EVALUATION OF RECLAIMED DRYWALL FOR SOIL AMENDMENT AND CARBON SEQUESTRATION

by

Fabien Besnard

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Approved by:

Dr. Helene A. Hilger

Dr. John L. Daniels

Dr. Martha C. Eppes

Dr. Sara K. McMillan

Dr. John F. Bender

ABSTRACT

FABIEN BESNARD. Evaluation of reclaimed drywall for soil amendment and carbon sequestration. (Under the direction of DR. HELENE HILGER)

Construction and demolition (C&D) activities produce 170 million tons of waste annually (US EPA 2009), 15% of which are drywall. Drywall from construction activities, virgin material too small to be reused and often disposed in landfills, is estimated at 1.7 million tons each year (Sandler 2003). Drywall in landfills leads to hydrogen sulfide emissions that can be lethal (Lee et al. 2006; Flynn 1998). The goal of this research was to evaluate two diversion options for reclaimed drywall: (i) as a soil amendment; and (ii) as a carbon sequestration driver. Canola, sunflower, wheat, and grass plants were amended with different doses of ground drywall. While the drywall did not significantly impact sunflower and grass growth, wheat seed yield increased 20%, and canola yield almost doubled relative to controls with no drywall amendment. Phytotoxicity tests performed on different drywall types revealed the potential inhibition effects of using mold and moisture resistant drywall as soil amendment, suggesting that careful sorting of reclaimed drywall may be necessary before land application. Wheat and corn amended with 3,208 kg S ha^{-1} as ground drywall in a climate receiving less than 33 in y^{-1} of rain proved able to sequester atmospheric carbon at a rate of 650 kg ha^{-1} y^{-1}. Presumably the plants transported atmospheric carbon to the soil via rhizosphere respiration, where the carbon reacted with drywall calcium to form calcium carbonate. This sequestration was confirmed by carbon isotope analysis.

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CHAPTER 1: INTRODUCTION

1.1 Background

The amount and diversity of waste materials produced in countries, states, and cities worldwide continue to drive flexibility and innovation among the professionals who must manage and treat such wastes. Each day, across the many categories of wastes produced -- municipal solid waste, industrial waste, agricultural waste, and construction and demolition waste -- even if per capita waste generation rates remain stable, total waste quantities tend to grow as population climbs.

As of 2009, construction and demolition wastes (C&D wastes) represented about one third of the U.S. waste stream. As the category label implies, these materials originated from construction, demolition, and renovation activities and include concrete, steel, bricks, wood, drywall, carpets, cardboard, and asphalt shingles. In 2009, annual U.S. C&D production rates were estimated at 170 million tons per year (US EPA 2009).

Drywall comprises 15% of the U.S. C&D waste, making it one of the main constituents of this waste sector (Sandler 2003). While demolition drywall is generally contaminated with paint and nails, waste construction drywall are typically pieces of virgin material too small to be reused on site. Both types of drywall are typically landfilled in dedicated C&D waste landfills. However, C&D landfills are often built to less stringent standards than municipal waste landfills because less biological activity is expected from the disposed wastes. When drywall, made primarily of calcium sulfate

($CaSO_4$), is emplaced, the sulfate can be oxidized to hydrogen sulfide (H_2S) (Lee et al. 2006), which is a gas that can be lethal even at low concentration (Flynn 1998). Thus, there is great interest in identifying reuse options for waste drywall that can divert it from C&D landfills and prevent or reduce hydrogen sulfide emissions.

The amount of virgin drywall waste generated from new building construction and renovation is not trivial. It is estimated that conventional construction of a standard 2000 ft^2 house yields about 1.5 tons of drywall (Gaskin et al. 2002); nationally, 1.7 million tons of waste construction drywall is generated every year in the US (Sandler 2003). Because this material is virgin and uncontaminated, it is estimated that as much as 50 to 80% of it could be reused or recycled (Chandrakanthi et al. 2002). Drywall is 10% paper, 90% calcium sulfate (gypsum) and specific product types contain trace amounts of additives to give them special properties (USG 2011a).Thus, the gypsum content – its chemical and physical properties – largely drives the reuse strategy options for drywall that have been proposed or that are under investigation.

Gypsum is widely used in modern agriculture (Olson 2000). It enhances soil qualities and delivers calcium and sulfate, both essentials for plants health and plant growth (USDA 2006, Scherer 2001). Its beneficial effects on canola and sunflower plants and overall crop yields are well documented (Bora 1997, Brennan et al. 2007, Ahmad et al. 2005, Intodia et al. 1997, Rani et al. 2009). Other studies have also demonstrated the beneficial uses of gypsum on wheat, corn, and grass (Toma et al. 1999, Rashid et al. 2008, Kruse et al. 2009). Drywall, composed of 90% gypsum, seems a good candidate for reuse as a soil amendment, yet few studies have been completed that investigate this option. Burger (1993) demonstrated that pulverized drywall applied to a corn field increased crop yield by 25%. Wolkowski (2003, 2009) used ground drywall on alfalfa and potatoes with positive results, and Gaskin et al. (2002) authored a guide on using waste construction drywall on-site for grass enhancement and soil erosion control to avoid to waste hauling or landfilling.

These studies were all published about a decade ago, and there is no evidence of replication or expansion to other crop investigations since then. Considering the lack of replication of these studies; the fact that there are new drywall products on the market; and the fact that certain plants that benefit from sulfur addition were not included in these studies; some new assessments of waste virgin drywall amendments on crops seem warranted. A plant that would greatly benefit from a sulfur amendment is Canola; which requires high level of sulfur for proper growth (Scherer 2001). It is a crop of increasing interest because it is cultivated, often in rotation with sunflower, for biofuel production. It will be interested to evaluate the use of ground drywall on crops such as canola and sunflower and see if a waste product could enhance biofuel production.

Another interesting role for waste construction drywall may be that it promotes sequestration of atmospheric carbon as it serves as an agricultural amendment. This role is linked not to the sulfur it contains but to the calcium it can provide to soil to produce calcium carbonate precipitate. Geologists expect to find soil calcium carbonate formation in arid and semi-arid climates, where high temperature and low rain precipitation coincide (Schlesinger 1985, Salomons et al. 1976). Recently, Manning (2008) and Renforth et al. (2009) described observing the phenomenon under unlikely conditions in England, where calcium carbonate formed in a compost pile placed in a quarry. They attributed the sequestration to the combination of vegetation that populated the compost and the calcium-rich environment provided by the quarry. They used stable isotope analysis to confirm that the source of the carbon in the carbonate precipitate (pedogenic carbonate) was atmospheric carbon dioxide that had traveled through the plants (Manning 2008, Monger et al. 2001).

This mechanism of carbon sequestration begins with the transfer of atmospheric carbon (carbon dioxide, CO_2) into the soil via vegetation. The carbon taken up by the plant ultimately leaves via the plant roots and, if conditions are right, reacts with calcium in the soil to form calcium carbonate precipitate (Monger et al. 2001) but only when very specific conditions are met, and there are few places where all of them occur simultaneously. The calcium originates from minerals weathering, rain, or wind, and it is often the limiting factor for soil calcium carbonate formation (Manning 2008, Landi et al. 2003). Thus, if waste construction drywall proved to be valuable for certain crops, and this functionality could be coupled to both carbon sequestration and landfill waste disposal avoidance, those would be worthy accomplishments. The goal of this dissertation is to evaluate the reuse potential of waste construction drywall as part of a carbon sequestration system and as a soil amendment.

1.2 Objectives

The goal of this research is to evaluate two different reuse options for waste construction drywall: (i) as a soil amendment; and (ii) as part of a carbon sequestration system. The specific research objectives used to accomplish this goal are described below.

Objective 1: Determine the phytotoxicity of three common types of drywall on six plant seed types.

The phytotoxicity of various doses of a regular drywall, a fire retardant drywall, and a mold and moisture resistant drywall will be assessed with respect to canola, corn, wheat, sunflower, lettuce, and cucumber seeds. The phytotoxicity of these drywalls will be evaluated using a standardized germination scoring protocol.

Objective 2: Measure the effects of waste construction drywall amendments on plant characteristics and yields of several crop plants grown in North Carolina.

Canola, sunflower, and wheat plants will be grown in soil amended with different doses of waste construction drywall to assess the effect of the drywall on plant yields. An experiment growing canola plants in pots rather than at field scale will also be performed to provide more details about the effects of ground drywall amendment on canola growth, a plant widely grown for biofuel.

Objective 3: Evaluate the feasibility of the on-site use of waste construction drywall as a soil amendment for lawn growth and erosion control.

The use of waste drywall on a construction site would reduce the need for the waste hauling and landfill disposal. The third objective of this research will be to evaluate the effect of a waste construction drywall amendment on the growth and root development of tall fescue grass. Tall fescue will be grown in one gallon pots with different doses of regular, fire retardant, and mold and moisture resistant drywall.

Objective 4: Investigate the carbon sequestration potential of a system composed of actively growing vegetation (a crop) and calcium-rich soil (waste construction drywall amendment).

The release of atmospherically-derived carbon into the soil rhizosphere by plants makes it available for long-term sequestration if the carbon reacts with calcium present in soil to form calcium carbonate precipitate. The combination of crop (wheat and corn), to pump atmospheric carbon into the soil, and waste construction drywall, to provide calcium, will be evaluated in a large scale experiment for its capability to sequester atmospheric carbon. Different doses of regular drywall will be amended in large soil columns containing wheat. Soil samples will be collected at different depths and analyzed for calcium carbonate. A stable isotope analysis will be performed on the calcium carbonate formed to confirm the atmospheric origin of the inorganic carbon.

CHAPTER 2: LITERATURE REVIEW

2.1 C&D Waste

Construction and demolition (C&D) wastes are the result of construction, demolition, and renovation of buildings, bridges, and roads. In the U.S. the precise definition of what constitutes C&D waste can vary from state-to-state; North Carolina describes it as “solid waste resulting from construction, remodeling, repair, or demolition operations on pavement, buildings, or other structures, not including inert debris, land-clearing debris, or yard debris” (US EPA 1998). Such definitions become important when disposal options for different waste categories are considered (Figure 1).

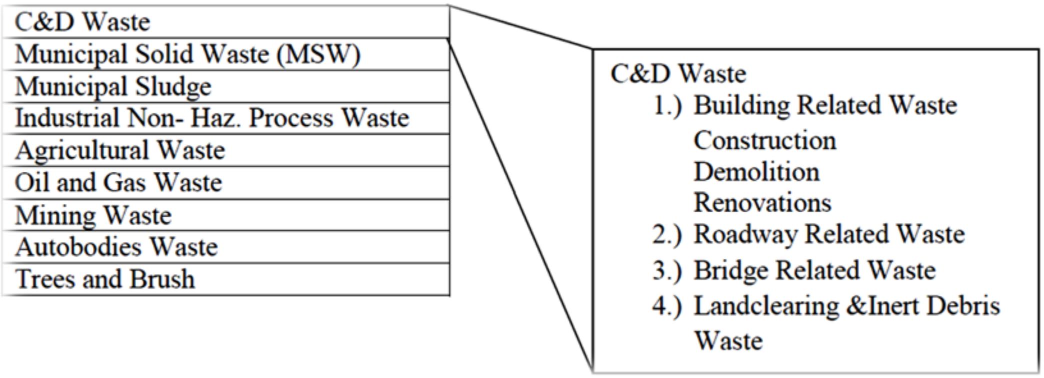


Figure 1: C&D waste in perspective (US EPA 1998)

C&D waste streams can include concrete, asphalt, wood, metal, cardboard, plastic, soil, and drywall (Townsend et al. 2001). However, clearly the quantity and quality of particular loads are affected by a variety of factors, including the activity being performed (construction, demolition, renovation, or repair), the methods used, the target structure type (residential, commercial, industrial building, road, or bridge) and size (Low-rise or high-rise), whether work involves interior or exterior building components, (Curro 1991; US EPA 1995), the timeline of the project, and the contractor practices (US EPA 1995).

Construction debris, the scraps produced from over purchase or cutting of virgin materials, are the smallest fraction (by weight) of C&D waste streams (US EPA 2011a). Residential debris contains cardboard, wood crates, wood and metal stud trimmings, wire scraps, pipe scraps, drywall leftovers, and pieces of carpet, tiles, temporary construction materials, dust, and other general trash (Curro 1991).

Demolition debris (typically wood, concrete, and drywall), on the other hand, is the most prevalent component in the C&D waste. Interior demolition debris includes gypsum drywall, wood studs, steel studs, doors, lighting fixtures, wires, plumbing fixtures, pipes, ceiling tiles, furniture, carpeting, dust, and general trash (US EPA 2011a). Exterior demolition debris is generated during structural dismantling, deconstruction, or demolition and includes pallets, damaged or cut concrete blocks, damaged or cut bricks, soil pipes, conduit pipes, roofing materials, siding materials, soil, landscaping materials, windows, doors, and temporary construction materials (Curro 1991). Demolition debris reflects the building trends of the past; construction materials used 40 years ago are today’s demolition debris (Sandler 2003). Because they are so widely viewed as “wastes”, C&D materials are often contaminated with hazardous materials, including the empty containers from use of such materials. Waste oils, greases, machine fluids, batteries and treated lumber can all be found mixed with C&D waste streams (US EPA 1995).

2.2 C&D Landfill

2.2.1 Regulations

C&D wastes management is not governed by the federal Resource Conservation and Recovery Act (RCRA) for hazardous waste nor by RCRA for municipal solid waste. As a consequence, the debris from construction and demolition activities is not subject to federal management criteria (Tchobanoglous 2002). However, once they are targeted to be landfilled, they subject to regulation 40 CFR part 257 and part 258 of Subtitle D of RCRA. It is left to the discretion of each state to set the requirements for C&D landfills, and some require liners for environmental protection against leachate migration into groundwater (Tchobanoglous 2002). States can also apply specific C&D landfill restrictions as long as they are consistent with 40 CFR Part 258 (US EPA 1995). Most states require a permit for the design, operation, post-closure, financial assurance and sitting of a C&D landfill. Such landfills have to be set away from airports, wetlands, floodplains, ground and surface water, endangered species habitats, seismic zones, and unstable zones, and there are a variety of other restrictions that are applied (US EPA 1995). Tipping fees at C&D landfills tend to be lower than at MSW landfills because the cost of developing C&D landfills and the liabilities associated with them are lower than those of MSW landfills (US EPA 2004).

Half of U.S. states have completely banned all hazardous waste from being disposed in a C&D landfill (US EPA 1995), yet even in these states, there can be exceptions for small quantity generators. Construction and demolition companies gathering less than 220 lbs. per month of hazardous waste are classified as Conditionally Exempt Small Quantity Generators (CESQG), and they are exempt from most of the hazardous waste regulations (US EPA 2004). As a result, C&D waste such as old lead pipe, used oil, toxic paints, solvents, and asbestos based materials, considered hazardous waste, can still be found in C&D landfills.

2.2.2 C&D Landfill in the U.S and in N.C.

In 1994, it was estimated that 1,889 C&D landfills were active in the U.S (US EPA 1994), but in 2004 this number had dropped 17% to only 1,571 (Simmons et al. 2006). This national trend was also evident in North Carolina, where the number of registered C&D landfills fell from 153 in 1994 to only 94 in 2010, a 39% decline over 15 years (US EPA 1994; NC DENR 2010). In recent years, states have encouraged the recycling of C&D waste resulting in the decrease of C&D landfills (Bricker 2011). In the case of the North Carolina, C&D waste generation rate have also fall down due to the effect of the economy on construction activities. Moreover, in North Carolina, C&D waste can be disposed in MSW landfill decreasing the need to C&D landfill (NC DENR 2012).

2.3 C&D Waste Generation

2.3.1 Amount of C&D Waste in the US

In 2003, approximately 170 million tons of C&D waste were generated in the United States (US EPA 2009), which represents about one third of all waste generated in the US that year. This is typical of most industrialized nations, where as much as 50% of the waste stream is from C&D ativities (Schachermayer et al. 2001). The amount of C&D waste per capita increased from 2.8 lbs per person in 1998 to 3.2 lbs per person in 2003 (US EPA 1998; US EPA 2009). This increase is due to a good economic growth during early 2000, promoting construction activities.

C&D wastes have many origins, adding to the complexity of sorting C&D waste. C&D waste can be classified into construction, renovation, and demolition waste, but each of these categories of C&D can additionally be sorted into residential and non-residential categories (Table 1). Among the 170 million tons of C&D waste produced in 2003, 9% were produced by construction projects, 42% by renovation projects and 49% were produced by demolition projects. (US EPA 2009; Sandler 2003)

Table 1: C&D waste generated in the U.S. by categories in 2003 (Sandler 2003)

	Residential (10^6 tons)	Non-Residential (10^6 tons)	Sum (10^6 tons)
Construction	10	5	15
Demolition	19	65	84
Renovation	38	33	71
		Total	170

2.3.2 Amount of C&D Waste in North Carolina

North Carolina disposed 2,519,000 tons of C&D waste in 1997; 2,272,967 tons in 2002 (NC DENR 1998); and about 3,500,000 tons in 2007 (Ewandinger 2010). This is an increase of about 100,000 tons over 10 years of C&D waste per year since 1997. Wood, drywall, concrete, and brick represent about 65% of the total C&D waste disposed (Figure 2). The remaining C&D wastes are plastics, cardboard, roofing materials and other wastes.

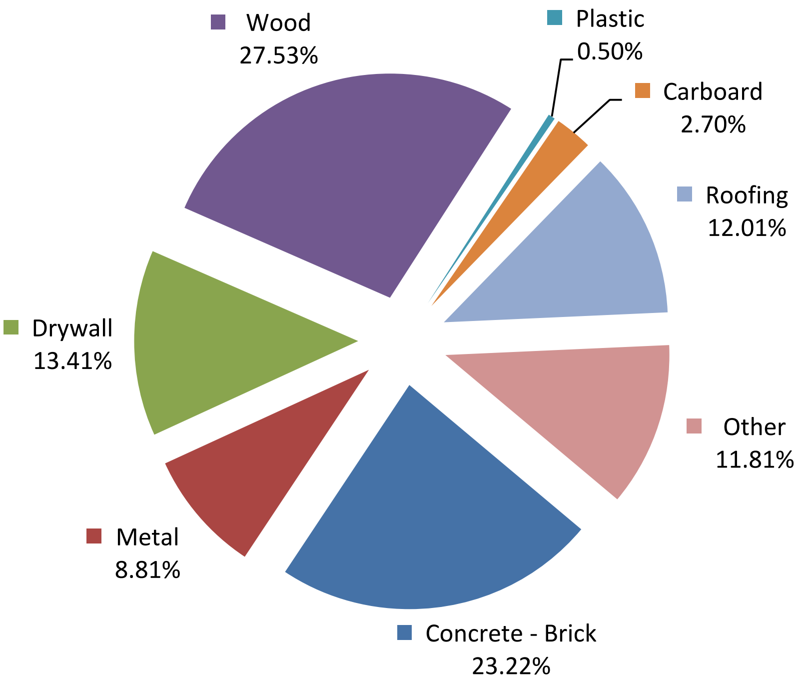


Figure 2: Composition of construction and demolition waste in the state of North Carolina in 1998 (NCDENR 1998).

2.3.3 Amount of C&D Waste in Mecklenburg County

Mecklenburg County disposed 377,120 Tons of C&D waste in 2008 (Talbert 2010). Similar to the trend of North Carolina C&D waste composition, the three main categories of materials disposed in Mecklenburg County are wood, drywall, and concrete and bricks representing also 65% of the waste (Figure 3).

2.4 C&D Waste Recycling Opportunities

There were approximately 3,500 C&D recycling facilities in the United States in 2003. The same year, the US EPA estimated that about 48% of C&D waste materials were recovered (US EPA 2011). Materials that are currently recycled and reused include: wood, cardboard and paper, concrete, asphalt, bricks, drywall, plastic, low grade soil, and metals (steel and non-ferrous). The amount of materials recycled will likely increase over time as C&D landfill tipping fees increase, as mandatory landfill diversion legislation is put into action, and as entrepreneurs find new ways to make recycling profitable (Tchobanoglous 2002).

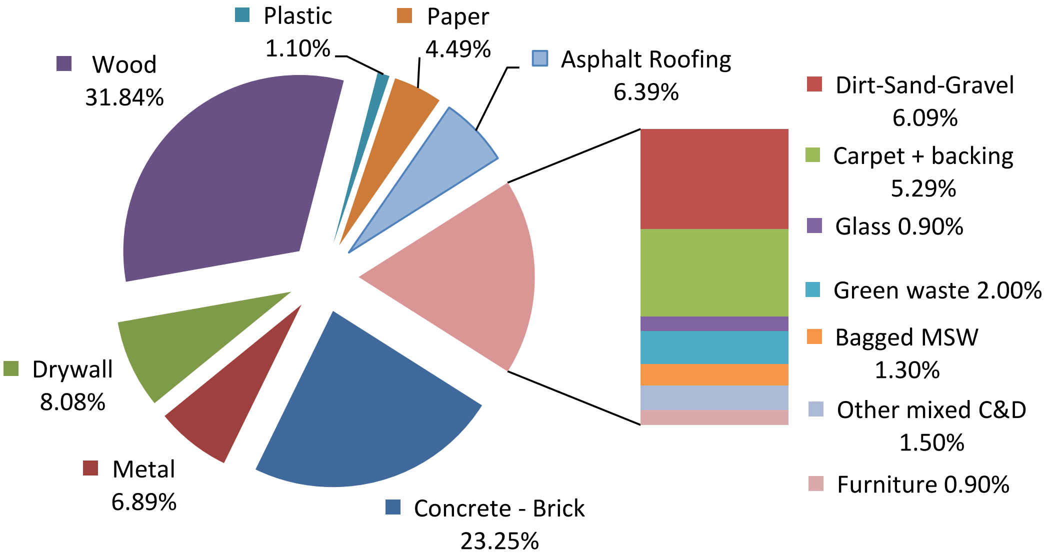


Figure 3: Composition of the C&D waste diposed in Mecklenburg County in 2008 (Talbert 2010)

Contractors are already realizing cost savings from C&D recycling, stimulated by LEED (USGBC 2005) and other certification systems that reward waste sorting and reclamation. Sorted wastes are more valuable, and their deposition with C&D recyclers typically involves lower transportation costs and eliminates landfill tipping fees. (Chandrakanthi et al. 2002). Sorting is particularly important for identifying and removing contaminants, as the kind and degree of contamination are key factors for valuing the materials (Lawson et al. 2001).

While construction debris is mostly virgin material with a high potential resale value, demolition debris typically brings much less revenue because the materials are old, contaminated, and difficult and costly to sort. The economic feasibility of recycling demolition waste depends on the size of the project, with larger projects yielding better prospects for revenue than smaller ones. For example, 22,000 ft^2 of office space was demolished at Central Piedmont Community College in Charlotte N.C. in 2001, and 79% of the demolition debris was recycled. However, the same company will not engage in efforts to recycle materials from smaller projects, because they judge it to be unviable economically (personal communication).

2.4.1 Wood

Wood waste from construction is typically converted to wood chips for use as landscaping bark, mulch, composting bulking agent, animal bedding, or soil amendment (Curro 1991). In 1998, the American Forest and Paper Association located 315 wood processing facilities in the US (US EPA 1998). C&D wood waste is also highly desired as fuel due to its low moisture content (US EPA 1998) and its high BTU value (7,750 to 8,200 btu dry lb^{-1}) (US EPA 2011).

Wood from demolition activities has a lower reuse value than waste wood from construction because of the contaminants it can contain. These include paint, metals, and plastics, which can be tolerated in most modern wood boilers but are problematic when the wood is used for soil amendment or landscaping (Curro 1991). Such wastes also tend to have high heavy metal content (US EPA 1998). Lumber treated for outdoor durability is particularly difficult to recycle because of its heavy metal content. Treated Such wood is generally subjected to chrome, copper and arsenic (CCA wood) to make it resistant to insects, and as a result, it contains high heavy metal concentrations (US EPA 2011b).

Treated wood is consider a hazardous materials and is subject to hazardous waste regulation (US EPA 2004).

2.4.2 Asphalt Shingles

Asphalt shingles are sometimes used as fuel, particularly in cement kilns where the mineral residue after combustion is in turn used in the cement manufacturing process (US EPA 2011). Asphalt shingles are also used as supplement to hot or cold mixes asphalt for paving. However, scrap asphalt shingles from construction activities (virgin material) are usually preferred to scrap asphalt shingles from demolition activities because the latter are not uniform and can be contaminated with other materials (US EPA 1998; Tchobanoglous 2002). Since the supply of used shingles greatly exceeds the amount of waste virgin shingle, there is a continued need for evaluating new uses for this waste stream. An house redoing its 15 ft^2 roof will produce about 6000 lbs. of waste shingles during demolition that will mostly ended up in a landfill (US inspect 2012).

2.4.3 Concrete

Concrete, the heaviest C&D waste component, is typically processed in an impact crusher and screened to produce “recycled aggregate,” which can replace virgin aggregate in concrete production. Such concrete must meet ASTM standard specifications, and concrete made with recycled aggregate is typically less resistant to crushing and impact forces. As a result, recycled aggregates are generally used as base material for sidewalks, driveways, or parking lots but not in structural applications. Larger pieces of waste concrete can be used as riprap on roads and lagoons (US EPA 1998; Tchobanoglous 2002; US EPA 2004).

2.4.4 Asphalt

In 1998, it was estimated that there was more than 1,000 asphalt and concrete crushing facilities processing 50 million tons per year of discarded pavement (US EPA 1998). Processed asphalt pavement can be readily recycled in a cradle-to-cradle or closed loop fashion, and the technology is such that recycling can take place at the site of demolition (called “cold in-place”) (Missouri DOT 2009).

The cold in-place recycled asphalt paving process uses a milling machine, a screening or sizing unit, a mixing unit, and a paver. The milling machine grinds off existing asphalt and passes it on to the screening unit, which sorts the asphalt by size and passes it to the mixing unit. The mixing unit weighs the asphalt emplaced in it and adds an appropriate amount of emulsified liquid asphalt binder. After the binder has been spread uniformly throughout the mix, the mixer will pass the asphalt to a paver unit, which reapplies it to the road (US EPA 2004; Missouri DOT 2009).

2.4.5 Bricks

Concrete, bricks and masonry products are often processed together and used as base materials. In instances, when large amounts of brick are available, it may be recovered and used as landscape stone or in a building façade (Curro 1991). New investigations are exploring the use of brick as aggregate for concrete (Cavalline 2012).

2.4.6 Alternative Daily Cover (ADC)

Construction and demolition wastes can be screened to generate a low grade soil substitute that can be used as alternative daily cover (ADC) in landfills. ADC is highly valued in states that do not have access to large amounts of soil or states that want to reduce the amount of soil dedicated to daily cover. However, this use may become less viable as municipalities press to find alternatives to landfilling (Spencer et al. 2006).

2.4.7 Incineration

The U.S. EPA has strong interest in C&D waste such as plastics and rubber for their "refuse-derived fuel" RDF applications (US EPA 2011). It has been estimated that about 4.7 million tons of C&D waste were burned in 2009 (US EPA 2011). Some contaminated residuals or materials from C&D waste present in small quantities can also be used as a RDF in an incinerator or boiler. However, careful pre-testing is required to ensure that there is no hazard associated with the emissions and that the ash disposal is conducted properly (Curro 1991).

2.4.8 Metals

There are strong markets for ferrous metals, copper, and brass. In 1996, the Steel Recycling Institute estimated that 85% of steel from construction activities, demolition activities, streets, bridges, and highways were recycled (US EPA 1998). Steel is being recycled into new steel and as a result, steel that is sold on the market today is made of 90% recycled content (SRI, 2011). During deconstruction, steel beam can be salvaged and reused for another project, reducing the environmental cost of processing scrap steel into new steel (Winters-Downey, 2010)

2.5 Waste Drywall

2.5.1 Fabrication and Composition

Drywall or gypsum wallboard is made by sandwiching a ¼ to 1 inch thick layer of gypsum ($CaSO_4,2H_2O$) between two thin layers of paper, so that its composition by weight is typically about 90% gypsum, 8% cellulose (as paper), and 2% of starch, crystalline silica, and other components specific to the type of drywall (USG 2011a). Special drywalls contain others materials. Fire retardant drywall has fiberglass embedded in the paper (USG 2011b), while mold resistant drywall has a fungicide and bactericide (USG 2011c).

2.5.2 Waste Drywall Quantity

For the past 40 years, drywall has been heavily relied upon as the material for constructing interior walls (Musick 1992). In 2000, about 1.6 million new homes were built in the US, and most of them used drywall for interior walls (Marvin 2000). As of 2006, annual drywall sales were about 36 million tons in the United States (Founie 2006). In 2006, the world production of gypsum drywall was estimated at 8 billion square meters. Almost half of the drywall was produced in the US, while the rest was made in Asia and Western Europe. The rapid economic development occurring in India and China is expected to further increase drywall production over the next decade (Founie 2006).

Nationally, drywall averaged only 5-15% of C&D waste (Sandler 2003). In 2002, renovation projects produced more drywall waste (11.3 million tons) than construction (1.7 million tons) or demolition (1.0 million tons) (Table 2). However, demolition activities will produce an increasing amount of drywall in the future due to the increase uses of drywall in the seventies (Sandler 2003).

Table 2: Waste drywall generated in the U.S. in 2002 (Sandler 2003)

Categories	% in the C&D Waste Stream	Amount (10^6 tons y^{-1})
Residential construction	21	1.4
Nonresidential construction	8	0.3
Residential renovation	20	1.8
Nonresidential renovation	34	9.5
Residential demolition	5	1
Nonresidential demolition	0	0

2.5.3 Drywall from Construction

Drywall from construction waste is usually partial pieces of virgin drywall panels that are discarded during a construction project. In general, each square foot of new construction produces between half a pound and one pound of waste virgin drywall (Ewandinger et al. 1998; Gaskin et al. 2002; Wolkowski 2003). This is equivalent to 1980 lbs. of wasted new drywall for the construction of an average home. Clearly, the amount of such discards could be reduced if construction managers planned strategically to do so. Raw material costs, waste transport costs, and landfill tipping fees would all decline as a result. It is estimated that as much as 50-80% of virgin drywall could be reused or recycled (Chandrakanthi et al. 2002).

2.5.4 Drywall from Demolition

Demolition drywall is often contaminated with materials like nails, lead-based paint, and asbestos (especially for houses build before 1970) (NC DENR 1998). Such contamination reduces its potential for some of the easiest reuse options, such as agricultural applications (NERC 2006).

2.5.5 Drywall Related Problems

2.5.5.1 Hydrogen Sulfide Production

In the 1980s, waste gypsum drywall was discarded in landfills as part of the municipal waste stream. However, it became apparent that sulfate reducing bacteria (SRB) were present in the moist, anaerobic, and organic-rich environment of a MSW landfill, generating H_2S gas according to Eq. 1.

$$2CaSO_4 + 4H_2O + organic\ matter \xrightarrow{SRB} 2H_2S + 5CO_2 + CH_4 \qquad (1)$$

There were also metallic sulfides leaching into groundwater as a result of landfilled drywall (Musick 1992a; Townsend et al. 2001). In general, one pound of hydrogen sulfide gas is produced from every four pounds of disposed drywall. This phenomenon is particularly problematic in municipal solid waste landfills, where organic content is high (Tchobanoglous 2002), but it is also occurring in C&D landfills (Lee et al. 2006).

Hydrogen sulfide has a rotten egg smell at concentrations of 0.1-10 parts per million (ppm). Interestingly, it is less odiferous at higher levels but becomes more of a health risk as concentrations increase. It is a human irritant at levels above 10 ppm and can have life threatening effects at 100 ppm (Flynn 1998). Moreover, hydrogen sulfide erodes landfill equipment, corrodes gas recovery equipment, increases SO_x production from flares, and explodes very easily (Flynn 1998; Heguy et al. 2005).

Monitoring at ten Florida C&D landfills revealed varying H_2S levels (3 ppbv - 12,000 ppmv in the soil vapor phase and ambient air around the landfill) as well as the presence of other reduced sulfur compounds (RSCs) such as methyl mercaptan, carbonyl sulfide, and carbon disulfide at each landfill. H_2S was found in higher proportions than the other RSCs. In some case, the ambient H_2S was higher than OSHA and NIOSH worker exposure limits (Lee et al. 2006).

2.5.5.2 Drywall Dust

Waste drywall usually produces dust when it is handled, and the dust can be a health hazard for workers if it contains fiberglass, asphalt wax emulsions, or asbestos (Townsend et al. 2001, NERC 2006).

2.5.5.3 Marketability

Although landfilling waste drywall as C&D waste is no longer considered innocuous or desirable, the economic incentives to divert it are not particularly strong. The factors that influence these economics include tipping fees, transportation costs, separation costs, any processing costs, comparable product costs, and the cost of raw gypsum; also to be factored in, are stakeholders’ motivations (Cochran 2003, Townsend et al. 2001, Marvin 2000). If the cost of raw mined gypsum is low, landfilling waste drywall will be cheaper than to reclaim it.

Incentives and services exist to encourage and help the recycling of drywall and C&D waste in general. Certain building certification programs such as LEED (USGBC 2005) incentivize contractors to sort C&D wastes on-site. When C&D waste are sorted, they are more likely to be recycled than landfilled (Cordeiro 2006). In Florida, specialized service companies exist that will come to a construction site to remove waste drywall. Drywall manufacturing companies such as Union Gypsum in Charlotte, NC are offering lower tipping fees for drywall ($20 per ton) than the local C&D landfill ($25 to $30 per ton). These services and incentives have improved the economics of drywall capture (Townsend et al. 2001).

2.5.6 Waste Drywall Collection

Although C&D waste collection sites exist where drywall and other waste streams can be recovered transport fees and contamination rates are high. On-site sorting where construction is occurring is most economical and stationary compactors are available that can box more than twice the capacity of conventional open containers and protects drywall from rain (Ewandinger et al. 1998). The number of pulls to empty the containers on the site can compete with the low tipping fees of landfilling (Ewandinger et al. 1998). On site collection requires more effort but yields a purer final product with a higher market value (Cochran 2003).

2.5.7 Drywall Recycling Opportunities

Waste virgin drywall can be reused in construction project when an entire panel can be saved. If so, the panel can be donated to nonprofit organization to build affordable houses (in the case the drywall sheets are either half size or larger). Ground drywall is also used as a soil amendment for home gardening, on golf courses, in horticulture applications, in city parks and recreational facilities, in forestry, and for mine reclamation. It is also used as an absorbent for spills, animal wastes, and cat litter products (Ewandinger at al. 1998, NWR 2013). If the calcium sulfate is pure enough, it can be used for industrial applications related to food production and glass, paper, and pharmaceutical manufacture (Wyatt et al. 1992; Founie 2006; Cordeiro 2006).

2.5.7.1 Recycled as New Drywall

The economic feasibility of recycling drywall into new drywall depends mainly on the regional demand for gypsum drywall and the cost of gypsum ore (Marvin 2000; Townsend et al. 2001). In this case, the crushed waste drywall should be low in contamination (moisture and paper) (Cochran 2003). If the gypsum powder is pure enough, it is blended with raw gypsum and used to produce new drywall. The paper layer is often recycled and reused in the fabrication of gypsum drywall (Musick 1992a), or used in the fabrication of office paper (Codeira 2006).

2.5.7.2 Recycling Opportunity of National Gypsum

National Gypsum Company has a recycling program for waste virgin drywall. The company takes back waste drywall from construction activities and uses it as raw material for new drywall and as soil amendment for agricultural uses. The National Gypsum Company plant in New England, with the help of a third-party processor, collects and processes construction drywall into a fine powder. This fine powder is then used for the fabrication of new drywall representing up to 10% of National Gypsum Company production at the New England plant. In a similar fashion, the National Gypsum Company plant near San Francisco collects construction drywall and grinds it for agricultural uses (National Gypsum 2011). Recycled calcium sulfate from waste gypsum could be a competitive option to virgin gypsum ore (Ewandinger et al. 1998). In addition of these recycling programs, the company has an internal recycling program at their plants. The drywall scrap produced during the fabrication of new drywall is reused into the production chain for the fabrication of new drywall (National Gypsum 2011).

2.5.7.3 On Site Reuse of Waste Drywall

Collection costs, transportation costs, and landfill tipping fees can be a significant expense for a contractor. In order to reduce these costs, the drywall can be crushed on site and used as soil amendment on the land surrounding the construction site (Marvin 2000). Marvin (2000) suggests that pulverized drywall should be spread evenly on a soil with good drainage and good aeration to avoid hydrogen sulfide formation. Gaskin et al. (2002) established a guideline for onsite land application of scrap drywall taking into account the size of the house and the size of the surrounding land (Table 3). This practice requires a portable grinder and small applicator, adding to the processing cost (Cochran

2003) but it eliminates collection costs, transportation costs, and landfilling fees. A similar recycling technique is currently used for wood debris which is processed into mulch and applied on site (Block 2000).

Table 3: Guidelines to calculate area needed for on-site reuse of scrap drywall[1] (Gaskin et al. 2002)

House Size (ft^2)	Scrap Drywall (lbs.)	Area Needed for Application (ft^2)	(acre)
1,500	2,250	9,000	0.20
2,000	3,000	12,000	0.30
2,500	3,750	15,000	0.35
3,000	4,500	18,000	0.40
3,500	5,250	21,000	0.50
4,000	6,000	24,000	0.55

[1] Assumes typical application rate of 250 lbs/1000 ft^2

2.5.7.4 Waste Drywall in Cement Manufacturing

Gypsum ore is used in new cement (about 10%) to control the set time. Crushed calcium sulfate from waste drywall can be used in place of virgin ore if the reclaimed material has low paper content and low moisture content (Marvin 2000, Cochran 2003, Corderio 2006).

2.5.7.5 Waste Drywall in Animal Litter

Waste drywall alone or in combination with wood chips (to avoid dust production) has been used as litter material for cows and chickens because it reduces foot problems, increases udder health of cows (Marvin 2000). Wyatt et al. (1992) showed that it is also a good litter material for chickens because of the gypsum capacity to absorb and release moisture.

2.5.7.6 Waste Drywall as Soil Enhancer

Gypsum amendment improves some physical and chemical properties of certain soils. Calcium ions promote flocculation of clay particles (USA gypsum 2009), which increases water and air penetration as well as drainage (Marvin 2000). The increased water penetration capacity can reduce water runoff and erosion, and enhance slope stabilization (Nadler et al. 1986; Sumner 1993; Block 2000; Founie 2006; USA gypsum 2009). Soil dispersion was reduced and crop establishment was enhanced when gypsum was used on massive brown and grey soils (Jarwal et al. 2001). Likewise, soil crusting was reduced when gypsum was surface applied to California San Joaquin Valley soil; crust strength declined an average of 24% and soil aggregation increased 46%. Additionally, Composts lacking sufficient calcium or sulfate can benefit from the addition of calcium sulfate from waste drywall, but if there are anaerobic regions in the pile, hydrogen sulfide can be produced (Marvin 2000).

