DISSERTATION

TOWARDS THE SYSTEMATIC IDENTIFICATION OF LOW-COST ECOSYSTEM-MEDIATED CARBON SEQUESTRATION OPPORTUNITIES IN BIOENERGY SUPPLY CHAINS

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ABSTRACT

TOWARDS THE SYSTEMATIC IDENTIFICATION OF
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Because the dedicated production of terrestrial biomass feedstocks involves the fixation of atmospheric carbon, carefully managed biofuel and bioenergy supply chains are increasingly recognized as an opportunity for carbon sequestration in soils or geological reservoirs in addition to their climate change mitigation value via the displacement of fossil fuel use. Bioenergy involves the coupling of agricultural systems and industrial supply chains, and finding optimal system designs often requires navigating a fundamental tension between maximizing overall system productivity while simultaneously limiting the intensification of feedstock exploitation to sustainable levels. Bioenergy sustainability analyses are further complicated by strong spatial heterogeneities in feedstock production performance, fundamentally different emission mechanisms across the agricultural and industrial phases of the biofuel lifecycle, and the tendency to perform environmental assessments and economic analyses in isolation. Well-designed integrated assessments are necessary to identify the total amounts and time dynamics of sequestration possible in such systems, to put those results in context relative to other supply chain impacts, and to understand tradeoffs between various environmental impact criteria and production costs.

This dissertation starts with a thorough review of the bioenergy lifecycle assessment (LCA) literature to identify outstanding climate impact accounting challenges and inform the

integration of production cost estimates. Two integrated assessment case studies are then undertaken to identify low-cost opportunities for improving carbon sequestration at different points in the bioenergy supply chain. The first focuses on feedstock production, assessing the potential for increasing soil carbon sequestration in bioenergy landscapes based on the cultivation of perennial grasses. A spatially-explicit landscape analysis system is created around a newly-parameterized version of the DayCent biogeochemistry model, and switchgrass productivity and soil greenhouse gas balance are assessed across gradients of land quality and cultivation intensity in a real-world bioenergy landscape in western Kansas. Integrating these ecosystem simulation results with existing LCA, farm enterprise budget, and biomass transport models allows for the quantification of landscape level cost – mitigation tradeoffs under various system design strategies and policy constraints. The second case study focuses downstream in the supply chain, considering the use of low-value conversion co-products as soil amendments to improve agroecosystem sustainability. The biochar co-product from a hypothetical thermochemical conversion system in the Colorado Front Range is assessed using simplified models of biochar recalcitrance and agronomic benefits as a function of feedstock material and conversion method. Together, these case study results are illustrative of the potential costs of improving ecosystem-mediated carbon sequestration in bioenergy systems, and the ongoing work required for full global supply chain optimization.

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CHAPTER 1

INTRODUCTION

1.1. Introduction to Ecosystem-Mediated Carbon Sequestration Assessment

Bioenergy is unique among renewable energy technologies in that it relies on carbon derived from the fixation of ambient atmospheric CO_2 as an energy carrier, and requires manipulation of the natural carbon cycle in the course of cultivating biomass feedstocks. Careful management of bioenergy supply chains introduces the potential for enhancing carbon storage in the biosphere or diverting biomass-derived carbon into geological storage, thus leading a sequestration of atmospheric carbon over various timescales (e.g., Lehmann, 2007a), in addition to displaced fossil fuel use. Such technologies have often been lumped under the geoengineering umbrella, termed Carbon Dioxide Removal in order to differentiate them from more aggressive geoengineering interventions meant to modify the radiative balance of the planet (so-called Solar Radiation Management, Shepherd, 2009).

As concerns over total global anthropogenic greenhouse gas emissions exceeding the limits implied by internationally-agreed temperature targets (Allen *et al.*, 2009) grow, so too does interest in carbon-sequestering bioenergy production pathways. Today, a large fraction of the climate-stabilizing Representative Concentration Pathways developed by the Intergovernmental Panel on Climate Change assume significant deployment of carbon-sequestering bioenergy technology in order to compensate for the anticipated overshooting of acceptable atmospheric CO_2 concentrations (Fuss *et al.*, 2014). Such systems are often described as 'carbon-negative' to the extent that supply chain carbon sequestration outweighs other lifecycle GHG emissions, implying that increasing production rates contribute to decreasing net atmospheric CO_2 concentrations (Keith & Rhodes, 2002; Rhodes & Keith, 2008; Kraxner *et al.*, 2014).

There are at least three mechanisms by which bioenergy supply chains could achieve significant levels of carbon sequestration. BioEnergy with Carbon Capture and Storage (BECCS) involves capturing and liquefying bioenergy system CO_2 emissions and then injecting them into suitable geological formations for permanent sequestration, a technology originally designed for coal and other stationary fossil energy sources (Creutzig *et al.*, 2015). BECCS could potentially be integrated to sequester emissions from the combustion of biomass at a stationary power plant, or waste CO_2 from the production of biofuels through biochemical or thermochemical conversion pathways. Several regional-scale analyses of the former scheme have been recently been conducted (Kraxner *et al.*, 2014; Sanchez *et al.*, 2015), and a demonstration of BECCS is currently underway at a corn ethanol facility in Illinois (Lusvardi, 2015).

A second mechanism for bioenergy supply chain carbon sequestration lies is improving the carbon storage of soils on which feedstock crops are cultivated. The amount of carbon stored in soil organic matter globally is several times larger than the total carbon storage in live biomass or of CO_2 in the atmosphere (Lal, 2004), and reflects a balance between site net primary productivity and the turnover rate of dead organic matter as determined by its original chemical composition, environmental controls on microbial activity and soil carbon stabilization potential, and disturbance due to management such as tillage. The cultivation of bioenergy feedstocks can either enhance or degrade these carbon sinks depending on the crop, the environment and site where it is cultivated, and how it is managed (Davis *et al.*, 2013). The cultivation of dedicated perennial grass feedstocks on marginal or degraded lands in particular is thought to have great potential for carbon sequestration through increasing soil organic matter, which would be a major contributor to the net GHG mitigation value of such a supply chain (Tilman *et al.*, 2006a; Robertson *et al.*, 2011; Wang *et al.*, 2012).

The third sequestration mechanism involves a hybrid of the first two, in which carbon-rich bioenergy conversion co-products are applied to agricultural soils as amendments, a strategy with potential to valorize those material streams and improve overall system GHG performance and sustainability (Cayuela *et al.*, 2010). Thermochemical conversion systems produce a solid carbon-rich byproduct which, when used as a soil amendment, is referred to as biochar. Biochar has received great attention in the last decade as strategy for improving fertility and reducing trace GHG emissions in agroecosystems while simultaneously directly sequestering additional carbon (Lehmann, 2007a, 2007b; Laird, 2008). Direct analogs exist for biochemical conversion systems as well. Biochemical conversion of lignocellulosic material to ethanol produces significant amounts of lignin by-product, a complex heterogeneous bio-polymer resistant to biological conversion (Tanger *et al.*, 2013). While it is typically assumed that this lignin by-product would be burned on-site to provide process heat and electricity (e.g., Dutta *et al.*, 2011), it has recently been suggested that, like biochar, this highly-recalcitrant fraction could persist for long timescales in soils and thus improve system GHG performance when applied as a soil amendment (Pourhashem *et al.*, 2013). Likewise, a similar sequestration may be possible with the anaerobic digester slurry co-product of biogas production (Smith *et al.*, 2014). In each case, the more volatile or labile fractions of the biomass are exploited for the production of high-value liquid or gaseous biofuels, while the more recalcitrant left over fraction is used to mitigate the effects of the original biomass removal and potentially improve soil health and productivity (Lal, 2004). Thus, this carbon sequestration strategy is potentially more robust and durable than increasing ordinary soil organic matter levels, and represents a potential source of value in contrast to the additional costs required for CCS.

The latter two sequestration mechanisms can be termed ecosystem-mediated, as the total amount and/or the stability of carbon storage is a function of ecosystem processes. Such effects represent a challenge for lifecycle assessment, as they require a completely different set of analytical tools to evaluate than those used to tabulate supply chain inputs of material and energy. Soil organic matter balance is a strong function of both environmental and management factors, and shows strong spatial variability even within the boundaries of a single bioenergy production system. Sequestration based on co-product soil amendments is even more challenging, as the biogeochemical recalcitrance of such materials is often not well quantified and the mechanisms underlying their potential agronomic value are difficult to identify and model.

In addition, while each of these mechanisms has potential to improve the net greenhouse gas performance of bioenergy systems, their implementation has strong implications for the economics of the systems in question. Implementation of BECCS requires significant additional equipment and energy use at the conversion facility. Maximizing soil carbon sequestration under biomass feedstock crops implies targeting particular types of land for cultivation and adjusting agronomic management, with associated implications for land costs and overall crop productivity. Use of co-products as soil amendments introduces an opportunity cost of not using them as process fuel or for electricity production for internal use or export (Dutta *et al.*, 2011). In both of the ecosystem-mediated mechanisms, increasing soil organic matter levels can introduce a feedback of improved agronomic performance and increased system productivity. As a result, lifecycle assessment performed in isolation has limited value, and integrated assessments that simultaneously consider the greenhouse gas and the economic implications of a given biophysical scenario are necessary to estimate the practicality of implementation. Such studies can be useful in identifying and quantifying the lowest-cost opportunities for reducing GHG emissions through various bioenergy supply chain modifications or substitutions, determining the so-called marginal carbon abatement costs of such systems.

1.2. Organization of Dissertation

This dissertation is organized as six separate chapters, including this introductory chapter to introduce and highlight the linkages between the following chapters. Chapter 2 is a detailed review of the bioenergy lifecycle assessment literature. Chapter 3 and 4 describe a case study focusing on bioenergy feedstock landscape design for optimal soil carbon sequestration, with Chapter 3 presenting model parameterization and methods for landscape-scale assessment, and Chapter 4 devoted to interpreting ecosystem simulation results within an integrated assessment framework and developing optimal system performance tradeoff curves under various design strategies and policy constraints. Chapter 5 introduces an additional case study around co-product management, estimating the cost and system GHG performance implications of using biochar as a soil amendment rather than a process fuel. All chapters 2-5 are written as stand-alone journal articles, with separate introductions and discussion sections putting the individual results and insights into a broader context. The dissertation is completed with a brief conclusion chapter recapitulating the results of the two case studies in the context of broader bioenergy assessment efforts.

Chapter 2 – Understanding GHG mitigation in bioenergy systems: A review of epistemic, methodological, and system design factors

Lifecycle assessment techniques have been applied for quantitative sustainability analysis in bioenergy systems for more than three decades (Silva *et al.*, 1978; Chambers *et al.*, 1979), though broad new challenges to bioenergy system sustainability are still being raised with disconcerting frequency (Rosenthal, 2008; Searchinger *et al.*, 2008; Liska *et al.*, 2014; The Associated Press, 2014; Gillis, 2015). Bioenergy lifecycle assessment is more complex than that for other energy technologies due to biogenic emissions from feedstock production that vary widely based on both environmental factors and agronomic management factors (Davis *et al.*, 2013), and evolve over timescales very different from that of fuel production (Schulze *et al.*, 2012). In addition, large-scale feedstock cultivation potentially puts pressure on a limited global arable land base, likely introducing market-mediated leakage effects (Searchinger *et al.*, 2008). These effects are central to the sustainability of the bioenergy concept, but are fundamentally different from emissions due to supply chain material inputs or energy use and thus are not easily represented in most standard lifecycle assessment models.

This chapter presents a review and classification of the different types of emissions included in existing bioenergy lifecycle assessment studies. A simple taxonomy is developed to classify emissions based whether they are industrial or biogenic in nature, whether they occur directly within or indirectly outside of the physical boundaries of the supply chain, whether their temporal nature is discreet or continuous, and whether they represent real observable emissions or avoidance of emissions relative to a non-observable counterfactual scenario. These different classification criteria each have important accounting implications, questions around which are often not yet well resolved. The review and synthesis ends with a discussion contrasting carbon-negative bioenergy supply chains versus those that do not sequester carbon but nonetheless have high fossil fuel displacement value.

Chapter 3 – Analyzing variable feedstock productivity and soil GHG emissions balance across a cellulosic bioenergy landscape

While it is recognized that large-scale production of dedicated biomass crops will likely be required to meet current bioenergy mandates, it is not clear where in existing agricultural landscapes such production would best be integrated, or how intensively such production should be managed. These choices have huge implications for the overall environmental performance of a bioenergy supply chain, with potential to 'swing' the system from one that mitigates emissions to one that increases them relative to a fossil fuel baseline (Davis *et al.*, 2013). Heterogeneity in land quality and land use history lead to large spatial variability at landscape scales, and correlations between the two complicate assessment efforts and make generalizations difficult.

This chapter develops methods for using biogeochemistry process models for high-resolution assessment of bioenergy landscape productivity and associated biogenic greenhouse gas emissions balance. First, detailed parameterizations for both upland and lowland switchgrass are developed for the DayCent model using a large dataset of US field trials collected from the literature, with independent validation of model performance conducted where possible. Next, an illustrative case study is conducted for the cultivation of switchgrass in the heterogeneous landscape around a new commercial-scale cellulosic biorefinery in southwestern Kansas. Existing spatial databases of required model data inputs are leveraged to characterize the case study landscape and specify the tens of thousands of simulation runs necessary to compare switchgrass cultivation across a range of management intensities (nitrogen fertilizer application rates) to 'business as usual' land management at the full resolution possible with these inputs. A set of tools is then developed in Python and using SQLite relational databases in order to automate the execution of multiple model runs in parallel and the processing and integration of simulation results in a consistent and transparent manner. The case study results serve to illustrate the potential variability in switchgrass yield and biogenic emissions footprint as a function of which parts of the landscape are cultivated and how intensively they are managed.

Chapter 4 – High resolution assessment identifies low-cost mitigation opportunities in bioenergy landscapes

The choices around feedstock siting and cultivation intensity investigated from a biogeochemical perspective in the previous chapter have important implications for the overall costs and lifecycle emissions performance of a feedstock supply chain. The level of nitrogen fertilizer represents an important input cost for farmers, and the resulting crop productivity determines whether the farming operation is profitable enough to cover input and operational costs. These factors can be investigated in the context of a farm enterprise budget in order to determine the minimum farm-gate break-even price necessary to cover costs for any given set of input intensity and resulting crop yields (Jain *et al.*, 2010). Synthetic nitrogen fertilizer carries a high embodied emissions burden, and also results in significant emissions of the potent greenhouse gas nitrous oxide (N_2O) due to soil microbial activity when applied to agricultural soils (Wang *et al.*, 2011). To the extent that costs and lifecycle feedstock production emissions are each minimized at different levels of management intensity or at different positions on the landscape, a landscape performance tradeoff will exist and optimization can be performed.

This chapter starts with a review of landscape design priorities from a logistics, farm enterprise budget, and a general biogeochemical perspective. The biophysical simulation results developed in the previous chapter are then integrated with a crop production budget, a simple biomass transport model, and a lifecycle assessment framework in order to translate yields and biogenic emissions into production costs and supply chain lifecycle emissions, considering opportunity costs of feedstock production and baseline landscape emissions assessed spatially for business-as-usual land management. The resulting multi-dimensional assessment considering both costs and emissions as a function of both spatial location of cultivation and intensity of agronomic management is then solved with a simple weighted solution approach based on applying a price for carbon and determining the minimum total social cost (minimum delivered biomass costs + valorized lifecycle greenhouse gas emissions) of meeting biorefinery feedstock demand. Pareto tradeoff frontiers illustrating the range of cost-minimizing and carbon sequestration-minimizing landscape designs possible are then constructed for a variety of different system design strategies and policy constraint scenarios.

