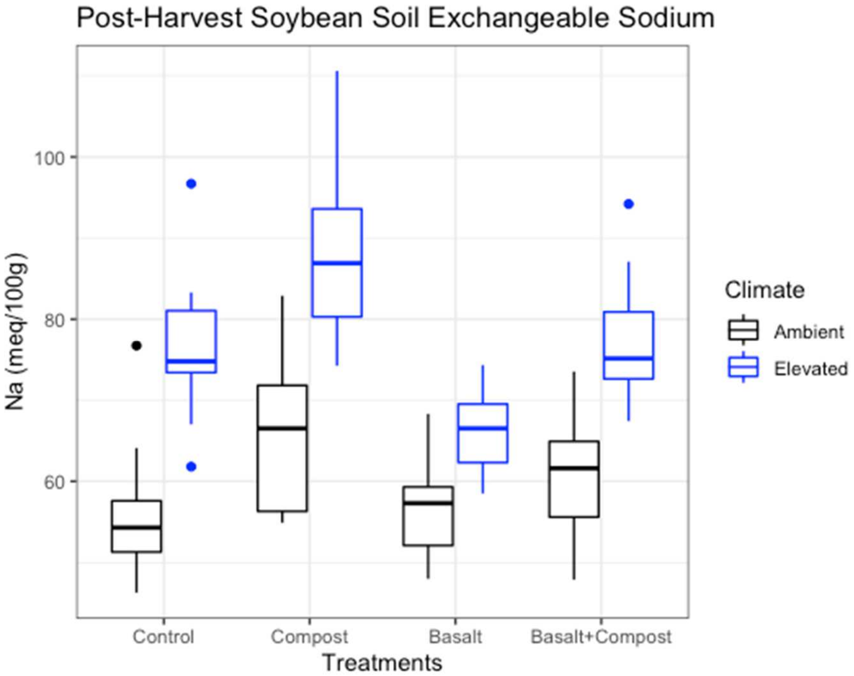

Figure 3.34. Soybean soil Na concentration (µg/g) in ambient CO_2+Temperature (black) and elevated CO_2+Temperature (blue) with the different treatments studied (control, compost, basalt, and basalt+compost).

Table 3.13. Exchangeable Ca (µg/g), Mg (µg/g), and Na (meq/100g) in soybean soil and standard error of each from control and treated samples in ambient and elevated CO_2 and temperature (n=12).

Soybean soil nutrients							
Climate	Treatment	Ca	Ca (se)	Mg	Mg (se)	Na	Na(se)
Ambient	Control	981.5	28.25	807.2	21.81	44.61	2.23
	Compost	1013.9	26.84	798.5	19.63	53.78	2.66
	Basalt	1040.7	14.75	692.3	15.05	57.17	1.75
	Basalt+Compost	1040.7	25.27	694.5	17.17	60.24	1.99
Elevated	Control	978.0	23.63	797.0	18.99	61.07	2.22
	Compost	1047.0	19.89	838.3	14.74	70.53	3.02
	Basalt	929.9	16.83	740.4	12.05	66.18	1.34
	Basalt+Compost	890.2	17.04	691.5	11.81	77.23	2.14

Discussion

I examined the hypothesis that elevated CO_2 and temperature lead to accelerated dissolution of rock dust, with corresponding ESW effects imparted on plants, soils and dissolved alkalinity. My findings confirmed this expectation in terms of alkalinity generation, increased pH, increased soybean biomass, and nutrients pools, particularly for Ca, Mg, K, Mo and Si. In contrast, I did not find evidence for substantial or systematic changes in nutrient concentration in plants, implying that increased plant productivity mediated by ESW under elevated CO_2 and temperature does not change the relative quality of nutrients in soybean biomass. Rather, soybean responds to ESW products through productivity increases that enhance C biomass rather than concentrating nutrients released in my growth chamber experiments. These findings demonstrate robustness in enhanced weathering technology to potential future changes in CO_2 and warming, which is critical given the need to deploy billions of tons of CO_2 removal through the array of negative emissions technology over the 21st century (IPCC, 2019).

4.1 Soybean yield

Dry soybean biomass did not improve with amendments in ambient conditions. In elevated CO_2 and temperature, soybean biomass increased in both basalt and basalt+compost amended treatments compared to control. We also measured a significant yield increase in the elevated CO_2 and temperature trial compared to ambient conditions (Figure 3.1). The increase in yield in elevated CO_2 and temperature is due to the CO_2 fertilization effect (Iverson and Norby, 2014). Sakurai et al. (2014) found a 7.5% increase in soybean yield with every 50 ppm increase in CO_2, which reflects the yield response we observed in elevated CO_2 and temperature. Past studies have observed significant increases in soybean yield in response to rock dust amendments, which has largely been traced to pH changes that optimize productivity (Beerling et al. 2018).

It is difficult to disentangle which nutrients had the greatest impact on soybean yield, or if pH was the principal driver, however it is noteworthy that Mo concentration in soybean biomass amended with basalt and basalt+compost increased substantially compared to the control. Molybdenum is a key control on nitrogen fixation (Rasnake, 1982) and could therefore have stimulated soybean productivity in response to higher symbiotic nitrogen fixation. Future work could focus on rates of nitrogen fixation in response to rock dust inputs and the mechanism behind plant productivity increase.