2.5.7.7 Waste Drywall to Reclaim Sodic Soil

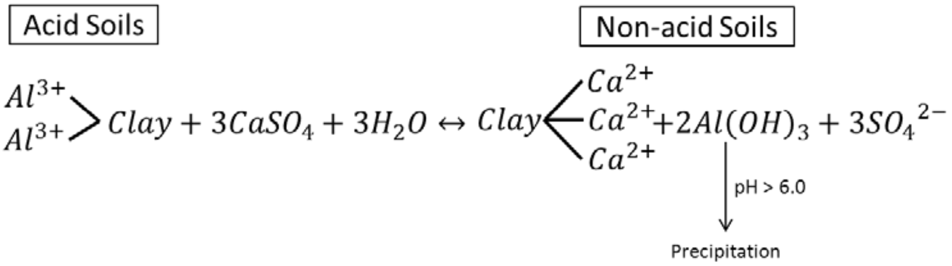
Sodic soils are those with high sodium content. They drain poorly, so that they are either too wet or too dry for the establishment of vegetation (Franzen et al. 2006). Calcium ions from gypsum application have the ability to replace sodium ions attached to clay soil particles (Eq. 2) (Rengel 2002), and the sodium can then be flushed out by rain water.

$$\left.\begin{matrix}Na^{+}\\ Na^{+}\end{matrix}\right> Clay + CaSO_4 \leftrightarrow Clay{-}Ca^{2+} + \underset{\text{Leached}}{\underset{\downarrow}{2Na^{+}}} + {SO_4}^{2-} \qquad (2)$$

Such sodium displacement increases soil drainage and reduces swelling and cracking, so that seed emergence improves (Sumner 1993; USA gypsum 2009). A gypsum application rate of 1-3 tons acre^{-1} is sufficient to treat sodic soil (Ron 2003), although high rates of gypsum (27 tons acre^{-1}) tilled three feet deep yielded very marked reductions in soil sodium saturation relative to lower gypsum application rates (10 tons acre^{-1}) tilled in at a shallower depth (Franzen et al. 2006).

2.5.7.8 Waste Drywall for Red Mud Reclamation

Red mud is a soil residue from the aluminum industry that is characterized by many aluminum ions attached to soil clay particles and a low soil pH. Application of gypsum to such soils provides calcium ions that replace the aluminum, allowing the latter to precipitate as aluminum hydroxide (Eq. 3) (Smith et al. 1994; Block 2000; Rengel 2002).



$$\left.\begin{matrix}Al^{3+}\\Al^{3+}\end{matrix}\right> Clay + 3CaSO_4 + 3H_2O \leftrightarrow Clay\left<\begin{matrix}Ca^{2+}\\Ca^{2+}\\Ca^{2+}\end{matrix}\right. + 2Al(OH)_3 + 3SO_4{}^{2-} \qquad (3)$$

The pH must be greater than six for the precipitation to occur, but if it is successful, soil exchangeable Al can be decreased by 10 to 20% (Liu et al.2001) with this method. Wong et al. (1991) used gypsum and sewage sludge amendments to revegetate red mud (Wong et al. 1993) and found that the amendments improved both the soil structure and hydraulic properties of red mud as it leached aluminum and sodium concentrations. (Wong et al.1991).

2.5.7.9 Waste Drywall as pH Enhancer

Typically the addition of gypsum causes little to no soil pH change (Burger 1993, Scott et al. 1993; Smith et al.1994). Even copious amounts of gypsum application to soil yielded only slight (0.2-0.7) declines due to the release of hydrogen ions from the clay surface replaced by calcium ions (Wolkowski 2000; Liu et al. 2001; Wolkowski 2003; Wolkowski 2009). There are a few instances when gypsum addition will significantly influence pH. When soil has a high pH (>8.4) due to the presence of sodium carbonate, a gypsum addition will lower the pH as sodium carbonate is converted to sodium sulfate (Franzen et al. 2006). Red mud with an initial pH of 10.6 and sodic soil with a starting pH of 9 both showed pH declines after gypsum addition. The change is not due to sulfuric acid formation but to hydrogen ion displaced from the clay and released into the soil solution (Wong et al. 1993; Wolkowski 2003; USA gypsum 2009). Soils, whose pH is lower than 4.5 will see their pH increased by the addition of gypsum (Franzen et al. 2006). Barnard (1989) observed that an addition of two tons per hectare of gypsum in an orchard soil slightly increase the pH of the top soil.

2.6 Gypsum

The Greeks used gypsum to amend soil, and its modern use can be traced back to 1768 in Switzerland, when an experiment showed that its application increased clover yields (Tabatabai 1984). Today, the use of nitrogen fertilizer containing little to no sulfur, the decrease of pesticide containing sulfur, and the decrease of atmospheric sulfur due to increasing stringent law on coal power plant, accentuate the need for a sulfur amendment in crop cultivation (Tabatabai 1985; Scherer 2001). Consequently, gypsum is the most used sulfur fertilizer in the American agriculture and 357,000 tonnes were used in the US in 2010 (USGS 2012).

Overall, gypsum application results in increased yields of several plants, including alliums, almonds, barley, citrus, coffee, cranberries, desert salt grass, ginseng, grapes, lawns, marsh vegetation, papaw, peanuts, tomatoes, raspberries, sugarcane, cabbage, broccoli, cauliflower, radishes, turnips, kale, onions, and wheat (Sumner 1993; Townsend et al. 2001; NWR 2013). Sumner (1993) and Toma et al. (2005) suggest that crop yield increases are likely due to increased Ca^{2+} and to detoxification of the soil (see sec 2.5.7.7 and 2.5.7.8). Gypsum may also improve crop yields by improving soil texture before tillage (see sec 2.5.7.6) and helping seed emergence (USA gypsum 2009; Chen et al. 2011).

2.6.1 Gypsum and Drywall Elemental Composition

Ground drywall contains about 21.9% calcium, 18.1% sulfur, 0.2 % magnesium, with small amounts of boron, iron, manganese and phosphorus (Table 4). The latter have the potential to provide plant micro-nutrient demands (USA gypsum 2009). Ground drywall nutrient levels are comparable to those found in FDG (flue gas desulfurized) gypsum and gypsum ore.

Surface application of gypsum increases the exchangeable calcium (Toma et al. 2005, Liu et al. 2001) and sulfate (Nadler et al 1986) throughout the entire soil profile because gypsum is highly soluble (0.264g / 100ml) (Musson et al. 2008). The average concentration of calcium in soil is 10g kg^{-1} (1,000 ppm) or 0.1% (Rengel 2002). Two percent gypsum in soil favors plant growth, gypsum addition to 2-25% has little or no negative effect on plants. It is only when gypsum levels exceed 25% that significant reductions in plant yields occur, and they are likely due to imbalances in K:Ca and Mg:Ca ratios that occur (FAO, 1990).

Table 4: Macro and micro-nutrients concentrations from different gypsum sources (Dontsova et al. 2005)

	Units	FDG Gypsum	Gypsum Ore	Drywall
Calcium	%	23	19.1	21.9
Magnesium	%	0.03	1.35	0.22
Sulfur	%	18.7	15.1	18.1
Boron	ppm	26.7	9.4	7.3
Iron	ppm	264	1045	547
Manganese	ppm	5.5	14.6	9.4
Phosphorus	ppm	16.7	30.6	51.6

Gypsum benefits extend beyond nutrition to include enhanced soil aggregation and hydraulic conductivity. As a result there is less resistance to root penetration and greater, root proliferation (Wong et al. 1991; Sumner 1993; Block 2000). The young roots may have easier access to nutrients, especially nitrogen (USA gypsum 2009).

2.6.2 Benefit of Calcium

Calcium plays an essential role in cell division cellular membrane formation, (Wolkowski 2003; White et al. 2003). Calcium strengthens the cell wall rigidity by forming cross-links within the pectin polysaccharide matrix (Easterwood 2002). It contributes to nutrient uptake processes by stimulating the protein channels of the root (White et al. 2003). It also influences fruit quality and the way plants respond to environmental and disease stresses because plant pectin levels is changed (USA gypsum 2009; Patterson 2013). However, Excessive calcium levels in soil can prevent seed germination and stunt plant growth (White et al. 2003).

Plants vary in their responses to calcium and in the amount of calcium they retain. Dry weight calcium loads range from 0.1 to 5 g of calcium per 100g of dry weight (White et al. 2003). Some plants are calcifuges, grow at low calcium concentrations, and are not stimulated by calcium additions but are rather inhibited by high calcium doses. Conversely, some plants are calcicoles and contain high calcium levels and are stimulated by calcium additions to soil. These plants include the Crassulaceae (stonecrop), Brassicaceae (broccoli) and Fabaceae (soybean, pea) (Rengel 2002; White et al. 2003).

2.6.3 Benefit of Sulfur

Sulfur is considered the fourth most important element for proper plant cultivation after N, P, and K. It is typically absorbed by plant roots as sulfate (SO_4^{2-}) but occurs in the soil as organic sulfur (a sulfate ester or other carbon-bond sulfur) that must be released by microbial activity (Scherer 2001). Sulfur in plants activates enzymes and is important for synthesis of amino acids and proteins, vitamins, and glucocide oils (Tabatarai 1984). Nitrogen and sulfur uptake are often related because they are both necessary for protein synthesis. If sulfur becomes limited, uptake of nitrogen tends to slow (Tabatarai 1984). Hence, sulfur is the limiting soil nutrient in many parts of the world (Scherer 2001). Further, it can be challenging to maintain sulfur availability in soil, because it leaches readily especially if soil is not vegetated. Annual leaching losses in the US can reach about 15 kg S ha^{-1} and additional atmospheric sulfur losses occur as well (Tabatarai 1984).

2.6.4 Soil Elements Lost Due to Gypsum Amendment

Calcium applied to soils decreases the amount of exchangeable aluminum, sodium, (Nadler et al. 1986), potassium, and magnesium that is available on soil binding sites (Burger 1993; Sumner 1993; Caires et al. 2002) because it displaces them, allowing them to leach through the soil along with sulfate ions (Liu et al. 2001).

The leaching of Al and Na can be a positive outcome when the soil is acid (high level of aluminum) or sodic (high level of sodium). However, the leaching of potassium and magnesium is usually not desirable, and Burger (1993) argued that the addition of calcium via ground drywall amendment would reduce the available soil potassium and magnesium levels, requiring fertilizer applications to balance the losses. The University of Wisconsin-Extension expressing similar concerns for sandy soil and medium-textures soil recommended limits of only 2 Mg ha^{-1} and 5 Mg ha^{-1} of gypsum be allowed to sand and silt loam respectively every three to four years (Wolkowski 2003). However, agricultural doses recommended for crops are as high as 4.4 Mg ha^{-1}, just at the limit recommended. Higher dose, such as 22 Mg ha^{-1}, can be recommended but in only specific case where soil are acidic or sodic (Chen et al. 2011)

Concerns about detrimental effects from ground drywall applications proved to be unfounded. Further, it has been shown that there are some additional constituents in drywall beyond those in gypsum and the additions appear to be innocuous or beneficial. On a pound for pound basis, ground drywall contains more potassium, magnesium, phosphorus, iron, and manganese than agricultural gypsum (Gaskin et al. 2002) (Table 5).

Table 5: Constituent comparison of ground wallboard and agricultural gypsum (Gaskin et al. 2002)

Constituent (Lbs./ton)	Ground Wallboard	Agricultural Gypsum
Calcium	444 – 456	534 – 570
Sulfur	320 – 238	402 – 424
Phosphorus	0.4 – 0.6	0.4
Potassium	1	0.1 – 0.2
Magnesium	11	3.0 – 3.8
Iron	4.24 – 4.82	0.94 – 1.61
Manganese	0.2 – 0.3	0.07 – 0.10
Boron	0.03 – 0.04	0.17 – 0.19
Sodium	1.8	1.8 - 20

2.7 Gypsum Uses in Agriculture

2.7.1 Drywall as Agricultural Amendment

Drywall is about 90% gypsum, with the remainder as paper binder. Drywall can be used as an agricultural soil amendment with little interference from the paper fraction, although there is some concern that when surface applied, the lighter paper particles may be subject to wind dispersion (Gaskin et al. 2002; Wolkowski 2003; Cochran 2003). When ground, the particle sizes typically range from powder to ½ inch diameter (Cordeira 2006, Dontsova et al. 2005), and a wet lime spreader is suitable for spreading it on soil (Dontsova et al. 2005). Among the few studies investigating construction drywall as a soil amendment, one showed it to be equivalent to agricultural gypsum for achieving a 25% yield increase in corm (Burger 1993), and another saw no difference in drywall and agricultural gypsum performance on alfalfa and potato crops (Wolkowski 2003).

2.7.2 Gypsum as a Replacement for Lime

Gypsum is often compared to lime as a source of calcium. However, gypsum-sourced calcium tends to migrate deeper into the subsoil than calcium from lime (Toma et al. 2005). Liu et al. (2001) showed that only 7.6% of the latter moved 10 cm beyond the subsurface, whereas 60% of calcium applied as gypsum moved to that depth. Toma et al. (2005) found gypsum as deep as 80 cm below surface in Andisol after 16 y of surface treatment, and the gypsum was still having beneficial impact on the subsoil exchangeable aluminum. The availability of calcium in the entire soil profile can be beneficial for plants with deep root system.

2.7.3 Effect of Gypsum on Wheat

Although wheat does not have high sulfur demands and typically removes only 15 kg S ha^{-1} (Scherer 2001), there are times when sulfur can be a limiting nutrient and gypsum addition will stimulate wheat production. Jarwal et al. (2001) reported seeing an increase in wheat yield with 2.5 t ha^{-1} of gypsum amendment (relative to controls) when wheat was grown on a sodic soil but no yield increase was observed when wheat was grown on a calcareous soil. Khan et al. 2007 found 66% yield increases with 2 t ha^{-1} gypsum doses, and Rashid et al. 2008 observed that an amendment of 2.5 t ha^{-1} of gypsum during the rainy season in Pakistan increased yields by 46%. The latter results were attributed in part to soil moisture conservation effects of the gypsum. Caires et al. (2002), in a distrophic clay soil, noticed that the optimum gypsum amendment was 8.2 t ha^{-1} with an increase of wheat grain yield by 12%. The distrophic soil lacking in Ca, Mg, K, and Na greatly benefitted from gypsum addition. In a pot study, Brennan et al. (2007) observed an increase in wheat grain yield by 25% increases with only a gypsum amendment of 0.3 t ha^{-1}. The wheat responded positively to such a small rate because the plants were provided with all the necessary nutrients (K, P, S, Cu, and Zn) except calcium, rendering calcium the limiting element.

2.7.4 Effect of Gypsum on Corn and Sunflower

When pulverized regular construction drywall was applied to a corn field at a rate of 24.6 Mg ha^{-1}, the corn yield was 25% greater than that of a control plot and the same as that of a plot similarly amended with agricultural gypsum (Burger 1993). Toma et al. (1999) also observed positive responses from corn dosed with gypsum amendment levels of 10 and 35 t ha^{-1} even after 16 y, which significantly improved corn yields by 29% and

50% respectively relative to unamended controls. Similarly, sunflower yields improve in response to gypsum amendments. When 40 and 60 kg S ha^{-1} were supplied as gypsum, the yields increased 27% and 31%, respectively, relative to controls that were unamended and the gypsum appeared to outperform elemental sulfur dosing (Intodia et al. 1997; Rani et al. 2009). Gypsum amendment surpassed other sulfur amendment sources effect on sunflower (e.g. pyrite, elemental sulfur, lignite fly ash) with respect to plant height leaf area index, seed yield, and stalk yield (Poomurugesan et al. 2008).

2.7.5 Effect of Gypsum on Grass

Gypsum has proved to be a beneficial amendment for lawn growth, increasing both grass thickness and root growth. It is a recommended product for fertilizing golf courses (Soil Solution 2011). Kentucky bluegrass and creeping bent grass clippings increased in weight by 22% and 32% respectively when grown in sand amended with gypsum (relative to controls with no gypsum (Soil Solutions 2011)). In a hydroponic setup, tall fescue was grown in media containing different doses of gypsum. The root mass of tall fescue was significantly affected by gypsum and almost doubled when compare to a control with no gypsum (Kruse et al. 2009). However, Wood (2008) used ground scrap drywall as a soil amendment for tall fescue grass. The drywall amendment resulted in no change in grass growth compare to the control treatment. The non-effect of such amendment was not correlated to the use of ground drywall but to the extremely high dose used in the experimentation and the rough climatic conditions.

2.7.6 Effect of Gypsum on Canola

A number of plants, including cabbage, cauliflower, kale, turnips, radishes, asparagus, alfalfa, and canola have a high demand for sulfur. Canola is of particular interest because it is used as a seed oil crop to make biodiesel fuel. Canola is the result of several years of rapeseed breeding done in Canada. The consequent breeding produces a rapeseed plant better suited for oil production. The US adopted this new rapeseed as canola, a contraction of Canada and oil (US Canola Association 2012). The relative degree of sulfur demand among Canola varieties depends on the proteins synthesized and the growth stage of the plant (Tabatarai 1984; Scherer 2001; Atkinson et al. 2006). Some canola plants can uptake 30 kg S ha^{-1} of soil (Scherer 2001). This makes it a synergistic target for waste gypsum drywall.

Canola plots amended with 0 to 10 t ha^{-1} gypsum doses yielded an average of 60% more seeds than control plots (Jarwal et al. 2001). Similarly, Bora (1997) showed that the application of gypsum at 20 kg S ha^{-1} and 40 kg S ha^{-1} significantly increase seed yield, seed oil content, and oil yield compared to a control by 7 and 14% respectively. Ahmad et al. (2005) showed that the fertilization timing was also important. The application of gypsum in split doses (50% at planting, 25% at vegetative, and 25% at flowering stage) resulted in a higher biomass accumulation, larger leaves, and higher seed yield that the same dose applied at once. In greenhouse trials, Brennan et al. (2007) observed a large increase of shoot yield and grain yield of canola exposed to gypsum. However, two different varieties of canola had different responses. In general a gypsum dose between 20 and 60 kg S ha^{-1} is enough to observe a positive response in canola growth.

In several studies, the response of canola to sulfur was compared when different sources of sulfur were applied. Canola yields were higher when sulfur was supplied as gypsum rather than as ammonium sulfate, ammonium thiosulfate, and elemental sulfur

(Swan et al. 1986; Withers et al. 1994; Wen et al. 2008). In some cases, ammonium sulfate outperformed gypsum (Withers et al. 1994). Bora (1997) compared two classic soil amendments: lime and gypsum. He observed that the gypsum amendment significantly yields more oil than lime amendment due to the addition of sulfur from the gypsum. Bora argued that the sulfate provided by gypsum was the key to the better yield. This is in line with the fact that canola is highly responsive to sulfur amendment rather than calcium amendments.

2.7.7 Biofuel Production Using Canola

Biofuel is an emerging alternative to regular diesel and has numerous advantages. Cars using biofuel have emissions with lower content of carbon monoxide, particles, and hydrocarbons and similar level of NO_x than regular diesel emissions. Biofuel contains almost no sulfur and consequently sulfur emissions are greatly reduced (0.29 % for conventional diesel against 0.005% for biodiesel). Moreover, biodiesel is biodegradable (Van dyne et al. 1993).

Canola is grown for the production of cooking oil and biofuel. It has been specifically grown for its biofuel potential since 1986. In 2003, there were 1,500,000 acres of canola grown in the US resulting in 187,500,000 gallons of oil produced (canola yield is between 110 and 145 gal acre^{-1}) (Atkinson et al. 2006).

Canola is usually preferred to soybean for biofuel production for several reasons. Canola has twice the oil yield per acre than soybean. Biodiesel from canola oil has a better cold flow property and higher cetane number than biodiesel from soybeans oil allowing biodiesel from canola oil to run engines quieter and at lower temperature (Atkinson et al. 2006, Myers 2002). Moreover, the co-product of canola oil production can be used as high quality protein and glycerin product for feed stock (Van dyne et al. 1993).

2.7.8 Potential Toxicity of Drywall in Soil

The material safety data sheets of one manufacturer's (USG Company) regular drywall, fire-resistant drywall (type X fire code), and mold resistant drywall (Mold Tough ™ gypsum panels) describe these products as having "no adverse impacts on ecology" (USG 2011b, USG 2011c). However, this part of the MSDS refers only to the calcium sulfate constituent of the drywall and not any potential chemical added such as sodium pyrithione or fiberglass. USG Sheetrock® Mold Tough ™ gypsum panels contains about 2% of sodium pyrithione, which could potentially harm plants (USG 2011c). Sodium pyrithione is classified as a fungicide and bactericide agent. USG has completed field amendment testing using this mold resistant drywall and concluded that sodium pyrithione was a poor pesticide (USG 2007). Moreover, the US EPA has approved its use in drywall (USG 2011c). In his use of regular gypsum drywall as soil amendment for corn, Burger (1993) worried that the use of wallboard type X containing fiberglass as soil amendment could have a negative impact. However, Wolkowski (2001) showed that crushed type X wallboard mixed with soil does not have a negative impact on living organisms such as earthworms. Gypsum also contained micro-nutrients and metals. Dontsova et al. (2005) compared different sources of gypsum for their metal concentration with the US EPA biosolids limits (Table 6). Dontsova et al. (2005) compared synthetic gypsum (gypsum from the flue gas desulfurization of coal plant), gypsum ore, and gypsum from drywall. The major differences between these three sources of gypsum are that gypsum from drywall contained more mercury and less copper than the over sources of gypsum.

Table 6: Trace metal content of different gypsum sources compared with U.S. EPA Part 503 pollutant concentration limits for excellent quality biosolids (Dontsova et al. 2005)

Pollutant (mg kg^{-1})	Synthetic Gypsum	Natural Gypsum	Drywall gypsum	US EPA Part 503
Arsenic	0.56 (0.05)	< 0.52	0.98 (0.11)	41
Cadmium	< 0.48	< 0.48	< 0.48	39
Chromium	1.30 (0.85)	1.38 (0.32)	1.09 (0.09)	1200
Cobalt	< 0.48	0.53 (0.04)	< 0.48	NR
Copper	1.16 (0.66)	1.33 (0.30)	0.95 (0.14)	1500
Lead	0.80 (.30)	2.92 (0.30)	0.70 (0.02)	300
Mercury	< 0.26	< 0.26	< 0.26	17
Molybdenum	0.51 (0.26)	1.28 (0.04)	< 0.24	
Nickel	0.73 (0.18)	1.42 (0.23)	0.83 (0.12)	420
Selenium	5.51 (3.47)	< 1.45	1.85 (0.04)	36
Zinc	3.88 (2.78)	0.91 (0.49)	3.08 (0.45)	2800

Similar to the other sources of gypsum, gypsum from drywall contains several heavy metals including lead, cadmium and mercury. However, each heavy metal concentration is below the U.S. EPA requirement for biosolids land application which does not exclude drywall as soil amendment.

2.8 Waste Drywall Reuse for Carbon Sequestration

2.8.1 Global Warming and Greenhouse Effect

The increase of earth's surface temperature by 0.6 °C since the late nineteenth century and the current temperature rise of 0.17 °C per decade have been linked to the increase of atmospheric greenhouses gases (Lal 2004). Atmospheric levels of greenhouse gases such as methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) have increased since 1750 at a rate of 0.4%, 0.4% and 0.25% per year respectively (Lal 2004) (Table 7).

Table 7: Atmospheric trace gas concentrations since the industrial revolution (Lal 2004).

Gases	Current concentration	Percent Increase since 1750	Current Rate of Increase (% y^{-1})
Carbon dioxide (CO_2)	379 ppm	31	0.4
Methane (CH_4)	1745 ppb	151	0.4
Nitrous oxide (N_2O)	314 ppb	17	0.25

2.8.1.1 Carbon Dioxide

Carbon dioxide is often targeted for greenhouse gas reductions. From 1750 to 2004, atmospheric CO_2 concentrations rose 31% from 280 to 379 ppmv largely due to fossil fuel combustion and land use changes (Lal 2004). In absolute amounts, 240 to 300 Pg (petagram = 10^{15}g) of carbon from fossil fuel combustion and cement production and 81 to 191 Pg of carbon was from land use change, deforestation, biomass burning, agriculture, drainage of wetland, and soil cultivation have been released into the atmosphere since the industrial revolution (Lal 2004).

Table 8: Global and U.S. CO_2 emissions due to fossil fuel combustion (Lal 2004).

Year	Emissions (10^6 tons carbon y^{-1})	
	Global	U.S.
1750	3	-
1800	8	0.007
1850	54	5
1900	534	180
1950	1630	692
1970	4075	1152
1980	5297	1263
1990	6096	1314
1998	6608	1487

The emissions of carbon dioxide from fossil fuel combustion have been increasing globally (Table 8). Likewise, building energy consumption and transportation are also major sources of urban CO_2 emissions (Dahkal 2010). It is estimated that urban sources contributed 71% of global CO_2 emissions in 2006 and this will rise to 76% in 2030 (Dhakal 2010). In the US, urban areas were responsible for 80% of the CO_2 emitted in 2006, and globally, as the population increases and there is migration from rural to urban areas, this number is expected to rise (Dhakal 2010).

Modern agricultural methods, while highly successful at increasing yields, have often done so at the expense of depleting soil organic matter. In the range of 66-90 Pg of carbon release from soil to the atmosphere is attributed to changing agricultural practices since the industrial revolution (Lal 2004). Such depletion of soil organic matter is expected to continue and even intensify due to the temperature sensitivity of the soil carbon cycle. Increases in temperature will create feedback loops whereby greater releases of carbon dioxide from the soil will occur, further contributing to the problem (Johnston et al. 2004).

2.8.1.2 Methane

Methane, together with nitrous oxide, is responsible for 37% of the greenhouse effect (Gillett et al. 2010). Methane has increased from 700 to 1774 ppbv between the years 1750 and 2004 and it is still increasing at the rate of 11 ppb y^{-1} (Foster et al. 2007). Anthropogenic methane emissions are responsible for about 60% of the total atmospheric methane emissions (Solomon et al. 2007). Anthropogenic methane sources include agriculture, natural gas distribution, landfills, livestock, waste treatment, and fossil fuel combustion (Foster et al. 2007; Solomon et al. 2007). It is estimated that 7-14% of anthropogenic methane emissions are from urban areas (Dhakal 2010). Since methane absorbs terrestrial infrared radiation 25 times more effectively than carbon dioxide

(Lelieved et al. 1993), it is sometimes more efficient and less expensive to plan a multi-gas mitigation strategy rather than to mitigate only CO_2 (Gillett et al. 2010).

2.8.2 Active Carbon Sequestration

The scientific community considers it unequivocal that anthropogenic emissions of greenhouse gases are responsible for the increasing temperature of the earth (Lal 2004), and strategies for addressing climate changes have taken two paths. The first is adaptation – how to cope with the changes occurring. The second path is mitigation – how to stop continued rises in greenhouse gas concentrations in the atmosphere. To date, only few viable mitigation options are available, although many research avenues are being investigated. The main categories of mitigation approaches include: (i) improving the energy efficiency of machines; (ii) switching from fossil fuel to renewable energy; and (iii) using carbon sequestration techniques (Abu-Khader 2006). Carbon sequestration methods can be classified either as active or passive. Active carbon sequestration techniques involve engineered systems that capture carbon. Passive carbon sequestration methods are natural carbon sequestration processes.

Active carbon sequestration methods are often linked to coal-fired power plants, and they can be chemically, physically or biologically based. Chemical absorbents such as amine solutions, limestone, lime, and sulfur dioxide are effective in capturing carbon dioxide. However, the regeneration of the chemical absorbents is an endothermic reaction, consuming energy and reducing the net output power of the plant (Abu-Khader 2006). More recently, chemicals such as polystyrene-bound diethanolamine based ionic liquids and polyethylenimine (PEI) are being tested for their high CO_2 absorption capacity (Schuette et al. 2006; Chen et al. 2012)

Physical methods such as nano-porous absorbents act as molecular baskets to capture CO_2 in the condensed form. Membrane separation technology is also used to capture carbon dioxide from exhaust gases using membranes and vacuum pumps (Abu-khader 2006). Biological methods use special enzymes in a CO_2 scrubber. The enzyme carbonic anhydrase accelerates the hydrolysis of carbon dioxide, which is then fixed into stable mineral carbonates (Abu-Khader 2006).

The burying of carbon dioxide underground or in the ocean is another method being proposed for active carbon sequestration. Of course, the method presumes that favorable conditions would and could be sustained for millions of years. Deep ocean storage is particularly favored as a source of highly unsaturated water into which low purity CO_2 dissolved into shallow sea water would be transported. The gas can also be injected directly at 500m deep (Abu-Khader 2006). The storage of carbon dioxide underground in porous reservoir rocks is technically feasible but not yet practiced (Abu-khader 2006). Carbon could also be stored as carbonate mineral by having CO_2 react with calcium and magnesium to form carbonate minerals for a long-term sequestration in gas reservoirs and oil fields (Matter et al. 2009).

Stolaroff et al. (2005) investigated the use of fine droplets of steel slag and concrete waste ($Ca(OH)_2$ and CaO) dissolved in water to react with and capture atmospheric CO_2. The reaction would generate calcium carbonate as a stable solid. After modeling several possible methods of sequestration, Stolaroff estimated that as of 2005, the cost of such sequestration would be $8/ton of CO_2 (Stolaroff et al. 2005).

2.8.3 Passive Carbon Sequestration – Carbon Pool

The Earth’s carbon content is distributed among several pools, the largest of which is the oceans with about 40,000 Pg (Figure 4), 38,000 Pg are stored in intermediate and deep ocean depths and 1,020 Pg are stored near the surface. The ocean carbon is apportioned as dissolved organic carbon (700 Pg); surface sediment (150 Pg); and marine biota (3 Pg).

The second largest carbon pool is the geological pool, which contains 5000 Pg. Within the geological carbon pool, 4000 Pg is coal; 500 Pg is oil; and 500 Pg is gas. The surface soil of the planet contains about 2300 Pg of carbon: 1,550 Pg as soil organic carbon (SOC) and 748 Pg as soil inorganic carbon (SIC). The rest of the carbon is divided between the atmosphere (750 Pg) and the biotic pool (610 Pg) (Batjes 1996; Lal 2002; Lal 2004; Kumar et al. 2006).

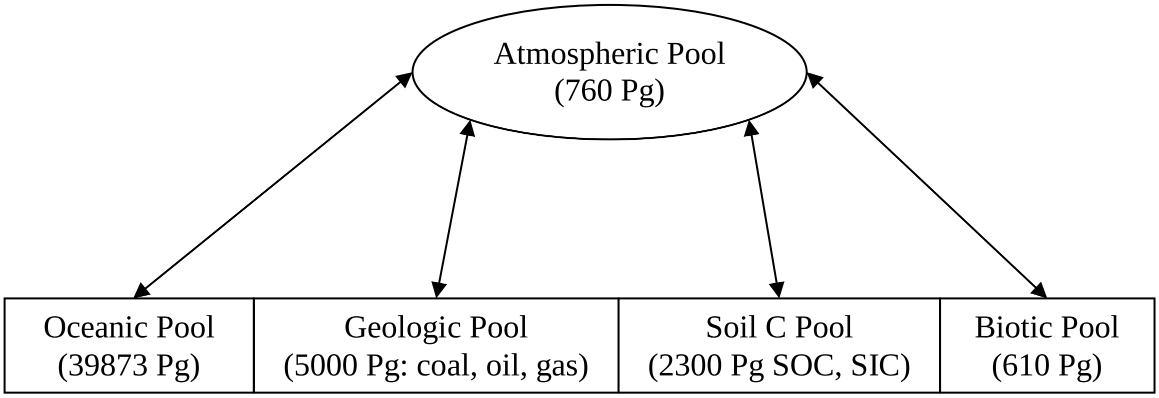


Figure 4: Earth’s carbon pool ecosystems

Carbon is constantly exchanged between the terrestrial pools and the atmosphere. The ocean pool takes up about 2 Pg of carbon from the atmospheric carbon pool every year (Lal 2004). The carbon exchange is particularly active between the soil carbon pool, the biotic pool, and the atmospheric pool. The flux of carbon from the soil to the atmosphere is between 75 and 100 Pg per year. This flux is principally due to soil respiration (plant roots and soil microbial respiration) (Bond-Lamberty et al. 2010). Nearly 10% of the total atmospheric CO_2 passes through the soil each year (Raich et al. 2000), and the average atom of carbon spend 10 years in the vegetation and 35 years in soil organic matter before returning into the atmosphere (Schlesinger 2002). Human activities such as fossil fuel combustion, and deforestation and land uses are responsible for a flux of 6.8 Pg and 1.6 Pg of carbon per year into the atmosphere respectively (Lal 2002). Human activities, such as land uses, also have a strong influence on the return rate of carbon atom. Agricultural irrigation has a negative impact on soil inorganic carbon accumulation. Moreover, acid rain due to human activities, lower the soil inorganic carbon pool by dissolving soil carbonates resulting in the production of carbon dioxide (Schlesinger 2002).

2.8.4 Soil Organic Carbon

2.8.4.1 Organic Carbon

Up to 8% of soil (by weight) is organic matter, depending on climate and vegetation types (Kumar et al. 2006). Plants, trees, and crops add carbon to the SOC pool by leaf deposition, and incorporation of other plant parts or crop residues (Kuzyakov et al. 2000). Moreover, during a plant's life, up to 50% of the carbon fixed through photosynthesis makes its way below ground as root exudate, root respiration, or through root decay (Rees et al. 2005) (Figure 5). About a ton of soil organic matter is generated for every 3.7 tons of atmospheric CO_2 taken up by plants (Kumar et al. 2006).

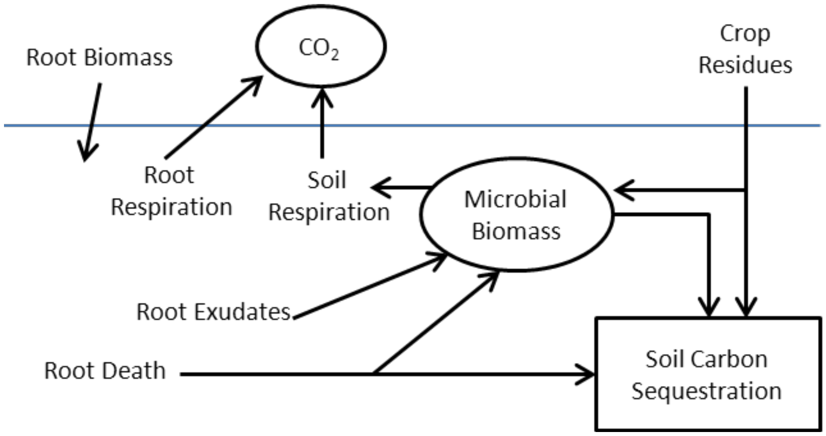


Figure 5: Carbon sequestration in soil via plant roots (Kumar et al. 2006)

The soil organic pool is sensitive and can quickly change due to human activities. Human land perturbations introduced through activities such as deforestation, agricultural practices, biomass burning, and wetland drainage are decreasing the SOC pools and increasing soil CO_2 emissions (Lal 2004).

2.8.4.2 Best Management Practices for Organic Carbon Sequestration

Soil management practices aimed at increasing SOC pools have been identified as “best management practices” (BMPs) and include conversion of marginal land into restorative land uses; use of conservation tillage; addition of compost and manure for nutrient recycling; reforestation; and irrigation aimed at proper water table management (Table 9) (Lal 2004). It is estimated that use of such BMPs could lead to sequestration of 50-1000 kg-$ha^{-1}y^{-1}$ of soil carbon (Lal 2004), which equates to 0.6-1.2 Pg-y^{-1} of soil carbon worldwide. These improvements offset about one third of the observed annual increases in atmospheric carbon dioxide (Lal 2004).

If a land management practice reverts from a sustainable to a non-sustainable state, the carbon sequestered will be released back to the atmosphere. As a result, land transformation for carbon sequestration is a good short to medium term method but cannot be considered a permanent solution for carbon storage (Smith 2004).

Table 9: Agricultural practices influencing the organic carbon pool (Lal 2002)

Practices that decrease loss of SOC	Practices that enhance SOC
• Soil erosion control techniques o Conservation tillage o Residue Management o Terrace and contour barriers o Improved cropping systems o Afforestation • Decreasing losses of dissolved organic carbon through leaching	• Improved soil fertility and integrated nutrient management o Nutrient cycling o Application of biosolids • Restoration of degraded soils o Eroded soils o Salt-affected soils • Water table management (drainage and sub-irrigation)

It is an unstable strategy for climate mitigation and cannot perform enough carbon sequestration to balance a continued rise of CO_2 (Schlesinger 2000). Moreover, if the sustainable practice is working, only a certain amount of carbon can be sequestered before the SOC reaches equilibrium (Smith 2004).

2.8.4.3 Modern Tillage Versus Conservative Tillage

Tillage practices have been recognized to greatly influence the soil organic content. Soil conventional tillage increases soil aeration and soil moisture, encouraging the biodegradation degradation of organic matter (Schlesinger 2000). The no-till methods and crop rotation increase the amount of carbon sequestered by modifying the soil physical and biological properties, creating soil aggregate, and slowing the decomposition rate of organic matter (Marland et al. 2004). Marland et al. (2004) studied 67 long-term crop experiments and observed that, on average, the change from conventional tillage to no-till methods resulted in 430 to 710 kg C ha^{-1} y^{-1} of carbon sequestered. Carbon sequestered by change of tillage methods is supposed to reach a maximum 5 to 10 years after the change and reach 0 kg C ha^{-1} y^{-1} after 15 to 20 years when the SOC content reaches equilibrium.

2.8.4.4 Increasing Nitrogen Availability

The use of nitrogen fertilizer could sequester carbon by enhancing vegetative growth (Schlesinger 2000). The application of nitrogen based fertilizer is often recommend to increasing the soil organic matter, especially for land poor in soil organic matter due to cultivation (Schlesinger 2000). However, each plant species have a different C/N ratio, as a result, plant with high C/N ratio such as trees have the potential to sequester more carbon than plants with low C/N ratio (Marland et al. 2004). However, the excess use of nitrogen can have negative effect. While accounting for carbon sequestered, it is important to account for the fabrication, transportation, and application of the nitrogen fertilizers. In conventional tillage cultivation, about 71% of the carbon sequestered is offset by the nitrogen fertilizer itself (Schlesinger 2000). Additionally, an excess use of nitrogen fertilizer is harmful for the environment as nitrogen fertilizer is responsible for N_2O production, a greenhouse gas (Schlesinger 2000).

2.8.5 Soil Inorganic Carbon

Inorganic soil carbon is primarily present as one of several carbonate minerals. Although there are 150 naturally occurring carbonates, 90% of soil carbonates are either calcium carbonate ($CaCO_3$) (also called calcite) or dolomite ($CaMg(CO_3)_2$). Siderite ($FeCO_3$) and ankerite ($Ca(Mg,Fe)(CO_3)_2$) are among the other more common carbonates (Ming 2002). Inorganic soil carbon is emplaced as part of geologic and soil forming factors, which, relative to organic soil carbon fluxes, are slow processes (Batjes 1996).

Table 10: Distribution of inorganic carbon in different earth climate (Wilding et al. 2002)

	Total Carbon		SIC		SIC/TC	SIC/TC
Moisture Conditions	Pg	% Global	Pg	% Global	% Region	% Global
Permafrost	405	16.4	18	1.9	4.4	0.7
Arid	877	35.5	732	77.8	83.5	29.7
Mediterranean	90	3.6	50	5.4	55.6	2.0
Semiarid	471	19.1	134	14.2	28.5	5.5
Humid	539	21.9	4	0.5	0.7	0.2
Perhumid	85	3.4	2	0.2	2.4	0.1
Total	2472	100.0	946	100.0		38.2

Globally, inorganic soil carbon constitutes 38% (697-946 Pg) of the total terrestrial carbon pool (Figure 4) (Batjes 1996; Wilding et al. 2002). The location of these inorganic pools is largely influenced by climate, with arid and semiarid regions claiming 78% and 14% of the total inorganic carbon pool respectively (Table 10).