Chapter 5 – Distributed biochar and bioenergy coproduction: a regionally-specific case study of environmental benefits and economic impacts

The efficiency of biomass feedstock conversion to liquid transportation fuels based on alkanes, alkenes, aromatics, or alcohols is ultimately constrained by stoichiometry, as getting from lignocellulosic biomass with hydrogen-to-carbon ratios in the range of 1-2 to liquid fuels with H:C of 2-4 requires either that surplus C is rejected or supplemental H is added (Tanger *et al.*, 2013). While many systems (fermentation, gasification) reject excess carbon in the form of CO_2, more mild thermochemical conversion systems such as slow and fast pyrolysis reject some of their excess C in a charcoal-like form, heavily enriched in aromatically-bound C compared to the original feedstock material. Preliminary studies suggest that using this recalcitrant material as a soil amendment rather than combusting it for process heat may be attractive from an economic and GHG mitigation value perspective, depending on the properties and agronomic performance of the char and the source of process energy that would be displaced (Gaunt & Lehmann, 2008; Hammond, 2009; Roberts *et al.*, 2010; Galinato *et al.*, 2011; Shackley *et al.*, 2011; Yoder *et al.*, 2011; Sohi, 2013).

Existing studies are generally based on reported average values for biochar performance from sometimes contradictory meta-analyses (Jeffery *et al.*, 2011; Biederman & Harpole, 2013; Crane-Droesch *et al.*, 2013; Liu *et al.*, 2013) and typically ignore the huge range of heterogeneity observed in biochar properties (McLaughlin *et al.*, 2009; Spokas & Reicosky, 2009). To the extent that biochar yield, recalcitrance, and agronomic performance are all related to the temperature and duration of the thermochemical conversion step (Brewer *et al.*, 2011; Rutherford *et al.*, 2012; Schimmelpfennig & Glaser, 2012), these existing efforts potentially fail to address a fundamental tension between designing a conversion system for favorable energy yields versus designing a system for good biochar performance (Woolf *et al.*, 2014). However, assessment capabilities are limited by an incomplete understanding of the mechanisms behind biochar agronomic and biogeochemistry effects, which are not yet represented in process-based models like DayCent.

This chapter presents an additional case study investigating tradeoffs in system economic and greenhouse gas performance between using char as a soil amendment versus as a process fuel, as a function of the conditions under which the char was created. The agronomic value of biochar is modeled conservatively as a simple liming effect based on its ash content, consistent with meta-analyses showing that positive yield effects are most often observed with biochar application to low-pH soils and in association with measured increases in soil pH (Jeffery *et al.*, 2011; Biederman & Harpole, 2013; Liu *et al.*, 2013). Similarly, biochar recalcitrance is simulated as a function of conversion temperature, with hotter conversion leading to lower yields of more aromatic and recalcitrant char. The resulting model is applied to a case study of biochar production in the Colorado front range from locally-sourced brewery spent grains or beetle-kill pine wood, with the resulting char exported to a neighboring state for use as an agricultural soil liming agent. While this case study is somewhat more exploratory than the first, it illustrates an important system performance tradeoff that is unlikely to emerge from existing meta-analysis efforts.

Chapter 6 – Conclusion

Finally, a brief concluding chapter summarizes the results of the two case studies in the context of other efforts estimating marginal carbon abatement costs in bioenergy supply chains. This chapter includes a discussion of how these case studies might be further refined in the future, and how they might be combined and linked with more detailed models of biomass conversion in order to generate 'global' optimizations for full bioenergy supply chains capable of identifying additional emergent opportunities for low-cost GHG mitigation. Ongoing work building off these preliminary results is also briefly introduced.

CHAPTER 2

ASSESSMENT OF BIOENERGY SYSTEM CLIMATE IMPACTS: A REVIEW OF CONCEPTUAL, METHODOLOGICAL, AND SYSTEM DESIGN FACTORS

2.1. Summary

A variety of renewable fuel and power standards at the local, state, and federal level encourage or mandate the widespread deployment of biofuel and bioenergy production, and many projected climate mitigation scenarios rely on such systems for their ability to sequester carbon. Lifecycle assessment (LCA) techniques have been applied to quantify the climate impacts of bioenergy systems for decades, and great progress has been made in understanding material and energy consumption and associated greenhouse gas (GHG) emissions and other climate impacts across bioenergy supply chains. However, the provisioning of biomass feedstocks ties these supply chains to agricultural and ecosystem processes that are central to overall bioenergy system sustainability yet not easily represented in standard LCA models. Over the last several years critical challenges have been raised around bioenergy climate impacts with regard to the proper accounting of changes in ecosystem carbon storage and other biogenic GHG emissions during feedstock production, leakage effects associated with increasing productive pressure from a limited global arable land base, and the need to consider direct biophysical climate impacts such as changes in surface albedo or evapotranspiration.

Here we review the bioenergy lifecycle assessment literature with a focus on climate impacts that are not well represented in many standard bioenergy assessment tools. We introduce a simple climate impacts taxonomy that highlights assessment challenges and opportunities for system climate performance improvement. For each type of climate impact we

explore the range of values reported in the literature (due to both real-world variability between systems, and uncertainty in assessment), the level at which system performance might be improved, and analogs in production cost analysis that should be treated consistently in the context of an integrated assessment. A select set of first- and second-generation bioenergy LCA studies are then reviewed and evaluated against the taxonomy to highlight assessment gaps and inconsistencies. We end with a discussion of trends in bioenergy LCA towards spatially-explicit biogeochemical feedstock cultivation modeling, integrated assessment and system optimization, and development of bioenergy system concepts with strong carbon sequestration potential.

2.2. Introduction

Biomass in its various forms is encountered in great quantities in both natural ecosystems and agro-ecosystems in all countries of the world. The burning of woody biomass is one of the earliest human exploitations of energy, and the combustion of biomass for cooking is still ubiquitous in many developing countries, accounting for approximately as much wood consumption as the global industrial lumber market (Chum *et al.*, 2011). In addition to the potential for improving biomass combustion for cooking (Smith, 2010), there is increasing interest in other advanced bioenergy applications in developing-country settings including small-scale electricity production based on combustion or gasification (Junginger *et al.*, 2001; Karve *et al.*, 2011), alcohol production from the fermentation of sugary or starchy crops (maize, sugarcane, cassava) for use in liquid fuel cookstoves or engines (Pennise *et al.*, 2009; Maroun & La Rovere, 2014), and the production of biodiesel from dedicated oil crops such as jatropha (Eckart & Henshaw, 2012; Muys *et al.*, 2014). Increased and improved bioenergy exploitation are viewed as important tools for sustainable development (Sagar & Kartha, 2007), and receive support through the IPCC Clean Development Mechanism (Ravindranath *et al.*, 2006) and other carbon financing programs (e.g., Simon et al., 2012).

In developed countries, bioenergy is present in a range of forms and scales including home heating based on pellet stoves, coal supplementation with biomass in large power stations, and the production of first-generation liquid biofuels based on the fermentation of maize or the transesterification of various plant oils (Hill *et al.*, 2006; Wang *et al.*, 2011). It is estimated that 40% of the 2010 corn crop was consumed in domestic biorefineries, yielding 13.8 billion gallons of ethanol. This is equivalent to >6% of the US gasoline motor fuel supply on an energy basis, and the associated 60 million tons of distillers grains and solids (DGS) co-produced contributed approximately 17% of total equivalent corn and soy feed consumption by domestic cattle, swine, and poultry that year (World Agricultral Outlook Board 2012; Renewable Fuels Association 2012; US Energy Information Administration 2012; Hoffman and Baker 2011; Hoffman and Baker 2010). The 2007 Energy Independence and Security Act (EISA) mandates that this first-generation biofuel production be supplemented with 21 billion gallon a year of second-generation biofuels derived from cellulosic feedstocks or other 'advanced' sources (110th Congress of the United States, 2007), spurring work on a wide variety of biochemical (Peplow, 2014), thermochemical (Butler *et al.*, 2011), and hybrid (Daniell *et al.*, 2012) biomass conversion pathways. This national policy is complemented by a variety of local and state incentive programs or mandates for the production of biomass-derived fuels, electricity, or heat (http://www.aeltracker.org/).

In addition to incentivizing or mandating biofuel production, policies such as the US Renewable Fuel Standard (RFS) and the California Low Carbon Fuel Standard (LCFS) also require the quantification of associated climate impacts in order to ensure that environmental performance goals are met (Liska & Perrin, 2009). Lifecycle assessment (LCA) is the analytical process of tabulating the inputs and outputs of an industrial supply chain, tracing material and energy flows associated with production, use, and final disposal through to the margins of the physical economy and tabulating all exchanges with nature ('elemental flows') in order to determine total impacts associated with that production process. Formal guidelines for conducting LCAs are provided in ISO standards 14040 and 14044 (International Organization for Standardization, 2006a, 2006b), which specify processes around problem definition, modeling of material flows within and upstream of a supply chain (lifecycle inventory), interpretation of total elemental flows (lifecycle impact assessment), and iterative review by technology stakeholders. The impacts associated with elemental flows can be interpreted through a variety of lenses focusing on various aspects of non-renewable resource depletion, environmental damage, or impacts on human health or well-being (von Blottnitz & Curran, 2007; Bai *et al.*, 2010; Buratti & Fantozzi, 2010), with total lifecycle fossil energy use and greenhouse gas emissions balance being the most commonly-reported metrics in bioenergy LCA.

LCA studies typically take one of two accounting stances. Early LCA studies focused on determining the fraction of current overall industrial activity and associated energy use or GHG emissions that could be assigned to a given industry, a process known as attributional lifecycle assessment (ALCA). ALCA is conservative in the sense that combining ALCAs for all products and services generated within an economy should yield an accurate estimate of the overall environmental impact of that economy (Brander *et al.*, 2009), and is thus useful in regulatory settings. In contrast, the consequential lifecycle assessment (CLCA) approach evolved later in order to address 'what if' questions around the potential impacts of a hypothetical future expansion of a given production pathway, focusing on marginal rather than average emissions and including indirect and ripple effects, in order to inform policy decisions (Ekvall & Weidema, 2004). Consequential LCAs are non-conservative in that they include indirect effects that would be attributed to other production chains in an ALCA, but are casually linked to the expansion of the production chain in question and thus deserve consideration from policymakers (Brander *et al.*, 2009). CLCA is geared toward comparing the relative impacts of switching from one technology to another, an interference that is not possible from ALCA results (Plevin *et al.*, 2014). In practice, few bioenergy LCA studies adhere strictly to either definition, and most fall somewhere in between the pure ALCA and CLCA categories.

Efforts to understand the performance of bioethanol supply chains date back to the late 1970's (Silva *et al.*, 1978; Chambers *et al.*, 1979). Early studies focused on supply chain energy consumption to determine whether biofuel production was thermodynamically favorable (Patzek, 2004; Ponton, 2009) or contributed to domestic energy security by displacing petroleum (Farrell *et al.*, 2006; Dale, 2007). The recognition of biofuels as a renewable energy source capable of making a significant contribution to a national GHG emissions reduction strategy (Pacala & Socolow, 2004) has been associated with a refocusing of LCA efforts around climate metrics such as global warming impact (Adler *et al.*, 2007; Wang *et al.*, 2007a). Despite some irregularities in system boundary definition in early studies (e.g., Pimentel, 1991), subsequent work indicated significant convergence in LCA results from different studies after normalization with common boundary conventions and/or emission factor datasets (Farrell *et al.*, 2006; Plevin, 2009; Whitaker *et al.*, 2010). More recent lifecycle assessment literature trends, as assessed through Web of Knowledge (http://apps.webofknowledge.com/) search results, are shown in Figure 2.1. While the number of LCA studies on all topics in the literature has approximately quadrupled over the past decade and a half, the number of biofuel and bioenergy LCA studies in particular has surged, especially since the 2007 EISA legislation mandated that biofuels meet lifecycle greenhouse gas reduction targets relative to conventional fuels to qualify towards the US Renewable Fuel Standard. Such biofuel and bioenergy studies account for approximately 1/8 of all new lifecycle assessment studies published since 2011. In addition to these conventional bioenergy studies, LCA techniques have been applied to the production of bioplastics (Dornburg *et al.*, 2003), soil amendments (Roberts *et al.*, 2010; Woolf *et al.*, 2010), and air pollutant emissions associated with wood-fueled cooking in developing countries (Johnson *et al.*, 2009; Grieshop *et al.*, 2011; Singh *et al.*, 2014a).

Broadly, any bioenergy system based on terrestrial feedstocks (either dedicated crops or residues from other cultivation processes; algae and other aquatic feedstocks excluded) features a production chain consisting of biomass cultivation or procurement, biomass collection and transport to a centralized biorefinery or energy conversion facility, conversion of the raw biomass to energy products and non-energy co-products, and finally the distribution of these products to the point of use (Figure 2.2). Even as understanding of the material and energy inputs to this supply chain has improved, the production of biomass feedstocks links the supply chain to a range of difficult agricultural or ecological sustainability issues, giving rise to a variety of critical challenges to bioenergy sustainability over the past decade. Cultivation of dedicated bioenergy feedstock crops or removal of residues in conventional agricultural systems has important implications for the biogeochemical cycling of carbon, nitrogen, and water in these systems, often resulting in significant fluxes of CO_2 associated with changes in soil organic matter levels and nitrous oxide (N_2O) emissions associated with nitrogen fertilizer additions (Robertson *et al.*, 2011). These GHG emissions are strongly controlled by agronomic management decisions such as the type of crop cultivated, the rate of nitrogen fertilizer application, the intensity of tillage prior to replanting, and many others (Anderson-Teixeira *et al.*, 2012; Davis *et al.*, 2013), which can interact strongly with local environmental factors such as climate, landscape position, and soil type (Kim & Dale, 2005; Zhang *et al.*, 2010). Carbon stocks can take decades to reach equilibrium after a change in land use or management, introducing assessment challenges around properly accounting for emission timing (O'Hare *et al.*, 2009; Holtsmark, 2015). In addition to these biogeochemical impacts, changes in land use and land management can have a variety of direct biophysical impacts on surface albedo and evapotranspiration, with additional significant climate implications in some situations (Caiazzo *et al.*, 2014).

In addition to these direct biogeochemical and biophysical impacts, to the extent that feedstock production adds pressure to limited global area of arable land it becomes important to explicitly consider the 'business as usual' (BAU) uses of that land in the absence of bioenergy feedstock production, and indirect effects associated with any disruptions to agricultural commodity markets. The high GHG footprints associated with many types of conventional agriculture and land management imply that bioenergy system performance results can be very sensitive to assumptions around BAU scenarios (Davis *et al.*, 2012; Duval *et al.*, 2013; Field *et al.*, 2013). To the extent that any displaced commodity production affects prices in international commodity markets, this could contribute to deforestation and other land use change pressures domestically and in other countries, resulting in strong leakage effects (Fargione *et al.*, 2008; Searchinger *et al.*, 2008). While the likely magnitude of this so-call 'indirect land use change' (iLUC) effect has been revised down sharply from initial estimates (Wang *et al.*, 2011), there is still contentious debate around whether the effect is empirically observable or falsifiable (Babcock, 2009; Kim & Dale, 2011; O'Hare *et al.*, 2011) and whether there is enough assessment certainty for the effect to be considered in regulatory settings (Plevin *et al.*, 2010; Zilberman *et al.*, 2010; Warner *et al.*, 2013).