4.2 Soybean crop nutrients

We measured a suite of elements in soybean biomass, including potentially rock-derived elements. I expect basalt amended plants may show increased rock-derived nutrients, such as Fe, Ca, and Mg, if these elements are limited in the soil matrix. I also expect that silicates will break down more rapidly in future, elevated climates due to increased CO_2 and higher temperatures which increase reaction rates. Therefore, the likelihood of measuring an increase in rock-derived nutrients in soybean biomass is greater in the future climate scenario. On a µg/g basis, the concentration of Mg, Fe, Na, Cu, C, and N in soybean biomass range similarly in ambient and elevated conditions, which suggests that soybean assimilated these nutrients consistently in both climate conditions. Si and Ca decrease in elevated CO_2 and temperature, which suggests that the concentration of these elements in soybean biomass decreased in elevated CO_2 and temperature. P and K concentration in soybean biomass increased in elevated conditions but followed the same trends as in ambient conditions where compost and basalt+compost increased compared to the control and basalt. This indicated that compost supplied significant quantities of P and K. The concentration of Zn, Ba, and Mo increased systematically in elevated conditions. This suggested that soybean assimilated more of these elements in elevated CO_2 and temperature alone.

Total pools (mg/plant) of nutrients reflect total biomass increases. The increase in soybean yield is congruent with the total pools of nutrients including Mo, Cu, but not Al, Mg, Ca, Si, Fe, K, and P. This may be due to increased yield. Other treatment effects observed in soybean biomass include Compost increased Na in ambient conditions. Ba is lower in silicate amended soybean biomass in ambient conditions and higher overall in elevated climate conditions. There was no treatment effect on rock-derived nutrients in the composition of aboveground biomass. This suggests that nutrients that basalt may have provided were not depleted in the soil, therefore their addition had no impact on crop biomass composition.

Few studies have addressed changes in soybean composition with increased CO_2 and temperature, however other crops have been examined. One study found that CO_2 and warming did not affect total plant C:N in rice, but did alter N partitioning (WeiGuo et al. 2010). Wang et al. (2019) assessed the impact of elevated CO_2 and warming on rice and wheat C:N and C:P ratios and observed varying outcomes across crop type. They found that elevated CO_2 increased C content and decreased N content, thereby increasing C:N, in rice and wheat. P also decreased in rice, causing the C:P to decrease. Increased temperature alone however had no effect on C:N and C:P in rice and decreased C:P and N:P in wheat due to increased P assimilation (Wang et al. 2019). Another study observed warming could decrease K, Ca, and Mg in wheat biomass, reducing dietary nutrient content in wheat. Future research should focus on increasing CO_2 and temperature concurrently and assessing various crop and soil types.

4.3 Soybean weathering products

The extent of silicate dissolution in soil is measured in terms of the increase in soil alkalinity, pH, and potentially rock-derived cations Ca, Mg, and Fe in soil. I anticipated that the 2050 climate scenario with elevated CO_2 and temperature would have more alkalinity and a higher pH in soil. However, soil cations may show no change as background nutrient pools were very high compared to the amount of nutrients added via basalt and compost. Basalt and basalt+compost amended pots did not show a significant increase in alkalinity in ambient CO_2 and temperature. However, compost in combination with basalt did show elevated alkalinity in many samples compared to basalt alone. Basalt and basalt+compost amended plots showed increased alkalinity in the elevated CO_2+temperature scenario. Similarly, pH did not increase in ambient conditions, but increased significantly in elevated conditions.

It appears that increasing temperature and CO_2 substrate boosts silicate dissolution rate, thereby increasing pH and bicarbonate formation compared to the ambient CO_2 and temperature scenario. Results suggest that compost paired with basalt does further improve ESW rate compared to basalt alone. The rate of cation release from silicate chains is more rapid in acid than in basic solutions (Harley and Gilkes 1999), so ambient CO_2 and temperature may not show significant weathering because the soil pH is neutral. Although N-fixing soybean is an additional source of H^+ in soil through processes such as nitrification and ammonification (Beerling et al. 2018), a control with a non-N-fixer is required to determine if this factor was significant to silicate dissolution rate. Li et. al. (2016) used models to predict basalt weathering in the future and estimated a more rapid dissolution rate as temperature increases. Dimitar

(2017) predicts that high CO_2 in Earth's atmosphere would further enhance silicate weathering with N-fixers. Silicate weathering occurs via acid produced from various sources that fluctuate temporarily, spatially, and according to plant type, so CO_2 consumption estimates based on the assumption that silicate weathers via carbonic acid alone may underestimate silicate weatherability (Dimitar 2017).

As expected, there was no treatment effect in soil cations, likely because the native pool of nutrients was more robust than what was added with basalt and compost. Nutrients that are not utilized by crops and microbes are transported by leaching, especially with frequent leachate extractions. Future studies should utilize nutrient depleted soils for silicate addition to affect nutrient pools.

Summary and conclusions

The aim of this study was to determine how ESW may respond in future climates as CO_2 and temperatures increase. Although pH is a dominant control on silicate weathering, I anticipated that CO_2 and temperature were also major controls on mineral dissolution rate. In fact, we observed significant increases in alkalinity, soil pH, and crop yield with silicate additions under elevated CO_2 and temperature conditions. Although silicate rock powder does not contain significant amounts of nitrogen, phosphorus, and potassium, and therefore cannot replace standard fertilizers, they do carry micronutrients such as Ca, Mo, and Mg, which are not easily restored once they have been removed. My results indicate that silicates can act as a supplement to optimize yield in soybean. Future studies should allow crops to grow to maturity and assess biomass production and nutrient composition because there may be significant changes in nutrient partitioning. Future studies should also measure soil alkalinity more frequently to get a more precise understanding of weathering flux.

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