2.8.5.1 Natural Inorganic Carbon Sequestration

There are two types of carbonates in soil: primary carbonates and secondary carbonates. Primary carbonates have lithogenic or geogenic origins, which mean they were formed from rock material. Secondary carbonates, also called pedogenic carbonates, are formed within the soil. The formation of pedogenic carbonate using carbon from atmospheric origins is considered passive carbon sequestration (Kuzyakov et al. 2006).

Plants play an essential role in transferring atmospheric carbon dioxide into the soil. Root and microbial respiration (also called soil respiration) result in soil CO_2 with carbon atoms that originated from the atmosphere (Figure 5) (Kuzyakov et al. 2006). As the soil CO_2 concentration increases due to plant activity, more CO_2 dissolves in the soil water. During a heavy precipitation, the dissolved CO_2 can migrate down the soil profile to be stored in groundwater (Marland et al. 2004). The dissolved CO_2, in the deep aquifer or in the soil, can react with calcium minerals to form calcium carbonates and be stored for a long period of time (Portier et al. 2005). Clever irrigation management of agricultural crop can lead to soil inorganic carbon sequestration by leaching of dissolved CO_2 into the soil profile or even the groundwater (Lal 2004). In arid and semiarid region, soil inorganic carbon is increased by irrigation and application of gypsum. However, the use of NH_4 fertilizer decreases the soil inorganic carbon content (Suarez 2002).

High soil carbon dioxide concentrations can influence the dissolution of primary carbonates and the formation of secondary carbonates (Kuzyakov et al. 2006). Carbonic acid is formed as CO_2 dissolved in the soil solution resulting in the decrease of the soil pH. As a consequence, primary carbonates dissolved and have the potential to reform into secondary carbonates with the use of atmospheric carbon dioxide, sequestering carbon (Gocke et al. 2009).

These two processes described above are natural methods for sequestering atmospheric carbon as inorganic carbon. However, the formation of calcium carbonate for inorganic carbon sequestration can be forced by providing calcium to a soil rich in dissolved carbon dioxide. Renforth et al. (2009), in an experiment consisting of applying an engineered soil (quarry fines and compost) to produce soil for land restoration, observed that after five years, calcium carbonate had formed in the engineered soil. An isotope study of the calcium carbonate formed confirmed that the carbon was from atmospheric origin and was transferred into the soil via the vegetation grown on this soil during the five year period. It was considered passive carbon sequestration as no human interaction was involved, except the fabrication of the engineered soil (Renforth et al. 2009). Soil could be engineered to sequester carbon using the plants as a vehicle to transport carbon into the soil, and using calcium based materials to enrich for calcium to promote calcium carbonate precipitation.

2.8.5.2 Calcium Carbonate Formation

The precipitation of calcium carbonate requires a reaction between calcium and carbonate or bicarbonate ions. Gaseous carbon dioxide dissolves in the soil water phase to form three different species: carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) (Eq.4, Eq.5, Eq.6, Eq. 7) (Salomons et al. 1976, Salomons et al. 1978). The relative amounts of each species formed depend on soil pH, temperature, and CO_2 partial pressure, and the formation of calcium carbonate occurs when calcium ions react with carbonate (Eq.8) or bicarbonate ions (Eq.9).

Calcium carbonate formation

$$CO_2(g) \Leftrightarrow CO_2(aq) \qquad (4)$$

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3 \qquad (5)$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad (6)$$

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-} \qquad (7)$$

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3(s) \qquad (8)$$

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3(s) + H_2O + CO_2 \qquad (9)$$

Calcium carbonate dissolution

$$\begin{array}{c} CO_2(g) + H_2O \\ \downarrow \end{array}$$

$$CaCO_3(s) + H_2CO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (10)$$

$$CaCO_3(s) + 2H^+ \Leftrightarrow Ca^{2+} + H_2O + CO_2(g) \qquad (11)$$

The precipitation of $CaCO_3$ is usually triggered when the calcium ions and carbonate ions reach the limit of solubility (Eq. 8) or when calcium and bicarbonate ions move into a low soil CO_2 pressure zone (Eq. 9) (Salomons et al. 1976, Salomons et al. 1978). However, calcium carbonate can dissolve if the soil pH is low enough, usually due to the presence of carbonic acids from soil CO_2 dissolution (Eq. 10, Eq. 11) (Birkeland 1984). Multiple environmental and climatic factors influence the formation and dissolution of calcium carbonate. These factors are discussed in the following section.

2.8.5.3 Physical and Chemical Factors Influencing $CaCO_3$ Formation

Several physical and chemical factors influence the precipitation and dissolution of calcium carbonates in soil. Among these factors: pH, partial pressure of CO_2 (pCO_2), temperature, rain precipitation, ionic strength, soil sulfur content, and vegetation cover are the most influential.

2.8.5.3.1 pH

The pH, among variables such as the temperature of the soil solution (influencing the pK) and the partial pressure of CO_2 in soil, will determine which species of the carbon dioxide/water equilibrium predominates (Eq. 4-7) (Snoeyink et al. 1980). If the soil pH is basic, carbonate ions will be predominant and calcium carbonate will precipitate mainly according to the following equation (Eq.8). Bicarbonate ions will be predominant if the soil around a pH of 8. In such soil, calcium carbonate will precipitate mainly according to Eq.9. It is important to notice that in this case the partial pressure of CO_2 will also have an effect on the precipitation as it is noticeable on the (Eq. 9) (Manning 2008). As the pH decreases, fewer carbonate and bicarbonates ions will be available for the precipitation reactions to occur (Figure 6) (Birkeland 1984).

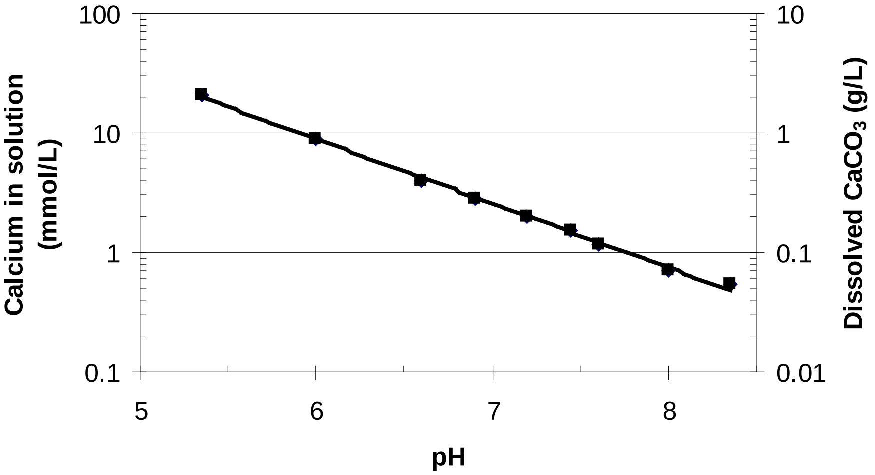


Figure 6: Calcium carbonate solubility as a function of pH (Birkeland 1984)

Plants activities will have an effect of the soil pH. When plant roots absorb cations for nutrition, they will release organic acids and hydrogen ions to maintain internal cell charge balances. The result is lower soil water pH and increased bioavailability of nutrients and metals (Grinsted et al. 1982; Hinsinger 2003; Kumar et al. 2006). For example, Hedley et al. (1982) observed this phenomenon in rapeseed when calcium (Ca^{2+}) was taken up by roots; and Bashan et al. (1989) reported it in wheat roots, where ammonium ions (NH_4^+) increased the proton efflux but nitrate reduced it. Organic acids release has less influence on soil pH than hydrogen ion release because organic anions (especially carboxylated higher-molecular-weight organic acids) play the role of buffers in soil (Hedley et al. 1982; Manning 2008)

The effects of root and microbial (soil) respiration on soil pH have been well-reviewed. Cereals transfer 30-50% of their atmospheric carbon uptake below ground, with 10-20% of that carbon released as carbon dioxide and the remainder as root biomass (Hinsinger 2003). Maize plants secrete about 20% of photosynthesized carbon as root exudates, and about 75% of the exudates are then consumed by microbes in the rhizosphere, which release CO_2. The CO_2 addition to the soil solution leads to carbonic acid formation and soil pH decline. This mechanism of lowering soil pH tends to be more pronounced than that resulting from proton efflux related to nutritional uptake of cations. Plant roots and microorganisms can also change the soil pH by redox-coupled reactions (Hinsinger 2003).

2.8.5.3.2 pCO2

The partial pressure of carbon dioxide in soil (pCO_2) can be up to 10-100 folds higher than atmospheric levels due to root and microbial respiration (Birkeland 1984). This can be a highly localized effect that tends to occur at root surfaces and quickly be less pronounced even 2-3 mm away (Gollany et al. 1993). It is also highly dependent on the type of vegetation present and the season (Birkeland 1984; Schlesinger 1985). Carbon dioxide is readily soluble in water, and the greater its partial pressure, the more soluble it becomes in the soil solution (Portier et al. 2005).

However, the pCO_2 has a complex effect on calcium carbonate formation. At high pCO_2 levels, more carbonate and bicarbonates ions will be present in the soil solution and available to form calcium carbonate, but increased CO_2 will also lowered pH, which is not favorable for precipitation. Further, the presence of high CO_2 may reflect the uptake of cations, such as Ca^{+2}, which makes the calcium unavailable for precipitation. (Kumar et al. 2006). As a result, vegetative soil will usually have a lower calcium carbonate content then un-vegetated soil (Birkeland 1984).

Calcium carbonate precipitation was modeled using equation 9. (Breecker et al. 2009). Equation 12 describes the relation between the calcite activity (a_{CaCO_3}), the aqueous concentration of calcium ($[Ca^{2+}]$), the soil partial pressure of CO_2 gas (pCO_2), and the temperature equilibrium constants K_1, K_2, K_{cal}, and K_{CO2} corresponding to the dissolution of carbonic acid, the dissolution of bicarbonate, the dissociation of calcite, and the hydration of CO_2 respectively.

$$a_{CaCO_3} = \frac{4[Ca^{2+}]^3}{pCO_2}\left(\frac{K_2}{K_1 K_{cal} K_{co_2}}\right) \tag{12}$$

Equation 12 is only valid assuming the activities are equal to the concentration and assuming the soil pH is lower than nine (Breecker et al. 2009). The equation shows that the precipitation of calcium carbonate ($a_{CaCO3} \geq 1$) will be favored if the calcium concentration ($[Ca^{2+}]$) is high, the carbon dioxide partial pressure is low, and the soil temperature is high (The product of the equilibrium constants increases with temperature). As a result, a degasing of soil CO_2, or low soil CO_2 in a dry and hot climate are the optimum conditions for calcium carbonate formation.

2.8.5.3.3 Temperature

Calcium carbonate solubility follows the trend of carbon dioxide solubility; both become more soluble as temperature declines (Figure 7) (Birkeland 1984). The relationship is not linear, so that a temperature changes from 25°C to 10°C results in a three-fold increase in solubility, while a doubling of temperature from 25°C to 50°C yields a four-fold decrease in solubility.

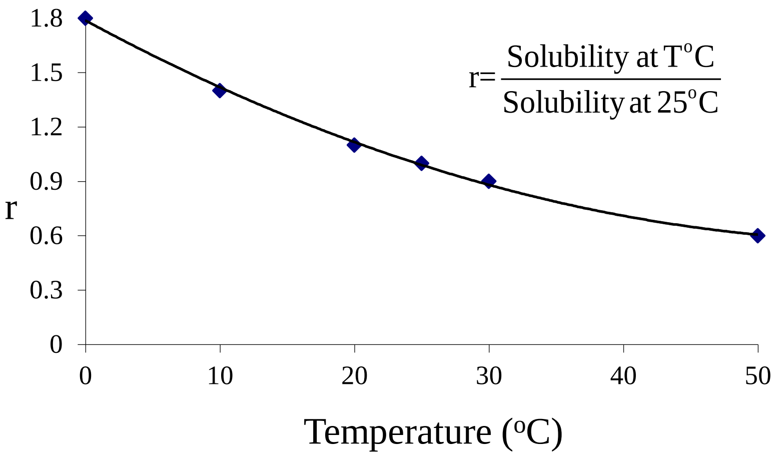


Figure 7: Influence of temperature on calcium carbonate solubility (Birkeland 1984)

There are some indirect temperature effects as well, since seasonal soil temperature changes influence microbial respiration rates. Such rates are usually highest during spring and summer (Hashimoto et al. 2006). This effect can combine with soil temperature impacts on water evaporation such that ionic concentrations increase and promote precipitation (Salomons et al. 1976, 1978). Together these phenomena may lead to calcium carbonate precipitation, especially in arid and semi-arid climates.

2.8.5.3.4 Rain Precipitation

Soils in the U.S. are designated as pedalfers if they receive more than 30 in of rain annually, and these occur in the eastern half of the country (Figure 8). Soils designated as pedocals receive less than 30 in of rain annually. In pedocal soil such as The Mojave Desert, heavy winter rains leave the soil saturated with carbonates and bicarbonates due to plant growth and root respiration. In the summer, the desert is subject to severe drought, which reduces biological activity and root respiration and enlarges soil pores, so that the soil CO_2 can readily escape (Schlesinger 1985; Hamada et al. 2001). The net decline in pCO_2 is sometimes the key for calcium carbonate precipitation. This mechanism appears to have mediated calcium carbonate formation in the Mojave Desert over the past 20,000 years (Schlesinger 1985).

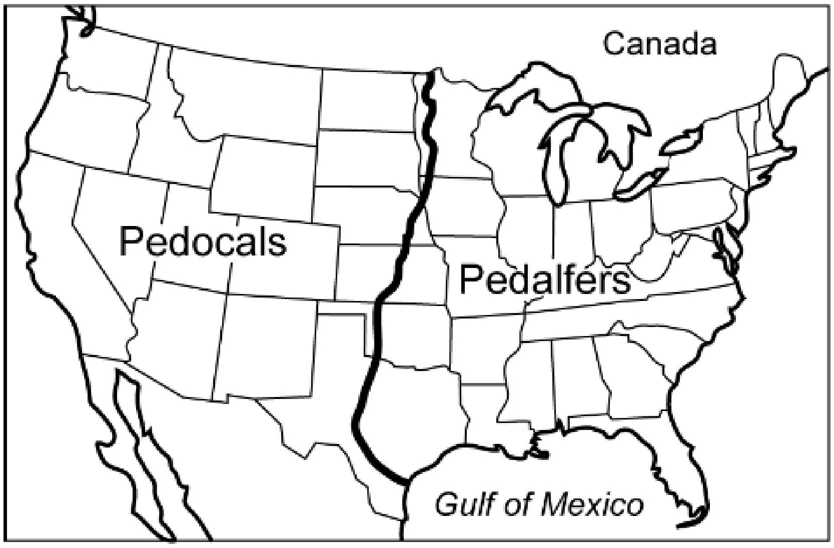


Figure 8: Pedocal and pedalfer soils in the US (Marbut 1935)

In pedalfer soils, high rain events leach calcium, carbonate, and bicarbonate ions deep into the soil profile. As the ions migrate through the soil, they reach a zone below the plant roots where both pCO_2 and moisture are low due to plant uptake and evaporation. These conditions favor calcium carbonate formation. Consequently, the depth of calcium carbonate formation in a pedalfer region depends on of the climate and rain events (Birkeland 1984) and can occur well below the root depth (Manning 2008). Gunal et al. (2006) noted this phenomenon in Kansas, where the amount of calcium carbonate decreased and the depth of its appearance increased from western Kansas to eastern Kansas, Eastern Kansas receiving more annual rain than western Kansas. The depth at which calcium carbonate forms increases with increasing annual rainfall as

Figure 9 shows (Jenny 1980, Birkeland 1984). At an annual precipitation rate of 85 cm (33 in), calcium carbonate can be anticipated at a minimum depth of 90 cm.

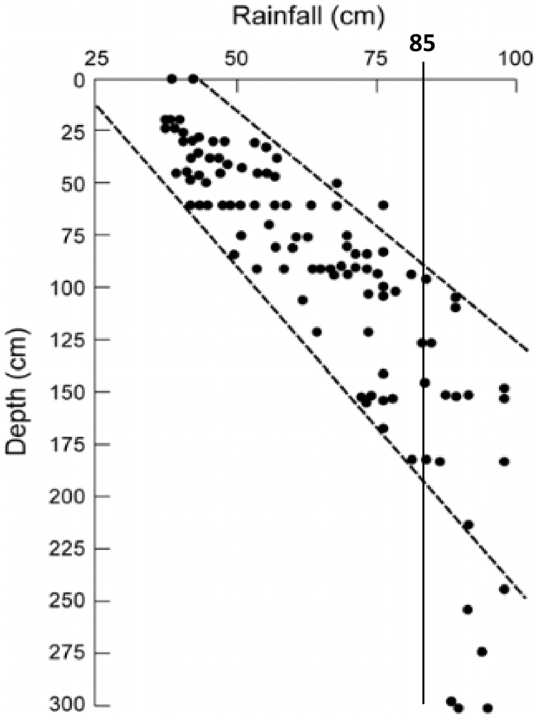


Figure 9: Depth of calcium carbonate occurrence according to rain precipitation

When annual precipitation exceeds 33 in or 85 cm, the wetting front will get deeper (the depth as which the water from rainfall penetrate in the soil) and the conditions for calcium carbonate formation may not be satisfied until depths of 3 m or more. Consequently, in regions with high water tables and high rainfall, calcium carbonate may leach into groundwater and never precipitate.

2.8.5.3.5 Ions

The presence of others ions in the soil solution will influence calcium carbonate formation. Moreover, as the ionic strength increases, the solubility of carbon dioxide decreases, lowering the amount of bicarbonate and carbonate ions available for the formation of calcium carbonate (Matter et al. 2009). Inorganic and organic ions such as metals ions, low molecular weight polyelectrolytes, and amino-polyphosphonates retard calcium carbonate crystallization, and phosphorus-containing compounds of any kind are particularly inhibitory (Sawada 1997).

2.8.5.3.6 Vegetation

Moulton et al. (2000) reported that the weathering rate of calcium and magnesium minerals in western Iceland was four-fold greater in vegetated areas than in bare regions. Enhancing weathering effects is one influence of vegetation on calcium carbonate formation along with acid production from plants (due to root respiration, exudates, and rhizosphere respiration) that can dissolve existing calcium carbonate and calcium-bearing minerals (Monger et al. 2002, Treatwell-Steitz et al., 2000). Further, plants with a high requirement for calcium can accumulate calcium in the rhizosphere and create conditions favorable for calcium carbonate formation (Rengel 2002). Dawood (1989) observed that the addition of agricultural grade sulfur to soil containing high levels of calcium carbonate significantly increased the dissolution of calcium carbonate. Some of the freed calcium then recombined with sulfate to form gypsum.

2.8.5.4 Forms of Calcium Carbonate

Calcium carbonate in soil occurs as: nodules, filaments, coatings, and horizons (Birkeland 1984). Table 11 describes the evolution of calcium carbonate accumulation in soil as a function of other materials present in the soil. When present in small amounts, calcium carbonate tends to be found as nodules or filaments. As more is formed, it may appear as a coating on pebbles and sand grains. When it constitutes more than 40% of the soil, an entire band of calcium carbonate can be visible in the soil profile, and this is designated as the K horizon (Birkeland 1984).

There are several reports of such calcium carbonate forms in the literature. Gunal et al. (2006), in his calcium carbonate evaluation of Kansas soil, observed calcium carbonate as clay coating and nodules. Manning (2001) found calcite in the leachate of a municipal solid waste landfill as discrete grains and coatings of quartz sand. Treatwell-Steiz et al. (2000) reported finding large pebbles with thick coatings due to the amount of water they could retain but smaller sand and particles did not have any coating. Additionally, calcium carbonate has different crystalline shapes: calcite, valerite, and aragonite. Calcite is the most stable form and therefore the predominant one (Ogino et al. 1987). The crystal form in which calcium carbonate precipitates can vary depending upon the temperature and the pH at which it is formed. At low temperature (14-30^{o}C), calcium carbonate appears as valerite and calcite crystals, while at high temperature (60-80^{o}C), aragonite and calcite crystals are favored. Gebauer et al. (2009) showed that high alkalinity conditions yield valerite and aragonite, the less stable form of calcium carbonate, will gradually transform over time into calcite (Ogino et al. 1987).

Table 11: Stages of calcium carbonate morphology (Birkeland 1984)

Stages of Carbonate Morphology		
Stage	Gravelly parent material	Non-gravelly parent material
I	Thin discontinuous clast coatings; some filaments; matrix can be calcareous next to stones; about 4% $CaCO_3$.	Few filaments or coatings on sand grains
I+	Many or all clast coatings are thin and continuous	Filaments are common
II	Continuous clast coatings; local cementation of few to several clasts; matrix is loose and calcareous enough to give somewhat whitened appearance	Few to common nodules; matrix between nodules is slightly whitened by carbonate (15-50% by area), and the latter occurs in veinlets and as filaments; some matrix can be non-calcareous; about 10-15% $CaCO_3$ in whole sample, 15-75% in nodules
II+	Same as stage II, except carbonate in matrix is more pervasive	Common nodules; 50-90% of matrix is whitened; about 15% $CaCO_3$ in whole sample
Continuity of fabric high in carbonate		
III	Horizon has 50-90% K fabric with carbonate forming an essentially continuous medium; color mostly white; carbonate-rich layers more common in upper part; about 20-25% $CaCO_3$	Most grains coated with carbonate; most pores plugged; >40% $CaCO_3$
III+	Most clasts have thick carbonate coats; matrix particles continuously coated with carbonate or pores plugged by carbonate; cementation more or less continuous; >40% $CaCO_3$	Most grains coated with carbonate; most pores plugged; >40% $CaCO_3$
Partly or entirely cemented		
IV	Upper part of K horizon is nearly pure cemented carbonate (75-90% $CaCO_3$) and has a weak platy structure due to the weakly expressed laminar depositional layers of carbonate; the rest of the horizon is plugged with carbonate (50-75% $CaCO_3$).	
V	Laminar layer and platy structure are strongly expressed; incipient brecciation and pisolith (thin, multiple layers of carbonate surrounding particles) formation	
VI	Brecciation and recementation, as well as pisoliths, are common	

2.8.5.5 Natural Rate of Calcium Carbonate Formation

The rate at which calcium carbonate forms in soil depends on the process of formation, the leaching rate of the soil, and, most importantly, the availability of calcium from either rock weathering, wind dust, or rain (Birkeland 1984; Manning 2008). Several studies have measured the rate of pedogenic calcium carbonate formation in different climates. The deposition rate in the Mojave Desert over the past 20,000 y ranged from 1.6-3.5 g m^{-2} y^{-1} (Schlesinger 1985). In Saskatchewan Canada soils, the rates of pedogenic carbonate formation varies from 8.3-14.3 g m^{-2} y^{-1} and increases as rain and snow precipitation increases (Landi et al. 2003). Presumably this is due to the weathering of lithogenic carbonate, providing calcium that is limited in this region. The weathering of lithogenic carbonate “freed” calcium ions that will be reformed as pedogenic carbonate. As a result, the more rain, the more calcium will be freed from the dissolution of primary carbonate and then the more pedogenic carbonate will form. Birkeland et al. (1984) suggested that, on average, the rate at which calcium carbonate can form is about 2 g m^{-2} y^{-1}.

Others studies estimate the re-crystallization rates of calcium carbonate. In the laboratory, wheat plants were grown in the loess soil sample under a ^{14}C atmosphere. Wheat provided a high flux of CO_2 into the soil (from root and rhizosphere respiration) to enhance the weathering and reformation process. Kuzyakov et al. (2006) measured the ^{14}C in the freshly formed pedogenic calcium carbonate to measure the rate of re-crystallization. The rate of re-crystallization was 0.0029% per day. According to the model develop by Kuzyakov et al. (2006), between 100 and 2000 years will be necessary to convert 99% of primary carbonates to pedogenic carbonates. However, the authors suggested that the re-crystallization of calcium carbonate in the natural environment will be smaller than the model is predicting. Several variables such as mean annual precipitation, temperature, and vegetation types were not taken into account in the laboratory experiment (Kuzyakov et al. 2006).

Gocke et al. (2009) observed that the atmospheric carbon dioxide concentration had a strong influence on the re-crystallization rate. An atmospheric carbon dioxide concentration of 380 ppm, 5000 ppm, and 50,000 ppm was producing a re-crystallization rate of 0.000043 % per day, 0.000082% per day and 0.00017% per day respectively in a loess soil. The authors suggested that the field condition should show a faster re-crystallization rate due to the constant production of carbon dioxide in soil by root and microbial respiration. It is also expected that re-crystallization will be faster near the root due to the higher pCO_2 near the roots, and during the spring and the summer when the temperatures are higher and the plant activity is the greatest (Gocke et al. 2009).

2.8.6 Potential Calcium Source in the System

Calcium ions in soil have different origins. The main sources are calcium-rich minerals, soluble calcium in dust, calcium in rain, and gypsum (Birkeland 1984; Schelsinger 1985; Manning 2008). The calcium-rich minerals are silicate parent rocks, plagioclase feldspar, calcic ferromagnesian silicates, and limestone (Manning 2008). In many places where natural calcium carbonate forms, the source of calcium is external. In the New Mexico regions, dust and rain are the main source of calcium. In this region, calcium from rain precipitation contributes to the formation of calcium carbonate two to three-fold more than calcium from dust (Birkeland 1984). Soil calcium in Kansas derives mainly from Aeolian dust and the weathering of calcium rich-minerals (Gunal et al.

2006). In some semiarid and arid regions, atmospheric gypsum is a source of calcium (Birkeland 1984). It has been suggested that soil calcium carbonate formation could be enhanced by creating an engineered soil mix rich in calcium that could support plant growth. The vegetation effects described in section 2.8.5.1 could provide carbon dioxide partial pressure and the soil mix could provide calcium via concrete fines, portlandite within mortar, calcium silicate from cement, or gypsum from drywall (Renforth et al. 2009). Geologists have employed different models to explain the formation of calcium carbonate, including: the per descendum model, the per ascendum model, the transversal model, and the on-site model. These models are described below with a fifth model, the biogenic model which involves the formation of calcium carbonate by micro-organisms.

2.8.6.1 Per Descendum Model

In the per descendum model, calcium ions on the soil surface introduced by rain water or aeolian dust in conjunction with pre-existing calcium carbonates may be carried in with rainwater and migrate downward with the soil solution. They can encounter biogenic CO_2, and if conditions are right, precipitation can occur. (Schlensinger 1985; Monger et al. 2002; Gunal et al. 2006). At the surface, soil water depletion may occur due to wind and sun mediated evaporation or evapotranspiration and water uptake by plants. Such depletion leads calcium carbonate to reach its limit of solubility (Eq. 8) so that precipitation occurs (Schlesinger 1985). Calcium carbonate can also be formed as the solution moves below the vegetation roots where carbon dioxide pressure is low (Eq. 9) (Birkeland 1984; Boettinger 2002). The per descendum model is often observed in non-calcareous soil and is strongly correlated with wind dust and calcium rich rain (Monger et al. 2002).

2.8.6.2 Per Ascendum Model

In the per ascendum model, calcium, carbonate, and bicarbonate ions from a shallow water table moves upward due to water evaporation from the sun, wind, and plant water uptake (capillary rise effect). The precipitation of calcium carbonate in the upper profile of the soil occurs when the favorable formation conditions are met such as high concentration of calcium and low CO_2 pressure (Birkeland 1984; Monger et al. 2002). Calcium carbonate will formed following equation 9 where a low CO_2 pressure will unbalanced the equation forcing the reaction from left to right. The surface water evaporation will also increase the calcium concentration and contribute to the formation of calcium carbonate.

2.8.6.3 Transversal Movement Model

In the transversal movement model, soil solution containing carbonate, bicarbonate and calcium ions migrates transversally from an upslope position to a lower landscape position where there are favorable conditions for calcium carbonate formation (evaporation, low carbon dioxide pressure…) (Monger et al. 2002).

2.8.6.4 In-Site Model

The in-site model describes the dissolution and re-precipitation of carbon-based bedrock such as marine carbonate (limestone). Calcium-bearing igneous rocks dissolve due to a high acidity liberating calcium ions in the soil solution. These calcium ions react with carbonate and bicarbonate ions of root origin to form calcium carbonate. It is the transformation of lithogenic carbonate to pedogenic carbonate (recrystallization). Calcium-bearing igneous rock has a really slow rate of dissolution calcium (Gocke et al.

2009, Monger et al. 2002). As a result, this model presents a calcium carbonate precipitation rate much slower than the per descendum model (Monger et al. 2002).

2.8.6.5 Biogenic Model

Certain bacteria have the ability to form calcium carbonate. Cacchio et al. (2003) tested 31 bacteria strains and found that *Bacillus spp*. strains were the most common bacteria forming calcium carbonate. These strains were able to raise the pH of the medium, necessary for calcium carbonate formation, by hydrolyzing urea. Moreover, certain species of plant, fungi, and termites are also able to precipitate calcium carbonate (Monger et al. 2002).

2.8.7 Carbonate Ion Sources

Soil carbon dioxide dissolves in the soil water phase to form bicarbonate and carbonate ions (Eqs. 4, 5, 6, and 7). These ions are necessary for the calcium carbonate formation process. Carbon dioxide exists in soil due to atmospheric input or root and microbial respiration. Atmospheric CO_2 input occurs when a positive gradient is created between the atmosphere and the soil (Kumar 2006). However, root and soil microbial respiration generate a great amount of CO_2 often several times greater than atmospheric CO_2 concentration (Birkeland 1984). As a result, the majority of soil CO_2 is due to rhizosphere activities.

Atmospheric CO_2 is taken up by plants during photosynthesis. The carbon is either used for plant biomass or released into the soil via the roots as CO_2 (root respiration), root exudates (various chemicals compounds), or root debris (Kumar et al. 2006). The consumption of root exudates and root debris by rhizosphere microbes contributes to soil as the microbes consume the organic exudates and release CO_2

(microbial heterotrophic respiration). The combined phenomena of root respiration and microbial respiration are referred to as soil respiration (Raich et al. 2000). During one growing season, crops can transfer 1500 kg ha^{-1} carbon into the soil (Kumar et al. 2006).

2.8.7.1 Microbial Degradation of Root Exudates and Organic Matter.

There are more than 100,000 different plant-derived compounds that are metabolic by-products released as root exudates into soil. (Walker et al. 2003). They include low molecular compounds such as amino acids, organic acids, sugars, and phenolic compounds, and high molecular weight compounds such as mucilage (polysaccharides) and proteins (Walker et al. 2003; Rovira 1969). The rhizosphere microbial population releases CO_2 as a by-product of metabolizing root exudates and other organic matter that might include root matter and fungal biomass. (Prikyl et al. 1980; Ryan et al. 2001; van Hees et al. 2005, Marhan et al. 2008). Soil respiration is highly influenced by the type and amount of soil organic matter as well as the methods of field management used. It has been found that soil respiration of a crop field varies from 4 to 26 t ha^{-1} y^{-1} of carbon depending on whether tillage, drainage, grazing or manure application was employed (Raich et al. 2000; Rees et al. 2005).

2.8.7.2 Root Respiration

Plants release carbon dioxide through their roots as a result of cellular respiration in the plant roots. Root respiration plays an important part of soil respiration in any type of climate. In temperate zones, about 33-50% of soil respiration is due to root respiration (35-62% in pine forests and 17-40% in grasslands) (Raich et al. 2000). Root respiration can be influenced by an elevated atmospheric CO_2 concentration, and ambient temperature increases (Schlesinger 2000; Rees et al. 2005; Hill et al. 2007). It is estimated that root respiration from crop fields only contributes 12-38% to overall soil respiration (Raich et al. 2000).

CHAPTER 3: MATERIALS AND METHODS

3.1 Phytotoxicity Test

3.1.1 Drywall and Seeds Tested

The phytotoxicity of three commonly used gypsum drywall materials was assessed using a germination test (Wang et al. 1990; US EPA 1996; Wang et al. 2001) that consisted of measuring the germination rate and root elongation of seeds exposed to different concentrations of dissolved ground drywall solutions.

3.1.2 Seeds Used During Germination Tests

The germination test was performed on six kinds of plant seeds: lettuce (Grands Rapids, Ferry-Morse); cucumber (Straight Eight, Freey-Morse); wheat (NC05-20814, NC State, Raleight); canola (Dwarf Essex Rape seed, Wammock Farm Service, Inc.); Corn (Dwarf Open pollinated corn, Athens Seed Co., Inc); and sunflower (*Hellianthus annuus*). Lettuce and cucumber are usually recommended for germination tests due to their high chemical sensitivity (US EPA 1996). Wheat, canola, corn, and sunflower were tested because they are commonly cultivated in North Carolina and could benefit from a ground drywall amendment.

3.1.3 Drywall Tested

Three types of drywall were tested: a conventional drywall (USG Sheetrock® Gypsum Panel); a fire retardant drywall (National Gypsum’ Gypsum Board Gold Bond, XP, fire retardant ½”); and a mold and moisture resistant drywall (National gypsum, Mold, Mildew and Moisture resistant ½”). For convenience, these drywall types will subsequently be referred to as Type “C” for conventional drywall; Type “F” for fire retardant drywall, and Type “M” for mold, mildew, and moisture resistant drywall. Drywall samples were prepared in a similar fashion for each germination experiment. Every sample was commercial drywall that was ground (with its paper layer included) in a laboratory mill (Thomas-Wiley, Laboratory Mill, Model 4, Thomas Scientific USA).

3.1.4 Germination Test Procedure

Phytotoxicity was measured by exposing seeds to increasingly stronger solutions of dissolved ground drywall. First, stock solutions of drywall in water were prepared: 10 g of each ground drywall were dissolved in 400 mL of deionized water (DI). The solutions were stirred for 24 h and then allowed to settle for another 24 h. The supernatants were collected and poured into a bottle to comprise the stock solutions. Stock solutions were labeled XC, XF, and XM. Full strength stock solutions were then diluted 10, 100, and 1000-fold, so that there were four different concentrations of ground drywall in water for each of the three drywall types.

Table 12: Theoretical gypsum concentration in the drywall solutions[†]

Solution Label	Gypsum Concentration in Solution
X	2000 mg L^{-1}
X/10	200 mg L^{-1}
X/100	20 mg L^{-1}
X/1000	2 mg L^{-1}
control	0 mg L^{-1}

[†] based on Wood 2003 calculations

For instance, four solutions from fire retardant drywall were prepared and labeled XF, X/10 F, X/100 F, and X/1000 F. The theoretical gypsum concentration of each solution was based on Wood (2003) calculations (Table 12). Secondly, seeds were shaken in a 10% bleach solution for 20 minutes and then rinsed three times with DI water to wash away any traces of bleach. According to the seed size, five to ten seeds were placed in a Petri dish lined with a #1 Whatman filter. A 5 mL aliquot of drywall solution was poured in each dish (Figure 10), and then the dishes were incubated at 25°C in the dark for 72 h. Petri dishes were randomly distributed inside the oven to control for any uneven heat effects. Triplicates were prepared for each drywall type (C, F, and M), and in control dishes seeds received DI water only.

Figure 10: Petri dishes prepared for incubation

The number of seeds germinated per dish after 72 h was averaged for the triplicate trials and converted to a percentage. A seed was considered germinated if, after 72 h of incubation, it had grown more than 5 mm of root (US EPA 1996) (Figure 11). In addition to reporting the crude germination rate, a germination score (GS) was also reported. This parameter reflects both the number of seeds that germinate and the length of the rootlets after 72 h. The GS of each Petri dish was calculated by multiplying the germination rate of the Petri dish by the average root length of the seed germinated in this Petri dish.

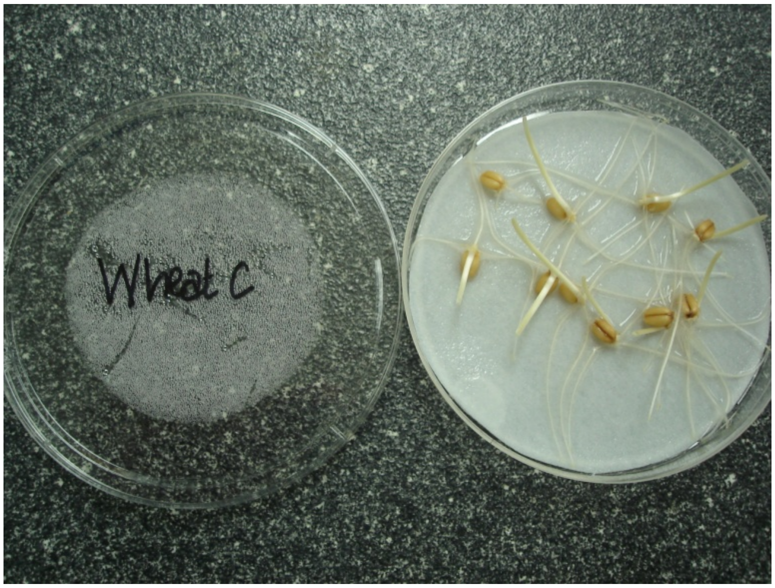


Figure 11: Wheat seeds germinated after 72 h in a dark 25°C oven

3.2 Drywall as an Amendment for Grass

3.2.1 Experiment Design

Pot experiments were conducted using three types of drywall and fescue grass. The drywall types tested were those described in Sec. 3.1.3, Types C, F and M. A commercial fescue grass seed (Tall fescue, Pennington Smart Seed) was used throughout the experiment.

Figure 12: Gypsum drywall amended tall fescue pot experiment

The experimental design used 52 one-gallon pots filled with a mix of topsoil (Organic valley and Scott topsoil brand) and potting soil (Timberline potting brand) at a ratio of 4/2/1 and a dose of drywall (Figure 12). Four doses of each drywall type were tested (Table 13) and replicated four times. The ground gypsum drywall was mixed thoroughly within the soil before filling the pots, and control pots received no ground drywall (Dose A). The ground drywall doses were based on previous research done at UNC Charlotte on the use of ground drywall-amended fescue for erosion control (Wood 2008). Due to the limited success of the doses tested in that study, lower doses were tested here. The highest dose used in this experiment was the lowest dose used in the Wood (2008) study.

On April 23, 2010 (Day 0), the commercial fescue grass seed was sown at a rate of 0.712 g per pot based on a sowing rate of 8 lbs./1000 ft^2 recommended by the vendor on the packaging. The pots were fertilized with 0.531 g of 20-20-20 fertilizer (Jack's Classic All Purpose) dissolved in 75 ml of DI water. The pots were maintained in a sunny outdoor location and watered daily either by a natural rain event or with tap water. The experiment was terminated on July 21, 2010, which was Day 89 of the trial.

Table 13: Ground drywall doses applied to grass plants in pots[†]

Dose	Ground Drywall per Pot (g)	Drywall Dose (g m^{-2})	Drywall Dose (kg ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	0.00	0	0	0
B	1.82	100	1,000	168
C	7.30	400	4,000	670
D	14.59	800	8,000	1,341
E	22.25	1220	12,200	2,044

[†]Note: These dosages repeated for each gypsum drywall type: C, F, and M.

3.2.2 Growth Parameters Measured

In order to monitor the effect of ground drywall amendments, several parameters were measured: the accumulated grass height, the biomass accumulation, and the final root coverage (Wood 2008). The soil pH was also measured to monitor any change in soil pH due to the ground drywall amendment.