The various biogeochemical, biophysical, counterfactual, or leakage effects associated with feedstock production are not easily represented in standard supply chain LCA models such as the Greenhouse gases, Regulated Emissions and Energy in Transport (GREET) model (Wang, 1999; Wang *et al.*, 2011). These climate impacts require a fundamentally different set of analytical tools to estimate, predicated on a different set of underlying assumptions and introducing a strong interdisciplinary aspect to bioenergy lifecycle assessment. The consideration of biogeochemical and biophysical effects that evolve over different timeframes than biomass harvest and conversion even implies the need for a different approach to climate impact accounting metrics. To the extent that likely land use change, landscape design, and crop management scenarios are not yet well-established for dedicated feedstock crops (Zhang *et al.*, 2010; Anderson-Teixeira *et al.*, 2012; Wu *et al.*, 2012; Roth *et al.*, 2015), the integration of economic production cost estimation tools becomes important to estimate which system design scenarios are most likely.

This manuscript reviews the range of climate impact factors included in existing bioenergy LCA studies, and classifies them in a simple taxonomy that highlights issues important for impacts assessment and accounting. Associated discussion highlights the range of values associated with each climate impact reported in the literature due to system variability and assessment uncertainty. Within each category we highlight opportunities for improving climate performance, and identify key assumptions that must be harmonized for consistency between an LCA and associated cost estimates within an integrated assessment framework. Illustrative examples are provided with the tabulation of the climate impacts associated with nitrogen management in the cultivation of first- and second-generation bioenergy feedstocks in order to illustrate the relative contributions of different kinds of climate impacts to a given aspect of the biofuel lifecycle. A variety of first- and second-generation bioenergy LCA studies are then reviewed against the previously-identified assessment and accounting issues identified in order to highlight gaps and inconsistencies across assessments in the literature. We end with a discussion of carbon sequestration potential in bioenergy systems, discussing the relative merits of 'carbon-negative' systems where carbon sequestration outweighs other net lifecycle-attributed climate impacts.

2.3. Classification of Bioenergy Lifecycle Emissions

Typically the climate impacts measured in bioenergy LCA are described and reported based their position in the supply chain, for example, during feedstock cultivation, harvest and transport, or conversion to energy products. Here we instead categorize the different lifecycle climate impacts encountered in bioenergy LCA in an alternate classification scheme based on:

- The nature of their origin (industrial versus biogenic)
- Their location in relation to the system boundary (direct versus indirect)
- The mechanism of climate impact (greenhouse gases versus biophysical effects)
- Their physical nature and direction (real positive and negative emissions fluxes versus avoided emissions)
- The temporal profile of their release (continuous versus time-dependent)

These distinctions have important repercussions for climate impacts accounting with regard to the assessment methods used, the climate impact metrics applied, and the underlying explicit and implicit analytical assumptions made. These classification dichotomies are independent, thus yielding a potential 32 combinations of attributes that might be encountered in bioenergy LCA practice. Individual classification categories and the associated repercussions for lifecycle accounting are explored in detail below. Table 2.1 shows how climate impact factors cited in the bioenergy lifecycle assessment literature fit in to the taxonomy.

2.3.1. Classification by origin- industrial vs. natural

Is this climate impact derived from an engineered process, or from an agricultural or biogeochemical process?

Industrial Impacts

Industrial impacts can be defined as those derived from engineered processes associated with the production and consumption of energy products (fuels and electricity) and manufactured materials (fertilizers, industrial enzymes, farm machinery, etc.) throughout the bioenergy supply chain. Much of the climate footprint of these inputs can be traced back to fossil fuel use and thus tabulation is often done on an energy basis, hence the persistence of the widely-criticized (Farrell *et al.*, 2006; Dale, 2007) net energy metric as a primary bioenergy LCA output (Pimentel, 2003; Patzek, 2004; Schmer *et al.*, 2008). While it is straightforward to convert fossil fuel use to CO_2 emissions based on fuel stoichiometry, the production of finished energy products such as refined liquid fuels involves inputs of primary energy in the extraction, refining, and distribution stages; thus there are upstream emissions associated with the production of the fuel beyond what is physically released at the point of use. Estimates suggest that upstream energy consumption in the production gasoline and diesel fuel is responsible for CO_2 emissions equal to ~16% those generated when those fuels are burned; the figure is 3% and 6% for the industrial fuels coal and natural gas, respectively (West & Marland, 2002). For electricity production, all direct GHG emissions occur upstream of the point-of-use, and low thermal conversion factors and high transmission losses for electricity generation imply that approximately 2.9 units of primary energy (much of it in the form of carbon-intensive coal) are consumed for every unit of electrical energy delivered (West & Marland, 2002).

In addition to CO_2 emissions, any real-world combustion-based energy conversion process also releases products of incomplete combustion and other air pollutants including N_2O, CH_4, non-methane hydrocarbons, and black carbon (soot), all of which have significant lifetime climate impacts relative to that of an equivalent mass of CO_2 (Bhattacharya & Abdul Salam, 2002; Grieshop *et al.*, 2011). The magnitude of such emissions depends on the fuel type, energy conversion technology, and pollutant mitigation technologies in place. The GREET model estimates criteria air pollutant emissions, including CH_4 and N_2O, for all combustion-based energy conversion processes modeled (Shapouri *et al.*, 2002; Wang *et al.*, 2003), and finds that on-farm use of LPG for grain drying produces 65 g CO_{2eq} of non-CO_2 emissions in addition to the 2.58 kg CO_2 released during the combustion of 1 kg of LPG, adding ~2% to the overall GHG emissions at the point of combustion. This factor varies from as low as 0.4% in the case of diesel-fueled farm tractors, or as high as 14% for on-farm natural gas-fuelled stationary reciprocating engines.

Accounting of industrial climate impacts is further complicated due to some supply chain material inputs having additional supply chain emissions not tied to combustion or energy use. Production of nitrate-based fertilizers from the oxidation of ammonia (NH_3) is a notable example. Synthesis of the ammonia feedstock uses methane as both a source of hydrogen reactant (with the associated carbon rejected in the form of CO_2) and a process fuel to drive the high temperatures and pressures required in the Haber-Bosch production process. Even though the subsequent oxidation reaction of ammonia to nitrate is itself exothermic and requires no significant energy inputs, N_2O can be emitted as a reaction byproduct in large enough quantities to dwarf the GHG footprint of the original ammonia synthesis (Wang *et al.*, 2003; Wood & Cowie, 2004), with the magnitude of N_2O emissions varying greatly between different fertilizer production facilities depending on the level of emissions control technology employed (Kongshaug, 1998).

Since industrial climate impacts tend to derive from point source emissions of GHGs and other climate forcing agents resulting from highly-engineered and precisely-controlled production processes and combustion technologies, and their associated emissions factors are generally well-characterized and easily amenable to representation through databases of emissions factors. This is the approach of the GREET model, which tracks industrial inputs on an energy basis and then applies fuel- and technology-specific emissions factors, corrected for incremental technological advances over time, to convert energy into GHG and other air pollutant emissions (Wang *et al.*, 2007b). Such a modeling exercise is in many ways similar to techno-economic assessment (TEA) in which industrial process models are integrated with enterprise budgeting tools to identify most cost-effective system designs (Gnansounou & Dauriat, 2010).

Reducing the magnitude of these climate impacts requires improving the performance of the underlying production processes, either by increasing the amount of product yield per unit of process input, or by reducing products of incomplete combustion and other non-CO_2 air pollutants associated with combustion-based process energy use (Wang *et al.*, 2011). LCA and TEA results are often aligned to the extent that process efficiency improvements improve performance on both metrics, though this relationship can break down in the case of fuel-switching to cheap but carbon-intensive fuels (Hill *et al.*, 2009; Wang *et al.*, 2011).

Natural impacts

We define natural impacts as those resulting from perturbations of natural background biogeochemical cycles or ecosystem processes during feedstock production, impacts that occur as a direct result of human activities on the farm but outside of engineered processes (Kendall & Chang, 2009). Natural climate impacts resulting from the cultivation of bioenergy feedstocks are dominated by biogenic emissions of GHGs from soils due to the metabolic activity of soil micro-organisms (Johnson *et al.*, 2007; Robertson *et al.*, 2011) and thus are non-point-source emissions. In addition to biogenic processes, the abiotic dissolution of agricultural lime (carbonate) to CO_2 is an additional natural non-point emissions source significant in many agricultural systems (West & McBride, 2005) and often included in LCA exercises (Adler *et al.*, 2007; Landis *et al.*, 2007).

Agriculture is the primary anthropogenic source of the potent greenhouse gas nitrous oxide (N_2O), an intermediate of microbial metabolic reactions involving either the oxidation of ammonia to nitrate (nitrification) or the anaerobic reduction of nitrate to N_2 (denitrification) (Mosier, 1994; Pachauri & Reisinger with Core Writing Team, 2007; Davidson, 2009). The rates of these microbial nutrient transformations in soil are increased above background levels as microbially-available N concentrations in soils increase with the application of synthetic or organic fertilizers or the cultivation of legumes, with N_2O emissions increasing non-linearly as soil N levels exceed plant demands (Hoben *et al.*, 2011; Shcherbak *et al.*, 2014). Direct N_2O emissions resulting from nitrogen fertilizer application are typically one of the largest contributors to the GHG footprint of corn production (Adler *et al.*, 2007), and thus are a significant driver of the overall climate impacts of the corn ethanol supply chain (Wang *et al.*, 2011).

Nitrous oxide emissions are anticipated to be significant in cellulosic ethanol systems based on fertilized crops as well (Bai *et al.*, 2010), though fertilizer requirements of dedicated biomass crops are not always well undestood (Arundale *et al.*, 2014a). The amount of nitrogen fertilizer application associated with different feedstock crops can vary widely (Table 2.2), depending on how much nitrogen is removed when the crop is harvested (grain tends to have higher N concentration than green biomass, which in turn has more N than senesced biomass), how efficient the crop is at capturing mineral nitrogen from the soil (related to how extensive a root system it has), and whether the crop is associated with rhizosphere nitrogen-fixing bacteria. Site-level environmental factors such as soil texture and climate are important as well, as they determine how mobile mineral nitrogen is within the soil profile and its vulnerability to leaching, as well as the activity level of nitrogen-metabolizing soil microbes.

Nitrous oxide emissions are often estimated based on a Tier 1 approach in which it is assumed that 1% (uncertainty range 0.3 – 3%) of any N applied to the system is directly emitted in the form of N_2O independent of the crop or site (Eggleston *et al.*, 2006). A glance at the experimental literature suggests that this is a reasonable assumption for annual bioenergy feedstock crops, but that perennial crops are characterized by even lower emission factors (Table 2.3). This is not surprising, as perennials tend to have more extensive root networks that are better able to take up applied N before it can be metabolized by microbes. For a given level of soil nitrogen and crop, N_2O emissions rates are also strongly dependent on soil moisture level and texture, and thus characterized by wide spatial and temporal variability with soil pedology and climate (Del Grosso *et al.*, 2006). Note that in addition to these direct N_2O emissions, indirect N_2O emissions associated with downstream nitrification/denitrification of N lost from the system due volatilization, leaching, etc. are discussed in a later section.

Terrestrial ecosystems store large amounts of carbon in living and dead plant tissues, and fluxes of CO_2 associated with changes in these carbon stocks due to human land management activities are significant in many agricultural systems. While aboveground standing biomass is often very transient in agroecosystems of interest for bioenergy feedstock production, soil organic matter (SOM) is used as a more stable proxy for total ecosystem carbon storage. Composed of the partially-degraded remnants of dead plant material, SOM makes up only a small fraction (typically < 5%) of the mass of most soils, yet exerts a disproportional influence on multiple soil properties including bulk density, water holding capacity, aggregation, and nutrient storage capacity, hence SOM level often being used as a general proxy for soil health and fertility (Paustian *et al.*, 2006). Perspectives on SOM formation and stabilization have evolved over time, with the old view of stabilization of decaying plant material as humic compounds as a function primarily of its initial chemical composition giving way to a new more nuanced view including additional stabilization mechanisms through SOM association with silt and clay particles or physical isolation within microaggregate structures (Six *et al.*, 2002; Schmidt *et al.*, 2011). Globally, soils contain several times more carbon as SOM than all living biomass or atmospheric CO_2, and the historical depletion of soil carbon in intensively-cultivated agricultural systems has made a significant contribution to anthropogenic GHG emissions (Schlesinger, 1997; Paustian *et al.*, 2000; Lal, 2004). As such, land with depleted soil carbon stocks due to past land-use practices represents an opportunity for carbon sequestration with progressive bioenergy feedstock cultivation practices (Paustian *et al.*, 1998).

The level of SOM in a soil represents a balance between inputs of organic matter and the decomposition of that matter to CO_2 through microbial respiration, and in any human-managed system SOM levels can change significantly with changes to input rate (e.g. due to fertilizer application or the harvest of biomass for bioenergy production) or litter decomposition rate (e.g. the effects of tillage, fertilization, and irrigation on microbial activity) (Paul *et al.*, 1997). While corn production using conventional tillage practices and/or high residue removal rates will often exacerbate soil carbon depletion (Anderson-Teixeira *et al.*, 2009), transitioning to no-till corn or perennial cellulosic feedstocks has the potential to significantly increase soil carbon levels (through both increases in litter inputs and decreases in decomposition rates), improving the overall GHG balance of the bioenergy feedstock production process (Kim & Dale, 2005; Tilman *et al.*, 2006a; Adler *et al.*, 2007; Qin *et al.*, 2015a). Such systems are slow to come to equilibrium, and response to a discreet change in land use or management plays out over decadal time scales. As with N_2O emissions, the CO_2 fluxes associated with changes in SOM levels are microbially-mediated and show a similar spatial variability with environmental factors such as climate and soil type (Hillier *et al.*, 2009). Bioenergy feedstock crops are associated with a range of SOM changes depending on the crop selected, the previous land use at the site of cultivation, and the agronomic management of the crop, with background environmental factors providing additional variability (Table 2.4). Bioenergy feedstock crops are generally associated with soil carbon sequestration at initial rates of up to 0.74 t CO_2 per ton of feedstock produced when grown on previously-cultivated land, though this flux attenuates as soil carbon comes to equilibrium. In contrast, the conversion of grasslands to bioenergy crops is at best carbon-neutral and at worst associated with carbon losses greater than 0.82 t CO_2 / t feedstock in the case of annual feedstock crops.