3.2.2.1 Accumulated Grass Height

The grass height was measured on Days 25, 39, 54, 76 and 89. The tallest strand of grass in each pot was measured from the soil surface to the tip of the grass blade. The grass was cut back at the end of each measurement episode (see Biomass accumulation, Sec.3.2.2.2 below), so the five grass heights measured over the course of the experiment were added to calculate the accumulated grass height.

3.2.2.2 Biomass Accumulation

The grass biomass was also measured on Days 25, 39, 54, 76 and 89 after the grass height measurement. The grass was trimmed to a height of 2.5 in., as recommended for lawn maintenance. The grass clippings were dried for 2 h at 104°C in a drying oven and weighed. The dry biomass increased for each time interval and accumulated over the duration of the experiment was calculated.

3.2.2.3 Root Coverage

The amount of root covering the bottom of the pot was evaluated as an indicator of the total amount of root grown during the entire length of the experiment. At the end of the experiment, the plastic pots were removed exposing the bottom of the soil. A set of five pot bottoms was presented to four observers. Each observer individually ranked the pot bottoms from 1 to 5, with a rating of 1 reflecting high root coverage, and a rating of 5 reflecting very little root coverage. After ranking the pot bottoms, another set of five pots was presented to the observers, with one of the second series being a pot from the previous set to assess their rating reliability.

3.2.2.4 pH

Soil pH was measured on Days 14 and 89. The “Pourthru” procedure (Bilderback 2001) was used, wherein two hours after having watered the grass as usual, 120 ml of DI water is poured into each pot, and the water leaching out of the pots is collected. A direct measure of the leachate pH is then conducted.

3.3 Drywall as an Amendment for Canola

3.3.1 Experiment Design

The drywall types tested were those described in Sec.3.1.3, Types C, F and M. One gallon pots were used for the experiment (Figure 13). The pots were filled with a mix of topsoil (Organic valley and Scott topsoil brand) and potting soil (Timberline potting soil brand) at a ratio of 4/2/1 and a dose of ground drywall.

Figure 13: Gypsum drywall amended canola pot experiment preparation

Four doses for each drywall type were tested (Table 14) based on the application rate of ground drywall used for crop growth (Wolkowski, 2003). Control pots received no drywall additions (Dose A). Each treatment was replicated five times.

Table 14: Ground drywall doses applied to canola plants in pots

Dose	Ground Drywall per Pot (g)	Drywall Dose (g m^{-2})	Drywall Dose (kg ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	0.00	0	0	0
B	0.91	50	500	84
C	2.74	150	1,500	251
D	5.48	300	3,000	503
E	8.21	450	4,500	754

†Note: these dosages repeated for each gypsum drywall type: C, F, and M.

Five canola seeds (Dwarf Essex Rape seed) were planted in each pot on April 26, 2010 (Day 0) and 1.327 g of 20-20-20 fertilizer (Jack's Classic All Purpose) into 378 ml of tap water was applied on Day 16. On Day 25, when cabbage worms were evident, the plants were sprayed with a garlic/onion solution deterrent which succeeded in setting back the worm population. The pots were maintained in direct sunlight from Day 0-96 (April 26-July 31, 2010), but because they were showing signs of sun damage, they were moved into a shaded area until the end of the experiment. On Day 149 the plants were thinned from five to three plants per pot, and a second dose of fertilizer (0.277 g per pot) was applied. The experiment was terminated on Day 186.

3.3.2 Growth Parameters Measured

The effect of drywall amendments on the canola plants were assessed by measuring the number of leaves per plant and the dry root mass of the plants (Ahmad et al. 2005). The number of leaves per plant was counted and photographed on Days 16, 25, 36, 51, 64, and 78. Dry root mass was measured at the end of the experiment (Day 186). Canola plants were harvested and delicately taken out of the soil with their roots. The roots were removed, dried for 24 h at 104°C, and weighed.

3.3.3 Soil Parameters

Soil pH and soil conductivity were measured six times over the course of the experiment (Days 11, 25, 36, 57, 71, and 140). The procedure used to measure the pH and the conductivity was based on the "Pourthru" procedure (see Sec. 3.2.2.4).

3.4 Canola Field

3.4.1 Huntersville

The first field scale drywall amendment experiment started in November 2009 and ended in June 2010. The field, located in Huntersville N.C., is owned by Charlotte Mecklenburg Utilities. The experimental plot was part of a larger field experiment being cultivated with a canola crop for biofuel production. Several problems occurred during the growing season. The crop was planted later than recommended, and the cold winter of 2009 killed about 25% of the plants. Moreover, during the spring 2010, it was estimated that about 50 deer fed on the canola for two weeks, destroying about 95% of the remaining crop. Growth measurements of the crop were made on the few remaining plants.

3.4.1.1 Field Experimental Design

The field was prepared, seeded, and fertilized by a professional farmer (Mr. Gary Duckworth). Soil preparation and liming (Appendix A) were done on October 7, 2009 (Day -29). Fertilizer (18-24-0) was applied on October 23, 2009 (Day -13), and the canola seeds were planted on November 5, 2009 (Day 0). Ground virgin drywall amendment was surface applied on November 7, 2009 (Day 2) (Figure 14: Ground drywall after surface application November 7, 2009). Four doses of ground conventional drywall (USG Sheetrock® Gypsum Panel) and a control consisting of no drywall amendment were used (Table 15). The treatment doses were based on the doses of ground drywall used for crop growth reported by Wolkowski (2003).

Figure 14: Ground drywall after surface application
November 7, 2009

Table 15: Ground drywall application rates for canola at the Huntersville field site

Dose	Drywall Dose per Plot (g)	Drywall Dose (g m^{-2})	Drywall Dose (kg ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	0	0	0	0
B	632	158	1,580	265
C	1263	316	3,160	530
D	1895	474	4,740	794
E	2526	632	6,320	1059

The experimental layout consisted of 20 2-m x 2-m plots arranged in a rectangle shape (16 m by 13 m) with a one meter buffer between each plot (Figure 15). Each treatment and the control were replicated four times and randomly distributed among the 20 plots.

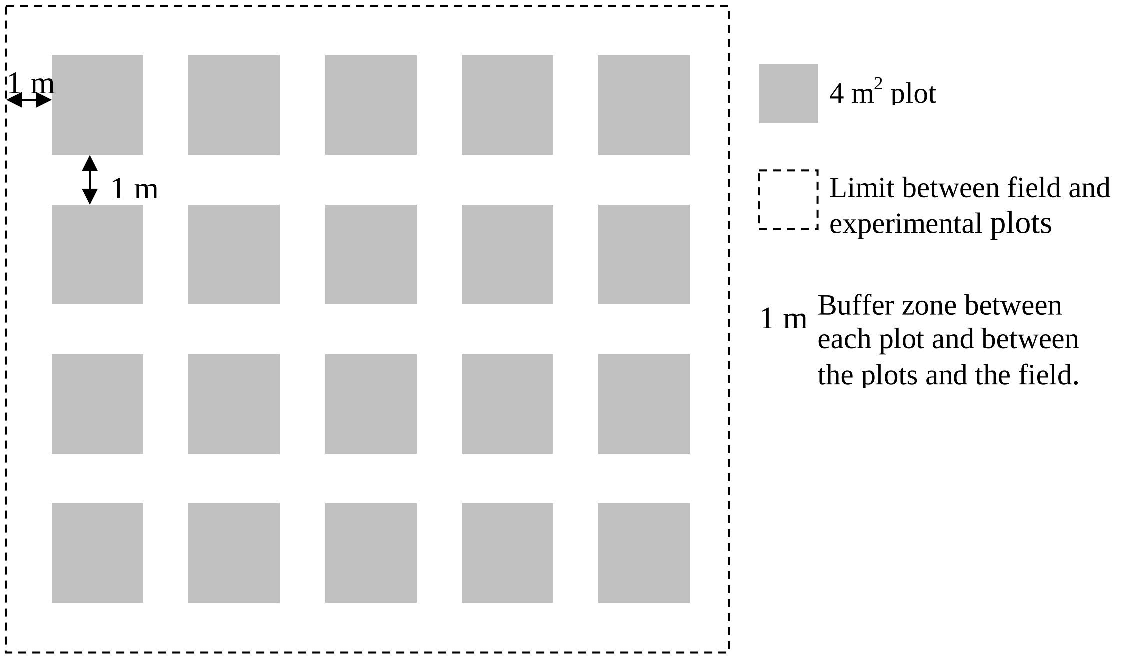


Figure 15: Experimental configuration of field trial plots

3.4.1.2 Growth Parameters Measured

The effect of the ground drywall amendment on the early growth of canola was evaluated by measuring the dry root biomass, the number of pods per plant, and the seed weight (Ahmad et al. 2005). On June 4, 2010 (Day 211), 15 plants were randomly selected for harvest from each plot; in some cases, plots only had 10 healthy plants due to the frost and deer damage. First, the roots of these plants were removed, dried for 24 h at 104°C, and weighed to calculate the dry too biomass. Then the pods per plants were counted and the weight of 1000 seeds was measured.

3.4.2 Newton

The first field scale experiment was greatly damaged by the frost and the deer. The opportunity to redo a field experiment was offered in October 2011. The Catawba EcoComplex in Newton, N.C. offered the use of their canola field for another field experiment (Figure 16). The seeds were planted in early October, about one month earlier than the first field trial planting, and frost damage was avoided. Moreover, the site used at the Catawba EcoComplex was fenced, and no deer were able to access the field.

Figure 16: Newton canola field April 13, 2011

3.4.2.1 Field Experimental Design

The field was prepared and fertilized by Mr. Whisnant, a Catawba Valley farmer contracted by the Catawba County Engineering and Utilities Department to manage their biodiesel crop production (Appendix A). Canola seed were sown on October 5, 2010 (Day 0). Four doses of ground conventional drywall (USG Sheetrock® Gypsum Panel) were surface applied to different plots on October 29, 2010 (Day 24). Control plots received no ground drywall amendment (Table 16). Each treatment dose was replicated four times, so that there were four plots receiving each of the doses shown in the table. The doses were selected based on gypsum application rates found in literature (Withers et al. 1994; Wen et al. 2003; Ahmad et al. 2005; Wen et al. 2008). The plot design was similar to the one used in the Huntersville field experiment and contained 20 2-m x 2-m squares arranged in a rectangle (16 m by 13 m) with a one meter buffer between the squares (Figure 15).

Table 16: Ground drywall doses applied to canola plots at the Newton site

Dose	Drywall Dose per Plot (g)	Drywall Dose (g m^{-2})	Drywall Dose (kg ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	0.00	0.00	0.00	0.00
B	19.92	4.98	49.8	8.3
C	59.75	14.94	149.4	25
D	119.50	29.88	298.8	50.1
E	199.17	49.79	497.9	83.4

3.4.2.2 Seed Yield Measurement

The effect of the ground drywall amendment on canola plant growth was evaluated by measuring the number of pods per plants, the number of seeds per pods, the weight of 1000 seeds (Ahmad et al. 2005), and the leaf area of young canola plants. On June 21, 2011 (Day 259), ten plants per plot were randomly selected for harvesting. First, the pods per plant and the seeds per pods were counted. Then, the weight of 1000 seeds per treatment dose was measured.

3.4.2.3 Leaf Area Measurement

On December 2, 2010 (Day 58), three plants per plot were randomly selected for harvest. The leaf area of these plants was measured using Photoshop CS3 (Jarou 2009), a graphic editing software. The leaves of each plant were cut from the main stem and set on a white piece of paper. A yellow rectangular label was placed next to the leaves as a reference. A photograph of the white piece of paper (with the leaves and the label) was taken, and the software was used to compare the number of pixels of the label with the number of green pixels of the leaves. Knowing the surface area of the label (9 in^2), the software computed the surface area of the leaves.

3.5 Sunflower Field

3.5.1 Field Experimental Design

The effect of a ground drywall amendment on sunflower plant growth (*Hellianthus annuus*) was evaluated on a sunflower crop grown for biofuel at the Catawba County EcoComplex in Newton, NC (Figure 17). As with the canola crop previously described, the soil preparation, fertilizer application, and seed planting were contracted by the county to a local farmer, Mr. Whisnant. The sunflowers were planted on June 5, 2010 (Day 0). Four different application rates of ground regular drywall (USG Sheetrock® Gypsum Panel) were tested in quadruplicate, and four control plots were maintained that received no ground drywall amendment (Table 17). The ground drywall was surface applied on June 10, 2010 (Day 5). The doses selected for testing were based on rates found in the literature (Intodia et al. 1997; Poomurugesan et al. 2008; Rani et al. 2009). The plot design was the same as that used for the Newton canola field trials (Figure 15).

Figure 17: Sunflowers at Newton site August 3, 2010

Table 17: Ground drywall application rates for sunflower at the Newton field site

Dose	Drywall Dose per Plot (g)	Drywall Dose (g m^{-2})	Drywall Dose (kg ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	0.00	0.00	0.00	0.00
B	19.92	4.98	49.8	8.3
C	59.75	14.94	149.4	25
D	119.50	29.88	298.8	50.1
E	199.17	49.79	497.9	83.4

3.5.2 Growth Parameters Measured

The effect of ground drywall on the growth of sunflower was evaluated by measuring plant height, sunflower head girth, dry stalk biomass, plant density (Intodia et al. 1997; Poomurugesan et al. 2008), and leaf surface area using Adobe Photoshop CS3 (Jarou 2009). These evaluations were performed on Days 34 (July 9, 2010) and 59 (August 3, 2010) after seeding. A last measurement was scheduled on September 14, 2010 (Day 101) during the final harvest. However, the sunflowers were completely overrun by Japanese Honeysuckle, which precluded any manual harvesting of the sunflower heads or plants.

3.5.2.1 Plant Height and Head Girth

Three plants per plot were marked using surveyor tapes at the start of the experiment. The height of these plants was measured 34 and 59 days after seeding. Plant height was measured from the soil to the start of the head. The head diameters of these plants were measured on Day 59. The girth of the sunflower head was calculated using the diameter measurements.

3.5.2.2 Leaf Surface Area and Dry Biomass

Three random plants per plot were harvested on Days 34 and 59. The 5th, 6th, 7th, and 8th leaves downward from the head of each plant were cut from the main steam. The leaves were subjected to pixel measurement as described in Sec.3.4.2.3 for canola leaves. Briefly, leaves were placed on a white background next to a yellow label and photographed. Adobe Photoshop CS3 software calibrated the number of green pixels (leaf pixels) measured on the leaves to the number of yellow pixels on the known surface area of the label to calculate the leaf surface area. The plants harvested on Day 59 were used for the dry stalk biomass measurement. The sunflower stalks were stripped of their leaves, roots, and head, hung to dry for three months and then weighed.

3.5.2.3 Plant per Hectare

On July 9, 2010 (Day 34), the number of plants per plot was counted. The plant density of each plot was calculated knowing the surface area of each plot (4 m^2).

3.6 Carbon Sequestration Experiment

An engineered soil system composed of ground drywall and cereals was tested to evaluate its carbon sequestration potential (section 3.6.3). The calcium brought into the system by the ground drywall amendment and the atmospheric carbon added to the system by the cereals crop could result in the formation of calcium carbonate, the product of passive carbon sequestration. Wheat was grown on a soil amended with ground drywall as part as this carbon sequestration experiment. The opportunity was taken to evaluate the effect of drywall on wheat growth and wheat yield (section 3.6.2).

3.6.1 Outdoor Experimental Design

3.6.1.1 Cylinder Columns

Wheat and corn were grown in circular 12-inch diameter cardboard cylinders (QUIKRETE® QUIK-tubes) that were 4 ft high. Each cylinder contained a commercial premium soil blend consisting of screened topsoil, creek sand, & compost (Garden Max Blend, BlueMax Materials, Charlotte, NC (Appendix B)) that filled it about 4/5 full. The bottoms 6 in. of each cylinder were filled with brick nuggets (Blue Max materials, Charlotte, N.C.) for drainage. Some cylinders received 3% concrete fines (D.H. Griffin Grading and Crushing, Charlotte N.C.) at about 2 ft deep to increase soil pH by 1 unit (Figure 18).The tubes were covered inside and outside with a 3 mil thick 55 gal plastic contractor bag to protect the cardboard tube from water and extend its life. The bottom of the tube was covered with a liner made of two thickness of a soil separator tarp (25µm nylon mesh nitex sefar). Finally, a plastic milk crate (Staples store brand) 11.5 in wide, 16.75 in long and 13.75 in tall was placed at the bottom end of the tube to add some structural strength and to ease transport. The cylinders were housed outdoors, where they were exposed to natural lighting and temperature conditions, but they were located under a shelter so that watering could be controlled.

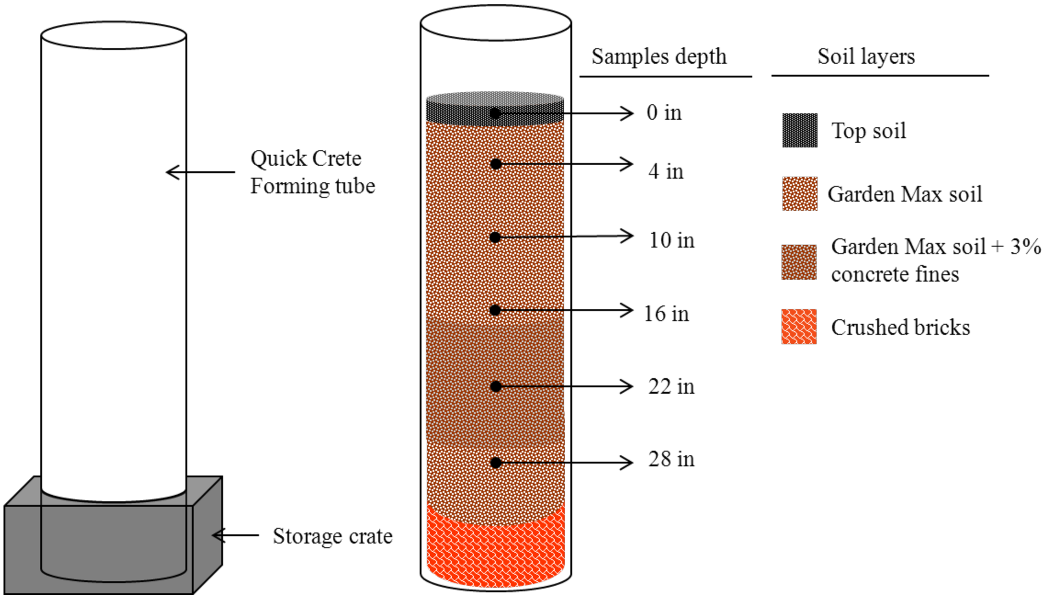


Figure 18: Soil layers inside a column

3.6.1.2 Shelter

The annual precipitation of North Carolina is about 44 in. (average over seven years of data obtained from the Ready Creek Environment Center rain gauge). This high precipitation classified North Carolina as a pedalfer soil where calcium carbonate is hardly formed. In order to control and reduce the level of precipitation to below 33 in y^{-1} (pedocal soils), a shelter was built under which the experiment took place. The shelter was built with a roof but no walls to allow the air circulation to cool down the plants in the hot North Carolina summer. The shelter was made of construction lumber and was 12 ft wide, 16 ft long, and 10 ft high. The roof was made of greenhouse plastic tarp. Wooden racks were also built to elevate the tubes and collect potential leachate. The racks were 14 ft long and 1.25 ft wide and were on average 1 ft above the ground (Figure 19). The plants were watered weekly. Some plants were tested at a watering rate of 33 in y^{-1} while others were grown using a watering rate of 28 in y^{-1}. The North Carolinian precipitation pattern was respected (wet summer and dry winter).

Figure 19: Shelter for carbon sequestration experiment

3.6.1.3 Drywall Dose

The construction of the shelter and the cylinders was completed on October 27, 2009 (day -3). The cylinders were filled on October 29, 2009 (Day -1) and October 30, 2009 (Day 0). Finally, the ground drywall (USG Sheetrock® Gypsum Panel) doses were added. Three different doses of regular gypsum drywall were tested in triplicate, under different precipitation levels, and with or without a concrete fines addition (Table 18). The doses selected were based on recommended literature values for agricultural gypsum application rates for wheat. (Sundahri et al. 2001; Caires et al. 2002; Rashid et al. 2008). Half of this dose was mixed with the first 8 in of the soil and half was surface applied when the seeds were planted. Control cylinders did not receive any drywall amendment.

Table 18: Ground drywall doses for carbon sequestration experiment

Dose	Precipitation Level (in. y^{-1})	Concrete Fines	Drywall Dose per Column (g)	Drywall Dose (g m^{-2})	Drywall Dose (t ha^{-1})	Sulfur Equivalent (kg S ha^{-1})
A	33	N	0	0	0	0
B	33	N	35	480	4.8	804
C	33	N	70	960	9.6	1,609
D	33	N	140	1,920	19.2	3,218
E	33	Y	70	960	9.6	1,609
F	33	Y	140	1,920	19.2	3,218
G	28	N	940	0	0	0
H	28	N	70	960	9,6	1,609
J	28	N	140	1,920	19,2	3,218
I	28	Y	70	960	9,6	1,609

3.6.2 Drywall as an Amendment for Wheat

Wheat seeds (NC05-20814, NC State, Raleigh, NC) were germinated in the laboratory on October 27, 2009 (Day -3). On October 29, 2010 (Day -1), half of the drywall doses were mixed into the top 8 in. of soil. On October 30, 2010 (Day 0), seeds were applied at a rate of 35 seeds ft^{-2} (Bitzer et al. 1994), so that 27 seeds were planted in each cylinder in a bed of vermiculite, perlite, and peat moss (ratio of 1/1/4) that was mixed with the remaining half dose of ground drywall and placed atop the soil in the cylinders. The wheat was harvested on May 17, 2010 (day 199). The effect of a drywall amendment on wheat growth was measured only for the first 4 treatments (A, B, C, and D).

3.6.2.1 Growth Parameters Measured

The wheat growth was continuously monitored using an industry standard developed in Germany called the BBCH (Biologische Bundesanstalt, Bundessortenamt and CHemical) scale (Meier 2001). The scale converts growth stages of cereals (number of leaves, tillers, node, flower emergence...) into numerical values so that growth of different plants can be compared. In addition to growth, the effect of ground drywall on weight height and yield were assessed on Day 199. Yield was measured in terms of number of ears per columns, number of kernels per ears, and the weight of 100 kernels (Sundahri et al. 2001).

3.6.2.1.1 BBCH Scale

On December, 22, 2010 (Day 53), five plants per cylinder were randomly selected and graded using the BBCH scale. On March 9, 2011 (Day 130), the same five plants were graded again using the BBCH scale.

3.6.2.1.2 Ears per Columns, Kernels per Ear, and Mass of 100 seeds

On May 17, 2010 (Day 199), wheat plants were harvested. The number of ears produced in each cylinder, and the number of seeds per ear were recorded. Finally, 100 seeds per cylinder were randomly selected and weighed.

3.6.2.1.3 Wheat Height

The height of the wheat was measured on May 17, 2010. During the harvest, some plants were cut above the 4th node; therefore, the height of each plant was measured from the plant tip to the 3rd node so that comparisons could be made between plants.

3.6.3 Carbon Sequestration

A series of plantings was continued over two years after the initial wheat planting because the process of $CaCO_3$ was likely to be slow, the amounts produced were likely to be small, and we wanted to optimize our ability to detect its presence (Gocke et al. 2010). Wheat plants were used as crop because their exudates are among the few that have been characterized in the literature (Kuzyakov et al. 2000; Ryan et al. 2001; Pearse et al. 2006). For the first crop rotation, wheat seeds (NC05-20814, NCSU, Raleigh, NC) were used (section 3.6.2). Wheat plants were harvested May 17, 2010 (Day 199). On June 3, 2010 (Day 246), three corn seeds (dwarf open pollinated corn, Athens Seed Co., Inc. Watkinsville, GA.) were planted in each cylinder in about 2 in of top soil (The Scotts Company LLC). The same day, another dose of ground drywall was added to the cylinders using amounts shown in Table 18. Corn was harvested on September 27, 2010 (Day 332). On October 27, 2010 (Day 362), another rotation of wheat was planted following the same protocol used in the first rotation. Another dose of ground drywall was added to the cylinders using amounts shown in Table 18. On May 26, 2011 (Day 573), the second rotation of wheat was harvested, while a second rotation of corn was planted that included an additional dose of drywall. The second rotation of corn was harvested on October 7, 2011 (Day 707). Over the 707 day duration of the experiment, the weekly watering rate was continued whether or not plants were growing in the cylinders.

3.6.3.1 Soil Sampling and Analysis

On October 21, 2011 (day 721), soil samples were taken from each cylinder. Six samples were taken along the soil profile for each cylinder at a depth of 0, 0.10, 0.25, 0.41, 0.56, and 0.71 m. The samples were obtained by cutting a window on the side of the cardboard cylinder. Then, using a sampling auger, three samples were taken and placed in a plastic bag. The plastic bag was then labeled and stored at 4°C. In the lab, the samples were air dried, crushed, and then sieved to a 2mm opening. The samples were finally analysis for the following parameters.

3.6.3.1.1 Soil pH

The pH was measured by placing a 10 g portion of soil in a conical tube, with 20 ml of 0.01 M of $CaCl_2$ solution. The tube was sealed and vortexed for 1 min. After a 15 min settling period, the pH of the supernatant was measured (Eppes 2011).

3.6.3.1.2 Calcium Carbonate Content

Calcium carbonate ($CaCO_3$) content in the soil was measured using a method described by Amundson et al. (1988). The principle of the test is that acid is introduced into a soil sample contained in a gas-tight bottle. The acid generates a reaction with the carbonate that results in CO_2 production. The percent CO_2 in the bottle headspace rises, and this increase can be detected using gas chromatography (GC) measurements. The CO_2 increase for a given amount of acid addition can be compared to that generated by standards, where known amounts of $CaCO_3$ additions to soil are correlated with measured CO_2 headspace changes.

Figure 20: Bottle and cap used in the GC method

The GC method procedure used here was as follows: A 5 g portion of soil sample was placed in a 120 ml bottle, which was sealed gas-tight with a specially designed cap fitted with a silicone septum (Figure 20). A 6 mL portion of 6 M HCl + 5% $FeSO_4$ was injected into the bottle with a syringe. ($FeSO_4$ was included with the acid to reduce the amount of carbon dioxide that might be produced by the oxidation of any organic matter present) (Loeppert et al. 1996). The bottle was shaken for 5 min, and then a gas-tight syringe was used to withdraw 50 µL of headspace gas from the bottle for GC analysis. To make standard curves for the samples tested, soil samples from the 33in y^{-1} trial control cylinders (treatment A) were collected and composited. A similar composite was made using soil from the 28 in y^{-1} trial control cylinders (treatment G cylinders). A specific amount of calcium carbonate representing 0.3%, 0.5%, 1%, and 1.5% of $CaCO_3$ in soil was added to the soil mixes. These standards were used to build standard curves to correlate the percent CO_2 in the bottle headspace to the amount of calcium carbonate in soil (Figure 21).

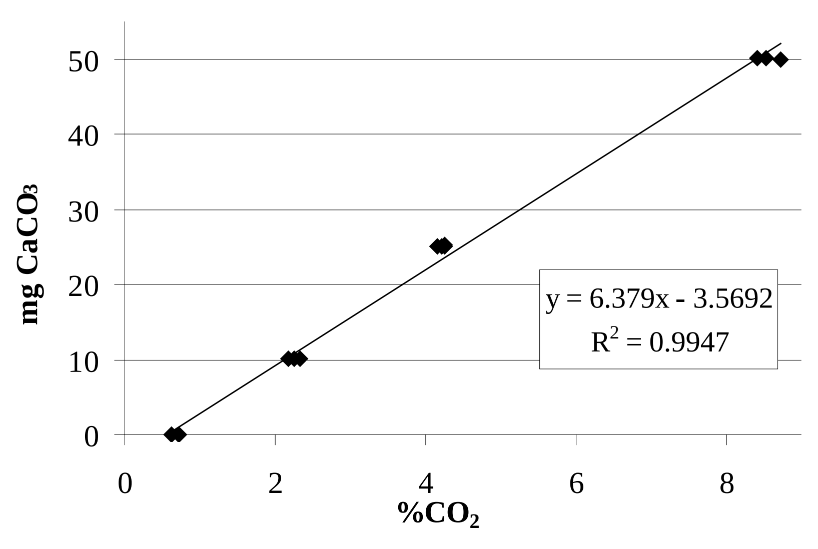


Figure 21: Standard curve made with the 33in y^{-1} trial control

3.6.3.1.3 Calcium and Sulfate Soil Content

The calcium and sulfate ions contained in each soil sample were measured using an ion chromatograph (IC). The measurement was performed in the Earth Science Laboratory of UNC Charlotte.

3.6.3.1.4 Stable Isotope Analysis

The stable isotope analysis of calcium carbonate formed in soil was done at the soil, water, and plant analysis laboratory of Georgia University. The Ratio ^{13}C to ^{12}C was measured to investigate the origin of the carbon atom of the freshly form calcium carbonate.

3.7 Statistical Analysis

Data collected during this research were statistically analyzed using the software OriginPro 8. ANOVA and LSD (Least Significant Difference) tests were used to determine any significant differences among the treatments. The significance level used was 0.05. However, it was necessary to use a significance level of 0.1 in certain cases due to the low number of replicates. The use of a significance level of 0.1 increased the power of the analysis, lowering the risk of “missing a significant difference” (type II error).

CHAPTER 4: RESULTS

4.1 Germination Tests

4.1.1 Lettuce

Lettuce is typically recommended in toxicity tests due to its high sensitivity to chemicals (US EPA 1996). As a result, lettuce was among the seeds tested for phytotoxicity (Figure 22).

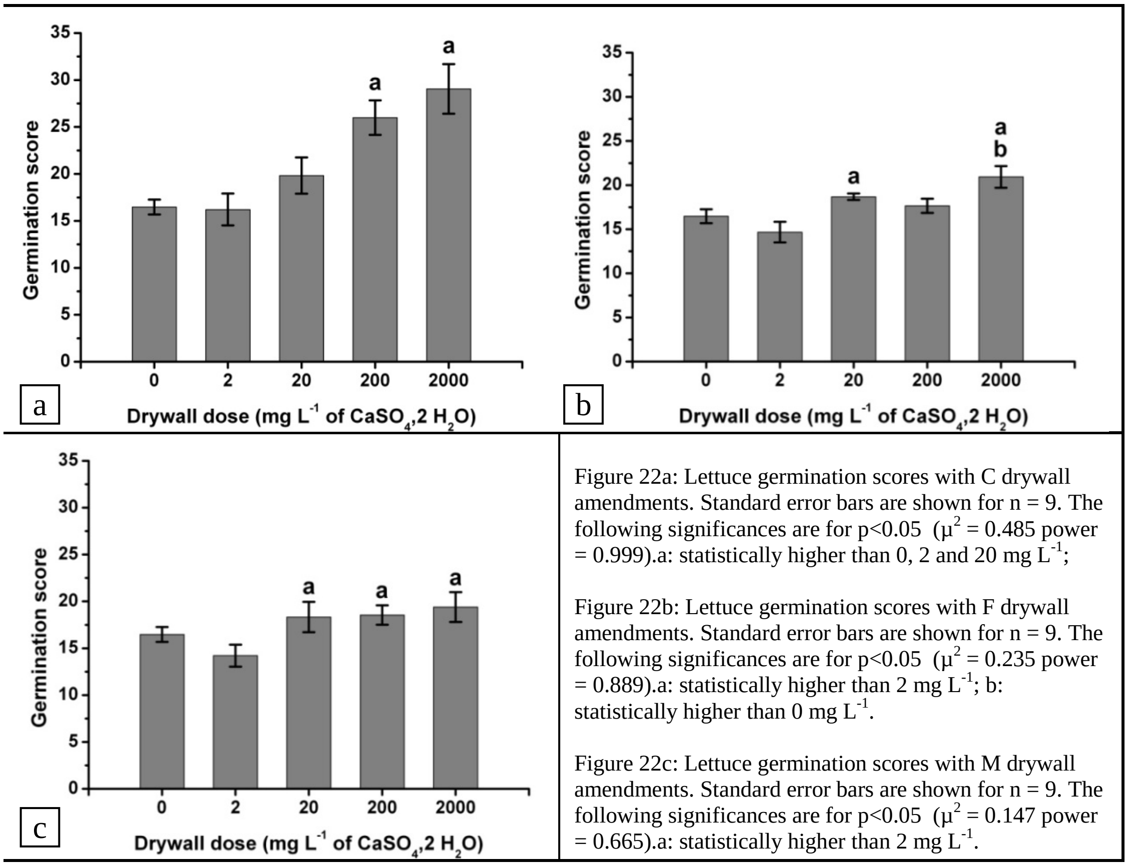


Figure 22a: Lettuce germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.485$ power = 0.999).a: statistically higher than 0, 2 and 20 mg L^{-1};

Figure 22b: Lettuce germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.235$ power = 0.889).a: statistically higher than 2 mg L^{-1}; b: statistically higher than 0 mg L^{-1}.

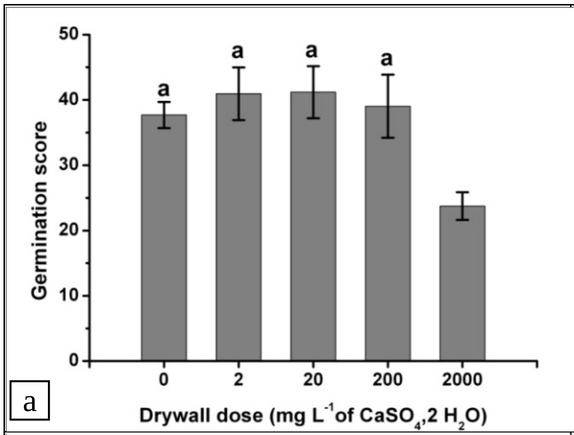
Figure 22c: Lettuce germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.147$ power = 0.665).a: statistically higher than 2 mg L^{-1}.

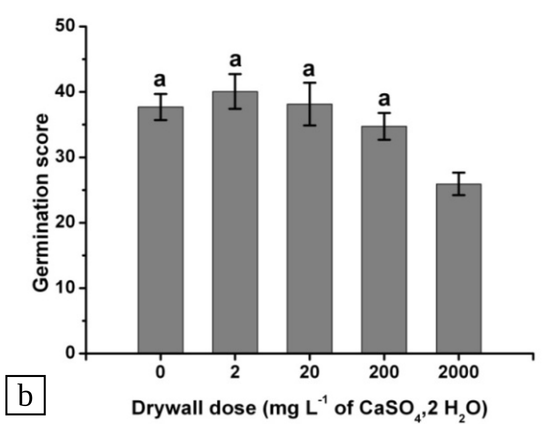
Figure 22: Germination scores of lettuce seeds exposed to drywall

Overall, all drywall types stimulated the germination score (GS) of lettuce seeds relative to the control. The two highest doses of C drywall significantly ($p<0.05$) increased the germination score compared to the control and the lowest doses. The highest doses increased the GS by 76% compare to the control while the dose of 200 mg L^{-1} increased the GS by 58%. Although this phenomenon was not repeated with F and M drywall, the highest doses of these drywalls significantly ($p<0.05$) improved GS of lettuce seeds compare to the control by 27% and 18% respectively. A two-way ANOVA analysis revealed that the C drywall significantly improved ($p<0.05$) germination compared to F and M drywall. Moreover, the same analysis showed that the two highest doses, regardless of drywall types, significantly ($p<0.05$) improved the germination score compared to the control and the lowest dose.

4.1.2 Cucumber

Cucumber seeds are also recommended for germination testing (U.S. EPA 1996). Unlike lettuce, cucumber seed germination was inhibited by high doses of drywall (Figure 23). At full strength, all drywall types significantly ($p<0.05$) inhibited cucumber seeds GS relative to controls and the lower doses. The C drywall inhibited cucumber seeds GS by 37%, the F drywall by 31%, and the M drywall by 56% compared to the control. The M drywall showed more inhibition, with the 10-fold dilution dose having a significantly lower GS ($p<0.05$) than the control. A two-way ANOVA analysis revealed that M drywall had a significantly ($p<0.05$) greater inhibition effect on GS than C drywall. The same analysis revealed that, regardless of the drywall types, the highest dose significantly ($p<0.05$) inhibited cucumber seed GS compared to the controls and the lower doses.





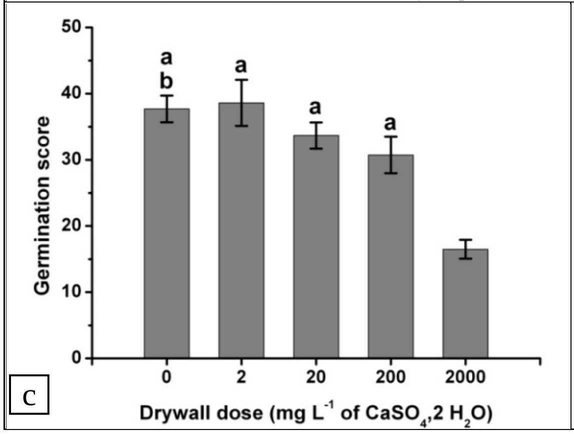


Figure 23a: Cucumber germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ (μ^2 = 0.212 power = 0.877). a: statistically higher than 2000 mg L^{-1}.

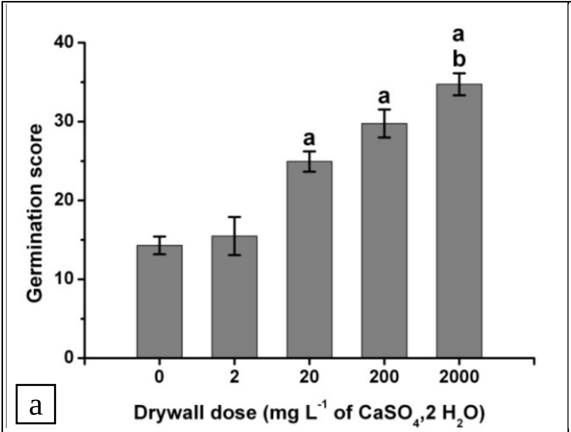
Figure 23b: Cucumber germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ (μ^2 = 0.205 power = 0.862). a: statistically higher than 2000 mg L^{-1}.

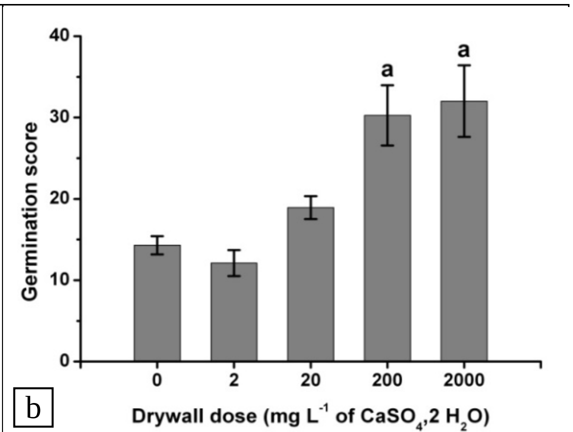
Figure 23c: Cucumber germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ (μ^2 = 0.419 power = 0.999). a: statistically higher than 2000 mg L^{-1}; b: statistically higher then 200 mg L^{-1}.

Figure 23: Germination scores of cucumber seeds exposed to drywall

4.1.3 Canola

Canola seed germination responses to drywall doses were similar to those observed with lettuce seeds exposed to drywall, with germination scores increasing with increasing drywall dose (Figure 24). Full strength C, F, and M drywall doses significantly ($p<0.05$) increased the GS relative to the control by 143%, 124% and 125% respectively. Full strength C, F, and M drywall effects on germination were also significantly different ($p<0.05$) from those associated with the 1000-fold dilution doses. The full strength C drywall dose resulted in a significantly ($p<0.05$) higher GS than the GS of canola seeds dosed with 100-fold doses.





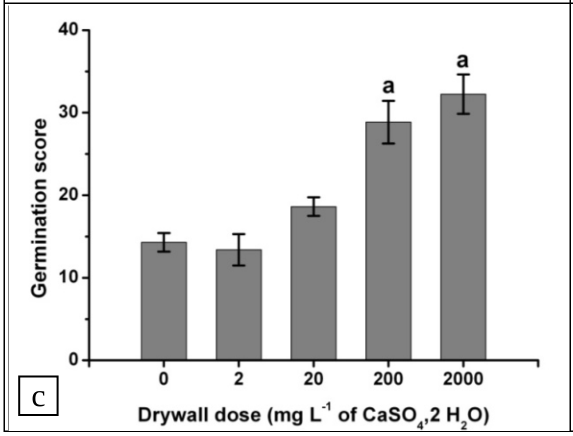


Figure 24a: Canola germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.671$ power = 1). a: statistically higher than 0 and 2 mg L^{-1}; b: statistically higher than 20 mg L^{-1}.

Figure 24b: Canola germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.506$ power = 1). a: statistically higher than 0, 2, and 20 mg L^{-1}.

Figure 24c: Canola germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.616$ power = 1). a: statistically higher than 0, 2, and 20 mg L^{-1}.

Figure 24: Germination scores of canola seeds exposed to drywall

The GS of canola seeds dosed with full strength F and M drywall solutions likewise differed significantly ($p<0.05$) from seeds dosed with 100-fold dilution doses of F and M drywalls. The 10-fold dilution doses of each drywall type also resulted in significantly higher ($p<0.05$) canola GS than the controls. Although the stimulatory effects of the F and M type drywall materials were not as robust as that of C drywall, all types enhanced the GS of canola seeds. A two-way ANOVA analysis confirmed that the effect of the types of drywall on canola seeds was not statistically different ($p<0.05$). The same analysis confirmed that regardless of the type of drywall, the two highest doses of drywalls statistically ($p<0.05$) resulted in higher GS than the lower dose and the control.

4.1.4 Wheat

Wheat seeds were subjected to the GS protocol (Figure 25) due to their relevance to the experiment exploring carbon sequestration impacts of drywall soil amendments. The wheat GS resulting from additions of various drywall types trended much like those of the cucumber seeds, with the highest dose of M drywall yielding significantly lower ($p<0.05$) GS than any other treatments and the control.

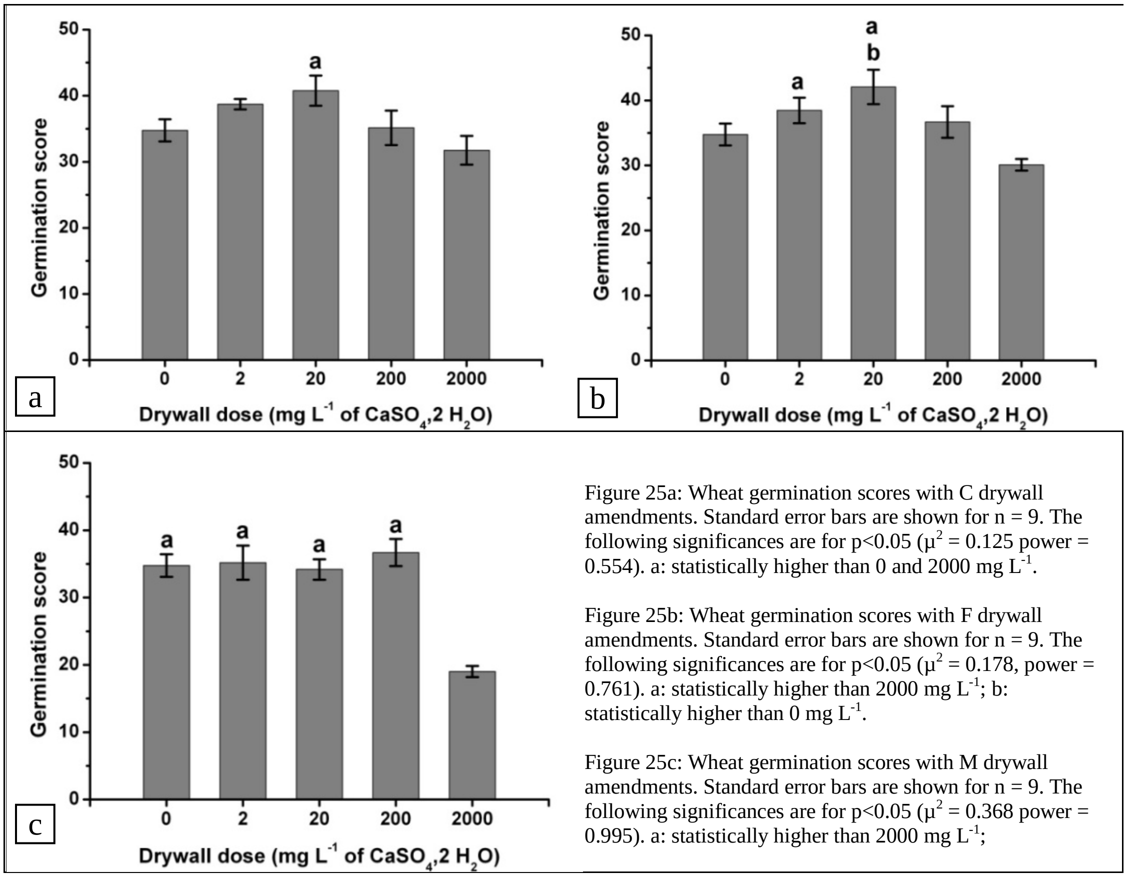


Figure 25a: Wheat germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.125$ power = 0.554). a: statistically higher than 0 and 2000 mg L^{-1}.

Figure 25b: Wheat germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.178$, power = 0.761). a: statistically higher than 2000 mg L^{-1}; b: statistically higher than 0 mg L^{-1}.

Figure 25c: Wheat germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.368$ power = 0.995). a: statistically higher than 2000 mg L^{-1};

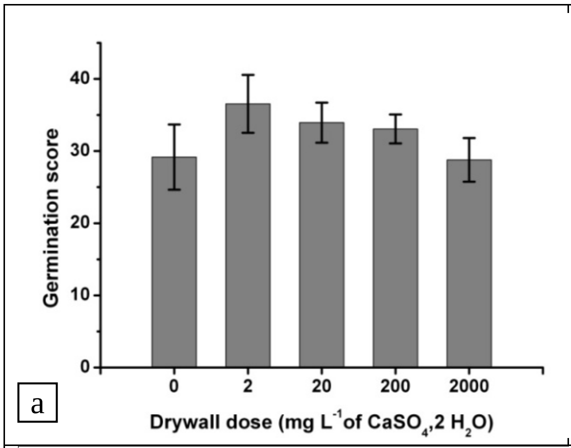
Figure 25: Germination scores of wheat seeds exposed to drywall

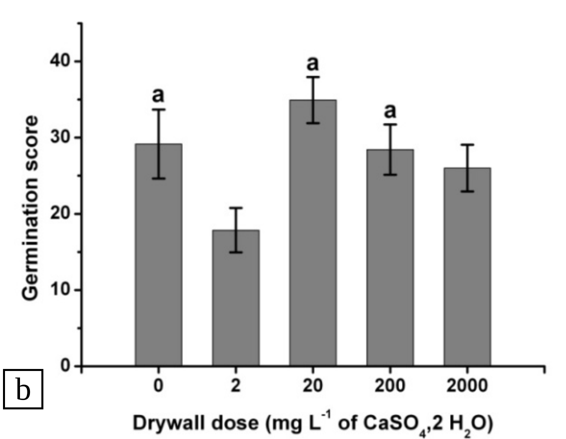
At full strength, the C and F drywall treatments were inhibitory relative to the controls. C drywall reduced wheat seed GS by 9%, F drywall by 13%, and M drywall by 45%. Interestingly, C doses at the 100-fold dilution doses significantly ($p<0.05$) stimulated GS of wheat seeds relative to the control (17%) and the full strength C dose.

Likewise, the 100-fold dilution dose of F drywall showed significant ($p<0.05$) stimulatory effects relative to controls (21%) and the highest dose. A two-way ANOVA analysis of the data set revealed that, regardless of the types of drywall, the highest concentration of drywall significantly ($p<0.05$) inhibited wheat germination relative to lower doses while the 100-fold dilution dose significantly ($p<0.05$) improved it. This analysis also revealed that M drywall resulted in significantly ($p<0.05$) lower GS values than F drywall.

4.1.5 Corn

Corn seeds were subjected to the GS test because they were also relevant in the carbon sequestration experiment. Drywall C doses did not have any significant effect on





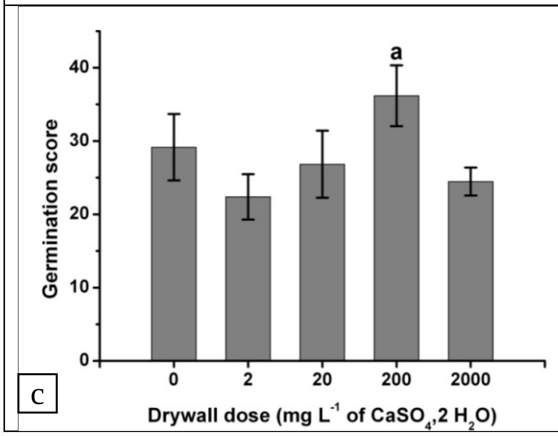


Figure 26a: Corn germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.089$ power = 0.259).

Figure 26b: Corn germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.231$, power = 0.706). a: statistically higher than 2 mg L^{-1}.

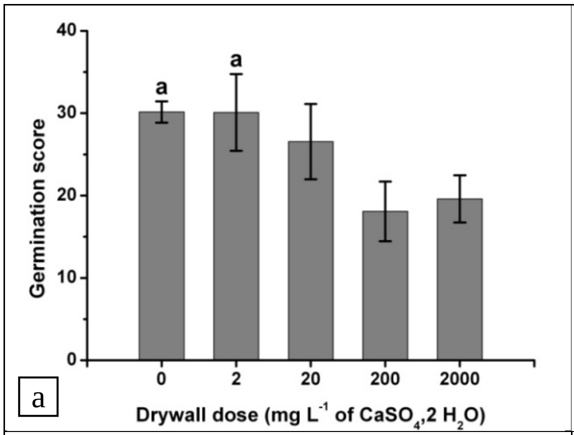
Figure 26c: Corn germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.165$, power = 0.529). a: statistically higher than 2 and 2000 mg L^{-1};

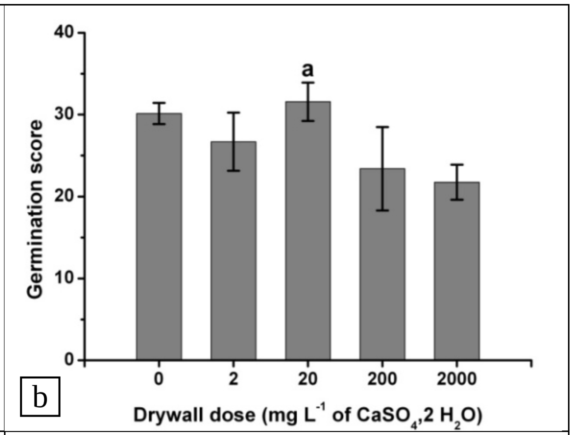
Figure 26: Germination scores of corn seeds exposed to drywall

corn seed germination at any levels (Figure 26). However, the 1000-fold dilution dose of F drywall yielded significantly ($p<0.05$) lower corn GS than the control (by 39%), the 100-fold (by 49%), and the 10-fold (by 37%) dilution treatments. Surprisingly, the GS results of corn seeds exposed to M drywall doses followed yet a third pattern. The 10-fold dilution dose yielded significantly ($p<0.05$) higher GS than the highest and lowest doses. Overall, the two-way ANOVA test revealed that the types of drywall did not have a significantly effect on corn seeds GS.

4.1.6 Sunflower

Sunflower plants were used in field experiments as a rotation crop with canola and were, therefore, included in the germination studies. Sunflower seeds responded to the drywall amendments much as the cucumber seeds did (Figure 27). The highest dose of C drywall yielded lower sunflower GS than the control. The 10-fold dilution dose yielded significantly ($p<0.05$) lower GS than the control and the 1000-fold dilution by about 40%. The M drywall doses results showed similar trends. The two highest doses of M drywall yielded a significant ($p<0.05$) sunflower GS decrease relative to the control. There was a 37% GS reduction from the 10 fold dilution and a 28% reduction from the full strength dilution. The F drywall trended toward decreasing GS with increasing dose. Overall, using a two-way ANOVA analysis, the two highest doses of drywalls significantly ($p<0.05$) inhibited the GS of sunflower seeds relative to the control and the two lowest doses for all drywall types. The same test confirmed that the three drywall types were not statistically different in their effects on sunflower seed GS.





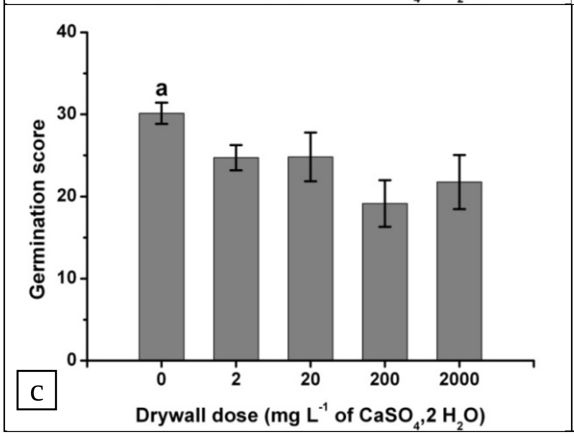


Figure 27a: Sunflower germination scores with C drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.194$ power = 0.611). α: statistically higher than 200 mg L^{-1}.

Figure 27b: Sunflower germination scores with F drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.144$, power = 0.435). α: statistically higher than 2000 mg L^{-1}.

Figure 27c: Sunflower germination scores with M drywall amendments. Standard error bars are shown for n = 9. The following significances are for $p<0.05$ ($\mu^2 = 0.194$, power = 0.597). α: statistically higher than 200 and 2000 mg L^{-1}.

Figure 27: Germination scores of sunflower seeds exposed to drywall

4.2 Grass Amendment Experiment

4.2.1 Accumulated Grass Height

The data generally showed that the C and F drywall amendments did not significantly affect grass height relative to controls (Figure 28). However, there was one treatment (1,341 kg S ha^{-1} of C drywall) that yielded significantly greater grass height ($p<0.05$), suggesting some minor drywall stimulatory effects. Sunflower seeds responded to the drywall amendments much as the cucumber seeds did (Figure 27). The highest dose of C drywall yielded lower sunflower GS than the control. The 10-fold dilution dose yielded significantly ($p<0.05$) lower GS than the control and the 1000-fold dilution by about 40%. The M drywall doses results showed similar trends. The two highest doses of

M drywall yielded a significant ($p<0.05$) sunflower GS decrease relative to the control. There was a 37% GS reduction from the 10 fold dilution and a 28% reduction from the full strength dilution. The F drywall trended toward decreasing GS with increasing dose. Overall, using a two-way ANOVA analysis, the two highest doses of drywalls significantly ($p<0.05$) inhibited the GS of sunflower seeds relative to the control and the two lowest doses for all drywall types. The same test confirmed that the three drywall types were not statistically different in their effects on sunflower seed GS.

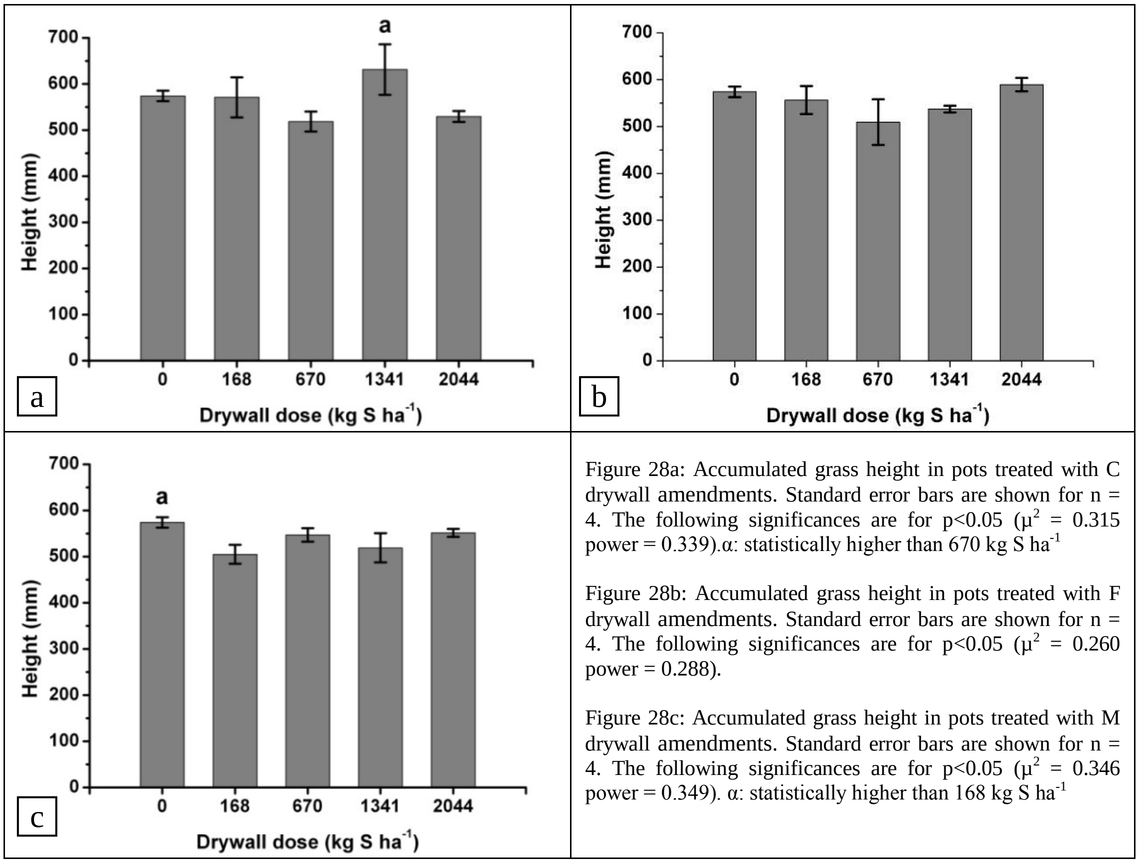


Figure 28a: Accumulated grass height in pots treated with C drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.05$ ($\mu^2 = 0.315$ power = 0.339).α: statistically higher than 670 kg S ha^{-1}

Figure 28b: Accumulated grass height in pots treated with F drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.05$ ($\mu^2 = 0.260$ power = 0.288).

Figure 28c: Accumulated grass height in pots treated with M drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.05$ ($\mu^2 = 0.346$ power = 0.349). α: statistically higher than 168 kg S ha^{-1}

Figure 28: Accumulated grass height in pots treated with drywall

Regarding the M drywall amendments, the lowest M drywall dose (168 kg S ha^{-1}) resulted in significantly ($p<0.05$) shorter grass than the control by a factor of 12%. A two-way ANOVA analysis suggested that there were no significant differences between the types of drywalls. The same analysis revealed that, regardless of the types of drywall, the dose rate does not significantly alter the grass height.

4.2.2 Accumulated Dry Biomass

The accumulated biomass data were much more variable than the accumulated grass height, so that although the data show some trend toward drywall inhibition (Figure 29), the statistics of both C and M drywall were not robust enough to reveal statistical differences.

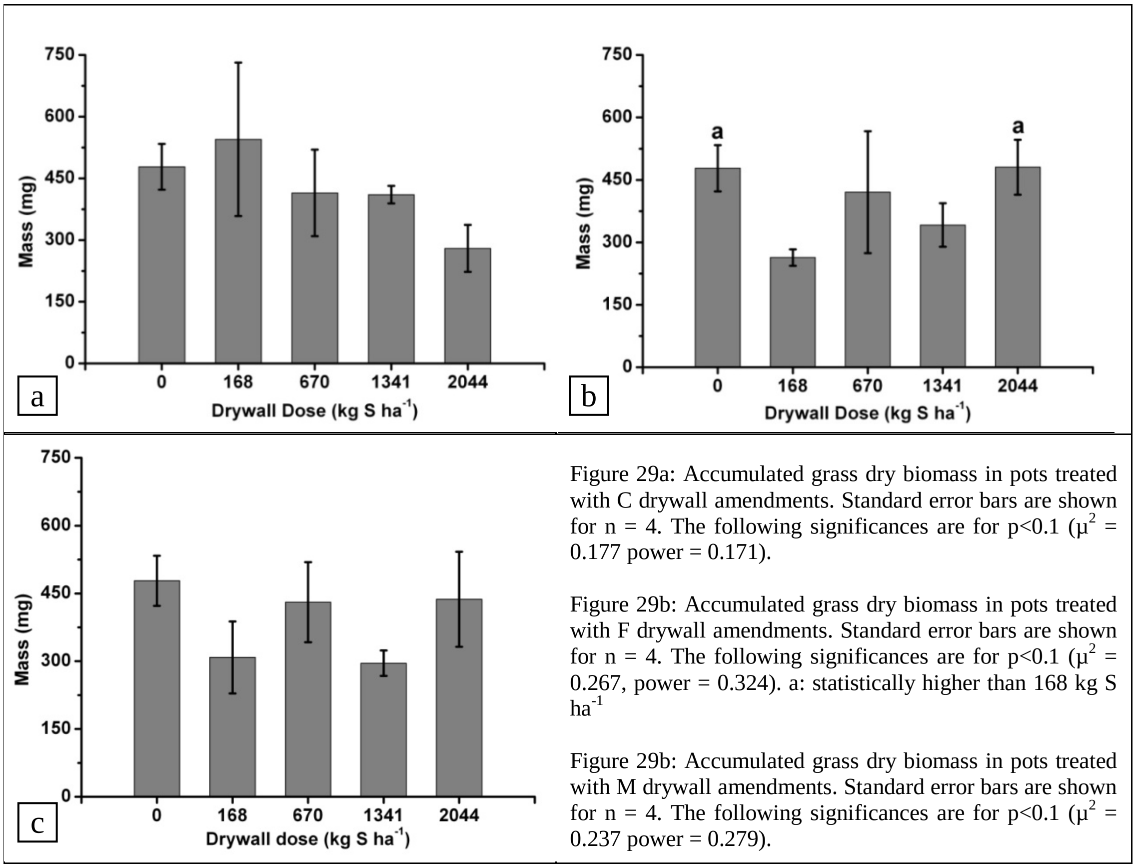


Figure 29a: Accumulated grass dry biomass in pots treated with C drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.1$ (μ^2 = 0.177 power = 0.171).

Figure 29b: Accumulated grass dry biomass in pots treated with F drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.1$ (μ^2 = 0.267, power = 0.324). a: statistically higher than 168 kg S ha^{-1}

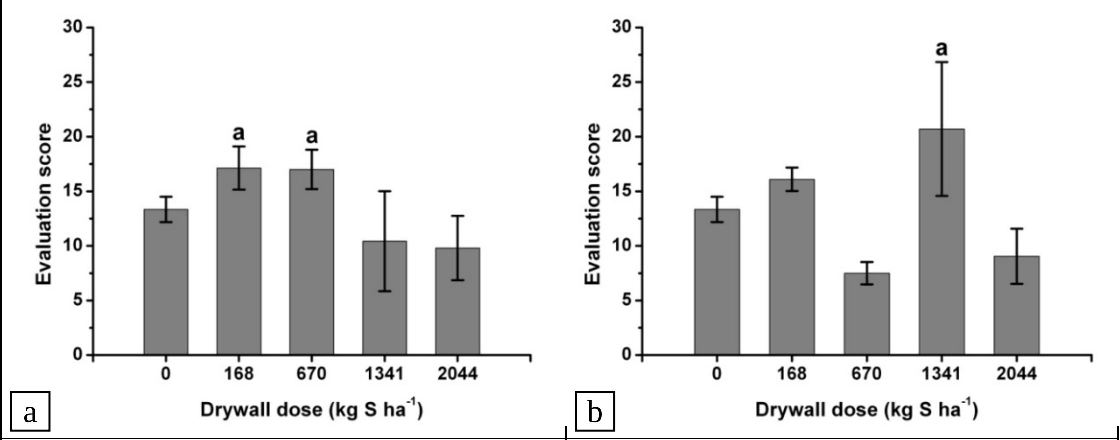
Figure 29b: Accumulated grass dry biomass in pots treated with M drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p<0.1$ (μ^2 = 0.237 power = 0.279).

Figure 29: Accumulated dry grass biomass in pots treated with drywall

There was significant inhibition ($p<0.1$) of biomass growth at the lowest and highest doses of F drywall relative to the control. The lowest F drywall dose reduced accumulated biomass by 45% relative to the control and to the highest dose. The statistics of both C and M drywall were not robust enough to reveal any differences. A two-way ANOVA analysis showed that neither the drywall types nor the doses were statistically different from each other.

4.2.3 Root Coverage

The relative degree of root coverage associated with each treatment was scored based on visual grading: the lower the score, the more the root covered the pot bottom.



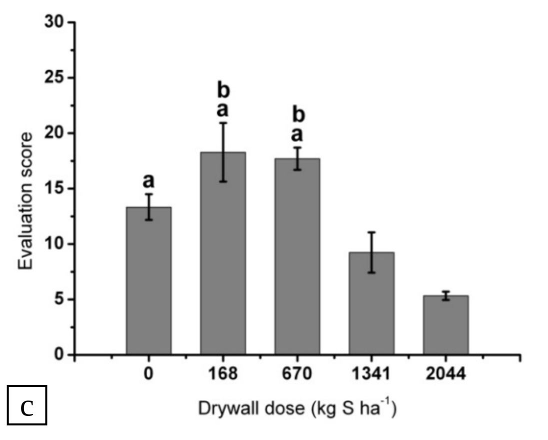


Figure 30a: Root evaluation score in pots treated with C drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p < 0.1$ ($\mu^2 = 0.380$ power = 0.556). a: statistically higher than 1341 and 2044 kg S ha^{-1}

Figure 30b: Root evaluation score in pots treated with C drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p < 0.05$ ($\mu^2 = 0.431$ power = 0.687). a: statistically higher than 670 and 2044 kg S ha^{-1}.

Figure 30c: Root evaluation score in pots treated with C drywall amendments. Standard error bars are shown for n = 4. The following significances are for $p < 0.05$ ($\mu^2 = 0.769$ power = 0.996). a: statistically higher than 2044 kg S ha^{-1}; b: statistically higher than 1341 kg S ha^{-1}.

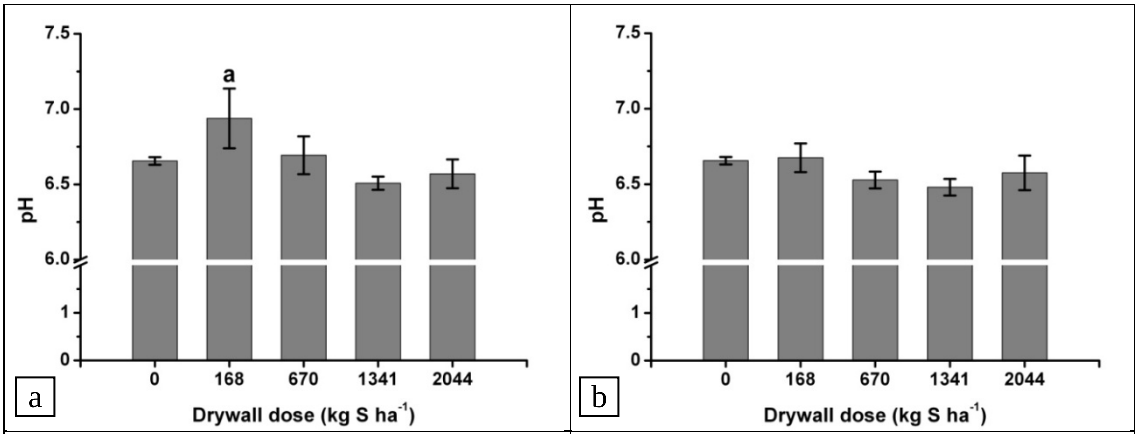
Figure 30: Root evaluation scores in pots treated with drywall

Figure 30 shows that the two highest doses of C and M drywall resulted in significantly ($p<0.1$ and $p<0.05$) higher root coverage relative to the control (for M drywall) and relative to the lower amendment doses (C and M drywall). The F drywall amendment of

1341 kg S ha^{-1} yielded sparser root coverage than the two high doses. The two-way ANOVA analysis ($p<0.05$) confirmed these results and revealed that drywall type did not affect root coverage. Nevertheless, visible inspection showed that grass in the control pots looked thicker and more robust than pots amended with drywall.

4.2.4 Soil pH

The two-way ANOVA analysis revealed that drywall type and pH effects were not related, after 14 days (Figure 31) and also 89 days after seeding (Figure 32).



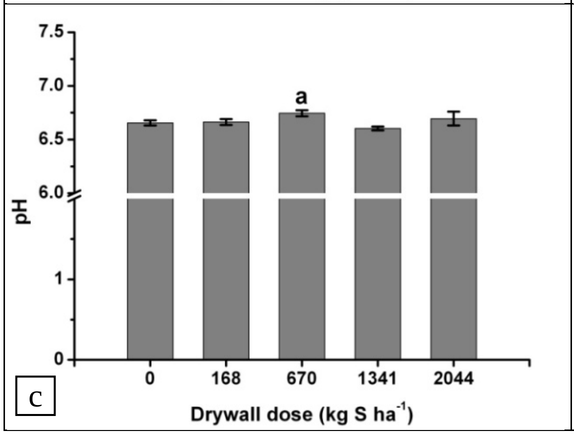


Figure 31a: Soil pH 14 d after amendment with C drywall. Standard error bars are shown for n = 4. The following significances are for $p < 0.05$ ($\mu^2 = 0.351$ power = 0.469). a: statistically higher than 1341 and 2044 kg S ha^{-1}

Figure 31b: Soil pH 14 d after amendment with F drywall. Standard error bars are shown for n = 4. The following significances are for $p < 0.05$ ($\mu^2 = 0.239$ power = 0.282

Figure 31c: Soil pH 14 d after amendment with M drywall. Standard error bars are shown for n = 4. The following significances are for $p < 0.05$ ($\mu^2 = 0.345$ power = 0.385). α: statistically higher than 1341 kg S ha^{-1}

Figure 31: Soil pH 14 d after amendment with drywall

M and C drywall tests showed that while no doses resulted in a pH significantly different than the control, among the doses there were differences; the highest doses of amendment yielded significantly ($p<0.05$) lower pH than the low doses. In the case of C drywall, the two highest doses resulted in a statistically lower soil pH than the lowest dose, but the pH difference was only 0.4 units. A similar pH response occurred in the M drywall tests, where the dose of 670 kg S ha^{-1} yielded a slightly but significantly ($p<0.05$) higher pH than the dose of 1341 kg S ha^{-1}. The two-way ANOVA analysis, which compared doses regardless of drywall types, indicated that the pH effects of the two highest drywall doses were significantly different from those of the lower dose ($p<0.05$).

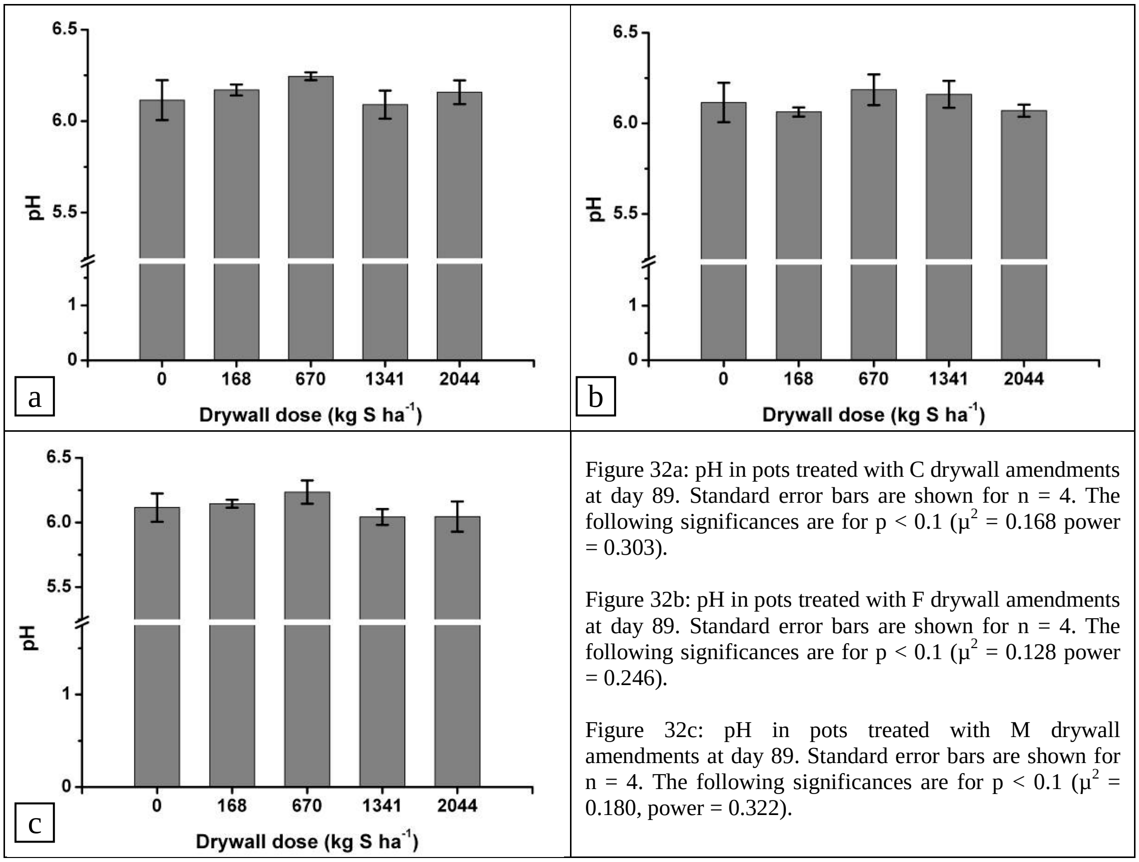


Figure 32a: pH in pots treated with C drywall amendments at day 89. Standard error bars are shown for n = 4. The following significances are for $p < 0.1$ ($\mu^2 = 0.168$ power = 0.303).

Figure 32b: pH in pots treated with F drywall amendments at day 89. Standard error bars are shown for n = 4. The following significances are for $p < 0.1$ ($\mu^2 = 0.128$ power = 0.246).

Figure 32c: pH in pots treated with M drywall amendments at day 89. Standard error bars are shown for n = 4. The following significances are for $p < 0.1$ ($\mu^2 = 0.180$, power = 0.322).

Figure 32: Soil pH 89 d after amendment with drywall

The soil pH on Day 89 was lower than on Day 14 for all treatments, including the control, but there was no evidence of further pH decline after Day 89.

4.3 Canola Pot Experiment

4.3.1 Leaf Count

Leaf counts were performed on canola plants on Days 16 and 25. On Day 16, the number of leaves per plant observed paralleled the results of the germination score test.

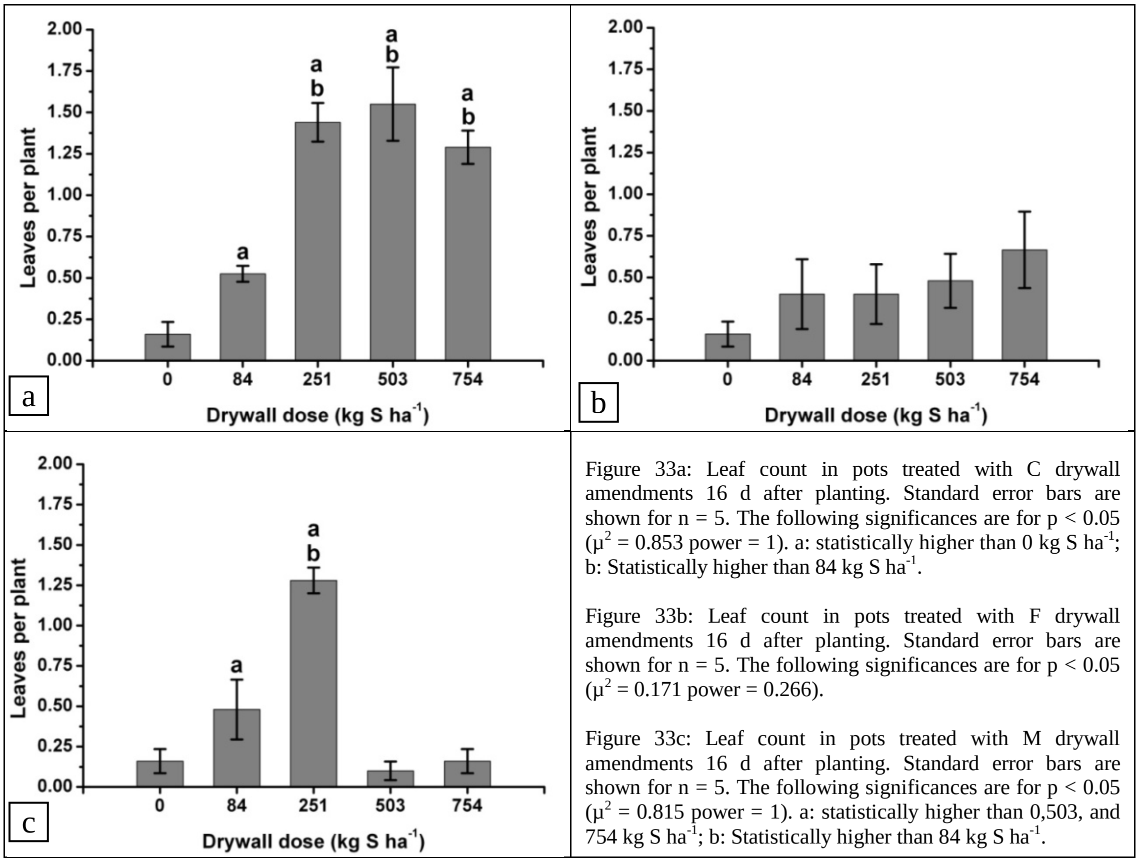


Figure 33a: Leaf count in pots treated with C drywall amendments 16 d after planting. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ (μ^2 = 0.853 power = 1). a: statistically higher than 0 kg S ha^{-1}; b: Statistically higher than 84 kg S ha^{-1}.

Figure 33b: Leaf count in pots treated with F drywall amendments 16 d after planting. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ (μ^2 = 0.171 power = 0.266).