Natural climate impacts from distributed biogenic GHG emissions present a fundamental assessment challenge as they are highly dependent on both a suite of environmental factors and historical land use practices, and thus show a high degree of spatial variability at sub-farm scales (Hillier *et al.*, 2009; Zhang *et al.*, 2010). Since soil carbon measurements and N_2O monitoring are expensive and laborious processes, such emissions are typically estimated using spatially-explicit biogeochemical process-based models capable of simulating plant growth, senescence and harvest, and litter decomposition for a specific local soil type, climate, and land use history, complemented with appropriate validation through field measurements (Parton *et al.*, 1987; Paustian *et al.*, 2009). A variety of these models have been applied to site-specific bioenergy LCA studies including the CENTURY (Kim & Dale, 2005), DayCent (Adler *et al.*, 2007), RothC (Hillier *et al.*, 2009), and EPIC (Zhang *et al.*, 2010) models.

Because these natural climate impacts are so variable, they represent an excellent opportunity for mitigation through careful bioenergy supply chain design. To the extent that biogenic GHG emissions are affected by climate, soil type, and landscape position, the careful siting of bioenergy conversion facilities and the selective contracting of feedstock production to farms with favorable locations can maximize the potential for carbon sequestration as SOM and avoid soil N_2O hotspots. At the level of individual farms, biogenic GHG emissions are a strong function of crop agronomic management intensity (Davis *et al.*, 2013), though the priority of maximizing economic returns often implies that farmers will manage more intensively than is optimal from a pure GHG perspective (Roth *et al.*, 2015). At landscape scales, there is still debate around the relative merits of pursuing less intensive feedstock cultivation over a large land area ('land sharing') versus concentration production on a smaller area of land cultivated at maximum intensity ('land sparing') (Anderson-Teixeira *et al.*, 2012).

2.3.2. Classification by location- direct vs. indirect climate impacts

Can I differentiate whether a climate impact is caused by my bioenergy system, as opposed to the neighboring system?

Direct impacts

We define direct climate impacts as those industrial and natural impacts originating from within a well-defined physical system boundary or identifiable as derived from a specific system. For liquid transportation biofuels such a boundary typically encompasses the farm where feedstock is cultivated, the transport network connecting farm to biorefinery, and biorefinery where it is converted to liquid fuel, as well as all upstream production processes for fuel, electricity, equipment, and chemical inputs consumed within the system (Figure 2.2). Such a scope is referred to as 'well-to-pump' (Wang *et al.*, 2012). When the scope is extended to include final use of the fuel in a vehicle it is termed either 'well-to-wheels' or 'field-to-wheels' (Laser *et al.*, 2009; Wang *et al.*, 2012). Attributional lifecycle assessment focuses primarily on these impacts, typically employing regional or country-level average estimated values for agricultural and industrial GHG emissions factors. However, the shift toward CLCA requires a refocusing on the marginal inputs that will be specifically affected by a particular bioenergy technology implemented at a particular site. This change of perspective is not a trivial one, as marginal electricity production is typically met with natural gas and renewable sources that have much lower impacts than average grid baseline power (Finnveden *et al.*, 2009), whereas marginal petroleum production involves a greater share of non-conventional sources including oil sands (Wang *et al.*, 2011).

While direct emissions (particularly direct industrial emissions) are often relatively well characterized, they are far from uniform across different bioenergy production systems. As we have previously observed, direct natural climate impacts associated with cultivating a particular crop at a particular geographic site can show large variance in response to climate, soil type, land use history, and management intensity. Industrial impacts, particularly those related to energy use at the biorefinery, can also vary greatly depending on the configuration of individual systems. It has been shown that the process fuel used at the biorefinery can have an large effect on the overall lifecycle GHG emissions: while many recent dry-mill ethanol production facilities are natural gas-fuelled, emissions are much greater when coal is used for heat production and much lower when biomass wastes are used instead (Wang *et al.*, 2007a; Hill *et al.*, 2009).

Projected direct emissions for future cellulosic ethanol production facilities using switchgrass feedstock still show a great range of uncertainty, with net GHG performance estimates ranging from similar to corn grain ethanol (Hsu *et al.*, 2010) to only a fraction thereof (Wang *et al.*, 2011). In addition, direct climate impacts are not static over time, but can be expected to evolve as technologies improve or changes in prices lead to substitution of different equivalent process inputs. It is well-recognized that energy efficiency of the corn ethanol production chain has steadily increased over time due to advances in agronomy (higher-yielding varieties) and biorefinery technology (dry milling over wet milling), as well as the movement towards low-energy-intensity co-products (i.e. wet distillers grains and solubles) (Liska *et al.*, 2009; Wang *et al.*, 2011).

Indirect impacts

The term 'indirect' is invoked very inconsistently across the lifecycle assessment literature. Sometimes it is used in the context of upstream impacts associated with the production of energy products and materials consumed in the supply chain under study (e.g., Yu *et al.*, 2014). Other times it is used to describe what we have termed 'natural impacts' associated with land management (as opposed to 'industrial impacts') in this review (Kilpeläinen *et al.*, 2012; Repo *et al.*, 2012). However, the term comes up most often in the context of indirect emissions of nitrous oxide (iN_2O) that occur outside the system boundary as a result of the transport off-farm of nitrogenous compounds derived from agronomic N additions, and indirect land use changes (iLUC) that occur as a result of market responses to changes in commodity production from the system. As such, for our purposes we define indirect climate effects as those occurring outside the physical boundaries of a bioenergy supply chain, causally related to bioenergy production activities yet not specifically differentiable between one individual bioenergy system or another.

Indirect nitrous oxide (iN_2O) emissions are the result of downstream nitrification/denitrification processes occurring on nitrogen that has crossed out of the system boundary, either in the form of volatilized ammonia, leached nitrate, or physically exported biomass used as an animal feed or soil amendment. While in most cases such emissions cannot be definitely be attributed to the activities of a specific farm within a given watershed or airshed, there is still a direct causal link between the bioenergy supply chain and the N_2O emission, and the only practical way to mitigate the emission is by changing the management of that farm. Estimating iN_2O rates requires that generic emission factors be applied to all N lost from the system through volatilization and leaching (factors of 1% and 0.75%, respectively; Eggleston *et al.*, 2006) as assessed using generic loss factors or based on more detailed agroecosystem process modeling (e.g., Del Grosso *et al.*, 2008). Because nitrogen can undergo a variety of biogeochemical transformations between the time it is first fixed from atmospheric N_2 and the time it is denitrified back to N_2 (Galloway *et al.*, 2003), careful accounting is necessary to properly close the mass balance and account for all indirect N_2O emissions. Recent top-down and bottom-up estimates converge around a combined direct and indirect global average N_2O emission factor of 3-5% (Crutzen *et al.*, 2008a; Del Grosso *et al.*, 2008; Smith *et al.*, 2012).

The most contentious topic in current bioenergy LCA practice is indirect land use change (iLUC). To the extent that diversion of part of the limited arable land base in the US to bioenergy feedstock production increases the price of agricultural commodities and reduces export levels, this is expected to drive up international commodity prices and thus incentivize the expansion of commodity agriculture in other countries, resulting in climate-intensive land use changes (Fargione *et al.*, 2008; Searchinger *et al.*, 2008; Liska & Perrin, 2009). As iLUC is at its core an economic effect, assessment of associated climate impacts per unit of biofuel produced is based on land use pattern predictions from large economic simulations of global trade coupled with estimates of land use change emission factors from biogeochemical process models (Plevin *et al.*, 2010). Such assessments are inherently complex and uncertain, requiring predictions about the relative likelihood of agricultural extensification versus intensification and the location and types of land converted, and likely changing in magnitude over time with improvements in technology and changing land use policy around the world (Zilberman *et al.*, 2010). The concept is complementary to that of the food-versus-fuel dilemma; to the extent that displaced food commodity production is replaced elsewhere, then iLUC emissions are incurred, and to the extent it is not, food prices may increase (Wise *et al.*, 2009; Zilberman *et al.*, 2011). First introduced in 2008, the concept of iLUC was rapidly codified into the quantitative LCA requirement of the US Renewable Fuel Standard (Liska & Perrin, 2009), despite early resistance among some in the assessment community and persistent reservations about the quality of the estimates and appropriateness of including consequential LCA effects in regulatory standards (Wang & Haq, 2008; Melillo *et al.*, 2009; Kim & Dale, 2011; Zilberman *et al.*, 2011). Warner *et* *al.* (2013) provide a comprehensive review of wide range of iLUC factor estimates in the literature, breaking them down by the bioenergy feedstock crop considered and the assessment method employed.

There are other potential indirect ripple effects of bioenergy production beyond iLUC. Transportation fuel demand is partially elastic, and to the extent that biofuels begin to take a large share of fuel markets, their price relative to business-as-usual gasoline prices will determine whether overall fuel consumption increases (biofuels cheaper than fossil fuels) or decreases (biofuels more expensive than fossil fuels, but their use mandated), a 'rebound'-type effect termed 'indirect fuel use change' (Rajagopal *et al.*, 2011). Similar ripple effects may already be happening to the extent that corn ethanol production co-products have already reached a scale large enough to distort animal feed markets (Liska & Perrin, 2009) and affect livestock production prices, an effect that was included in the co-product credit routine of earlier versions of the GREET model but was subsequently removed (Arora *et al.*, 2008). Co-product crediting by the displacement method and displacement of fossil fuel use in general are discussed in greater detail in section 3.4.2. In all these cases of indirect and market-mediated climate effects, the common thread is the effect having no specific provenance that distinguishes the impacts of one specific bioenergy system from another; thus the effects can only be assessed indirectly through universal emissions factors applied to mass fluxes across the system boundary.

Mitigation of bioenergy supply chain indirect effects can potentially occur at multiple levels. Indirect land use change is related to the amount of BAU agricultural commodity production displaced by bioenergy feedstock production, and as such it can be mitigated by targeting production on areas with low agricultural productivity or that are not current producing. This type of landscape-level design would likely be controlled by individual biorefinery facilities and their decisions around which local producers to contract with for feedstock provisioning. iLUC can potentially be mitigated more efficiently at the level of international policy by tying bioenergy mandates with land-use change and deforestation protections in the developing countries where iLUC emissions are feared to occur (Liska & Perrin, 2009; Zilberman *et al.*, 2010), for example through policies such as Reducing Emissions from Deforestation and Forest Degradation (REDD+; Fisher *et al.*, 2011). Likewise, indirect fuel use change effects could potentially be mitigated through the imposition of subsidies or taxes to blunt the difference in consumer price between fossil fuels and bioenergy alternatives (Rajagopal *et al.*, 2011). In contrast, iN_2O is not a market-mediated effect, and can only be reduced through more careful management of nitrogen fertilizer use at the scale of individual farms.

2.3.3. Mechanistic classification- GHGs vs. biophysical effects

Is the climate impacts due to a well-mixed greenhouse gas, or some other more geographically-specific radiative forcing effects?

Greenhouse gas emissions

Much of the climate impact of bioenergy supply chains is due to emissions of CO_2 associated with the combustion of fuel, and fluxes of CO_2 and N_2O associated with land management for feedstock production (see section 3.1.2). Such species of greenhouse gas are said to be 'well-mixed' in that their atmospheric lifetime is sufficient for them to be transported across the atmosphere far from their point of origin and make approximately the same contribution to the global greenhouse effect as emissions from any other location (Forster *et al.*, 2007). As such, accounting for climate impacts is relatively straightforward. The relative global warming impact of different species of GHG can be compared to one another using the metric of global warming potential (GWP), the calculation of which involves the integration of the radiative forcing potential of a pulse emission of the gas by its time-dependent concentration as it decays, normalized to that of a reference mass of CO_2 (Forster *et al.*, 2007). Since an emission of CO_2 to the atmosphere takes millennia to degrade fully, an arbitrary analytical timeframe across which to carry out the integration must be chosen. It is typical to report the GWP_{100} of a greenhouse gas as evaluated over a 100-year timeframe as this is thought of as a reasonable time period of interest for anthropogenic climate change policy, though the use of different time frames (e.g. 20- or 500-year) is equally justifiable and will change the relative weighting between short- and long-lived GHGs. The total GWP_{100} of a mixture of gases emitted together in a single pulse event can easily be computed by summing the individual GWP_{100} of each gas multiplied by the quantity released.

Biophysical effects and other forcing agents

Beyond the greenhouse effect, global climate is also sensitive to other factors that affect the radiative balance of the planet surface. Changes in land cover can significantly affect the reflectivity of the surface to incoming shortwave radiation, known as albedo. Albedo changes due to historic land use change have resulted in a small net negative contribution to global radiative forcing (Forster *et al.*, 2007). Bioenergy LCA studies are increasingly being expanded to consider albedo changes from land use change associated with feedstock production in addition to supply chain GHG emissions balance (Georgescu *et al.*, 2011; Cherubini *et al.*, 2012; Meyer *et al.*, 2012; Caiazzo *et al.*, 2014; Singh *et al.*, 2014b). Albedo effects can significantly reduce radiative forcings after biomass harvest in high-latitude systems where it encourages more consistent coverage of highly-reflective snow in winter months (Cherubini *et al.*, 2012;

Singh *et al.*, 2014b), with the magnitude of the effect similar to that of biogeochemical impacts of feedstock production. Others have simulated warming effects from albedo changes under certain feedstock production scenarios (Caiazzo *et al.*, 2014), particularly in bioenergy systems that co-produce biochar which then darkens the soil surface when used as an amendment (Meyer *et al.*, 2012). Albedo changes with feedstock cultivation also interact with other biophysical effects such as changing evapotranspiration rates, potentially magnifying climate impacts further (Georgescu *et al.*, 2011). Such effects are sensitive to latitude, climate, and baseline land cover, and thus must be assessed at similar levels of spatial resolution as are biogeochemical impacts (section 3.1.2)(Cherubini *et al.*, 2012).

There are additional air pollutants emitted during the bioenergy lifecycle beyond well-mixed GHGs that still act as important climate-forcing agents. Aerosol emissions such as SO_4 and carbonaceous particulate matter have important climate effects through directly absorbing or reflecting shortwave radiation, but are challenging to quantify because they tend to be extremely short-lived and have different impact depending on the latitude and geographic region in which they are emitted (Forster *et al.*, 2007; Rypdal *et al.*, 2009). Particulate matter (PM) is usually a mixture of weakly negative-forcing organic ('white') carbon or the strongly-absorbing elemental ('black') carbon, the ratios and net climate forcing effect of which can vary greatly between different PM sources (Bond *et al.*, 2004; Shen *et al.*, 2010). Emissions of oxides of nitrogen (NO_x) are similarly problematic. While NO_x is not a climate-forcer itself, it interacts with other species to promote the formation of tropospheric ozone (O_3, an extremely potent but short-lived GHG) and hydroxyl radical (OH-, which in turn promotes the destruction of the GHG CH_4), thus exerting a difficult-to-quantify forcing (Shine *et al.*, 2005; Forster *et al.*, 2007; Delucchi, 2010).

Like land use change biophysical effects, these other climate forcing agents are increasingly considered in bioenergy LCA, such as in the most recent update of the GREET model (GREET 2014, https://greet.es.anl.gov/greet/versions.html), and in studies of systems that include high rates of black carbon emissions such as small-scale combustion systems in developing countries (Grieshop *et al.*, 2011) or in systems based on waste biomass where the alternate management involves open-burning (Field *et al.*, 2013). Although these climate forcing agents were not included in the Kyoto protocol or associated emissions trading schemes, that may change in the future as recognition of their significance grows (Bond, 2007; Molina *et al.*, 2009; Shindell *et al.*, 2012) and policymakers make efforts to expand emission control efforts to include non-Kyoto climate forcers (Bureau of Public Affairs, US Department Of State, 2012). Rather than trying to compute GWP-equivalent metrics for these non-GHG species, some advanced climate impact studies couple emissions models directly into atmospheric process models to determine net impacts on climate, skipping the intermediary accounting metrics altogether (Shindell *et al.*, 2012).

2.3.4. Physical classification- observable vs. inferred or avoided climate impacts

Are the impacts based on tangible processes that can theoretically be observed, or are they based on an inference against a non-realized counterfactual scenario?

Observable emissions fluxes

All climate impacts discussed thus far have been observable in the sense that they are based on either releases of greenhouse gases to the atmosphere that could be physically measured through gas sampling of exhaust tailpipes or factory smokestacks or using a soil gas exchange measurement apparatus (Christensen *et al.*, 1996; Hansson *et al.*, 1999), or biophysical changes that could be assessed through direct measurements of albedo, evapotranspiration rates, etc. Focusing on GHG fluxes specifically, while we often think of ***emissions*** of gases from industrial processes and soils in the bioenergy supply chain to the atmosphere, removal of gases from the atmosphere via various ***sinks***, for example microbial oxidation of methane in soils or to carbon sequestration in terrestrial carbon stocks (Johnson *et al.*, 2007), are also important in bioenergy assessment (Guinée *et al.*, 2009). Such negative emission fluxes are also observable in the sense that they can be experimental measured and quantified using gas chambers, soil carbon measurements, or other techniques. Accounting of net GHG fluxes in bioenergy systems is typically as straightforward as subtracting the CO_2-equivalent (via a GWP calculation, see section 3.3.2) total of all sinks from the total system CO_2-equivalent emissions.

However, bioenergy LCA studies have shown inconsistency over the treatment of 'biogenic' carbon, i.e., carbon from atmospheric CO_2 fixed into biomass during photosynthesis, and then is subsequently released back to the atmosphere in part when the biomass is fermented or thermochemically converted into a liquid fuel and the remainder when that fuel is combusted in an engine. While some studies report these carbon fluxes explicitly (Sheehan *et al.*, 2003; Hsu *et al.*, 2010; Wang *et al.*, 2011), others adopt the convention of netting out this carbon fixation and subsequent release (Patzek, 2004; Dias De Oliveira *et al.*, 2005; Kim & Dale, 2005; Spatari *et al.*, 2005; Hill *et al.*, 2006; Hillier *et al.*, 2009). However, imbalances between carbon fixation and release can exist to the extent that standing biomass in the system changes over time, for example due to changes in soil organic matter levels. Therefore, whichever reporting stance is adopted, LCA results are only accurate to the extent that net changes to terrestrial carbon stocks are included in the analysis where applicable, effects that are only considered quantitatively in a subset of the above studies (Sheehan *et al.*, 2003; Dias De Oliveira *et al.*, 2005; Kim & Dale, 2005; Hillier *et al.*, 2009; Wang *et al.*, 2011) and ignored or assumed negligible in the rest (Patzek, 2004; Spatari *et al.*, 2005; Hill *et al.*, 2006; Hsu *et al.*, 2010). The same issue is encountered in GHG regulatory frameworks, many of which lack provisions to attribute changes in terrestrial carbon stocks to bioenergy production and thus erroneously treat all biomass feedstock production processes as inherently carbon-neutral (Searchinger *et al.*, 2009).

Inferred or avoided impacts

In contrast to observable emissions, inferred or avoided impacts are those that would occur in a hypothetical baseline or 'business-as-usual' counterfactual case but are avoided in the actual bioenergy production case; as such they are not based on actually-occurring GHG fluxes or biophysical effects that can be directly measured. Like indirect emissions, avoided emissions are a consequential lifecycle assessment concept, with corresponding focus on the marginal commodity suppliers directly affected by the new bioenergy technology (Schmidt, 2010). The trivial example of avoided emissions is emissions 'credits' for the displacement of fossil energy with bioenergy (e.g., Adler *et al.*, 2007), or crediting for co-products from a multiple-output production process based on the system expansion approach, also known as the displacement method (Kim & Dale, 2002; Kendall & Chang, 2009). In both cases, emissions savings are inferred relative to the burden from marginal additional production from other equivalent sources, assuming that the bioenergy production scheme didn't exist and that commodity demand would be satisfied through other production means.

More interesting examples of avoided emissions crediting occur when existing biomass resources are diverted from an alternate management scenario into the bioenergy production cycle. The GREET model includes a credit for N_2O that would otherwise be emitted after field incorporation when corn stover is used instead for bioenergy production, as explored further in Section 4 below (Wu *et al.*, 2006). Even greater GHG avoidance is possible in systems where waste biomass would otherwise be burnt with high associated emissions of air pollutants (Field *et al.*, 2013), or incorporated into anaerobic soils (Knoblauch *et al.*, 2011) or disposed of in landfills (Spath & Mann, 2004), which are associated with high methane emissions. The use of biochar as a soil amendment is a particularly interesting case, as it has been shown to dramatically affect nitrogen cycling, potentially increasing crop nitrogen use efficiency or suppressing soil emissions of N_2O (Steiner *et al.*, 2008; Singh *et al.*, 2010; Van Zwieten *et al.*, 2010; Lehmann *et al.*, 2011). Lifecycle studies of bioelectricity and biochar co-production from agricultural residues have thus credited for avoided N_2O and avoided fertilizer consumption on top of avoided alternate biomass management emissions and displaced fossil energy emissions (Gaunt & Lehmann, 2008; Woolf *et al.*, 2010). Similarly, when considering the diversion of feedstock away from some other productive use an into a bioenergy supply chain, some studies have credited any foregone GHG mitigation associated with the original use against the bioenergy supply chain (Mai Thao *et al.*, 2011; Melamu & von Blottnitz, 2011), directly analogous to considering opportunity costs in economic analyses such as techno-economic assessments or crop production budgets.

Establishment of a counterfactual baseline case against which to evaluate avoided emissions involves important explicit and implicit assumptions, economic as well as technical. Even in the simple case of crediting bioenergy production for an equal amount of fossil energy emissions on an energy basis, an implicit assumption is often made that consumer demand for fuel is constant, and that bioenergy will offset fossil fuel consumption. Empirical evidence across a variety of systems suggests this is often an unrealistically optimistic assumption (Bailis *et al.*, 2009; York, 2012). The same implicit assumption is built into any displacement-based co-product crediting, as discussed earlier in section 3.2.2. Definition of BAU land management in agricultural settings can also be challenging, as it requires predicting crop yields, agronomic efficiencies, and counterfactual SOM trends far into the future (Sheehan, 2009). Such technical assumptions can have a large impact on overall footprint results; for example the attribution of future projected improvements in crop yields exclusively to bioenergy production can offset projected bioenergy LUC emissions (Searchinger, 2010), greatly improving system sustainability. Choosing an appropriate counterfactual BAU scenario is analogous to establishing additionality as required in carbon offset trade (Lejano *et al.*, 2010), as crediting a bioenergy production scheme for GHG mitigation that would have occurred anyway (e.g. soil carbon increases due to increased adoption of no-till agriculture) distorts outcomes (Searchinger *et al.*, 2009; Searchinger, 2010).

2.3.5. Temporal classification- continuous vs. time dependent emissions

Do commitments to additional climate impacts stop accruing when the produce process ceases?

Continuous emissions

The GWP metric introduced previously is calculated based on estimates of atmospheric decay of a single temporally discreet ‘pulse’ of GHG emission. The production of a unit of biofuel or bioenergy involves many such pulses during input manufacture, energy use on the farm and at the biorefinery, and elsewhere along the supply chain, most of which occur close enough together to be considered simultaneous relative to a 100-year analytic framework. Thus, these emissions fulfill the requirements for a GWP calculation and are easily summed to estimate the total CO_2-equivalent emissions released per unit of energy produced (e.g., g CO_2eq / MJ EtOH). Continuous production of bioenergy yields a continuous stream of these emissions that cease completely when production stops, analogous to the concept of variable economic costs that occur continuously with production and scale with production output level.

Time-dependent emissions

Not all emissions associated with the bioenergy production cycle are continuous in nature, however. Some processes involve large one-time emissions releases analogous to fixed or capital costs in economics, while others feature emissions profiles that evolve over decadal timescales. Perhaps the most obvious example of the former are emissions associated with the manufacture of the capital equipment of the system, including farming equipment, the vehicles used to transport the feedstock, and the biorefinery facility itself. These embodied emissions occur only a single time prior to the start of production, though once amortized across a lifetime of bioenergy production they tend to account for only a very small contribution to the total footprint of production (Marland & Turhollow, 1991; Hill *et al.*, 2006). Changes in terrestrial carbon stocks such as SOM are a significant example of the latter case. As discussed previously, such changes reflect a changing dynamic equilibrium between litter inputs to and heterotrophic respiration rate within soils, and they develop slowly over yearly or decadal timescales as the system equilibrates to changes in management (Sheehan *et al.*, 2003).

Time-dependent emissions profiles raise temporal accounting issues related to proper integration of cumulative warming potential and the amortization of that potential across the fuel produced, with associated policy and regulatory challenges. Many studies of bioenergy land use change quantify the large initial carbon debt incurred from land clearing and then linearly amortize those emissions against annual avoided emissions from fossil energy displacement to compute a carbon 'payback period' (Fargione *et al.*, 2008; Searchinger *et al.*, 2008; Bernier & Paré, 2013; Mello *et al.*, 2014). However, this simple metric fails to account for the warming accrued by the initial CO_2 emissions across the years and decades before avoided emissions from fossil energy displacement catch up (O'Hare *et al.*, 2009). More recent studies develop dynamic GWP-type metrics appropriate for computing the cumulative radiative potential of time-dependent carbon fluxes (O'Hare *et al.*, 2009; Cherubini *et al.*, 2011; Kilpeläinen *et al.*, 2012; Repo *et al.*, 2012; Holtsmark, 2015), allowing them to be combined with GWP figures from continuous emissions to determine system net climate impacts. While many of these studies take a control volume approach tracking total ecosystem carbon storage level over time, others make an equivalent calculation by tracking the turnover times of various ecosystem components in a process more analogous to a control mass analysis (Repo *et al.*, 2012). Also, while much of the literature on this subject focuses on the payback of large upfront CO_2 emissions, the cultivation of carbon-sequestering perennial feedstocks on SOM-depleted land introduces the opposite problem of allocating a large initial CO_2 sequestration over future production.

Proper assessment of time-dependent emissions is an active area of research, and consensus around best methods is still evolving. When the EPA recently released their updated recommendations on biogenic CO_2 accounting they included a discussion of these accounting issues, but stopped short of making a strong endorsement of best practices (United States Environmental Protection Agency, 2014). While several studies have approached the problem by performing discreet or continuous integrative GWP-type calculations on evolving ecosystem CO_2 fluxes over time (O'Hare *et al.*, 2009; Cherubini *et al.*, 2011; Pierobon *et al.*, 2014), the GWP metric itself has been widely criticized (Shine, 2009), and a variety of alternatives suggested (Tol *et al.*, 2012).

2.4. Example: Climate Impacts of Nitrogen Fertilizers

In this section we focus in on one particular aspect of the supply chain for first- and second-generation biofuels in order to present an illustrative example of many of the accounting issues discussed in the preceding section. Specifically, the production and application of nitrogen-based fertilizers makes a significant contribution to the overall lifecycle environmental footprint of many bioenergy systems, covering a variety of the climate impact classifications discussed above. Ubiquitous in modern agricultural production systems, nitrogen application is associated with a variety of environmental externalities including greenhouse gas emissions (nitrous oxide), air pollutants (ammonia and oxides of nitrogen), and water pollutants (nitrate). The nature and magnitude of lifecycle greenhouse gas emissions associated with nitrogen fertilizer use in first- and second-generation ethanol production systems are explored below as an illustrative example using the GREET 1.7 model (Wang *et al.*, 2007b) and 2006 IPCC AFOLU guidelines (Eggleston *et al.*, 2006). Note that the climate impacts described are largely continuous rather than time-dependent in nature, and thus are easily converted to a GWI metric.

2.4.1. Nitrogen-associated emissions in 1st generation ethanol

The first case illustrates first-generation ethanol production from corn grain. The GREET model is used for estimates of crop and fuel yields, fertilizer application rates (with ammonia, nitrates, and urea rates specified individually), and emissions from fertilizer production. The industrial emissions associated with fertilizer synthesis are further disaggregated into emissions from combustion-based energy consumption versus process emissions from using methane as a hydrogen feedstock and stack emissions of N_2O during nitric acid synthesis using data from an associated technical report (Wang *et al.*, 2003). Natural climate impacts from soil N_2O emissions are estimated based on IPCC emissions factors for direct emissions associated with fertilizer application and residue incorporation (0.01 g N_2O-N/g N for each), as well as for indirect emissions associated with volatized and leached nitrogen (0.01 and 0.0075 g N_2O-N/g N, respectively), and assuming 10% of the applied nitrogen in fertilizer is volatized, 20% exported with the corn grain, 27% re-incorporated back into soil through crop residues, and the balance leached from the system as nitrate (Eggleston *et al.*, 2006).

Resulting GHG emissions are shown in Figure 2.3. Industrial emissions are dominated by process-derived sources including the use of CH_4 as a source of hydrogen for ammonia synthesis and the N_2O byproduct from ammonia oxidation to nitric acid for synthesis of nitrate-based fertilizer blends. Climate impacts from direct and indirect emissions of N_2O are approximately twice as high, for a combined climate impact of 20 g CO_2eq / MJ ethanol. Note that indirect emissions associated with the nitrogen in the corn grain that is harvested, retained in DGS through the ethanol fermentation process, and ultimately fed to livestock is not subjected to an iN_2O calculation as it is assumed that these would be negated through system expansion for co-product crediting (i.e., there is no additionality, as any livestock-derived emissions would still occur in the absence of DGS production).

2.4.2. Nitrogen-associated emissions in 2nd generation ethanol

The second case models a second-generation biofuel production system in which ethanol is produced thermochemically from lignocellulosic corn stover residues remaining after corn grain harvest (Figure 2.4). Since these residues are a byproduct of the production of corn for food or feed, all upstream, direct, and indirect emissions associated with the baseline fertilizer application rate are attributed to corn grain production as per the system expansion approach, and thus not considered in this analysis. However, GREET considers a ~10% increase in fertilizer application rate in order to offset nutrient exports in the stover and maintain soil fertility, and the associated marginal industrial and natural emissions increases are included here. Since the counterfactual scenario is traditional corn grain production in which the stover is left to degrade in the field, the diversion of that stover for bioenergy production results in the avoidance of N_2O emissions associated with the nitrification/denitrification of the nitrogen in the residue, credited as a negative avoided emission (it is assumed that all nitrogen in the biomass itself is converted to N_2 through pyrodenitrification during the thermochemical conversion process, and thus industrial feedstock-derived N_2O emissions at the biorefinery stage are negligible).