Figure 33c: Leaf count in pots treated with M drywall amendments 16 d after planting. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ (μ^2 = 0.815 power = 1). a: statistically higher than 0,503, and 754 kg S ha^{-1}; b: Statistically higher than 84 kg S ha^{-1}.

Figure 33: Leaf counts in pots treated with drywall 16 d after planting

The numbers of leaves were significantly ($p<0.05$) higher among plants receiving drywall amendment relative to the control pots (Figure 33). Pots receiving C drywall amendments generally outperformed those receiving R or M type amendment. This was statistically confirmed by a two-way ANOVA that showed the differences to be significant ($p<0.05$). The pots receiving a drywall dose equivalent of 503 kg S ha^{-1}

showed peak leaf numbers. Only the 251 kg sulfur ha^{-1} dose of M type drywall approached the stimulatory capacity of C drywall.

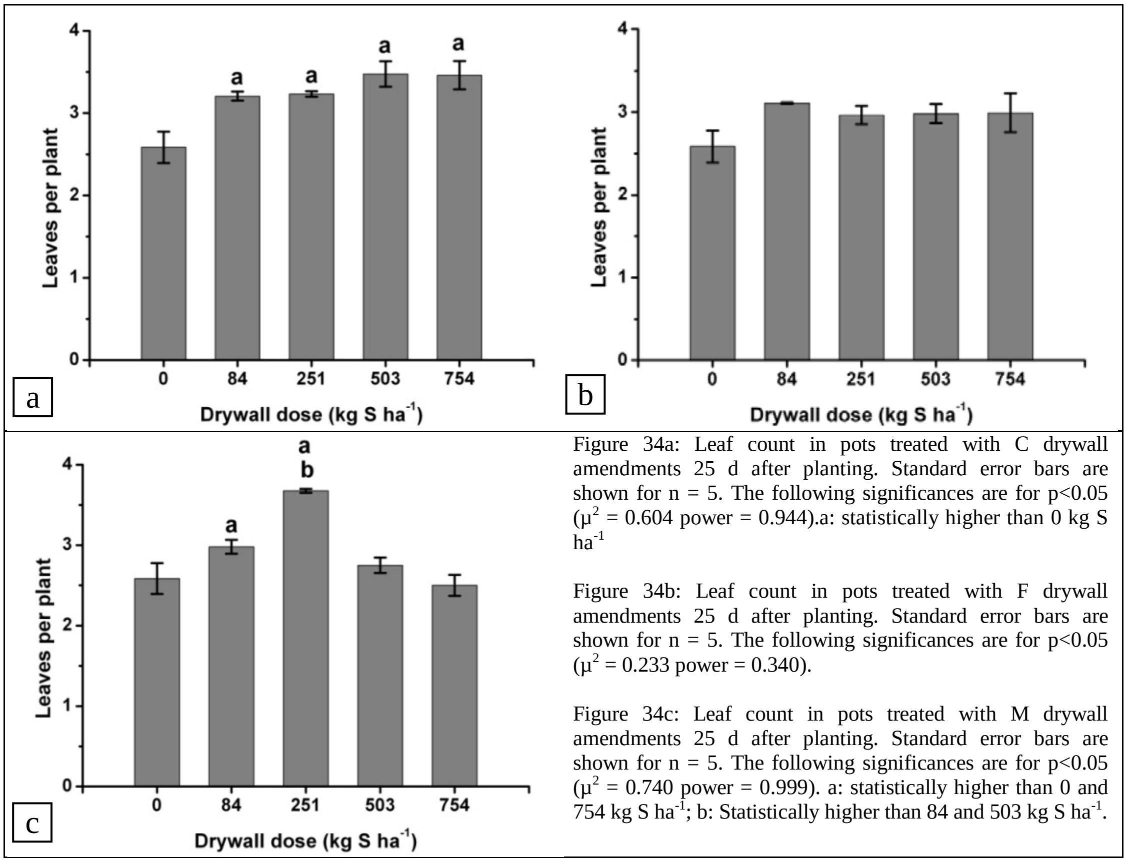


Figure 34a: Leaf count in pots treated with C drywall amendments 25 d after planting. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.604$ power = 0.944).a: statistically higher than 0 kg S ha^{-1}

Figure 34b: Leaf count in pots treated with F drywall amendments 25 d after planting. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.233$ power = 0.340).

Figure 34c: Leaf count in pots treated with M drywall amendments 25 d after planting. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.740$ power = 0.999). a: statistically higher than 0 and 754 kg S ha^{-1}; b: Statistically higher than 84 and 503 kg S ha^{-1}.

Figure 34: Leaf counts in pots treated with drywall 25 d after planting

The pattern of optimum doses within a drywall type varied, with the highest doses of C and F being stimulatory, but the highest dose of M yielding leaf counts similar to controls. F-type drywall tests showed increased stimulation of leaf production with increasing dose, although its impacts at maximum dosage was lower than the best dosage trials of R and M type drywall. The M drywall optimum dose was 251 kg of sulfur ha^{-1}, which was significantly ($p<0.05$) higher than the control. Overall, regardless of drywall types, the two-way ANOVA analysis revealed that every dose statistically increased the number of leaves per plants compared to the control pots. The second leaf count was performed on Day 25 of the experiment, and the treatment differences were less pronounced (Figure 34). Every dose of the C drywall resulted in a significantly ($p<0.05$) higher number of leaves per plant than controls. Consistent with the first leaf count, the optimum dose of C type drywall was 503 kg of sulfur ha^{-1}. F drywall amendment produced the smallest increase in leaves per plant relative to the controls, with no significant differences among them.

Figure 35: Visual comparison of replicate controls (top) and C-amended plants (503 kg sulfur ha^{-1}) (bottom) at Day 28.

However, the highest dose of M drywall resulted in the lowest number of leaves per plant among the trial treatments. There was a peak effect at the mid-range dose (251 kg of sulfur ha^{-1}), where the number of leaves per plant was significantly ($p<0.05$) higher than the control and the doses adjacent to it. The two-way ANOVA analysis of the Day 25 leaf count data revealed that, as with the Day 16 leaf count, C drywall amendments yielded statistically more leaves than drywall F and M drywall amendments. Moreover, regardless of drywall type, every dose resulted in statistically more leaves than the control treatment.

After the second leaf count, cabbage worms became a problem, and although they were ultimately brought under control (using a garlic/onion spray), it was decided that their damage to the plants compromised any future leaf count. Overall, the drywall amendments resulted in a greater number of leaves per plant relative to controls, especially for the C drywall. Further, by visual inspection, it was clear that plants amended with C drywall were more robust and had larger leaves than plants in the control pots (Figure 35).

4.3.2 Dry Root Mass

On Day 200, plant roots were collected, dried for 24 h at 100°C, and weighed (Figure 36). The two-way ANOVA analysis revealed that C drywall amendments yielded plants with statistically ($p<0.05$) heavier root masses than plants dosed with drywall F or M. The heaviest roots measured from plants that received C drywall amendments were 95g and 20g heavier than the heaviest roots from pots treated with F and M drywall amendments, respectively. Regardless of drywall type, the mid-range dose of 251 kg S ha^{-1} resulted in the heaviest roots. Moreover, for C drywall, this dose increased root mass by 86% relative to controls ($p<0.05$), and even the lowest dose resulted in a 47% increase. Similarly, the 251 kg S ha^{-1} dose of F drywall resulted in statistically ($p<0.05$) heavier average root masses that exceeded the mean associated with any other M drywall doses and the control by at least 50g. While the 251 kg S ha^{-1} dose of M drywall resulted in heavier roots, it was not significantly different from the other M drywall doses. The two-way ANOVA analysis also confirmed that the dose of 251 kg S ha^{-1} resulted in statistically ($p<0.05$) heavier root masses relative to all other doses and the control regardless of drywall type.

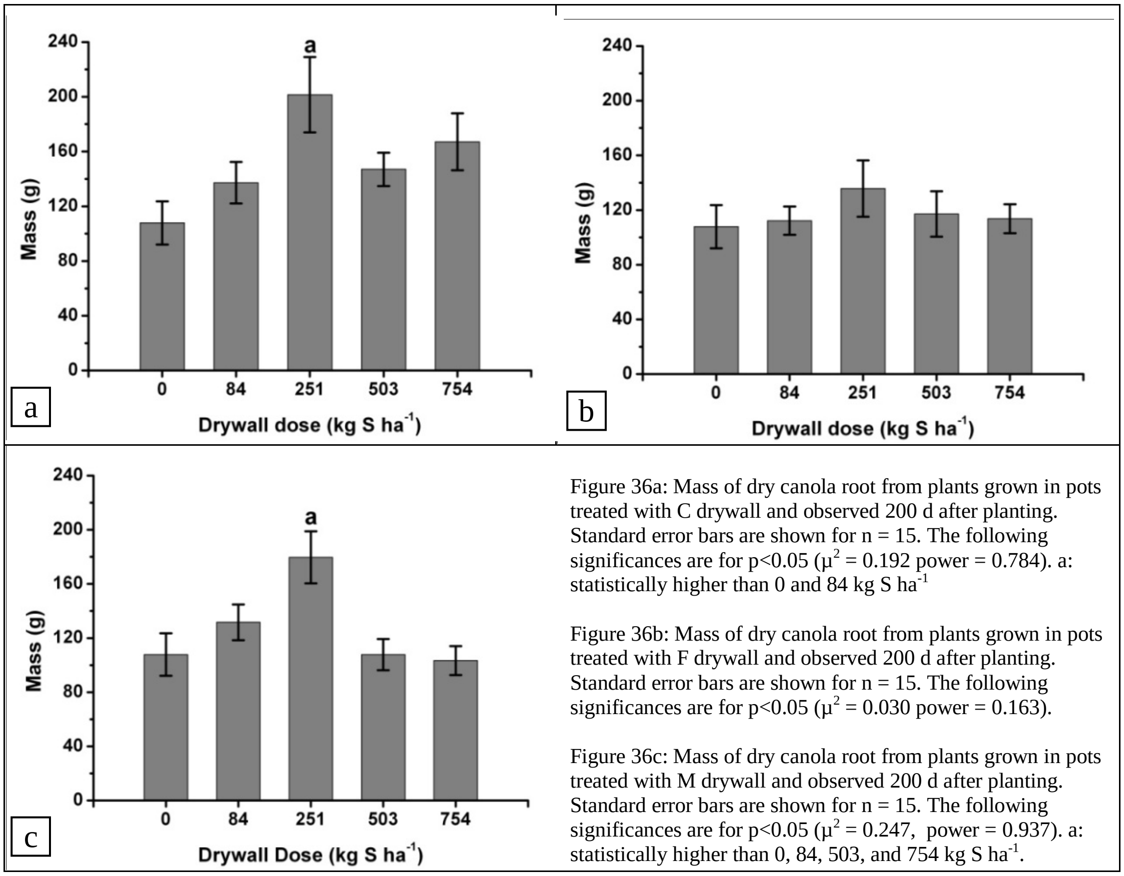


Figure 36a: Mass of dry canola root from plants grown in pots treated with C drywall and observed 200 d after planting. Standard error bars are shown for n = 15. The following significances are for $p<0.05$ ($\mu^2 = 0.192$ power = 0.784). a: statistically higher than 0 and 84 kg S ha^{-1}

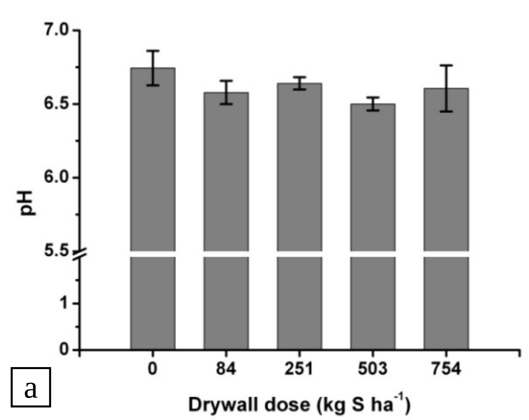
Figure 36b: Mass of dry canola root from plants grown in pots treated with F drywall and observed 200 d after planting. Standard error bars are shown for n = 15. The following significances are for $p<0.05$ ($\mu^2 = 0.030$ power = 0.163).

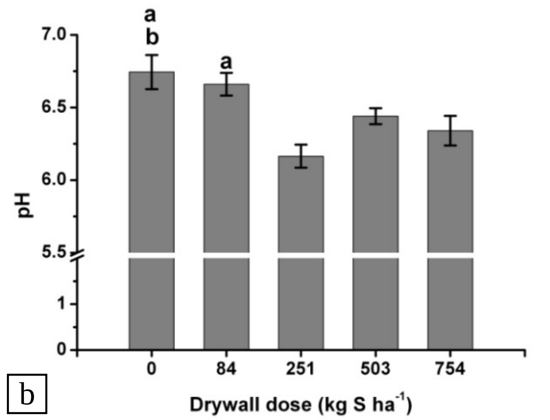
Figure 36c: Mass of dry canola root from plants grown in pots treated with M drywall and observed 200 d after planting. Standard error bars are shown for n = 15. The following significances are for $p<0.05$ ($\mu^2 = 0.247$, power = 0.937). a: statistically higher than 0, 84, 503, and 754 kg S ha^{-1}.

Figure 36: Mass of dry canola root from plants grown in pots 200 d after planting.

4.3.3 Soil pH and Soil Conductivity

Soil pH testing for the canola pot experiments was conducted as described in the grass pot experiments (see section 3.2.2.4). Figure 37 shows the soil pH 11 days after planting. Results from tests of each drywall type demonstrate a trend of lower pH at higher doses, which was statistically ($p<0.05$) confimed.





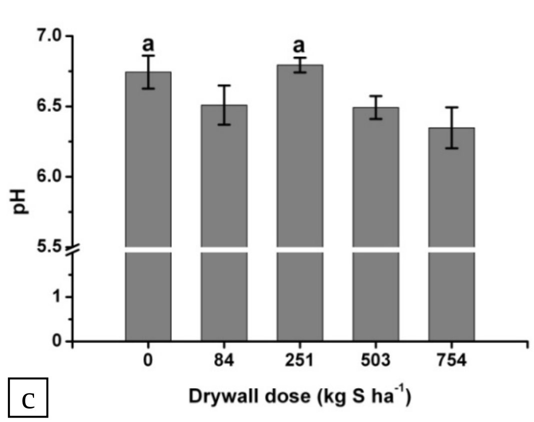


Figure 37a: Soil pH 11 d after amendment with C drywall. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ ($\mu^2 = 0.134$ power = 0.184).

Figure 37b: Soil pH 11 d after amendment with F drywall. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ ($\mu^2 = 0.584$ power = 0.958). a: statistically higher than 251 and 754 kg S ha^{-1}; b: statistically higher then 503 kg S ha^{-1}

Figure 37c: Soil pH 11 d after amendment with M drywall. Standard error bars are shown for n = 5. The following significances are for $p < 0.05$ ($\mu^2 = 0.353$, power = 0.644). a: statistically higher than 754 kg S ha^{-1}.

Figure 37: Soil pH 11 d after amendment with drywall

While the soil pH under different doses of drywall C was not statistically different, the pH of soil treated with the highest doses of F and M drywall were significantly ($p<0.05$) lower than the soil pH of the controls and the lower doses of F and M drywall. In the case of F drywall, 251 kg S ha^{-1} amendment resulted in a soil pH 0.6 unit lower than the control soil pH. In the case of the M drywall amendments, the highest dose resulted in a soil pH 0.3 unit lower than the control. A two-way ANOVA analysis confirmed that, regardless of the types of drywall, the three highest drywall doses yielded statistically ($p<0.05$) lower soil pH than the control. However, the soil pH is not affected by the type of drywall.

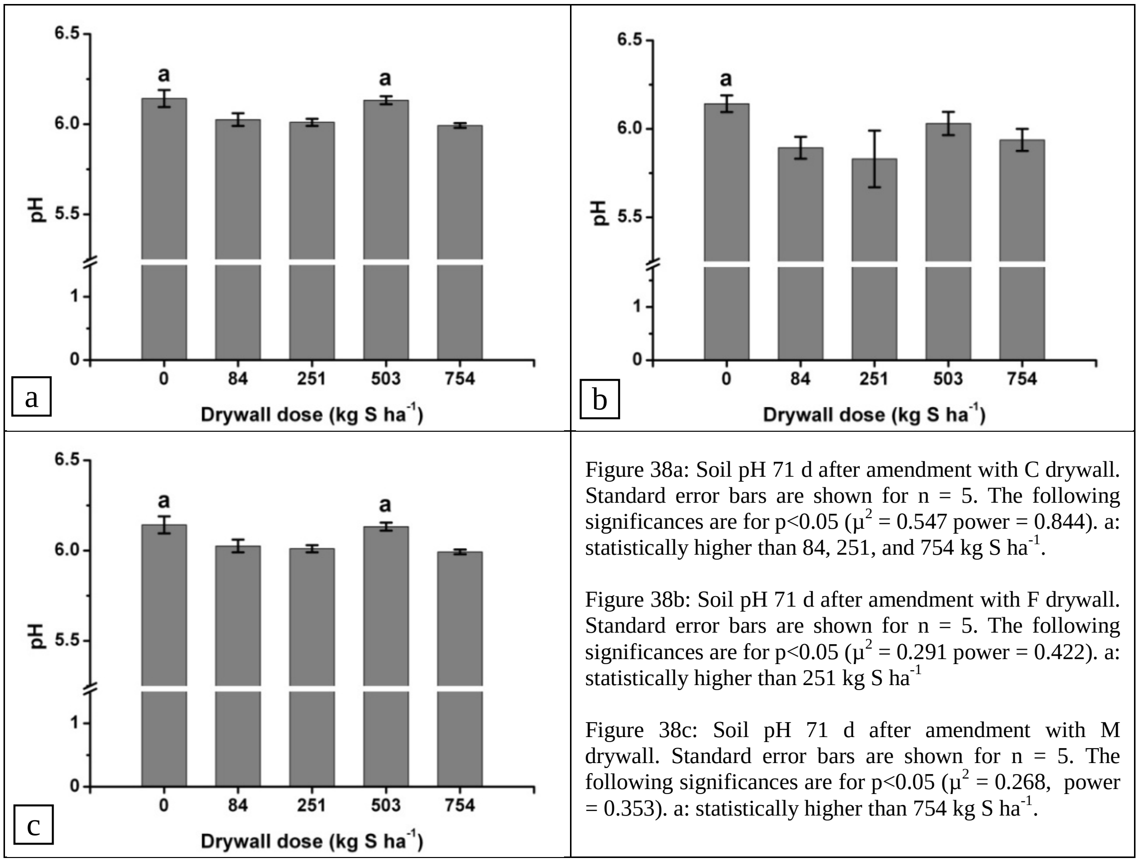


Figure 38a: Soil pH 71 d after amendment with C drywall. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.547$ power = 0.844). a: statistically higher than 84, 251, and 754 kg S ha^{-1}.

Figure 38b: Soil pH 71 d after amendment with F drywall. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.291$ power = 0.422). a: statistically higher than 251 kg S ha^{-1}

Figure 38c: Soil pH 71 d after amendment with M drywall. Standard error bars are shown for n = 5. The following significances are for $p<0.05$ ($\mu^2 = 0.268$, power = 0.353). a: statistically higher than 754 kg S ha^{-1}.

Figure 38: Soil pH 71 d after amendment with drywall

As observed in results from the grass experiments, the soil pH 71 days after planting (Figure 38) was lower than early (Day 11) soil pH readings. However, it is worth noting that this decrease was observed for each dose and the control. After 71 days of monitoring, the soil pH behaved in a similar fashion than at Day 11. The higher the drywall dose, the lower the pH. The soil pH difference between the control and the highest dose was only significantly different ($p<0.05$) with the C drywall amendments. The highest dose of C drywall decreased the soil pH by 0.15 pH unit. Moreover, similar to the soil pH at day 16, the two-way Anova revealed that the higher doses yielded statistically ($p<0.05$) lower pH than the control and than the 503 kg S ha^{-1}, a trend seen with the C and M drywall. The same analysis revealed that the F drywall amendments yielded significantly ($p<0.05$) lower pH than drywall C and M but the decline was only a few decimal points.

The soil conductivity was monitored in pots treated with C drywall throughout the experiment (Figure 39). The conductivity changes were as expected, with the highest treatment dose resulting in the highest conductivity and the control pot resulting in the lowest conductivity in the early days of the experiment. The highest dose yielded an initial soil conductivity five fold greater than soil in the controls.. However, over the duration of the experiment, the conductivity in the high dose treatment pots decreased, reaching the level of the control pots on Day 51, after which all conductivities converged.

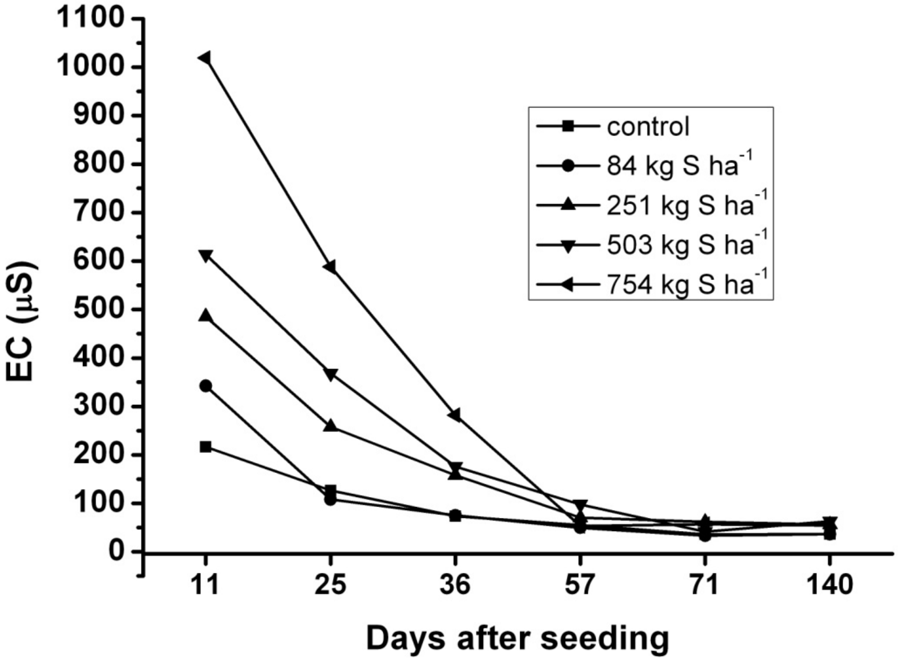


Figure 39: Soil conductivity during canola plant exposure in pots to C drywall amendments.

4.4 Canola Field

4.4.1 Huntersville

Canola plants grown at the Huntersville site suffered from cold damage during the winter months of 2009, and nearly 30% of the crop was lost to an unusually early frost. Moreover, during the months of March, April, and May 2010, the yield was greatly reduced by deer grazing on the flowering plants (Figure 40). Several deer-proofing remedies were employed, but none of them were entirely successful. As a result, of the 70% remaining after frost damage, only 10% of the crop was healthy enough for experimental analysis.

Figure 40: Typical canola plot appearance at the Huntersville site April 20, 2009.

4.4.1.1 Root Dry Biomass, Pods per Plant, and Mass of 1000 Seeds

Root dry biomass measures, pods per plant counts, and seed weighing were performed on the subset of canola plants suitable for harvesting. Clearly, the results must be judged with the understanding that the sample set was not a randomly selected set of plants but rather the survivors of frost and deer grazing. The analyses showed that the dry plant mass (Figure 41) and the number of pods per plants (Figure 42) were not affected by the ground drywall amendment. There were no obvious trends and no statistical differences. However, there was a slight difference in seed mass between the third and fourth highest doses that proved to be statistically significantly ($p<0.1$) (Figure 43); the mass of 1000 seeds from plants dosed with 794 kg S ha^{-1} were significantly heavier than 1000 seeds from plants dosed with 1059 kg S ha^{-1}.

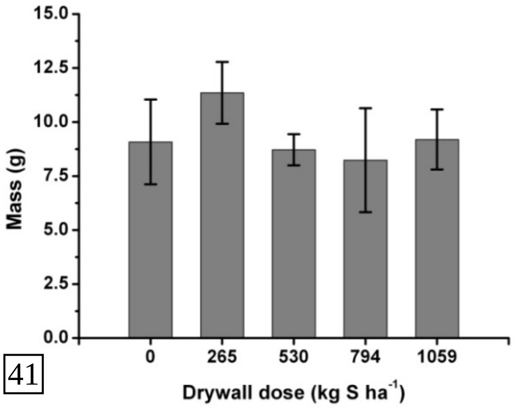


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Figure 41: Dry mass of 15 canola plants roots grown in soil at the Huntersville site that was amended with C drywall. Standard error bars are shown for n = 4. The following significances are for $p<0.10$ (μ2 = 0.127, power = 0.232).

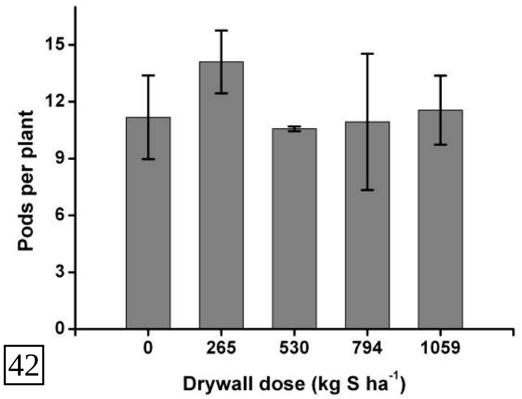

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Figure 42: Number of pods per canola plants grown in soil at the Huntersville site amended with C drywall. Standard error bars are shown for n = 4. The following significances are for $p<0.10$ (μ2 = 0.102, power = 0.192).

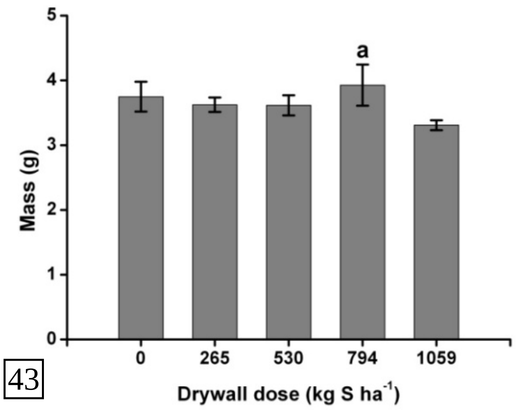

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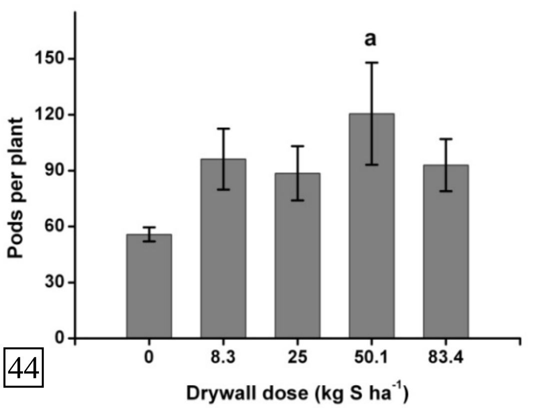
Figure 43: Mass of 1000 canola plant seeds grown in soil at the Huntersville site amended with C drywall. Standard error bars are shown for n = 4. The following significances are for $p<0.10$ (μ2 = 0.230, power = 0.378). a: statistically higher than 1059 kg S ha^{-1}.

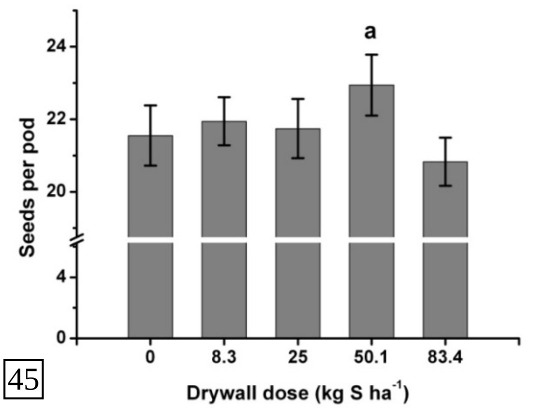
4.4.2 Newton

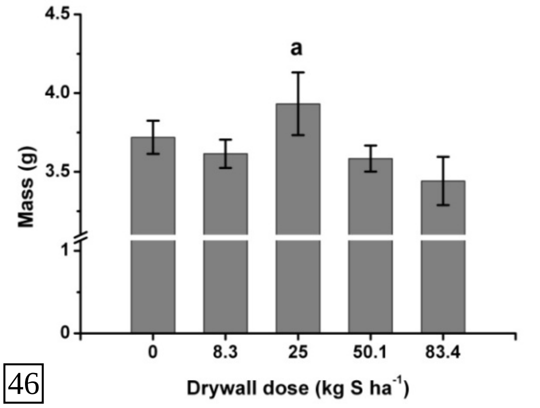
Plants at the Newton site did not suffer from frost damage or deer grazing, and thus, the results obtained from this experiment are likely more reliable than those from the Huntersville site.

4.4.2.1 Pod Count, Mass of 1000 Seeds, Seed Count, Leaf Areas

The number of pods per plant was positively affected by all ground drywall amendment doses (Figure 44). The dose of 50.1 kg S ha^{-1} significantly ($p<0.1$) increased the number of pods per plants 116% relative to controls.







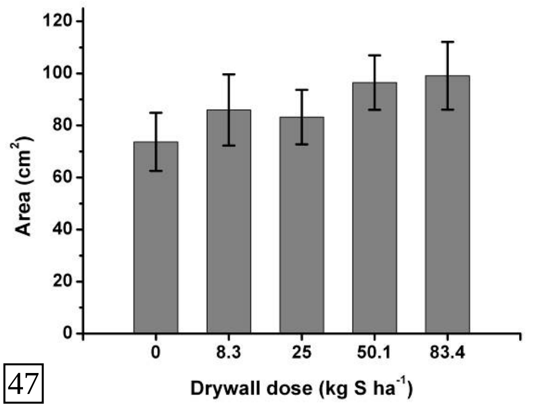


Figure 44: Pod counts of canola plants grown in a soil amended with C drywall. Standard error bars are shown for n = 12. The following significances are for $p < 0.10$ ($\mu^2 = 0.117$, power = 0.617). a: statistically higher than 0 kg S ha^{-1}

Figure 45: Seed counts of canola plants grown in soil amended with C drywall. Standard error bars are shown for n = 12. The following significances are for $p < 0.10$ ($\mu^2 = 0.070$, power = 0.410). a: statistically higher than 83.4 kg S ha^{-1}

Figure 46: Mass of 1000 canola seeds in soil amended with C drywall. Standard error bars are shown for n = 12. The following significances are for $p < 0.10$ ($\mu^2 = 0.119$, power = 0.659). a: statistically higher than 8.3, 50.1, and 83.4 kg S ha^{-1}

Figure 47: Leaf area of canola plants grown in soil amended with C drywall at the Newton site measured 58 d after planting. Standard error bars are shown for n = 12. The following significances are for $p < 0.10$ ($\mu^2 = 0.052$, power = 0.343).

The same dose also yielded significantly ($p<0.1$) more seeds per pod (Figure 45) than amendment higher dose of 83.4 kg S ha^{-1}. Figure 46 shows a negative dose-response trend with respect to seed mass. Doses of ground drywall resulted in lighter canola seeds. Interestingly, an ANOVA analysis revealed that the mid-range 25 kg S ha^{-1} dose yielded statistically ($p<0.1$) heavier seeds than resulted from the others drywall amendments but not the control. Leaf area tended to trend upward with increasing drywall dose (Figure 47). Unfortunately, there was high variability between replicates on these measures, and this trend did not confer any statistical relevance even though the highest dose resulted in an increase of 34% of the leaves area relative to the control to these results.

4.5 Sunflower Field

Sunflower plants were grown in Newton during summer 2011 on the same field used for the canola crop but at a different location to avoid any confounding effects from the previous ground drywall amendments. Although the experimental plan was to sample the plants three times during the course of the experiment, invasive honeysuckle plants overran the sunflower crop and rendered the third and final sampling campaign impossible. As a result, during the third sampling event, only growth parameters were measured.

4.5.1 Plant Height

Plant heights were measured on Days 34 and 59. The ground drywall amendments did not affect the height of the sunflower plants (Figure 48 and Figure 49). There was no statistical difference between the mean height of the treated sunflower plants and those grown in control plots.

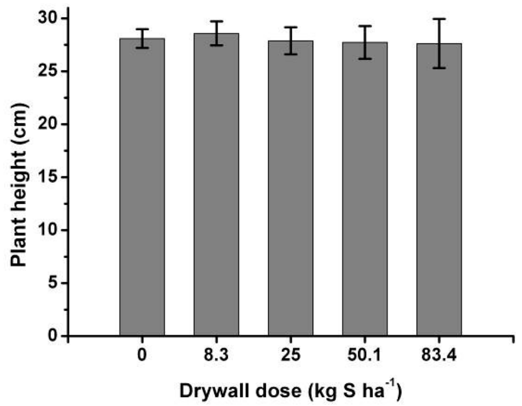


Figure 48: Sunflower plant height 34 d after planting. Standard error bars are shown for n = 12. The following significances are for $p < 0.1$ ($\mu^2 = 0.004$, power = 0.115).

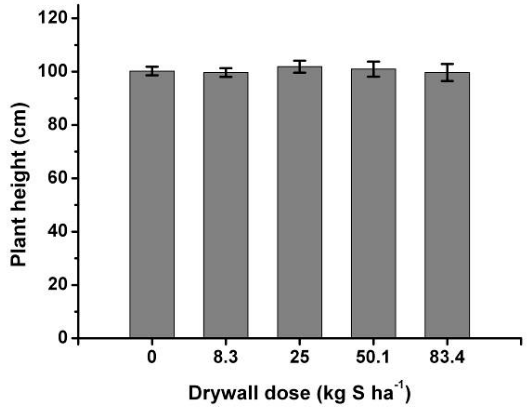


Figure 49: Sunflower plant height 59 d after planting. Standard error bars are shown for n = 12. The following significances are for $p < 0.1$ ($\mu^2 = 0.011$, power = 0.144)

4.5.2 Leaf Area

Leaf areas were measured on Days 34 and 59, and there were generally no differences between plants treated with ground drywall and those grown on control plots (Figure 50 and Figure 51). The exception was the plot amended with a 50.1 kg S ha^{-1} dose, which significantly increased ($p<0.1$) the leaf area more than did the lowest dose (8.3 kg S ha^{-1}) when sampled on Day 34.

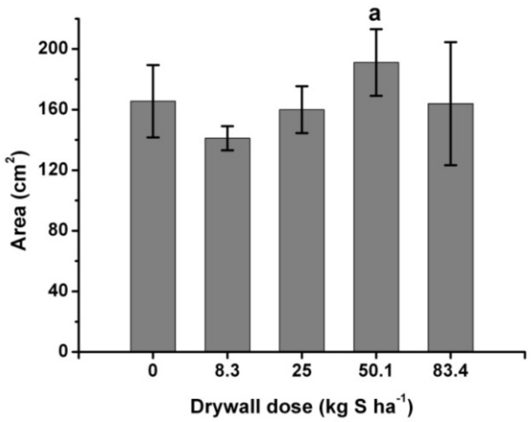


Figure 50: Sunflower top leaves area 34 d after planting. Standard error bars are shown for n = 9. The following significances are for $p < 0.10$ ($\mu^2 = 0.131$, power = 0.394). a: statistically higher than 8.3 kg S ha^{-1}

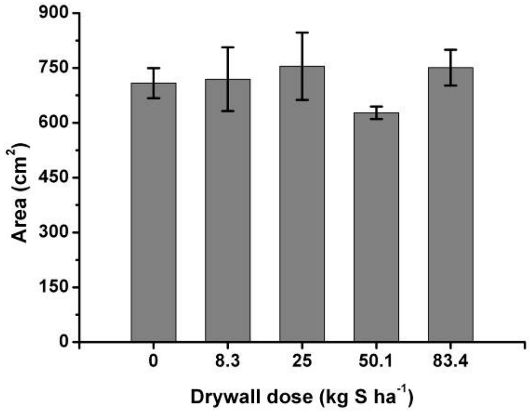
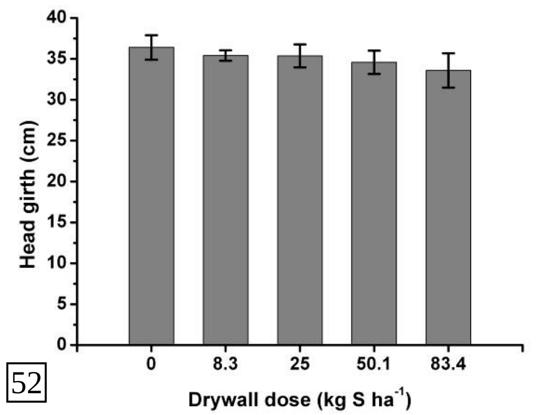
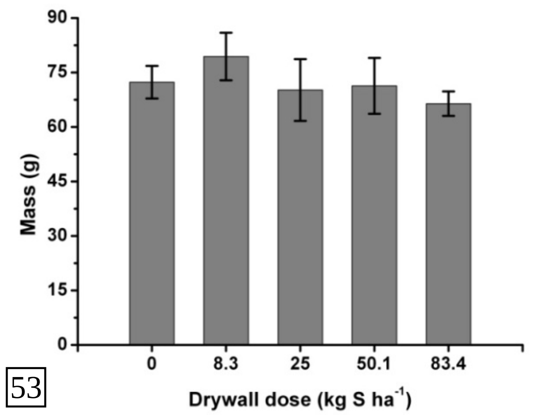


Figure 51: Sunflower top leaves area 59 d after planting. Standard error bars are shown for n = 9. The following significances are for $p < 0.10$ ($\mu^2 = 0.028$, power = 0.211)

4.5.3 Sunflower Plants per Hectare, Dry Stalk Mass, and Head Girth.

The sunflower plant density (Figure 54), dry stalk mass (Figure 53), and head girth (Figure 52) were measured on Day 59. For these three variables, the amendment of ground conventional drywall had no significant effect relative to controls. Nevertheless, there seemed to be a trend toward inhibition of head girth and the dry stalk mass with increasing drywall dose.





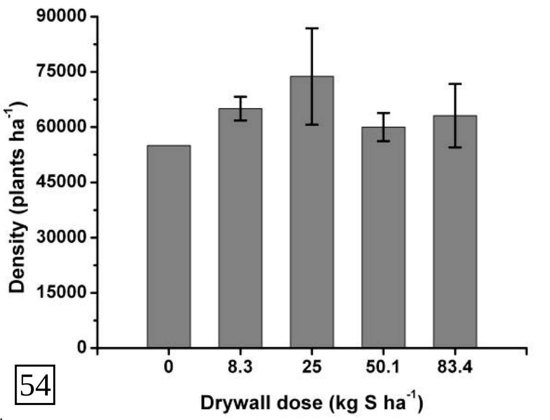


Figure 52: Sunflower head girth 59 d after planting. Standard error bars are shown for n = 12. The following significances are for $p<0.10$ ($\mu^2 = 0.036$, power = 0.249).