Note that the overall direct industrial and natural emissions rates are much lower than the corn ethanol case due to the lower rates of fertilizer application (offset partially by the lower mass conversion efficiency of stover to ethanol relative to corn grain), and the natural direct and indirect emissions are effectively cancelled out by avoided litter N_2O emissions of approximately equal magnitude. The resulting net footprint for N use of 1.5 g CO_2eq / MJ ethanol is more than an order of magnitude less than that of the 1st generation case.

2.5. Consistency in LCA Scope and Accounting Conventions

In order to highlight consistency or lack thereof in approach to the previously-introduced accounting challenges, in this section we reviewed a selection of prominent bioenergy LCA papers from the literature (Hill *et al.*, 2009; Cherubini & Jungmeier, 2010; Hsu *et al.*, 2010;

Wang *et al.*, 2012) in the context of the climate impacts taxonomy. These particular studies were chosen to be representative of the evolution of assessment efforts for the existing corn ethanol industry, as well as the potential performance of cellulosic ethanol production schemes that are expected to proliferate in response to the RFS2 mandate in the United States. Some of the studies describe new stand-alone assessments, while others are updates on longer-term projects in bioenergy LCA tool development. All of the studies are less than 6 years old, and have been cited on average at least 15 times per year since they were published.

Hill *et al.* (2009) study the climate and health impacts of corn and cellulosic ethanol from various feedstocks relative to gasoline. Lifecycle criteria air pollutant emissions are assessed spatially so associate impacts on populations can be evaluated. Monetizing both GHG and health impacts reduces the dimensionality of the assessment down to a single damage metric. The authors determine the combined climate and health impacts of corn ethanol are similar to or worse than gasoline, but cellulosic ethanol performance is substantially better. Cherubini & Jungmeier (2010) use LCA techniques to estimate the GHG performance of a biorefinery producing multiple energy and chemical products from a switchgrass feedstock. The analysis puts special emphasis on land use change and N_2O associated with switchgrass feedstock production. They determine that such a system would reduce GHG emissions in transport by 79% relative to a gasoline baseline initially, but by only 55% in the long term after soil organic matter levels come to equilibrium and carbon sequestration ceases. Additionally, they find the bioenergy system to out-perform the reference system on a variety of other environmental performance metrics except for eutrophication. Hsu *et al.* (2010) conduct an attributional LCA study for the production of ethanol from corn and a variety of cellulosic feedstocks in the US using the SimaPro lifecycle assessment software. They develop probability distribution functions for important model parameters, and perform a detailed Monte Carlo-based uncertainty estimation. Their results suggest broadly similar performance across both first- and second-generation biofuel production pathways, achieving 40-50% reductions in GHG intensity relative to gasoline. Finally, Wang *et al.* (2012) provides an update on the ethanol production pathways within the GREET model from a variety of first- and second-generation feedstocks. This update and the one directly preceding it (Wang *et al.*, 2011) emphasize the development of time series representing the increasing efficiency in both agricultural production (higher yields with lower fertilizer inputs) and biorefining (less process energy expenditure per unit of ethanol output) over time. In addition, the authors include an indirect land use change estimate for corn based on a composite of recent results from three different equilibrium models. They estimate that corn ethanol produced in the US does on average achieve lifecycle climate mitigation of greater than the 20% relative to a conventional gasoline baseline as required by the RFS, but this result is sensitive to the biorefinery process energy source. Cellulosic ethanol systems have even better performance, sensitive to farm nitrogen management and biorefinery efficiency assumptions.

The results of this review are shown in Table 2.5. While there is broad consistency in the way that biorefinery co-products are treated and increasing emphasis on assessment sensitivity and uncertainty analysis, there are broad inconsistencies and deficiencies on the other assessment issues. Only 3 of 4 studies account for changes in soil carbon associated with cellulosic feedstock crop production, but those that do find it to be an important contributor to overall system GHG balance. Only a single study explicitly accounts for iLUC effects, even though all were published after the effect was first identified in 2008. None of these studies address the accounting challenges around the time profile of biogenic GHG emissions or accounting for climate impacts of aerosol emissions or biophysical effects of land cover changes, though one of the authors has published extensively on those topics subsequently (Cherubini *et al.*, 2011, 2012). This simple review highlights the fact that bioenergy LCA techniques are evolving rapidly, and that well-cited studies published 5 years ago or more recently are lacking on methodological details that have since been identified as key determinants of system climate performance.

2.6. Discussion

Bioenergy lifecycle assessment has evolved greatly over the past decade in response to improvements in scientific understanding as well as changing policy imperatives. Specifically, bioenergy assessment practice among engineers, ecologists, and economists has moved towards emphasizing spatially-explicit biogeochemical modeling of feedstock cultivation, towards integrated assessment methods capable of predicting and optimizing both economic and environmental outcomes at landscape scales, and towards bioenergy system concepts with strong net carbon sequestration potential. These changing approaches and associated expansion of assessment scope necessitate further development and consistent application of the climate impact accounting points reviewed earlier.

2.6.1. Towards spatially-explicit biogeochemical modeling

Arguably the biggest recent shift in bioenergy LCA practice has come with the increasing understanding of the importance of biogeochemical GHG fluxes during feedstock cultivation (Davis *et al.*, 2009; Kendall & Chang, 2009; Gelfand *et al.*, 2013) and appreciation of their associated spatial variability (Kim & Dale, 2005; Hillier *et al.*, 2009; Zhang *et al.*, 2010). This trend is consistent with the changing focus of many biofuel LCA efforts from large-scale attributional studies toward consequential assessments examining the marginal impact of future system intensification or expansion (Brander *et al.*, 2009; Finnveden *et al.*, 2009). It has been hypothesized that the use of detailed biogeochemical assessment methods can facilitate the differentiation of low-impact feedstock producers (Kendall & Chang, 2009). Tools are already being developed toward this end; for example, the GHG signature of corn cultivation in the Midwestern US has been shown to be highly spatially variable at sub-county scales with distinct "hot-spots" of favorable production characteristics, and spatial optimization techniques have been applied to determine cultivation sites that minimize environmental impacts (Zhang *et al.*, 2010).

Though net GHG emissions remain the sole metric for many bioenergy LCA studies, there is increasing recognition that the process of bioenergy production also has significant repercussions for regional air and water quality (von Blottnitz & Curran, 2007; Kim & Dale, 2008; Bai *et al.*, 2010) and by extension for human and ecosystem health. While GHG mitigation and air pollutant mitigation in the energy sector generally show correlation (Smith & Haigler, 2008; Haines *et al.*, 2009), that relationship is far from exact, and a full accounting of the environmental footprint of agriculture requires consideration of nitrogen leakage in the form of gaseous NH_3, and NO_x and leached NO_3^-, in addition to CO_2 and N_2O fluxes (Follett *et al.*, 2011). Such pollutants can exhibit the same spatial variability observed from GHG emissions (Miller *et al.*, 2006), and can be evaluated on a site-specific basis using the same biogeochemical process models employed to model SOM changes and N_2O emissions (Kim & Dale, 2008; Egbendewe-Mondzozo *et al.*, 2011; Wu *et al.*, 2012).

2.6.2. Towards integrated assessment and landscape optimization

While spatially-explicit LCA methods are a powerful tool for identifying sites with favorable production potentials, a more complete understanding of the likely environmental impact of bioenergy production requires an assessment of human economic behavior at similar spatial scales in order to determine a) which cellulosic feedstocks are likely to be cultivated, b) which specific lands might be diverted from their current use and be put under feedstock cultivation, and c) the optimal level of crop management intensity (Davis *et al.*, 2013). Fortunately, economic assessments tools for cellulosic feedstock production have evolved in step with LCA efforts, and there are currently several methodologies available for the spatially-explicit estimation of production potentials and costs (Khanna *et al.*, 2008; Jain *et al.*, 2010) that can be employed to constrain LCA studies to only consider economically-feasible scenarios. Indeed, the state-of-the-art in this area is moving towards fully-integrated economic and environmental assessments (Egbendewe-Mondzozo *et al.*, 2011; Yu *et al.*, 2014) in which ecosystem models are paired with detailed crop production budgets to determine the yield potential of individual parcels of land, the extent of land conversion and cultivation intensification in response to an increasing price for cellulosic feedstocks, and the associated environmental footprint of that production.

A variety of biomass feedstock strategies have been suggested to maximize system performance while minimizing iLUC and food-vs.-fuel concerns (Robertson *et al.*, 2008; Tilman *et al.*, 2009). Agricultural residues have been advocated as low-impact feedstock, though the size of this resource is limited by the requirement of leaving enough residue in place to preserve SOM and minimize erosion (Sheehan *et al.*, 2003; Kim & Dale, 2004; Lal, 2005; Wilhelm *et al.*, 2007). To the extent that dedicated energy crops are needed, limiting their cultivation to marginal or abandoned lands (Kort *et al.*, 1998; Campbell *et al.*, 2008; Gopalakrishnan *et al.*, 2009; Blanco-Canqui, 2010; Kumar *et al.*, 2010; Spatari & MacLean, 2010; Cai *et al.*, 2011) is a strategy that minimizes disruption of existing food production but also avoids incurring land-use change carbon debt (Fargione *et al.*, 2008). It has been observed that the development of a cellulosic ethanol industry based on perennial grasses would allow land currently used for corn ethanol feedstock production to be used more efficiently with greater output of both food and fuel with a reduced environmental footprint (Davis *et al.*, 2012), though it is unclear if such a strategy is economically viable or compatible with existing RFS policy (110th Congress of the United States, 2007). Others have advanced even more innovative proposals to co-produce food and fuel from the same land based on multiple rotations (Heggenstaller *et al.*, 2008), or the extraction of valuable protein from cellulosic feedstocks prior to conversion (Dale *et al.*, 2009).

2.6.3. Towards carbon sequestration and carbon-negative system concepts

Bioenergy is unique among renewable energy technologies in using contemporary carbon fixed from the atmosphere as an energy carrier, and the possibility of managing bioenergy supply chains for carbon sequestration makes them of great interest as a tool for the stabilization of atmospheric CO_2 levels. Carbon-sequestering bioenergy technologies feature prominently in a large fraction of the IPCC's Representative Concentration Pathways that succeed in stabilizing climate change within internationally-agreed limits (Fuss *et al.*, 2014). Bioenergy systems can be managed for carbon sequestration through increasing soil organic matter storage during feedstock production (Tilman *et al.*, 2006a; Adler *et al.*, 2007), through using low-value carbon-rich conversion co-products as soil amendments (Laird, 2008; Pourhashem *et al.*, 2013; Smith *et al.*, 2014), or through the geological sequestration of the CO_2 by-products of biomass fermentation, thermochemical conversion, or combustion (Möllersten *et al.*, 2003; Rhodes & Keith, 2003; Spath & Mann, 2004; Kraxner *et al.*, 2014; Singh *et al.*, 2014b; Sanchez *et al.*, 2015). Pilot or greater scale experimental work is proceeding on all three options (Jirka & Tomlinson, 2014; Zimmermann *et al.*, 2014; Lusvardi, 2015), in parallel with the commissioning of the first set of commercial-scale cellulosic biofuel facilities worldwide (Peplow, 2014).

Systems in which carbon sequestration outweighs all other observable industrial lifecycle climate impacts are termed 'carbon-negative' (Tilman *et al.*, 2006a; Lehmann, 2007a). However, this terminology is somewhat non-descript, referring only to subset of rich taxonomy of bioenergy climate impacts discussed here. For example, it is perfectly conceivable that within a comparative LCA framework a non-carbon-sequestering bioenergy system generating large quantities of energy products that offset fossil fuel consumption could have greater climate mitigation value than a carbon-negative but low-energy generation scenario. Indeed, it has been shown that bioelectricity production will likely result in greater near-term climate mitigation value than carbon-negative biochar production in areas with coal-based electricity production (Woolf *et al.*, 2010). It is likely that the optimal climate-mitigating configuration of bioenergy systems will evolve over time, with near-term designs focusing on maximizing output of energy products in order to displace the greatest amount of fossil fuel usage, but with carbon sequestration becoming a more important system objective over time as the economy becomes less carbon intensive but as atmospheric CO_2 concentrations approach or exceed sustainable levels.

2.7. Conclusions

Bioenergy systems based on terrestrial feedstocks join agricultural processes associated with feedstock provisioning to industrial supply chains to process and convert that feedstock to fuels or other energy products. While climate impact assessment techniques are increasingly well-developed for the industrial supply chain parts of the bioenergy lifecycle, the additional sustainability questions around agroecosystem management challenge existing assessment methods and tools. This review presents a simple emissions taxonomy that highlights methodological challenges in lifecycle assessment of bioenergy system climate impacts, classifying impacts based on their nature of origin, location, mechanism, physical nature, and temporal profile. Of the climate impact effects included in the current bioenergy LCA literature, very few fall into the simplest classification category (direct, continuous, observable, industrial GHG emissions), and most rely on supplemental assumptions or calculations that are not well-integrated within existing supply chain LCA tools. Furthermore, reviewing a select set of recent prominent biofuel LCA studies from the past five years, we find them to be limited in scope and highly inconsistent in the application of climate impact accounting best practices around biogenic emissions, indirect effects, and biophysical climate impacts.

Bioenergy production is a complex systems problem in which there is inherent tension between the imperative of producing large quantities of energy to displace fossil fuel usage and the necessity of managing feedstock provisioning at sustainable levels of intensity. Further refinement of lifecycle assessment methods and metrics is necessary for fully understanding overall system environmental performance, and navigating performance tradeoffs to achieve optimal system designs. The potential for managing bioenergy systems for carbon sequestration will likely be a key driver for the future development of commercial-scale bioenergy facilities.

Table 2.1. Climate impacts taxonomy applied to commonly reported impacts from the bioenergy lifecycle assessment literature

Climate impact	**Origin**	**Location**	**Mechanism**	**Physicality**	**Temporality**	**Examples**
Supply chain energy, material inputs	Industrial	Direct	Either	Observable (positive)	Continuous	Wang *et al.* (2011)
Exhaust carbon capture & storage (BECCS)	Industrial	Direct	GHG	Observable (negative)	Continuous	Sanchez *et al.* (2015)
Capital embodied impacts	Industrial	Direct	Either	Observable (positive)	Time-dependent	Hill *et al.* (2006)
Fossil fuel displacement	Industrial	Indirect	Either	Inferred	Continuous	Plevin *et al.* (2014)
Co-product displacement	Industrial	Indirect	Either	Inferred	Continuous	Kim & Dale (2002); Farrell *et al.* (2006)
GHG mitigation opportunity costs	Industrial	Direct	Either	Inferred	Continuous	Melamu & von Blottnitz (2011)
Indirect fuel use change	Industrial	Indirect	Either	Either	Continuous	Rajagopal *et al.* (2011)
Direct soil N_2O emissions	Biogenic	Direct	GHG	Observable (positive)	Continuous	Nikièma *et al.* (2011)
Changes in ecosystem carbon stocks	Biogenic	Direct	GHG	Observable	Time-dependent	Hillier *et al.* (2009)
Avoided N_2O, CH_4 fluxes	Biogenic	Direct	GHG	Inferred	Continuous	Field *et al.* (2013)
Indirect land use change	Biogenic	Indirect	GHG	Observable	Time-dependent	Searchinger *et al.* (2008); Babcock (2009)
Indirect soil N_2O emissions	Biogenic	Indirect	GHG	Observable	Continuous	Del Grosso *et al.* (2008)
Aerosol emissions	Industrial	Direct	Other forcing	Either	Continuous	Grieshop *et al.* (2011)
Changes in farm albedo, transpiration	Biogenic	Either	Other forcing	Either	Time-dependent	Loarie *et al.* (2011)

Table 2.2. Typical nitrogen fertilizer application ranges for different bioenergy crops. Mean values with 10th and 90th percentile values as compiled by Wang *et al.* (2012)

Crop	**Typ. N application (kg N Mg^{-1} biomass)**
Corn	16 (12 – 19)
Corn stover removal	8.5 (6.5 – 10.5)
Sugarcane (Brazil)	0.8 (0.7 – 0.9)
Switchgrass	7.7 (4.8 – 10.6)
Miscanthus	3.9 (2.9 – 4.8)

Table 2.3. Direct nitrous oxide emission factors, comparing general IPCC Tier 1 emissions factor range with measurements from annual and perennial bioenergy feedstock production

Crop	N_2O-N (N applied)$^{-1}$	Reference
Tier 1		
NA	1.0 % (0.3 – 3 %)	Eggleston *et al.* (2006)
Observed*		
Corn	1.51 %	Hoben *et al.* (2011)
Canola/hemp	0.86 %	Kavdir *et al.* (2008)
Canola/rye	1.50 %	Kavdir *et al.* (2008)
Switchgrass	0.22 %	Hong *et al.* (2012)
Switchgrass	0.21 %	Nikièma *et al.* (2011)
Switchgrass	0.19 %	Schmer *et al.* (2012)
Miscanthus	0.47 %	Roth *et al.* (2015)
Willow	0.17 %	Kavdir *et al.* (2008)
Poplar	0.28 %	Kavdir *et al.* (2008)

Table 2.4. Typical soil organic matter changes (Δ SOM) under various land use changes to dedicated bioenergy feedstock crops, and associated direct land use change emissions factors (dLUC EF) per mass of feedstock cultivated. All values are medians, with 1st and 3rd quartiles reported.

Crop	Typ. Yield[1] (t ha^{-1} y^{-1})	Previous land use	Typ. Δ SOM[2] (t C ha^{-1} y^{-1})	Typ. dLUC EF (t CO_2 t^{-1})
Corn	9.8 (8.0 to 11.4)	cropland	1.2 (0.0 to 1.4)	0.45
		grassland	-2.2 (-2.9 to -1.1)	-0.82
Switchgrass	6.4 (5.1 to 10.2)	cropland	1.3 (0.5 to 2.9)	0.74
		grassland	-1.0 (-2.4 to 0.2)	-0.57
Miscanthus	14.8 (10.8 to 20.0)	cropland	1.1 (0.5 to 1.7)	0.27
		grassland	0.4 (-0.3 to 0.6)	0.10
Poplar	6.8 (5.2 to 9.8)	cropland	0.2 (-0.6 to 0.8)	0.11
		grassland	-0.6 (-1.4 to -0.2)	-0.32
Willow	8.7 (6.1 to 11.2)	cropland	1.0 (-2.3 to 3.2)	0.42
		grassland	0.0 (-6.6 to 0.5)	0

[1]Corn yield range from Lobell *et al.* (2014) for year 2011. Yield ranges for all other crops calculated from supplemental information provided in Searle & Malins (2014)

[2]From (Qin *et al.*, 2015a), 0-100 cm soil depth

Table 2.5. Survey of key assessment details across recent bioenergy LCA studies

	(Hill *et al.*, 2009)	(Cherubini & Jungmeier, 2010)	(Hsu *et al.*, 2010)	(Wang *et al.*, 2012)
Co-product crediting via displacement?	Y[6]	Y[5]	Y[3]	Y
Consider ecosystem C storage?	Y	Y	N	Y[1]
Dynamic GWP accounting?	N	N	N	N
iLUC included?	N[7]	N[4]	N	Y[1]
Aerosol emissions included?	N	N	N	N[2]
Biophysical land effects?	N	N	N	N
Sensitivity or uncertainty analysis?	N	Y	Y	Y

[1]Their methodology considers both changes in soil carbon during domestic production of feedstock biomass and market-mediated leakage effects due to crop displacement together as a single aggregate 'land use change' term

[2]The latest GREET.net model includes national-scale estimates of soil carbon a GWP factor of 600 for black carbon particulate matter emissions, and -69 for organic carbon PM

[3]Coproduct crediting is based on displacement for some processes, energy content allocation for others

[4]The assume that switchgrass feedstock production in limited to 'set-aside' land capable of sequestering carbon without displacing existing agriculture

[5]The functional unit of analysis is the basket of all biorefinery outputs, compared against an equivalent set of conventional fossil fuel-based equivalent products

[6]Using GREET model defaults

[7]Assumed that feedstock cultivation takes place on converted Conservation Reserve Program lands only

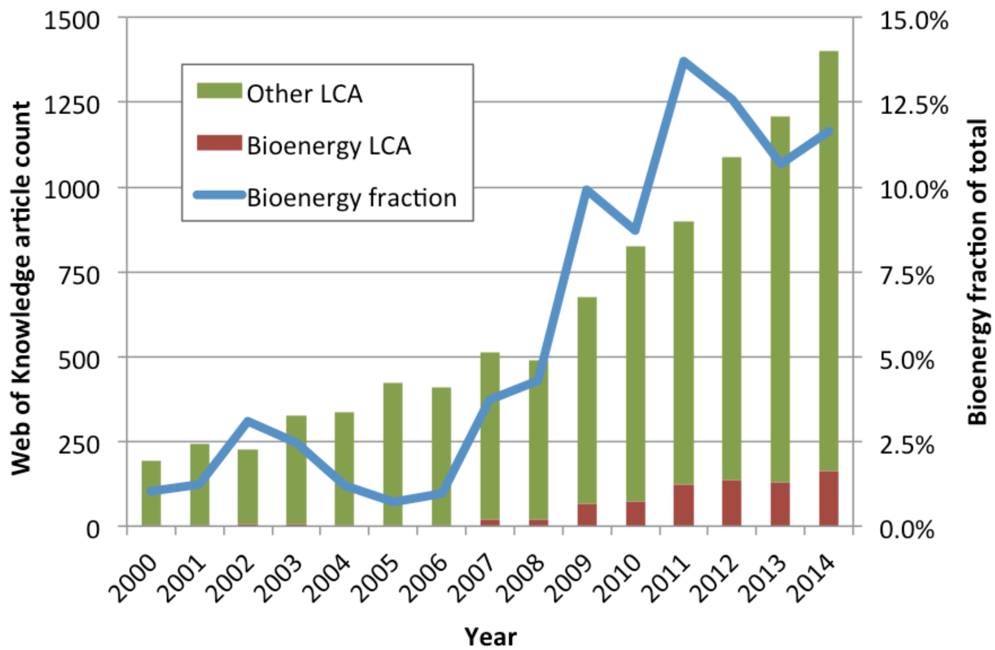

Figure 2.1. LCA literature trends based on Web of Knowledge search results. Bioenergy LCA study count based on the search string "TS=((lifecycle assessment OR LCA) AND (biofuel OR bioenergy OR ethanol OR biodiesel))"; non-bioenergy LCA studies identified by replacing 'AND' with 'NOT'.

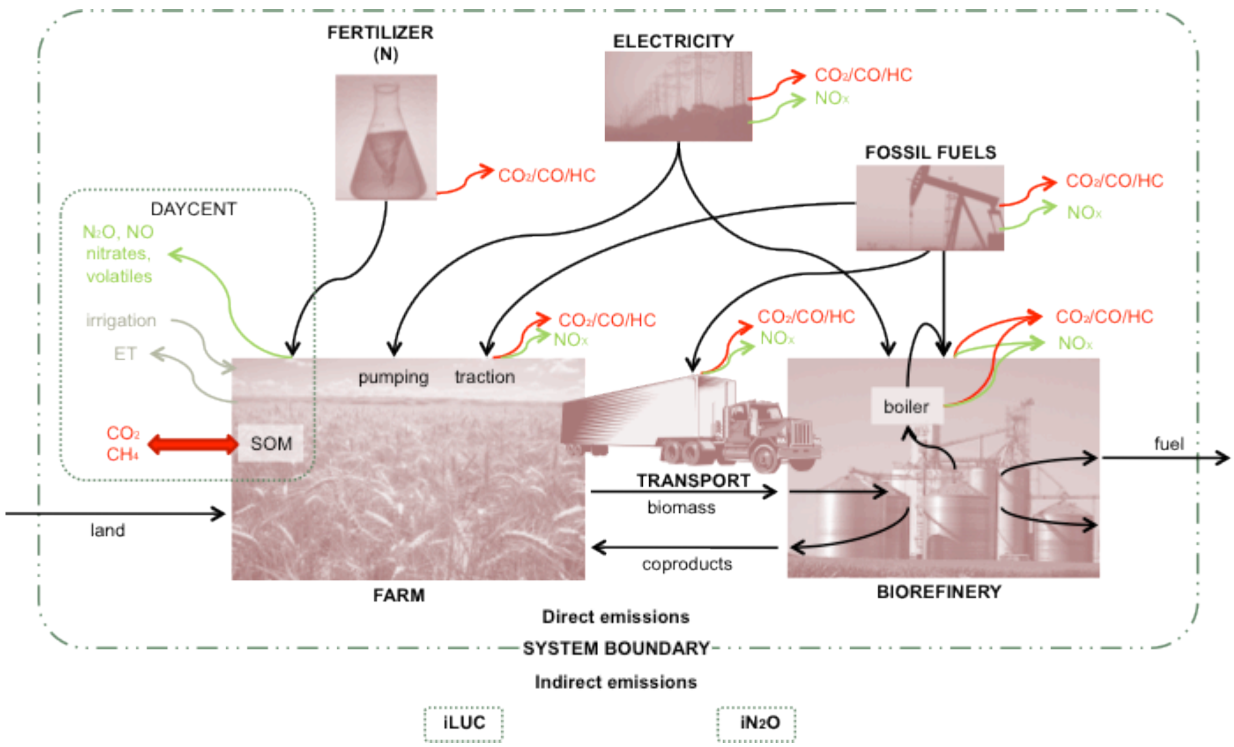

Figure 2.2. Schematic representation of the well-to-pump biofuel supply chain

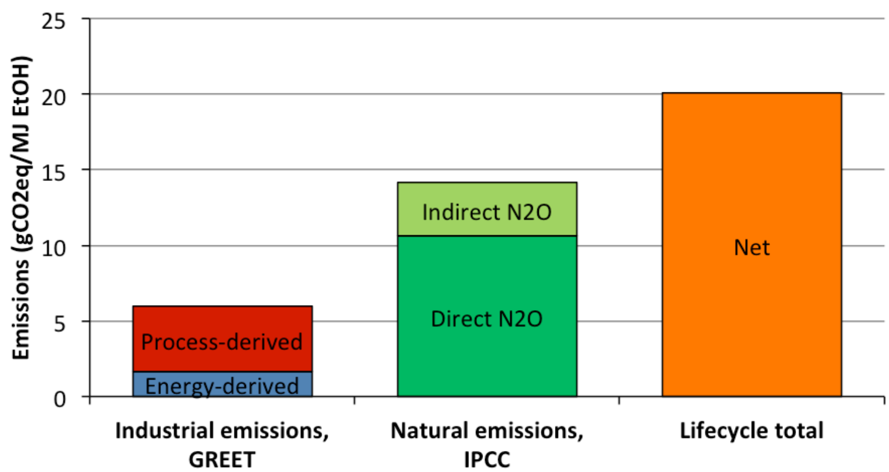

Figure 2.3. Greenhouse gas emissions associated with nitrogen fertilizer application in a first-generation corn ethanol production system

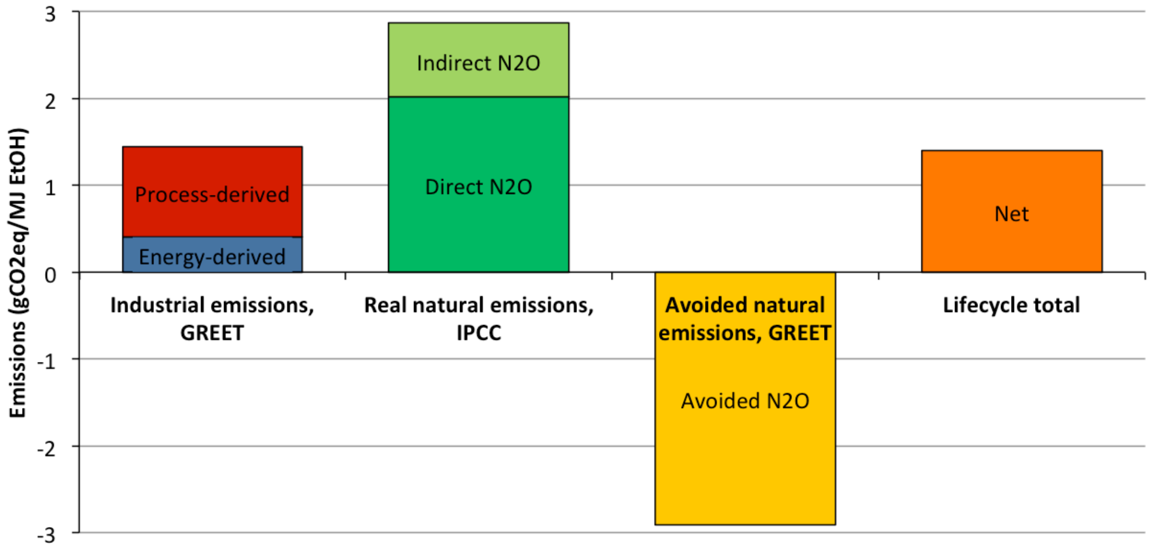

Figure 2.4. Greenhouse gas emissions directly associated with nitrogen fertilizer application in a second-generation corn stover cellulosic ethanol production system

CHAPTER 3

ANALYZING VARIABLE FEEDSTOCK PRODUCTIVITY AND SOIL GHG EMISSIONS BALANCE ACROSS A CELLULOSIC BIOENERGY LANDSCAPE

3.1. Summary

Renewable fuel standards in the US and elsewhere mandate the use of large quantities of cellulosic biofuels with low greenhouse gas (GHG) footprints, which will likely require extensive cultivation of dedicated bioenergy feedstock crops on marginal agricultural lands. Performance data for such production systems is sparse, and non-linear interactions between plant species, agronomic management intensity, and underlying soil and land characteristics complicate the development of sustainable landscape design and management strategies for low impact commercial-scale feedstock production. Process-based ecosystem models are valuable for extrapolating field trial results and making predictions of productivity and associated environmental impacts that integrate the effects of spatially variable environmental factors across diverse production landscapes. However, there are few existing examples of parameterizing such models against field trial results from both prime and marginal lands or conducting landscape-scale analyses at sufficient resolution to capture interactions between soil type, land use, and crop management intensity. In this work we used a data-rich, multi-criteria approach to parameterize and validate the DayCent ecosystem biogeochemistry model for upland and lowland switchgrass using data on yields, soil carbon changes, and soil nitrous oxide emissions from US field trials spanning a range of climates, soil types, and management conditions. We then conducted a high-resolution analysis of a real-world cellulosic bioenergy landscape in Kansas in order to estimate feedstock production potential and associated direct biogenic GHG

emissions footprint. Our case study results show that switchgrass yields and emissions balance can vary widely across a landscape large enough to supply a biorefinery, but that within a given land base both factors can be widely modulated by changing crop management intensity. This suggests great potential for bioenergy landscape design and optimization.