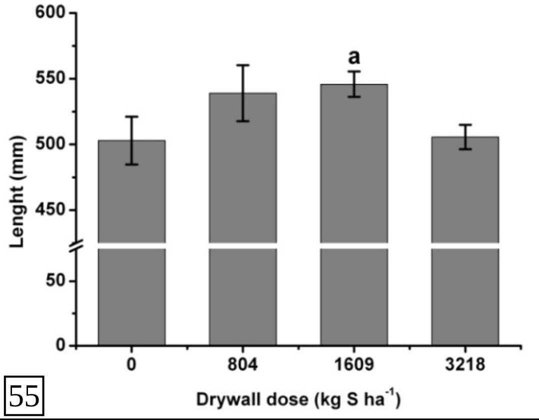
Figure 53: Sunflower dry stalk mass 59 d after planting. Standard error bars are shown for n = 4. The following significances are for $p<0.10$ (µ2 = 0.127, power = 0.244).

Figure 54: Sunflower plants density. Standard error bars are shown for n = 4.The following significances are for $p<0.10$ ($\mu^2 = 0.176$, power = 0.279).

4.6 Wheat Experiment

4.6.1 Wheat Growth and Yield Parameters

Although it was not the primary purpose of the carbon sequestration experiment to evaluate above-ground plant effects, data were collected to assess the effects of the conventional drywall amendment on wheat. The straw length, the number of ears per column, the number of kernels per plant, and the mass of 100 kernels were measured on plants grown with each of the treatment doses. The parameters straw length, number of kernels per ear, and mass of 100 kernels (Figure 55, Figure 57, and Figure 58) had similar responses to increasing drywall doses.



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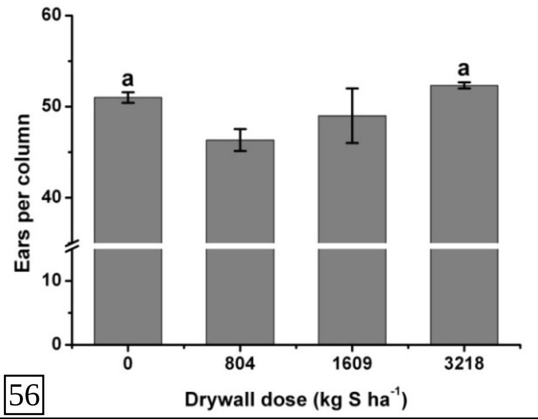

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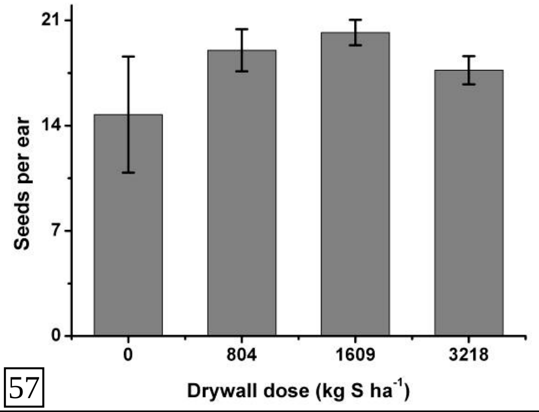

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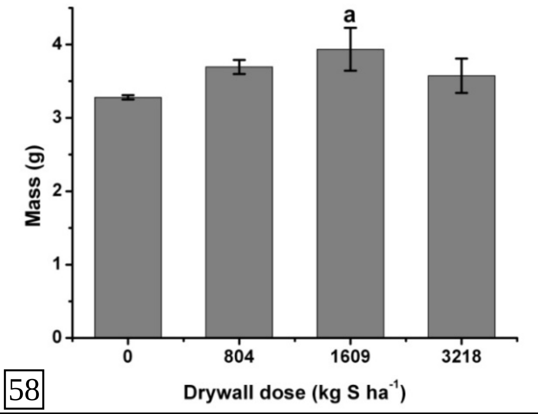

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Figure 55: Wheat stem length. Standard error bars are represented on the graph for n=3. The following significances are for $p<0.10$ ($\mu^2 = 0.433$, power = 0.501). a: statistically higher than 0 kg S ha^{-1}

Figure 56: Wheat ears count. Standard error bars are represented on the graph for n=3. The following significances are for $p<0.10$ (μ2 = 0.484, power = 0.579). a: statistically higher than 804 kg S ha^{-1}.

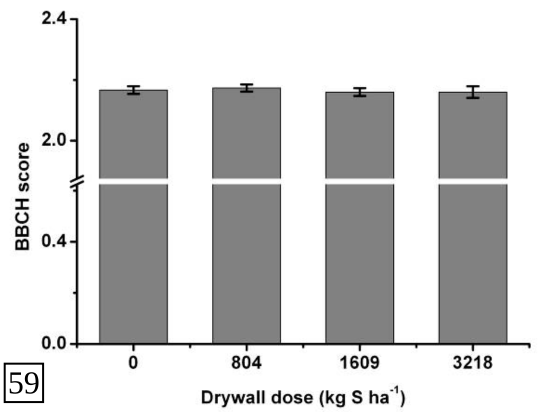
Figure 57: Wheat seed count. Standard error bars are represented on the graph for n=3. The following significances are for $p<0.10$ ($\mu^2 = 0.309$, Power = 0.342)

Figure 58: Mass of 100 wheat seeds. Standard error bars are represented on the graph for n=3. The following significances are for $p<0.05$ ($\mu^2 = 0.424$, Power = 0.489). a: statistically higher than 0 kg S ha^{-1}

The lowest and highest doses of drywall yielded plants with characteristics similar to controls, while the mid-range dose (1,609 kg S ha^{-1}) significantly ($p<0.10$ and $p<0.05$) improved the stem length (by 9%), and the seed mass (by 20%) relative to the controls. The same dose increased the number of kernels per ear by about 40% compared to the controls, but the difference was not significant due to the high variability of replicates. The number of ears per column (Figure 56) declined with the addition of ground drywall, increasing as the dose increased until it returned to the level of control columns at the highest dose. As a result, the highest dose yielded a significantly ($p<0.1$) higher number of ears (10% more) than the lowest gypsum dose of 804 kg S ha^{-1}.

4.6.2 BBCH Scale

As noted in 3.6.2.1.1, the BBCH scale converts plant growth stages to numerical values so that treatment effects on plant growth can be compared. The graphs of BBCH scale of wheat on Day 53 (Figure 59) and on Day 130 (Figure 60) show that on these days, the ground drywall treatments did not affect wheat growth relative to the controls. However, the rate of growth between these two dates (Figure 61) was statistically ($p<0.05$) faster for plants in the control columns and in columns receiving the highest drywall dose relative to the 1,609 kg S ha^{-1} dose. This is the same trend observed earlier where the control and the highest dose of drywall significantly increased the ears per column count relative to low doses.



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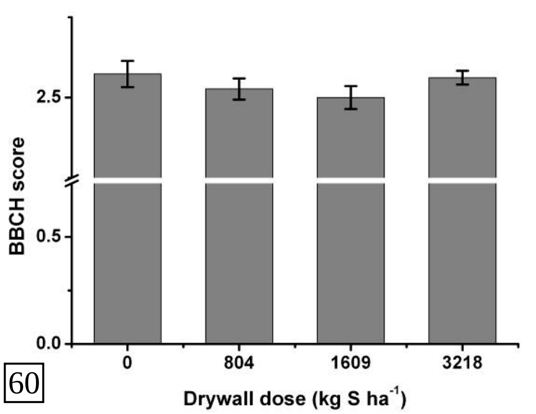

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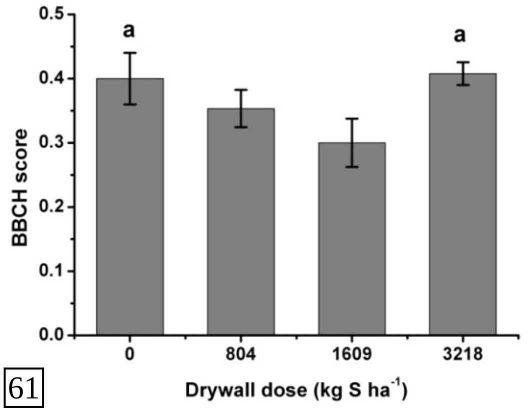

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Figure 59: BBCH score of wheat plants 53 d after planting. Standard error bars are shown for n = 3. The following significances are for $p < 0.1$ ($\mu^2 = 0.010$, Power = 0.153)

Figure 60: BBCH score of wheat plants 130 d after planting. Standard error bars are shown for n = 3. The following significances are for $p < 0.1$ ($\mu^2 = 0.051$, Power = 0.359)

Figure 61: BBCH score difference between 53 d and 130 d after planting. Standard error bars are shown for n = 3. The following significances are for $p < 0.05$ ($\mu^2 = 0.111$, Power = 0.653). a: statistically highier than 1609 kg S ha^{-1}

4.7 Carbon Sequestration

The carbon sequestration experiment was designed to evaluate the feasibility of using waste construction drywall to sequester carbon by exploiting the capacity of vegetation to transport atmospheric carbon into the soil and adjacent to microbial communities. The presence of calcium carbonate in the soil resulting from the reaction of the calcium and carbonate ions in the soil was monitored as well as soil pH, soil sulfate and soil calcium concentrations. Columns subjected to irrigation simulating 33 in y^{-1} of rainfall were designated the C-33 series, while columns receiving water at a rate of 28 in y^{-1} were designated the C-28 series.

4.7.1 Soil pH

Soil pH was measured because of its important role in calcium carbonate ($CaCO_3$) formation in soil; alkaline pH favors precipitation of $CaCO_3$. The pH was monitored at five different depths along the soil column profile after the columns were dismantled.

Table 19: Soil pH in C-33 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1})					
	0	804	1,609	3,218	1,609 (+)	3,218 (+)
0.10	6.94±0.08	6.91±0.17	7.00±0.05	6.96±0.10	6.98±0.07	6.78±0.15
0.25	7.19±0.05	7.17±0.06	7.18±0.03	7.12+0.01	7.09±0.05	7.10±0.07
0.41	7.18±0.07	7.16±0.04	7.19±0.05	7.06+0.06	7.08±0.07	7.08±0.16
0.56	7.21±0.05	7.21±0.03	7.22±0.02	7.14+0.18	[a] 7.51±0.05	7.29±0.06
0.71	7.17±0.07	7.22±0.05	7.19±0.07	7.09+0.09	[b] 7.36±0.01	7.22±012

Standard error bars are shown for n = 3.
(+) designates columns with concrete fines added.
(a) Statistically higher than 0, 804, 1609, and 3218 ($p<0.05$)
(b) Statistically higher than 3218 ($p<0.05$)

Table 20: Soil pH in C-28 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1})			
	Control	1,609	3,218	1,609 (+)
0.10	6.93±0.11	6.80±0.16	6.99±0.13	7.31±0.23
0.25	7.17±0.10	7.06±0.04	7.10±0.03	7.09±0.04
0.41	7.19±0.02	7.03±0.03	7.13±0.05	[a] 7.40±018
0.56	7.23±0.06	7.19±0.13	7.11±0.01	[b] 7.75±0.19
0.71	7.20±+0.03	7.15±0.14	7.10±0.05	[b] 7.84±0.20

Standard error bars are shown for n = 3.
(+) represents columns with concrete fines added.
(a) Statistically higher than 1,609 ($p<0.05$)
(b) Statistically higher than 0, 1609, and 3218 ($p<0.05$)

In C-33 columns, (Table 19), the drywall doses did not affect the soil pH at any depth compared to the controls. However, the addition of concrete fines to the dose 1,609 kg S ha^{-1} of drywall significantly ($p<0.05$) increased pH at a depth of 0.56 m by 0.3 unit compared to columns that did not receive any concrete fines. The same trend was evident in C-28 columns (Table 20). The lower layers of soil columns amended with concrete fines had a significantly higher ($p<0.05$) pH (a rise of about 0.6 pH units) than the lower layers of soil columns treated with ground drywall.

4.7.2 Soil Sulfate and Calcium Content

The sulfate and calcium ion concentrations in the soil column profiles were analyzed to detect evidence of gypsum migration downward over the course of the experiment. Table 21 and Table 22 show soil sulfate concentrations at various depths in C-33 columns and C-28 columns respectively.

Table 21: Soil sulfate ion content (g kg^{-1} of soil) in C-33 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1})				Comparison of sample depths regardless of doses ($p<0.1$)
	Controls	804	1,609	3,218	
0	0.21±0.11	7.62±6.92	5.71±2.75	8.96±4.97	-
0.10	0.02±0.01	0.18±0.01	0.35±0.05	$*^{ab}$1.06±0.51	-
0.25	0.03±0.01	0.14±0.03	1.07±0.38	$*^{a}$ 2.24±1.23	> 0.1,0.41,0.56,0.71
0.41	0.03±0.01	0.19±0.05	*0.30±0.08	$*^{a}$ 0.42±0.12	-
0.56	0.04±0.01	0.29±0.2	*0.32±0.04	*0.56±0.21	-
0.71	0.05±0.02	*0.40±0.01	*0.31±0.07	*0.46±0.14	-
Comparison of doses regardless of sample depths ($p<0.1$)	-	-	> control	> control, 804, and 1609	

Standard errors are shown for n=3.
(*) Statistically superior to the control ($p<0.1$)
(^{a}) Statistically superior to 804 kg S ha^{-1} ($p<0.1$)
(^{b}) Statistically superior to 1,609 kg S ha^{-1}($p<0.1$)

The higher drywall dose resulted in significantly ($p<0.1$) more soil sulfate under both watering rates. Moreover, at both irrigation rates, the sulfate ion concentration was highest at the top soil horizon where it was applied. This was likely due to the fact that some of it did not dissolve over the course of the experiment. In the C-33 columns, at the lowest dose the concentrations fell sharply after the top level increasing slowly with depth. At other doses, after the initial decline smaller peak values occurred at 0.25 m that were statistically significant at $p<0.1$, and then values fell to lower but steady values. The sulfate ion concentrations in C-28 columns showed greater variability among replicates, and as a result there were fewer differences that reached levels of statistical significance (Table 22). In many horizons, the 1,609 and 3,218 kg S ha^{-1} doses yielded significantly ($p<0.1$) higher soil sulfate ion levels than existed in the controls, but the differences between samples in the two dose treatments were not statistically different from one another. The sulfate ion concentrations depth of 0.56m contained statistically ($p<0.1$) more sulfate content than the depth of 0.41m.

Table 22: Soil sulfate content (g kg^{-1} of soil) in C-28 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1}) Control	1,609	3,218	Comparison of sample depths regardless of doses ($p<0.1$)
0	0.08±0.02	*8.27±0.94	*8.19±3.25	-
0.10	0.02±0.01	*0.74±0.35	0.26±0.12	-
0.25	0.03±0.01	0.57±0.20	0.64±0.48	-
0.41	0.04±0.01	*0.27±0.02	*0.31±0.14	-
0.56	0.05±0.01	0.25±0.05	*^{a}1.99±1.45	>0.41
0.71	0.10±0.04	*0.36±0.07	0.19±0.06	-
Comparison of doses regardless of sample depths ($p<0.1$)	-	> control	> control	

Standard errors are shown for n=3.
(*) Statistically superior to the control ($p<0.1$)
(^{a}) Statistically superior to 1,609 kg S ha^{-1} ($p<0.1$)

Table 23 and Table 24 show the calcium ion concentrations with depth C-33 columns and C-28 columns, respectively. As with the sulfate ion profiles, the surface layers had a highest calcium ion concentration. In C-33 columns, every drywall dose resulted in significant ($p<0.1$) increases in soil calcium ion levels relative to the controls. However, the treatments were not statistically different from each other. Calcium ion concentrations sub-peaks matched the locations of sulfate ion sub-peaks; for the C-33 columns, the second highest calcium ion peak in the column receiving the lowest drywall dose was in the deepest horizon (0.71 m). In the two higher doses, the second highest peaks both occurred at the 0.25 m depth.

Table 23: Soil calcium content (g kg^{-1} of soil) in C-33 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1})				Comparison of sample depths regardless of doses ($p<0.1$)
	Control	804	1,609	3,218	
0	3.52±0.01	*8.64±2.42	6.91±1.47	*8.93±1.51	-
0.10	1.62±0.10	1.83±0.08	1.87±0.06	*2.00±0.21	-
0.25	1.44±0.30	1.7±0.17	*2.17±0.27	*2.14±0.26	> 0.41,0.56
0.41	1.41±0.25	1.84±0.06	1.57±0.15	1.64±0.22	-
0.56	1.54±0.25	1.50±0.27	1.79±0.23	1.61±0.32	-
0.71	1.61±0.07	*2.17±0.33	*2.01±0.14	1.83±0.14	> 0.41,0.56
Comparison of doses regardless of sample depths ($p<0.1$)	-	> control	> control	> control	

Standard errors are shown for n=3
(*) statistically superior to the control ($p<0.1$)

In C-28 columns, there was much less distinction between treatment soil conditions and control soil. The only statistically significant ($p<0.1$) differences in calcium ion concentrations were between surface calcium ion levels in columns receiving the drywall doses relative to controls.

Table 24: Soil calcium content (g kg^{-1} of soil) in C-28 columns

Sample Depth (m)	Drywall Dose (kg S ha^{-1})			Comparison of sample depths regardless of doses ($p<0.1$)
	Control	1,609	3,218	
0	3.83±0.65	* 9.29±0.48	* 6.88±1.55	-
0.10	1.39±0.06	1.59±0.30	1.84±0.29	-
0.25	1.63±0.18	1.66±0.07	2.03±0.23	-
0.41	1.66±0.18	1.47±0.11	1.60±0.24	-
0.56	1.87±0.38	1.54±0.30	2.40±1.10	-
0.71	1.55±0.47	2.07±0.39	1.52±0.17	-
Comparison of doses regardless of sample depths ($p<0.1$)	-	-	-	

Standard error of the mean is indicated for n=3.
(*) Statistically superior to the control ($p<0.1$)

4.7.3 Soil Calcium Carbonate Content

The calcium carbonate content of the C-33 columns and the C-28 columns are shown in Table 25 and Table 26 respectively. The calcium carbonate content of the soil was measured at five different depths using the gas chromatography (GC) method. These tables show the total amount of calcium carbonate within the soil profile of each column. There is a high variability among the replicates, with columns that produced barely any calcium carbonate while its replicate produced a high amount of calcium carbonate. This phenomenon is seen in C-33 columns treated with 3,218 kg S ha^{-1} and C-28 columns treated with 1,609 kg S ha^{-1}. The three replicates of the C-28 columns with 3,218 kg S ha^{-1} did not show any calcium carbonate formed despite the same treatment in C-33 columns produces a high amount of calcium carbonate.

Table 25: Calcium carbonate content (mg kg^{-1} of soil) in C-33 columns

Sample Depth (m)	Treatments								
	0 kg S ha^{-1}			804 kg S ha^{-1}			1,609 kg S ha^{-1}		
0.10	0	0	0	0	0	0	0	1	0
0.25	0	0	30	720	72	0	1,187	280	0
0.41	0	0	0	0	5	0	83	0	401
0.56	0	0	28	53	26	0	356	57	0
0.71	34	0	6	325	119	154	0	19	276
Sum	34	0	64	1,098	222	154	1,626	357	677
	3,218 kg S ha^{-1}			(+) 1,609 kg S ha^{-1}			(+) 3,218 kg S ha^{-1}		
0.10	126	63	0	0	0	0	114	189	31
0.25	721	0	84	89	0	0	257	331	0
0.41	0	0	0	0	0	0	8	0	0
0.56	6,106	1,487	0	8,298	4,860	5,789	83	621	1,768
0.71	430	0	0	5,495	187	2,803	0	460	331
sum	7,383	1,550	84	13,882	5,047	8,592	462	1,601	2,130

(+) represents columns with concrete fines added.

Table 26: Calcium carbonate content (mg kg^{-1} of soil) in C-28 columns

Sample Depth (m)	Treatments					
	0 kg S ha^{-1}			1,609 kg S ha^{-1}		
0.10	0	0	14	0	29	0
0.25	256	0	297	344	0	449
0.41	75	73	27	0	0	0
0.56	0	0	333	2,434	51	116
0.71	1	0	0	1,446	44	0
sum	332	73	671	4,224	124	565
	3,218 kg S ha^{-1}			(+) 1,609 kg S ha^{-1}		
0.10	0	122	0	0	0	0
0.25	12	0	0	564	0	173
0.41	0	0	57	110	0	48
0.56	0	0	140	3,146	9,159	5,069
0.71	0	0	0	1,873	3,540	1,157
sum	12	122	197	5,693	12,699	6,447

(+) represents columns with concrete fines added.

In order to truly compare the treatment, calcium carbonate due to tap water uses, and concrete fines addition must be subtracted to the values in Table 25 and Table 26. First, the two bottom layer of the columns that received concrete fines have to be adjusted for the calcium carbonate originally present in the fines due to concrete carbonation. In the laboratory, the calcium carbonate content of the concrete fines was measured using the GC method. A 3% (w/w) addition of concrete fines corresponded to 2,422 mg kg^{-1} of calcium carbonate. The second adjustment has to be done regarding the tap water used to water the crop during the length of the experiment. The high alkalinity of the tap water added carbonate and bicarbonate ions to the system.

4.7.4 Tap Water Carbonate Ions Content

Wheat and corn plants in the carbon sequestration experiments were irrigated with municipal tap water produced by the City of Charlotte. It contains 20 mg L^{-1} as $CaCO_3$ of alkalinity and has a pH of 8.5. The amount of carbonate and bicarbonate ions added to the soil columns during irrigation was calculated to evaluate the importance of tap water into the formation of calcium carbonate. The following calculations are based on Snoeyink et al. (1980). Total alkalinity equation can be expressed as:

$$\text{Alkalinity (eq/l)} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{13}$$

Knowing the pH and the alkalinity of the tap water, the amounts of carbonate and bicarbonate ions present in tap water were calculated. The alkalinity equation (13) needed to be modified using the carbonate/water equilibrium equations (6) and (7) with a pK_{a1}=6.42 and pK_{a2} = 10.43 respectively.

From equation (6),

$$K_{a1} = \frac{[HCO_3^-].[H^+]}{[H_2CO_3]} \rightarrow [H_2CO_3] = \frac{[HCO_3^-].[H^+]}{K_{a1}}$$

And from equation (7),

$$K_{a2} = \frac{[CO_3^{2-}].[H^+]}{[HCO_3^-]} \rightarrow [HCO_3^-] = \frac{[CO_3^{2-}].[H^+]}{K_{a2}}$$

Using the above k_a calculations, the alkalinity equation (13) was modified:

$$Alkalinity = \frac{[CO_3{}^{2-}].[H^+]}{K_{a2}} + 2[CO_3{}^{2-}] + [OH^-] - [H^+]$$

$$Alkalinity = [CO_3{}^{2-}]\left(\frac{[H^+]}{K_{a2}} + 2\right) + [OH^-] - [H^+]$$

The alkalinity of Charlotte tap water is 20 mg L^{-1} as $CaCO_3$ with a pH of 8.5. 20 mg L^{-1} as $CaCO_3$ correspond to an alkalinity of $0.4.10^{-3}$ eq L^{-1}. As a result,

$$4.10^{-4} = [CO_3{}^{2-}]\left(\frac{10^{-8.5}}{10^{-10.43}} + 2\right) + 10^{-5.5} - 10^{-8.5}$$

$$\boxed{[CO_3{}^{2-}] = 4.55\ 10^{-6}\ \text{mol L}^{-1}}$$

Using the bicarbonate ions dissolution equation (7), it was possible to calculate the Charlotte tap water concentration in bicarbonate ions as follow:

$$K_{a2} = \frac{[CO_3{}^{2-}].[H^+]}{[HCO_3{}^-]} \rightarrow [HCO_3{}^-] = \frac{[CO_3{}^{2-}].[H^+]}{K_{a2}}$$

$$[HCO_3{}^-] = \frac{4.55\ 10^{-6} * 10^{-8.5}}{10^{-10.43}}$$

$$\boxed{[HCO_3{}^-] = 3.92\ 10^{-4}\ \text{mol L}^{-1}}$$

Using the carbonate acid dissolution equation (6), it is possible to calculate the Charlotte tap water concentration in carbonate acid as follow:

$$K_{a1} = \frac{[HCO_3{}^-].[H^+]}{[H_2CO_3]} \rightarrow [H_2CO_3] = \frac{[HCO_3{}^-].[H^+]}{K_{a1}}$$

$$[H_2CO_3] = \frac{3.87\ 10^{-4} * 10^{-8.5}}{10^{-6.42}}$$

$$\boxed{[H_2CO_3] = 3.21\ 10^{-6}\ \text{mol L}^{-1}}$$

To summarize, charlotte city tap water had the following ions concentration:

$[CO_3{}^{2-}] = 4.55\ 10^{-6}$ mol L^{-1}

$[HCO_3{}^-] = 3.92\ 10^{-4}$ mol L^{-1}

$$[H_2CO_3] = 3.21\ 10^{-6}\ \text{mol L}^{-1}$$

Knowing the carbonate content of the Charlotte tap water, the total amount of carbonate and bicarbonates ions added by the tap water to the system during the entire length of the experiment was calculated in order to estimate the amount of calcium carbonate formed due to tap water. The carbon sequestration experiment was done under two different precipitation levels: 28 in y^{-1} and 33 in y^{-1}, corresponding to 71 cm y^{-1} and 84 cm y^{-1} respectively. The column diameter was 12 in and its surface area was 730 cm^2. Consequently, the yearly water input was 61 L for each C-33 columns and 52 L for the C-28 series. The experiment lasted 707 days, which corresponded to a total water volume of 118.5 L for C-33 and 100.5 L for C-28. As a result, the C-33 columns received:

$$[CO_3^{2-}] = 4.55\ 10^{-6}\ \text{mol L}^{-1} = 5.39\ 10^{-4}\ \text{mol / column}$$

$$[HCO_3^{-}] = 3.92\ 10^{-4}\ \text{mol L}^{-1} = 4.64\ 10^{-2}\ \text{mol / column}$$

Considering the calcium carbonate formation equations (8) and (9), the theoretical amount of calcium carbonate formed in the entire column due to the tap water was calculated considering an unlimited amount of calcium. With equation (9), 2.32 10^{-2} moles of $CaCO_3$ could have been produced corresponding to 2.32 g of $CaCO_3$ per column. With (8), 5.39 10^{-4} moles of $CaCO_3$ could have been produced corresponding to 0.05 g of $CaCO_3$ per column. As a result, a maximum of 2.37 g of $CaCO_3$ could have been formed in the C-33 columns due to the tap water.

The C-28 columns received:

$$[CO_3^{2-}] = 4.55\ 10^{-6}\ \text{mol L}^{-1} = 4.57\ 10^{-4}\ \text{mol / column}$$

$$[HCO_3^{-}] = 3.92\ 10^{-4}\ \text{mol L}^{-1} = 3.94\ 10^{-2}\ \text{mol / column}$$

With equation (9), 1.97 10^{-2} mol of $CaCO_3$ could have been produced corresponding to 1.97 g of $CaCO_3$ per column. With equation (8), 4.57 10^{-4} mol of $CaCO_3$ could have been produced corresponding to 0.05 g of $CaCO_3$ per column. As a result, a maximum of 2.03 g of $CaCO_3$ could have been formed in the C-28 columns due to the tap water.

4.7.5 $CaCO_3$ Formed in Columns

Table 28 and Table 29 show a computation of the two most productive replicate for each treatment. The amount of calcium carbonate from the concrete fines and formed due to tap water are taking into account to have a conservative estimate of the amount of calcium carbonate formed. In order to calculate the total calcium carbonate in a column, the mass of the column had to be known. Table 27 shows the mass of each “slice” of the column corresponding to each sample taken. The total mass of the column was about 91.1 kg or 200.8 lbs.

Table 27: Calculation of the soil mass in a column

Sample Depth (m)	Corresponding Column Section (cm)	Section Thickness (m)	Section Mass* (kg)
0.1	0-17.5	0.18	20.43
0.25	17.5-33	0.16	18.10
0.41	33-48.5	0.16	18.10
0.56	48.5-63.5	0.15	17.51
0.71	63.5-78	0.15	16.93
		Sum	91.07

*based on a soil density of 1600 kg m^{-3}

Table 28: Total calcium carbonate formed in C-33 columns.

Sample Depth (m)	Treatments 0 kg S ha^{-1}			Average $CaCO_3$ per Section (mg/kg of soil)	$CaCO_3$ per Section (mg)	$CaCO_3$ (mg) per column adjusted for tap water input
0.10	0	0	0	0	0	
0.25	0	0	30	15	272	
0.41	0	0	0	0	0	
0.56	0	0	28	14	245	
0.71	34	0	6	20	339	
Sum	34	0	64	49	856	0
	804 kg S ha^{-1}					
0.10	0	0	0	0.0	0.0	
0.25	720	72	0	396	7,168	
0.41	0	5	0	3	54	
0.56	53	26	0	40	700	
0.71	325	119	154	222	3,759	
Sum	1,098	222	154	661	11,681	9,311
	1,609 kg S ha^{-1}					
0.10	0	1	0	0	0	
0.25	1,187	280	0	594	10,751	
0.41	83	0	401	242	4,380	
0.56	356	57	0	178	3,117	
0.71	0	19	276	138	2,336	
Sum	1,626	357	677	1,152	20,584	18,214
	3,218 kg S ha^{-1}					
0.10	126	63	0	95	1,941	
0.25	721	0	84	361	6,534	
0.41	0	0	0	0	0	
0.56	6,106	1,487	0	3,797	66,485	
0.71	430	0	0	215	3,640	
Sum	7,383	1,550	84	4,468	78,600	76,230

(+) represents columns with concrete fines added.

* The (+) doses are adjusted for calcium carbonate from concrete fines. The calcium carbonate content of concrete fines was substracted from the two bottom soil layers (0.56 and 0.71)

Table 28 (Cont.)

Sample depth (m)	Treatments (+) 1,609 kg S ha^{-1}			Average $CaCO_3$ per Section (mg/kg of soil)	$CaCO_3$ per Section (mg)	$CaCO_3$ (mg) per Column (adjusted for tap water input)
0.10	0	0	0	0	0	
0.25	89	0	0	45	815	
0.41	0	0	0	0	0	
0.56	8,298	4,860	5,789	4,622	80,931	
0.71	5,495	187	2,803	1,727	29,238	
Sum	13,882	5,047	8,592	6,394	110,444	108,074
	(+) 3,218 kg S ha^{-1}					
0.10	114	189	31	110	2,247	
0.25	257	331	0	166	3,005	
0.41	8	0	0	0	0	
0.56	83	621	1,768	0	0	
0.71	0	460	331	0	0	
Sum	462	1,601	2,130	276	5,252	2,882

(+) represents columns with concrete fines added.
* The (+) doses are adjusted for calcium carbonate from concrete fines. The calcium carbonate content of concrete fines was substracted from the two bottom soil layers (0.56 and 0.71)

In the C-33 columns, as the dose of drywall amendment increased, the amount of calcium carbonate formed also increases. Doubling the drywall dose results in more than doubling the amount of calcium carbonate formed. Moreover, it seems that calcium carbonate was formed mainly at two depths: 0.25m deep and below 0.56 m deep, which is the same depth at which sulfate and calcium, were found. The amendment of 1,609 kg S ha^{-1} coupled with concrete fines produced the highest amount of calcium carbonate, more than six times compare to the same dose but without concrete fines.

The dose of 3,218 kg S ha^{-1} coupled with concrete fines seemed to have formed only little calcium carbonate. Table 29 shows the amount of calcium carbonate in C-28 columns. As with the C-33 series, there are two depths at which calcium carbonate is evident. However, while a treatment of 1,609 kg S ha^{-1} yielded more calcium carbonate than the control, the treatment of 3,218 yielded little calcium carbonate.

Table 29: Total calcium carbonate formed in C-28 columns.

Sample Depth (m)	Treatments			Average CaCO$_3$ per Section (mg/kg of soil)*	CaCO$_3$ per Section (mg)	CaCO$_3$ (mg) per Column (adjusted for tap water input)
	0 kg S ha^{-1}					
0.10	0	0	14	7	143	
0.25	256	0	297	277	5,014	
0.41	75	73	27	51	923	
0.56	0	0	333	167	2924	
0.71	1	0	0	1	17	
sum	332	73	671	502	9,021	6,991
	1,609 kg S ha^{-1}					
0.10	0	29	0	0	0	
0.25	344	0	449	397	7,186	
0.41	0	0	0	0	0	
0.56	2,434	51	116	1,275	22,325	
0.71	1,446	44	0	723	12,168	
sum	4,224	124	565	2,395	41,679	39,649
	3,218 kg S ha^{-1}					
0.10	0	122	0	61	1,246	
0.25	12	0	0	0	0	
0.41	0	0	57	29	525	
0.56	0	0	140	70	1,226	
0.71	0	0	0	0	0	
sum	12	122	197	160	2,997	967
	(+) 1,609 kg S ha^{-1}					
0.10	0	0	0	0	0	
0.25	564	0	173	87	1,575	
0.41	110	0	48	24	434	
0.56	3,146	9,159	5,069	4,692	82,157	
0.71	1,873	3,540	1,157	0	0	
sum	5,693	12,699	6,447	4,803	84,166	82,136

(+) represents columns with concrete fines added.

* The (+) doses are adjusted for the calcium carbonate from concrete fines. The calcium carbonate content of concrete fines was substracted from the two bottom soil layers (0.56 and 0.71).

This does not mean that no calcium carbonate was formed under this treatment but rather the sampling “missed” the calcium carbonate. When comparing the dose of

1,609 kg S ha^{-1} but under different rainfall rates, the C-28 columns yielded twice as much calcium carbonate as the C-33 columns. The same treatment of 1,609 kg S ha^{-1} coupling with concrete fines produced more calcium carbonate than the same treatment without concrete fines and this for both precipitation.

Overall it seems that the ground drywall amendment on crop can formed calcium carbonate in soil. The use of concrete fines to increase the pH plays an important role in enhancing the formation of calcium carbonate as well as a drier environment increase calcium carbonate formation. Knowing the amount of calcium carbonate formed in each column, it is possible to calculate the amount of carbon sequestered by such system made of waste construction drywall and crops.

4.7.6 Carbon Sequestered by Columns

The amount of calcium carbonate in the column was converted into the amount of carbon the system could sequester per hectare and per year. These calculations are shown in Table 30 and Table 31 for the C-33 columns and C-28 columns respectively. The two treatments that sequestered the most carbon were the amendments of 1,609 kg S ha^{-1} coupled with the addition of concrete fines with a precipitation regime of 33 in y^{-1} and 28 in y^{-1}.

Table 30: Carbon sequestered by C-33 columns

Treatments (kg S ha^{-1})	Total $CaCO_3$ per Column (mg)	$CaCO_3$ Formed (kg ha^{-1} y^{-1})*	Carbon Sequestered (kg ha^{-1} y^{-1})
0	0	0	0
804	9,311	659	79
1,609	18,214	1,288	155
3,218	76,230	5,391	647
(+) 1,609	108,074	7,643	917
(+) 3,218	2,882	204	24

*Based on the experiment length of 707 Days and a column surface area of 0.073 m^2

Table 31: Carbon sequestered by C-28 columns

Treatments (kg S ha^{-1})	Total $CaCO_3$ per Column (mg)	$CaCO_3$ Formed (kg ha^{-1} y^{-1})*	Carbon Sequestered (kg ha^{-1} y^{-1})
0	6,991	494	59
1,609	39,649	2,804	336
3,218	967	68	8
(+) 1,609	82,136	5809	697

*Based on the experiment length of 707 Days and a column surface area of 0.073 m^2

These treatments sequestered respectively 917 and 697 kg of carbon ha^{-1} y^{-1}. The treatment without concrete fines that performed the best was the highest doses under a watering of 33 in y^{-1} with a sequestering capacity of 647 kg of carbon ha^{-1} y^{-1}. The control treatment of the C-28 series was able to sequestered 59 kg of carbon ha^{-1} y^{-1}.

4.7.7 Stable Isotope Analysis

Five soil samples from different treatments exhibiting large amount of calcium carbonate formed were send to the analytical chemistry laboratory of Georgia University for stable isotope analysis of the soil inorganic carbon. The laboratory run each sample twice and measured the δ^{13}C vs PDB. The results of the analysis are shown in Table 32.

Table 32: Stable isotope analysis of column samples

Sample #	Treatment (kg S ha^{-1})	Watering Level	Sample Depth (m)	δ^{13}C vs PDB 1	δ^{13}C vs PDB 2	Average (‰)	St. Dev.
1	1,609	33	0.25	-16.23	-16.62	-16.42	0.28
2	3,218	33	0.56	-17.39	-17.35	-17.37	0.03
3	(+) 3,218	33	0.56	-19.88	-19.83	-19.85	0.03
4	1,609	28	0.56	-18.03	-17.57	-17.80	0.33
5	(+) 1,609	28	0.56	-16.14	-15.80	-15.97	0.24

The samples δ^{13}C vs PDB ranged from -15.80 to -19.88‰ indicating a depletion of ^{13}C in the inorganic carbon fraction of the soil. The highest depletion occurs in soil treated with the highest dose of ground drywall with concrete fines, and under 33 in y^{-1} of rain. The lowest depletion occurs with soil treated with 1,609 kg S ha^{-1} with concrete fines under the drier environment. Sample #1 was a soil sample taken at a depth of 0.25 m while the four other samples were taken at 0.56m deep. The difference in depth did not have any impact of the depletion of ^{13}C as the shallower sample had a δ^{13}Cvs PDB in the middle range. The addition of concrete fines did not to have any influences either on the δ^{13}C vs PDB. The only difference observable is that the sample receiving the highest dose of ground drywall (3,218 kg S ha^{-1}) had the smallest standard deviation.

CHAPTER 5: DISCUSSION

5.1 Drywall Phytotoxicity Effects

The phytotoxicity clearly revealed that seed types differ in their germination responses to the presence of drywall, and in some cases, the type of drywall influences germination responses. While lettuce and canola germination scores were markedly enhanced by dissolved drywall, corn and wheat seed germination was only slightly stimulated. On the other hand, cucumber and sunflower seeds responded negatively to a drywall amendment.

5.1.1 Canola and Lettuce

The germination scores of lettuce and canola were enhanced by the addition of ground drywall. A more details analysis of the germination scores shows that for these plants it was the root elongation more than the number of seeds germinated in the presence of drywall that boosted the score for samples in these treatments relative to controls. It is well known that canola responds positively to sulfur, and it is likely this nutrient was responsible for the strong early root development of theses seeds (Scherer 2001). Similarly, lettuce is known to respond well to sulfur supplementation; Thompson et al. (1939) observed that lettuce seeds were “awakened” from their dormant stage faster in a solution with sulfur than in a solution without it. While drywall type did not influence the GS of canola seeds, there was one difference observed among lettuce seeds dosed with the different drywall types. The C drywall doses resulted in higher GS than F and M drywall, suggesting that F and M drywall were slightly inhibitory to lettuce.

5.1.2 Corn

In corn seed germination tests, there was a trend for the presence of drywall at certain dosages to increase germination scores. Interestingly, the optimum dosages were different for the different types of drywall. The 1000-fold dilution of C drywall, the 100-fold dilution of F drywall, and the 10-fold dilution of M drywall, increased corn germination scores by 20 to 25% relative to controls. However, none of these differences were statistically significant relative to controls, nor were any differences between the different types of drywall on corn seeds statistically significant. While each dose of C drywall yielded at least the same corn GS as drywall-free controls, only the optimal dose treatments of F and M drywall yielded positive corn GS scores relative to controls. As with the lettuce seeds, it appears that F and M type drywall have some inhibitory effects on corn seeds, but unlike lettuce and canola, the mode of impact was on limiting seed germination rather than on shortening root length. When Burger (1993) studied corn yield on fields amended with drywall, there was a 25% increase in corn observed. Similarly, Toma et al. (1999) applied 10 t ha^{-1} of gypsum amendment to acidic soil and increased the corn yield by 29%. Although these studies did not isolate the germination impacts from overall crop success, they support the general trend observed here that drywall is not particularly inhibitory to corn.

5.1.3 Wheat

Wheat seed germination was slightly stimulated by C and F drywall amendment. Their dose-response profiles were similar, with a 20 mg L^{-1} optimal dose resulting in a

20% GS increase. Root growth rather than greater germination rates was largely responsible for higher GS values. From the literature, it is known that wheat has a relatively low sulfur requirement (Scherer 2001), which likely explains why wheat scores did not show the same robust response to drywall that was seen in tests with lettuce and canola seed. Brennan et al. (2007) observed that wheat shoot growth was not stimulated by gypsum, although wheat grain size increased by about 25%. Gypsum amendment did improve wheat yield in soil that was poor in Ca, Mg, K, and Na. Caires et al. 2002, suggesting that the root growth enhancement was a response to calcium in the drywall. As with the corn and lettuce seeds, M drywall inhibited wheat seed germination, with the highest dose lowering the GS 45% relative to drywall-free controls.

5.1.4 Cucumber and Sunflower

There was some enhanced cucumber root growth at low conventional drywall doses, which was likely due to the fact that cucumber plants are high calcium consumers (Ingestad 1972). However, as the doses of ground drywall increased, this effect reversed, and cucumber germination scores decreased due to shorter roots. Seed germination rates remained stable. It may have been due to cucumber seeds’ sensitivity to high conductivity (Papadopoulos 1994). The fact that germination scores for cucumber seeds exposed to M drywall doses were statistically lower than C drywall amendments suggests an additional inhibitory effect due solely to something in the M drywall.

Most of the seed tests showed that drywall amendment impacts were exerted along one of the two germination score dimensions – either root length changes or changes in germination rates. Sunflower seed test results were unique in that both root growth and germination rates were negatively affected at higher drywall doses.

Interestingly, field studies have shown up to 30% increases in sunflower plant seed yields in response to gypsum amendments applied at rates of 40 to 60 kg S ha^{-1} (Intodia et al. 1997; Rani et al. 2009). Sunflower seeds were also distinct from the other seed types in that while M drywall reduced the germination scores of lettuce, wheat, and cucumber seeds, no differences between M, C and F type drywall effects on sunflower seeds were evident.

5.1.5 Drywall Toxicity

The Material Safety Data Sheets (MSDS) is a document required by the Occupational Safety and Health Administration (OSHA) describing the physical properties of a hazardous substance. Although the MSDS for all of the drywall samples used in the germination tests and bench-scale experiments make no mention of potential harm to aquatic life (USG 2011a, USG 2011b, USG 2011c), the fire retardant drywall and especially mold, mildew, and moisture retardant drywall had a negative impact on the GS of lettuce, cucumber, wheat, and sunflower. These materials are marketed for resistance fire and to mold and mildew, and the results suggest that the product contains additives of some kind that lead to these effects. The MSDS sheets of the fire retardant drywalls (USG 2011b) show that these products contain fiber glass (about 1%) and ethylene vinyl acetate polymer (about 2%) acting as glue. Even if these constituents do not have a recorded impact on living organisms, they are constituents in greater proportion than in conventional drywall, making them the likely source of the mild toxicity observed. The MSDS of mold resistant drywall (MSDS 2011c) mentions that sodium pyrithione (about 2%) is added to mold resistant drywall. Sodium pyrithione is used to control mold, mildew, fungi, yeast, algae, and bacteria growth, and it is highly toxic to aquatic organisms at high concentration. It is very water soluble and could have been readily absorbed by the seeds (ARCH 2008).

5.2 Canola Plants at Bench Scale

5.2.1 Early Growth

The results of the canola bench-scale experiment confirmed some of the observations from the germination study. However, while in the germination tests, all types of drywall positively impacted the germination score, such positive effects on growing plants were not uniform across all drywall types. Conventional drywall outperformed fire retardant and mold and mildew resistant drywall in terms of more and larger leaves. Root mass was enhanced by drywall, indicating that the amendment can influence canola growth both above and below ground. The overall beneficial effects of conventional drywall on plant vigor are consistent the documented high S requirement of canola (Scherer 2001). Swan et al. (1986) observed significantly higher yields of canola in a growth chamber study when gypsum amendments were added. Interestingly, Warman et al. (1994), in their growth chamber study, did not observe any difference in yield between canola amended with gypsum (9.3 and 37.2 mg S kg^{-1} soil) and the control. However, he observed an increase in S uptake.

The finding that conventional drywall can stimulate early growth of canola is significant for good crop survival. Fast growth of young canola plants is an important asset because of the way they are typically cultured; they need to be able to withstand winter temperatures. Canola plants need to be exposed to cold temperatures to be able to flower in the spring. This process is called vernalization (Wright 2010). However, an extreme cold event can permanently damage the plants. The canola plants need to be well developed before the first frost occurs so that they can survive early freezes. The fact that not all drywall types can be relied upon to stimulate enhanced growth is a disappointing finding, because it suggests that careful sorting of waste wallboard will be necessary if this value-added property of conventional wallboard is to be exploited.

5.2.2 Soil pH and Conductivity

A soil pH change due gypsum amendment depends on two reactions where (i) Ca^{2+} replaces soil H^{+}; and (ii) SO_4^{2-} replaces soil OH^{-} on clay attachment sites (Liu et al. 2001). Typically, the effects of gypsum addition on soil pH are minimal, although in a rare case, Wong et al. (1993) observed a drastic drop from pH 10.5 to 8.6 when 5% gypsum was added to red mud, a byproduct of the bauxite refining industry. The soil pH values during the canola and grass experiments were not affected by the types of drywall but the amount of drywall had an impact. The pH did decrease slightly (relative to controls) in soil receiving the highest doses of drywall. Similar findings were reported by Liu et al (2001) when an acidic soil pH was lowered 0.7 unit when amended with gypsum and also by Smith et al. (1994) where soil pH was lowered by 0.2 unit when supplemented with 530 kg S ha^{-1} as gypsum.

Soil conductivity behaved predictably. The first days of sampling revealed high soil conductivity likely due to the freshly dissolved gypsum. However, as the experiment continued, the conductivity decreased, eventually reaching the same conductivity as that of the control pots. Decreased soil conductivity in pots with amended soil was likely due to salts leaching from the soil over the course of the experiment.

5.3 Grass Experiment

The grass experiment, in which the tolerance of fescue grass to drywall was tested, aimed to assess the feasibility of grinding waste virgin wallboard on a construction site and applying the ground material as a soil amendment. If the grass planted for erosion control showed good tolerance for the ground drywall, this method would eliminate the cost of hauling the waste drywall to the landfill or a reclamation facility. The results of this experiment showed that at the doses tested, the on-site application of drywall with erosion-control grass would not be particularly successful. While at a high drywall dose the root coverage was slightly better than the control, the grass was not as visually attractive as the control grass. Moreover, the grass biomass showed a negatively trend when amended with increasing dose of drywall.

The poor above-ground growth observed in this experiment is not consistent with trends seen in other studies where the same range of doses increased clipping weight for fescue grass, Kentucky blue grass, and bent grass (SoilSolutions 2011, Gaskin et al 2002). A similar study done at UNC Charlotte also showed that grass height and biomass accumulation were mostly inhibited by drywall doses (Wood 2008). This study used twice as much drywall as this project and suffered from the 2007 drought, which could have been the reason why above ground growth was impacted. However, the enhanced root growth reported here is consistent with other findings (Kruse et al. 2009, SoilSolutions 2011). Kruse et al. (2009) witnessed root enhancement of tall fescue due to gypsum amendments. The tall fescues were grown in a hydroponic system under several levels of aluminum. The gypsum addition was responsible for root development under aluminum contamination. The fact that root growth trends were opposite those of height and biomass suggests that the drywall may lead to plants shifting from investment in surface growth to investment in below-ground development. Unlike the seed experiments, there were no wallboard type-specific effects observed with the fescue grass responses to drywall. It is worth exploring this practice at lower doses or with different fertilizer and watering regimes, especially since the grass shows no sensitivity to the F and M type wallboards, so that no sorting would be necessary.

The area of lawn required to accommodate an entire load of drywall during construction will depend on the size of the house or project and the type of soil (Gaskin et al. 2002). The size of the project will define the amount of construction drywall reclaimed; a house produces about 1.5 lbs of construction drywall per square feet (Gaskin et al. 2002). The type of soil will define the application rate. Using the results of this study at the middle range dose (100 lbs / 1000 ft^2 or 5000 kg ha^{-1}), a house of 2000 ft^2 built would generate 3000 lbs (or 1360 kg) of construction drywall and it would require about 30,000 ft^2 of lawn to accommodate these load.

5.4 Canola in Field

5.4.1 Newton Field

While the field study of drywall impacts on canola crops at the Huntersville site yielded little practical information, the Newton field site produced some interesting findings. Drywall dosing at typical agricultural rates increased the number of pods and seeds as well as the leaf areas of plants relative to unamended controls. There was no change in seed mass. The 50.1 kg S ha^{-1} loading proved to be the most effective, more than doubling the pods per plant. This is consistent with other studies where 40 kg S ha^{-1} applied to canola significantly increased seed yield, seed oil content, and oil yield (Bora, 1997; Ahmad et al. 2005). Presumably the collective effect of the pod and seed increases observed in this study should result in enhanced seed oil yield. Taken together, the germination score test, the bench scale experiment, and the field scale experiment confirmed that canola seeds are positively affected by drywall supplementation. This is likely due to the high canola requirement for sulfur that the gypsum of drywall can provide. Data from this study describing the relative toxicity of different types of drywall products at different doses will allow greater confidence and wider use of waste construction drywall as soil amendment for canola. If this former waste material has the potential to increase oil yield to serve the growing biofuel industry, there is valuable synergy between waste management advantages and the agriculture benefits to such practices.

5.4.2 US Canola Production

The US Canola Association estimated that 703,182 hectares or 1,737,600 acres would be planted in canola seed in 2012 (US Canola Association 2012). If an optimum S dose was applied to this crop at a rate of 50.1 kg ha^{-1} y^{-1}, 210,250 tonnes or 231,761 tons of waste construction drywall would have been used. This would constitute a 13.7% diversion rate of waste drywall for the US (Sandler 2003).

5.5 Sunflower

Overall, the drywall amendment did not affect the growth of sunflower. This is in accordance with the germination test where sunflower germination and root elongation was not affected at low dose. Although sunflower seed yield was not documented in this study due to a weed infestation that rendered manual harvesting impossible, others have reported that gypsum amendments to sunflower crops increased seed yield, plant height, leaf area index, and stalk yield (Intodia et al. 1997, Poomurugesan et al. 2008, Rani et al. 2009). Therefore, a crop rotation of canola and sunflower would likely benefit in overall yields from applications of ground drywall.

5.6 Wheat Experiment

The germination study showed that conventional drywall has a positive effect on wheat growth. The large scale wheat experiment confirmed this result by showing that an amendment of 1,609 kg S ha^{-1} resulted in 9% longer stem growth, 40% more seed per flower, and 20% heavier seeds. However, the number of ears per pod and the wheat growth monitored with the BBCH scale were lower than the control for this dose. This suggested that wheat plant allocated more resources to seed production than to growth. This is in line with the Brennan et al. (2007) study that reported an increase of wheat yield by 25% but no increase of shoot biomass when plants were exposed to a gypsum amendment in a pot study. Overall, like in Brennan et al. (2007) study, wheat yield was significantly stimulated by ground drywall. This is also consistent with other studies where gypsum amendments resulted in increased wheat yield (Caires et al. 2002; Rashid et al. 2008). For instance, Rashid et al. (2008) applied 2.5 tons gypsum ha^{-1} and witnessed a 46% increase in wheat grain yield.

5.7 Carbon Sequestration

5.7.1 Soil pH

Calcium carbonate formation is highly favored at high soil pH. In order to create a zone of elevated pH, concrete fines, readily available from construction waste sites, were added to the column at a depth of 50 cm. The results showed that the addition of concrete fines successfully raised the pH by 0.5 pH unit compared to unamended soil. However, the concrete fines also contain carbonate due to concrete carbonation (Galan et al. 2010). As a result, the value of calcium carbonate found in the columns where concrete fines were added needed to be adjusted for the calcium carbonate originating from concrete fines.

5.7.2 Soil Calcium Carbonate Content

The carbon sequestration experiment revealed that with the proper elements present: calcium from waste construction drywall as a crop amendment; a crop such as wheat or corn that is capable of increasing soil CO_2; and precipitation limited to less than 33 in y^{-1}; an increase in drywall dose corresponded in an increase in soil calcium carbonate formed. The precipitation of 28 in y^{-1} also yielded calcium carbonate with the optimal dose being 1609 kg S ha^{-1}. The results also show that the columns with concrete fines formed more calcium carbonate than the pot without concrete fines. This is likely due to the increase in soil pH. This phenomenon can be observed with the dose of 1609 kg S ha^{-1} which was subjected to concrete fines amendment for both watering levels. This dose under the drier environment formed twice as much calcium carbonate than with 33 in y^{-1}. This is due to the fact that drier environment has higher calcium concentration in soil solution due to evaporation, enhancing the precipitation of calcium carbonate. This is a phenomenon seen in arid region of the US like the Mojave Desert (Schlesinger 1985). The use of concrete fines doubled the amount of calcium carbonate formed in the 28 in y^{-1} precipitation setting and formed more than six times the amount of calcium carbonate formed in the 33 in y^{-1} precipitation settings relative to the amendment without concrete fines.

The addition of concrete fines had a highly beneficial impact on the formation of calcium carbonate for both precipitations. However, some columns such as the C-33 dosed with 3.218 kg S ha^{-1} that received concrete fines and the C-28 dosed with 3,218 kg S ha^{-1} showed no evidence of calcium carbonate formation. In these cases, rather than conclude that it was absent, a more reasonable deduction, based on the fact that it was detected in several columns, is to conclude that the sampling technique likely “missed” the calcium carbonate that was formed in the column. The sampling method collected about 0.3 kg of soil samples at five different depths in a soil column that weighed more than 90 kg. As a result, it is highly probable that the calcium carbonate that formed in the column was not sampled. This experiment was not designed to accurately quantify the formation of calcium carbonate but rather to qualitatively demonstrate that the use of a waste material can help sequester carbon, which it successfully did.

The calcium carbonate detected appeared to be concentrated principally at two depths: below the surface at 0.25 m deep and deeper in the soil profile at 0.56 deep m and below. These two depths might correspond to two different processes of calcium carbonate formation (Salomons et al. 1976). The deeper layer may have formed well below the root zone where pCO_2 decrease enhancing the calcium carbonate formation according to the equation (9), while the shallower layer might be due to the capillary rise and evaporation of the soil solution. These depths also correspond to the depths at which sulfate and calcium ion concentrations were highest in the soil profile, suggesting that ground drywall penetrated at least 0.70 m into the column during the column experiments. It is also notable that the highest concentrations of calcium and sulfate ions occurred at the soil surface of each column, indicating that the drywall amendment did not completely dissolve and migrate into the soil; the full potential of the drywall amendment for carbon sequestration was not reached over the course of the experiment.

5.7.3 Precipitation Simulation

To simulate a fixed amount of precipitation, the water applied to the columns was controlled by placing the columns outdoors under a clear plastic tarp that was supported by a wooden frame. The columns were irrigated with tap water on a schedule. The tap water contained some alkalinity (20 mg L^{-1} as $CaCO_3$), and calculations were performed to subtract out any soil $CaCO_3$ contributions that could be attributed to drywall calcium combining with alkalinity introduced by the irrigation water. The calcium carbonate potentially formed due to the alkalinity of the tap water was 2.37 g and 2.03 g of calcium carbonate in the column watered with 33in y^{-1} and 28in y^{-1} respectively. This amount corresponded to only 11.5 % and 3% for the C-33 doses of 1,609 kg S ha^{-1} and 3,218 kg respectively. However, the tap water, with a pH of 8.5, higher than the pH of rain, could have enhanced the formation of calcium carbonate by increasing the soil pH.

5.7.4 Carbon Sequestered

The amount of calcium carbonate formed in the columns is used to estimate a carbon sequestration rate, The C-33, 1609 kg S ha^{-1} dose sequestered about 155 kg ha^{-1} y^{-1} of carbon, while the same drywall dose amended with concrete fines sequestered 917 kg ha^{-1} y^{-1}. The average car produces 612 kg y^{-1} of carbon (US EPA 2011c). A field of 4 hectares (9.9 acres) of wheat amended with 1,609 kg S ha^{-1} (the optimum dose for wheat growth) will offset the carbon dioxide production of an average car in a year. Moreover, about 1.5 million tons of waste construction drywall are produced annually in the U.S. (Sandler 2003). If this drywall was reclaimed and used as a wheat amendment (at the optimum dose of 1,609 kg S ha^{-1}) in the Western US, 178,000 ha (439,848 acres) of wheat could have been cultivated to sequester approximately 27,590 tonnes (30,350 tons) of carbon.

It is important to compare this sequestration rate to other natural and modern carbon sequestration techniques such as, soil organic carbon sequestration (crop residue), soil inorganic carbon sequestration (natural formation of pedogenic carbon), biotic carbon sequestration (forest growth) and chemical absorption for power plant emissions. The common unit used for comparison is g m^{-2} y^{-1} as carbon. Lal (2004, 2009) estimated that the use of best management practices (BMPs) in agriculture could sequester 50-1500 kg ha^{-1} y^{-1} of carbon as organic carbon corresponding to a rate of 5 to 150 g C m^{-2} y^{-1}. In the same study (Lal, 2009), it is suggested that inorganic carbon sequestration range from 0.15 to 1.5 g C ha^{-1} y^{-1}. Other studies evaluated the pedogenic carbonate formation in the US (Mojave Desert) at an average of 0.12 to 0.42 g C m^{-2} y^{-1} (Schlesinger 1985) and in the Saskatchewan soils of Canada at 1 g C m^{-2} y^{-1} (Landi et al. 2003). Biotic carbon sequestration is slightly higher. According to the type of tree, its age, and the climates, an average tree will sequester between 1,975 and 11,013 kg ha^{-1} y^{-1} of CO_2 (Tufts 2013). This corresponds to a range of 54 to 300 g m^{-2} y^{-1} of carbon. The modern carbon capture techniques used in power plant can sequester a large volume of carbon dioxide. Techniques such as wet amine scrubbing and solid adsorbent are designed to sequester 1,060 tons CO_2 day^{-1} (Schuette et al. 2006) or 95,724,500,000 g yr^{-1} of carbon per unit.

The carbon sequestration column study suggested that a system combining crops supplemented with waste construction drywall could sequester 79 to 917 kg ha^{-1} yr^{-1} of atmospheric carbon as inorganic carbon (7.9 to 91.7 g m^{-2} yr^{-1}). This range is at the low end of natural carbon sequestration rates, accomplishing about half that of agricultural BMPs and four-fold less than forest sequestration rates. However, the use of waste drywall increases the amount of inorganic carbon sequestered relative to natural rates of inorganic carbon sequestration. This is made possible by the drywall, which provides calcium, a mineral that would otherwise be a limiting factor (Manning 2008, Landi et al. 2003). The soil pH and rain levels characteristic of the western US (e.g. Kansas) are such that pedogenic calcium carbonate forms naturally (higher pH, lower precipitation). These experimental conditions used here approached these but were not as extreme. Therefore the experimental result strongly suggest that soil calcium supplementation with drywall would be highly productive in the western U.S., but that manipulation of calcium and pH conditions elsewhere might make it possible to enhance sequestration where it might otherwise hardly occur.

While organic carbon sequestration is dynamic with a high sequestration rate, it has a low mean residence time in soil. Trees rarely grow older than 200 years, and organic carbon is typically sequestered about 35 years (BHT 2013). Inorganic carbon mean residence time can reach 85,000 years (Schlesinger 2002). As a result, even though the rate of soil inorganic carbon sequestration is slow, once formed, it will stay sequestered for long periods.

Chemical methods to sequester carbon dioxide, especially those used to capture emissions from power plants, dwarf natural sequestration rates. Wet amine absorption or solid adsorbent can sequester 95,724,500,000 g y^{-1} of carbon per unit. Equivalent levels of sequestration with woods or wheat amended with drywall-supplied S (at 3,218 kg S ha^{-1} in a region with less than 33 in y^{-1} rainfall) would be 31,908 hectares and 105,191 hectares, respectively. However, the cost of chemical sequestration techniques is much greater (\$72 and \$129 per ton of CO_2 sequestered) and there are no ancillary benefits (Schuette et al.2006). In the case of the crop and drywall amendment system studied here, the ancillary benefits include the avoidance of S fertilizer life cycle costs and impacts; as well as the avoidance of drywall landfilling tipping fees and environmental impacts.

Plants can be categorized into three groups according to their photosynthesis pathway: C3-plants, C4-plants, and CAM plants. Briefly, these designations refer to the types of carbon compounds in which CO_2 is stored. C3 and C4-plants stored CO_2 in 3-carbon compounds and 4-carbon compounds while CAM plants stores CO_2 as acids. Wheat is a C3 plant, while corn is a C4 plant (Hopkins 1995). While the main difference between C3 and C4 plants lies in their photosynthesis pathway, another difference is the way different isotopes of carbon are processed or fractionated during photosynthesis. The amount of ^{13}C in plants is typically less than the amount of ^{13}C in atmospheric CO2, but the deficiency is of different magnitudes in different photosynthetic plant categories. The C3 plants tend to have an average deficiency of $\delta^{13}C$ of -27‰ while C4 plants have a deficiency of -12‰ (Deines 1980). $\delta^{13}C$ is the ratio of ^{13}C to ^{12}C in the sample to the ^{13}C to ^{12}C content in the official standard (Eq 14) In the carbon isotopic analysis, the official standard is the PDB standard (Pee Dee Belemnite) (Kendal et al. 1998).

$$\delta^{13}C(‰) = 1000 * \left(\frac{R_{sample}}{R_{standard}} - 1\right) \quad (14)$$

With R_{sample} = $^{13}C/^{12}C$ of sample and $R_{standard\,=}$ $^{13}C/^{12}C$ of a standard.

This depletion of ^{13}C due to plant photosynthesis is reflected in the plant tissue but also in the carbon released in the soil by the plant and rhizosphere respiration. In the case of pedogenic calcium carbonate, because its rate of formation is much slower than the rate at which CO_2 is supplied to the soil by the rhizosphere, the carbon isotope composition of calcium carbonate will be controlled by the carbon isotope composition of the soil CO_2, (Cerling 1984, Quade et al. 1989). Consequently, if the carbon isotope composition of calcium carbonate is similar to that of the plants, it would suggest that the soil calcium carbonate formed incorporated CO_2 of plant (and therefore atmospheric) origin.

Five samples of column soil containing $CaCO_3$ were sent to the Analytical Chemistry Laboratory at the University of Georgia (Athens, GA) for $\delta^{13}C$ analysis. The $\delta^{13}C$ values ranged from -15.97‰ to -19.85‰. The length of the carbon sequestration experiment was about 24 months with 14 of this month under C3 biomass (wheat), eight months under C4 biomass (corn), and two months of no vegetation. When this information is used to estimate a likely soil isotopic composition if plant CO_2 sources were used for $CaCO_3$ formation (Quade et al. 1989), Eq. 15 predicts a mean $\delta^{13}C$ of -19.74%.

$$\frac{14}{24} * (-27‰) + \frac{8}{24} * (-12‰) + \frac{2}{24} * (0) = -19.74‰ \qquad (15)$$

Cerling (1984) also suggests that during the winter, the soil CO_2 production through plants respiration might be reduced to zero, allowing atmospheric CO_2 to penetrate into the soil layer, hence increasing the carbon isotopic composition of the soil CO_2. The variation in winter temperature during the two years of the experiment could explain the range in $\delta^{13}C$ between the soil samples. The $\delta^{13}C$ soil sample at 0.25 m was not different from the other $\delta^{13}C$ at 0.56m deep. This is in accordance with the model developed by Quade et al. (1989) in which the decrease in $\delta^{13}C$ occurs just below the soil surface and the $\delta^{13}C$ stays constant below 0.20 m. There is no obvious explanation for the variations between the five sample readings. They were used to obtain some cursory indicator information about the source of the $CaCO_3$ carbon. The small sample size precludes drawing great inference from the data beyond confirmation that the results are within a range that is consistent with the hypothesis that the calcium-supplied drywall and plant system together provided some enhanced inorganic carbon sequestration.

CONCLUSION AND RECOMMENDATIONS

There are multiple benefits gained when waste drywall generated during construction and demolition activities can be diverted from landfills. This research built on some earlier studies to demonstrate that waste construction drywall can successfully be used as a soil amendment for canola and wheat crops. Specifically, a dose of ground drywall supplying 50.1 kg S ha^{-1} increased canola growth, which likely aided winter survival of young plants, and it increased canola yield, which is significant to the production of biofuel. Both the state of North Carolina and the U.S. government have launched aggressive initiatives to move the U.S. vehicle fleet to liquid biofuels (US DOE 2013).

The phyto-toxicity tests of three drywall types clearly demonstrated that fire retardant drywall and mold and moisture resistant drywall were not performing as well as a conventional drywall due to their additives. This will render drywall diversion more tedious, as waste construction drywall may require sorting before land application if certain seed types must germinate. If the amendment is applied after germination, field experiments may prove the specialty drywall products to be non-problematic. Experiments to determine the source of the problematic components of fire retardant and mold resistant drywall may determine that they are in a readily removable fraction of drywall (e.g. the outer paper layer that can be stripped), which might shift pre-processing from sorting to stripping..

The use of waste drywall ground and retained on a construction site for soil enrichment to support erosion control grass was not confirmed as an ideal use at the dosages tested here. While root development of tall fescue was enhanced, the above ground appearance of the grass was not as robust or aesthetically pleasing. Additional testing will be required at additional dosage ranges, with more extensive field testing, and over several seasons to further explore this option. Both stormwater filtration capacity and subsequent effects on final lawn health would need to be assessed.

The exploration of using waste drywall as a means to enhance vegetation-mediated carbon sequestration showed that this phenomenon could be enhanced using drywall amendments. When virgin drywall was coupled with plants in soil columns maintained over multiple crop cycles in soil columns, there was evidence that the system could sequester carbon as inorganic carbon (calcium carbonate) faster than would otherwise be expected. The fact that the vegetation mediated sequestration of atmospheric carbon dioxide was confirmed with stable isotope analysis. The formation of calcium carbonate using ground drywall was further enhanced by the addition of concrete fines, another waste product of construction and demolition activities that can be diverted from landfills for this purpose. However, it is important to point out that like the natural process, this phenomenon is only feasible in dry climates such as those found in the Western U.S. where rain precipitation is low and summer temperatures are high. While a crop and drywall amendment system alone will not solve the problem of increasing global accumulations of atmospheric carbon dioxide, it is a carbon sequestration strategy that is worthy of further consideration. It is easily implemented, relatively inexpensive, and converts a former waste to a value-added product. Future research will need to examine crop rotations, soil accumulations, soil and microbial ecology, pH effects, and other impacts that might accompany repeated use of drywall amendments in soil. This study focused entirely on waste construction drywall. Demolition drywall is the larger fraction of C&D drywall, and because it has paint and nails, it tends to be dealt with on a case-by-case basis. There is one example of demolition drywall with water based paint being diverted from landfilling in California (Richard. A. Ludt, personal communication, August 15, 2012).

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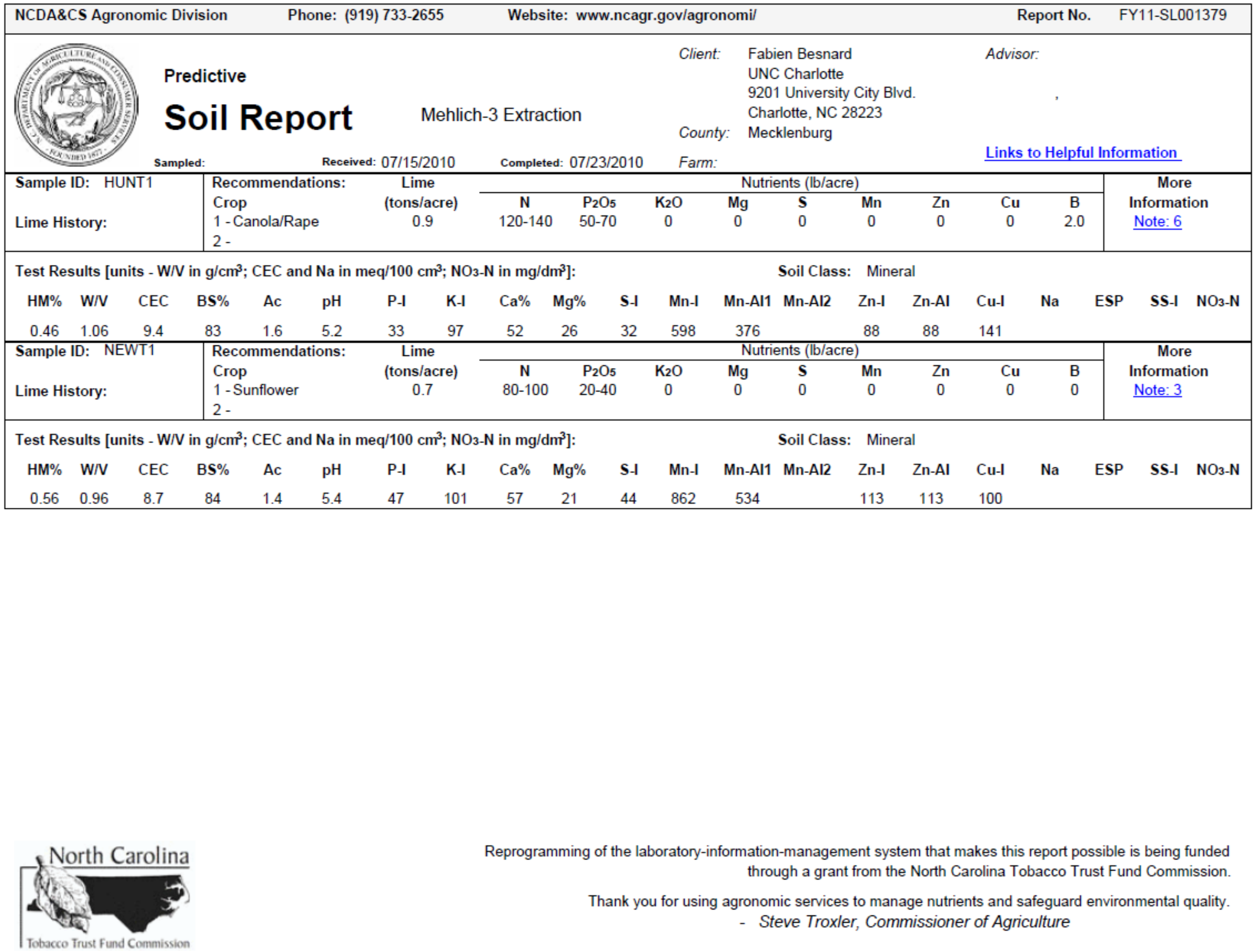
APPENDIX A: FIELD SOIL REPORT



NCDA&CS Agronomic Division **Phone:** (919) 733-2655 **Website:** www.ncagr.gov/agronomi/ **Report No.** FY11-SL001379

Predictive

Soil Report

Mehlich-3 Extraction

Client: Fabien Besnard
UNC Charlotte
9201 University City Blvd.
Charlotte, NC 28223
County: Mecklenburg
Farm:

Advisor:

Links to Helpful Information

Sampled: **Received:** 07/15/2010 **Completed:** 07/23/2010

Sample ID: HUNT1	**Recommendations:**	**Lime**	Nutrients (lb/acre)									**More**
Lime History:	Crop	**(tons/acre)**	**N**	**P2O5**	**K2O**	**Mg**	**S**	**Mn**	**Zn**	**Cu**	**B**	**Information**
	1 - Canola/Rape	0.9	120-140	50-70	0	0	0	0	0	0	2.0	Note: 6
	2 -											

Test Results [units - W/V in g/cm³; CEC and Na in meq/100 cm³; NO3-N in mg/dm³]: **Soil Class:** Mineral

HM%	**W/V**	**CEC**	**BS%**	**Ac**	**pH**	**P-I**	**K-I**	**Ca%**	**Mg%**	**S-I**	**Mn-I**	**Mn-AI1**	**Mn-AI2**	**Zn-I**	**Zn-AI**	**Cu-I**	**Na**	**ESP**	**SS-I**	**NO3-N**
0.46	1.06	9.4	83	1.6	5.2	33	97	52	26	32	598	376		88	88	141				

Sample ID: NEWT1	**Recommendations:**	**Lime**	Nutrients (lb/acre)									**More**
Lime History:	Crop	**(tons/acre)**	**N**	**P2O5**	**K2O**	**Mg**	**S**	**Mn**	**Zn**	**Cu**	**B**	**Information**
	1 - Sunflower	0.7	80-100	20-40	0	0	0	0	0	0	0	Note: 3
	2 -											

Test Results [units - W/V in g/cm³; CEC and Na in meq/100 cm³; NO3-N in mg/dm³]: **Soil Class:** Mineral

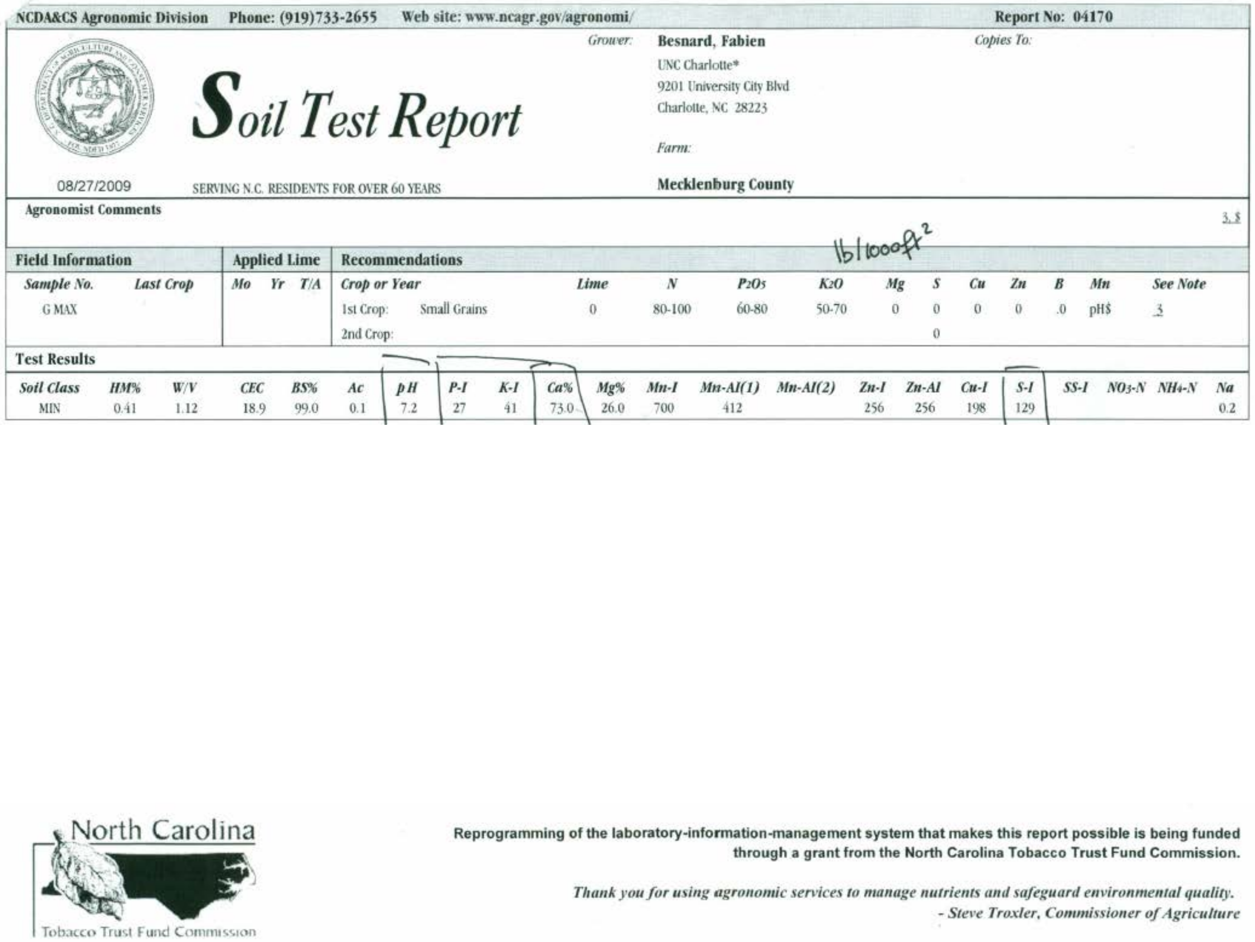
HM%	**W/V**	**CEC**	**BS%**	**Ac**	**pH**	**P-I**	**K-I**	**Ca%**	**Mg%**	**S-I**	**Mn-I**	**Mn-AI1**	**Mn-AI2**	**Zn-I**	**Zn-AI**	**Cu-I**	**Na**	**ESP**	**SS-I**	**NO3-N**
0.56	0.96	8.7	84	1.4	5.4	47	101	57	21	44	862	534		113	113	100				

North Carolina
Tobacco Trust Fund Commission

Reprogramming of the laboratory-information-management system that makes this report possible is being funded through a grant from the North Carolina Tobacco Trust Fund Commission.

Thank you for using agronomic services to manage nutrients and safeguard environmental quality.
- *Steve Troxler, Commissioner of Agriculture*

APPENDIX B: COLUMN SOIL REPORT



NCDA&CS Agronomic Division Phone: (919)733-2655 Web site: www.ncagr.gov/agronomi/ Report No: 04170

Soil Test Report

08/27/2009 SERVING N.C. RESIDENTS FOR OVER 60 YEARS

Grower: **Besnard, Fabien**
UNC Charlotte*
9201 University City Blvd
Charlotte, NC 28223

Farm:

Mecklenburg County

Copies To:

Agronomist Comments 3, $

lb/1000ft^2

Field Information		**Applied Lime**			**Recommendations**													
Sample No.	*Last Crop*	*Mo*	*Yr*	*T/A*	*Crop or Year*		*Lime*	*N*	*P_2O_5*	*K_2O*	*Mg*	*S*	*Cu*	*Zn*	*B*	*Mn*	*See Note*
G MAX					1st Crop:	Small Grains	0	80-100	60-80	50-70	0	0	0	0	.0	pH$	3
					2nd Crop:							0					

Test Results

Soil Class	*HM%*	*W/V*	*CEC*	*BS%*	*Ac*	*pH*	*P-I*	*K-I*	*Ca%*	*Mg%*	*Mn-I*	*Mn-AI(1)*	*Mn-AI(2)*	*Zn-I*	*Zn-AI*	*Cu-I*	*S-I*	*SS-I*	*NO_3-N*	*NH_4-N*	*Na*
MIN	0.41	1.12	18.9	99.0	0.1	7.2	27	41	73.0	26.0	700	412		256	256	198	129				0.2

North Carolina
Tobacco Trust Fund Commission

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Thank you for using agronomic services to manage nutrients and safeguard environmental quality.
- Steve Troxler, Commissioner of Agriculture