3.2. Introduction

The US renewable fuel standard has mandated quantitative environmental impact assessment for biofuel production since its expansion in the Energy Independence and Security Act of 2007, which requires the use of large quantities of ‘advanced’ and ‘cellulosic’ biofuels with lifecycle greenhouse gas (GHG) emissions reductions relative to a gasoline baseline of 50% and 60%, respectively (110th Congress of the United States, 2007). This requirement implies that biomass feedstocks can be provisioned with low direct environmental impacts, and with minimal disruption to commodity markets that could lead to indirect leakage effects (Searchinger *et al.*, 2008). A variety of low-impact feedstock strategies have been envisioned, including the collection of agricultural residues, forestry residues, and municipal wastes, as well as the cultivation of dedicated woody and herbaceous crops on marginally-productive lands (Campbell *et al.*, 2008; Robertson *et al.*, 2008; Tilman *et al.*, 2009). In particular, perennial grasses such as switchgrass, Miscanthus, bioenergy-optimized sugarcane, and mixed prairie species have been identified as promising cellulosic feedstock crops due to their high yield potential, relatively low input requirements, high nitrogen use efficiency, and ability to sequester carbon in soils (Vogel *et al.*, 2002; Tilman *et al.*, 2006a; Heaton *et al.*, 2008; Walter *et al.*, 2014). It has been estimated that biofuel supply chains based on these feedstocks will have highly favorable lifecycle GHG impacts as compared to first-generation biofuel technologies (Schmer *et al.*, 2008; Davis *et al.*, 2012; Wang *et al.*, 2012). A comprehensive review of US feedstock availability by the Department of Energy suggests that dedicated perennial grass feedstocks will likely play a significant role in meeting the national biofuel mandate (Perlack & Stokes, 2011).

Despite their promise, agronomic experience with such perennial grass feedstock crops is still relatively limited, and optimal agronomic management strategies to balance the often-competing goals of maintaining high yields while minimizing environmental impacts have not yet been resolved. The debate between the relative merits of low-intensity cultivation over large areas (often referred to as 'land-sharing' or extensive production strategy) versus more intensive production on a more limited land base ('land-sparing' or intensification) is still being waged, largely at a theoretical level (e.g., Anderson-Teixeira *et al.*, 2012). Process-based ecosystem modeling can play an important role in extrapolating limited existing field trial results to make more general estimates of productivity, environmental impacts, and optimal management and landscape design strategies.

3.2.1. Modeling cellulosic feedstock yields and environmental impacts

The use of crop models in assessing management-environment interactions and predicting bioenergy feedstock crop productivity was thoroughly reviewed by Nair *et al.* (2012). Crop models such as APSIM, BioCro, and ALMANAC have been applied at regional or national scales to assess the productivity of first- and second-generation feedstock crops as affected by broad-scale climate-soil associations (Bryan *et al.*, 2010; Miguez *et al.*, 2012; Behrman *et al.*, 2014). Bioenergy system design is not just a question of yield, however, and understanding changes in the biogeochemical cycling of carbon, nitrogen, and water is required to evaluate system sustainability (Robertson *et al.*, 2011). Perennial grass feedstock crops are typically associated with high potential for soil carbon sequestration. One recent meta-analysis suggests that switchgrass increases soil organic carbon (SOC) levels at a median rate of ~ 0.7 t C ha^{-1} year^{-1} when cultivated on carbon-depleted agricultural soils, though performance is more neutral when pastureland or other non-cropped land is converted (Qin *et al.*, 2015a). Application of nitrogen fertilizers is typically required to replace losses during harvest and to maintain yield levels, but N additions promote nitrous oxide (N_2O) emissions, which may increase non-linearly with N rate (Hoben *et al.*, 2011; Shcherbak *et al.*, 2014). This has been hypothesized to threaten the overall lifecycle GHG footprint of any bioenergy system based on feedstocks with inefficient nitrogen cycling (Crutzen *et al.*, 2008b). Biogeochemical cycling of C, N, and H_2O and associated fluxes of biogenic greenhouse gases are tightly linked in all agroecosystems by fundamental mechanisms including plant tissue stoichiometry, photosynthetic pathway, stomatal conductance, microbial mineralization/immobilization, and other factors that are affected by local climate, soil type, and land use history.

Detailed reviews of process-based biogeochemical models capable of capturing these interactions in the context of bioenergy system sustainability assessment are provided by Thomas *et al.* (2013) and Robertson *et al.* (2015). CENTURY and later the DayCent model were among the first to be applied to bioenergy sustainability assessment, and have been widely used to evaluate corn grain production, corn stover removal, and the dedicated cultivation of switchgrass and Miscanthus at scales ranging from individual sites to national scale (Sheehan *et al.*, 2003; Kim & Dale, 2005; Chamberlain *et al.*, 2011; Davis *et al.*, 2012; Lee *et al.*, 2012; Duval *et al.*, 2013). The Environmental Policy Integrated Climate (EPIC) model has also been applied extensively to bioenergy feedstocks in the context of economic (Jain *et al.*, 2010; Egbendewe-

Mondzozo *et al.*, 2011) and environmental (Gelfand *et al.*, 2013) sustainability assessment at scales from regional (Zhang *et al.*, 2010) to global (Kang *et al.*, 2014). Experience with biogeochemical models applied at finer spatial scales as driven by landscape factors such as soil types or topography is more limited. Several studies have attempted to parameterize crop production models based on switchgrass field trials across multiple soils under the warm, wet climate of the southeastern US, with results suggesting no clear differentiation of multi-year average productivity by soil type (Persson *et al.*, 2011), or higher productivity in silty and sandy soils relative to clays (Woli, 2012). A group at Idaho National Laboratory has linked DayCent with models of soil erosion (WEPS, RUSLE2) at the extremely high spatial resolutions (10m x 10m) associated with modern precision agriculture in order to determine the potential environmental benefits of replacing the low-yielding sections of individual corn fields with perennial grass for biomass (Abodeely *et al.*, 2013).

3.2.2. Modeling challenges

While biogeochemical models are increasingly used to simulate conversion of marginal agricultural lands to bioenergy feedstock cultivation (Bandaru *et al.*, 2013; Qin *et al.*, 2015b), these scenarios are especially challenging from a modeling perspective. The definition of 'marginal' land itself is not straightforward. In some cases this designation has been based on unfavorable biophysical properties as judged using land suitability ratings (Gelfand *et al.*, 2013) or remote sensing techniques (Cai *et al.*, 2011). Another basis for the designation considers past transitions in an out of agricultural production as inferred from land use datasets (Campbell *et al.*, 2008), remote sensing (Wright & Wimberly, 2013), or sector-level economic modeling (Swinton *et al.*, 2011). Bioenergy feedstock crops are not immune to the factors that make such lands marginal for conventional crops, and recent perennial grass field trials purposely conducted on marginal sites indicate reduced productivity relative to performance on the prime lands typically encountered at most agricultural field stations (Mooney et al., 2009; Shield et al., 2012; Boyer et al., 2013). From an ecosystem modeling perspective, accurate assessment is only possible to the extent that biophysical limitations on productivity (e.g., unfavorable climates, soil texture extremes, shallow soils, low soil organic matter levels, site drainage problems, slope, vulnerability to erosion, etc.) are represented directly or indirectly in model data inputs and modeled processes.

It is well understood that process-based ecosystem models require proper parameterization specific to the agroecosystems being simulated in order to achieve good performance, and that such models have limited predictive power when extrapolated far beyond their parameterization scope (Thomas *et al.*, 2013). However, given the limited amount of field trial data available and the challenges involved in specifying model runs for comparison with real-world data, many bioenergy assessment studies are based on models parameterized at only a very limited number of sites, parameterized under prime conditions and then extrapolated to highly marginal sites, or lacking an independent validation of performance (e.g., Gelfand *et al.*, 2013; Kang *et al.*, 2014). In the case of the DayCent model, parameterization typically involves adjusting site and crop parameters by hand in order to match observed real-world performance for a small number of field trial cases for which extensive data are available (Del Grosso *et al.*, 2011). While this approach can often yield a high degree of fidelity across a range of performance criteria for the sites in question (Hudiburg *et al.*, 2015), the very large number of empirically-determined crop and site parameters in the model makes the process vulnerable to over-parameterization. In such cases, model fit to the training dataset is improved via mechanisms that lack broader underlying ecological significance, reducing the generality of the resulting model for other geographic areas, environmental conditions, or management regimes (Necpálová *et al.*, 2015). It is also possible to introduce bias with the selection of the parameterization cases themselves, if the researcher gravitates to focus on studies that confirm *a priori* assumptions of how a system 'should' perform.

There are additional challenges around the spatial resolution of landscape modeling and assumptions about crop agronomic management. Management factors including tillage intensity (Adler *et al.*, 2007), fertilizer application rate (Davis *et al.*, 2013), and rotation length (Pyörälä *et al.*, 2014) can potentially change the lifecycle GHG performance of a bioenergy system from positive to negative, an effect termed the 'management swing potential' (Davis *et al.*, 2013). Management recommendations for bioenergy crops are not always well defined, and in the case of Miscanthus, nitrogen fertilizer requirements have been widely debated (Arundale *et al.*, 2014a), with important implications for the overall GHG footprint of production (Roth *et al.*, 2015). To the extent that there are interactions between best management and site-level ecosystem properties (soil texture, land use history, etc.), assumptions about management should ideally by implemented at the level of management decision-making, i.e., the field-scale. Some landscape modeling studies have started to endogenize management intensity questions by simulating productivity and environmental impacts at different rates of N application (Gelfand *et al.*, 2013) or different levels of tillage (Zhang *et al.*, 2010).

3.2.3. Study goals

Our study used the DayCent biogeochemical model to assess perennial grass productivity and associated biogenic GHG emissions as a function of land quality and management intensity. Implications for bioenergy landscape design are illustrated through a case study of switchgrass production around a newly constructed commercial scale cellulosic biorefinery in an area with substantial heterogeneity in soils and land use. This investigation expands on previous work in two main ways:

1. We conducted an extensive model parameterization and validation effort based on a data-rich, multi-criteria approach, using a large, unbiased parameterization dataset collected from the literature, that spans wide gradients of climate, soil texture, and management intensity.
2. We evaluated the impacts of management intensification at the full spatial resolution of the assessment, and optimal levels of nitrogen fertilizer application were computed for each simulation case in order to either maximize yield or minimize biogenic greenhouse gas emissions.

Our objective was to develop a rigorous, well-validated spatially explicit biogeochemical modeling capability that can serve as the basis for future integrated assessment and landscape optimization efforts, integrating productivity and biogenic GHG emissions estimates into full biofuel supply chain lifecycle assessments and economic analyses under real-world land ownership and policy constraints.

3.3. Methods

3.3.1. Case study introduction

We performed a landscape assessment case study simulating the cultivation of switchgrass (*Panicum virgatum*) to supply biomass to the Abengoa cellulosic biorefinery located outside the town of Hugoton in southwestern Kansas (Peplow, 2014), which began operations in fall 2014. While the plant will initially produce its 25 million gallons of ethanol per year using corn stover as the primary lignocellulosic feedstock, switchgrass has been mentioned as an advanced cellulosic feedstock of interest, and Biomass Crop Assistance Program Project Area 7 is sponsored by the company and targets the establishment of 20,000 acres of switchgrass production in the area (USDA Farm Service Agency, 2014). The Hugoton area has long been at the center of agricultural sustainability and energy issues, having been deeply affected by the Dust Bowl in the 1930s (Kansas Historical Society, 2014) and being the site of the earliest hydraulic fracturing trials in the U.S. (Borowski, 2012).

Today, the surrounding Stevens County is a highly diverse and productive agricultural area. In 2012, 21.4% of the county was dedicated to highly-productive irrigated corn cultivation (average yield of 12.1 Mg/ha, or 192 bushels/acre) and 11% to dryland wheat (1.1 Mg/ha, or 18 bu/acre), with smaller fractions devoted to other crops and pasture/rangeland, supporting an inventory of 45,500 head of cattle including calves (USDA NASS, 2014). In this study we investigated the biogeochemical implications of converting any cropland or rangeland in Stevens County and its six neighboring counties in southwestern Kansas and the Oklahoma panhandle to switchgrass cultivation (see Figure 3.1), examining tradeoffs between productivity and associated biogenic GHG emissions as a function of underlying soil type and management intensity. Issues of land ownership, conservation easement status, and policy limitations are excluded here, but explored in a subsequent publication dedicated to bioenergy landscape optimization.

3.3.2. DayCent model

Productivity and net fluxes of biogenic CO_2 and N_2O from soils under switchgrass cultivation were modeled with the DayCent biogeochemistry model (Parton *et al.*, 1987; Del Grosso *et al.*, 2011). DayCent is a semi-empirical process-based model that simulates cycling of C, N, and water in natural and agroecosystems based on site-specific biophysical factors, land use history, and management practices (e.g., tillage, fertilizer application, irrigation, etc.). The spatial and temporal scope of the model lies in between that of dedicated crop growth models (Miguez *et al.*, 2012) and generalized earth climate system models (Anderson *et al.*, 2013; Hallgren *et al.*, 2013). DayCent has been used extensively to predict yields and environmental impacts of cultivating switchgrass (Adler *et al.*, 2007; Chamberlain *et al.*, 2011; Davis *et al.*, 2012; Lee *et al.*, 2012) and is also used in the US agricultural soil GHG emissions (US EPA, 2014a).

DayCent computes soil temperature and moisture model using daily climate data inputs for different layers of the soil profile resolved separately based on soil texture, bulk density, and pH. Crop growth (net primary productivity, or NPP) is simulated using species-specific empirically derived parameters describing photosynthetic efficiency, tissue C/N ratio limits, above- and below-ground C partitioning, and phenology. Daily biomass growth potential (NPP_{pot}) is derived from top-of-atmosphere radiation (*srad*) corrected for atmospheric transmission losses, multiplied by a series of 0-1 factors that represent deviations from ideal temperature (f_{temp}) or soil moisture (f_{H2O}) or limitations due to canopy immaturity or self-shading (f_{canopy}). This potential growth is then adjusted down if available soil mineral nitrogen supply is limiting, as determined based on a maximum incremental biomass C:N ratio adjusted for plant maturity:

$$NPP = \max(NPP_{pot}, NPP_{Nlim}) \text{ where}$$

$$NPP_{pot} = srad \cdot transmission \cdot f_{temp} \cdot f_{H2O} \cdot f_{canopy}$$

$$NPP_{Nlim} = N_{avail} \cdot (C/N)_{max}$$

In addition to plant productivity DayCent also estimates soil carbon and nitrogen cycling including net changes in soil organic carbon (SOC) levels and nitrous oxide (N_2O) emissions, the major constituents of the agricultural soil greenhouse gas balance. Dynamics of soil organic matter (SOM) are simulated for soil surface pools and the top soil layer (here set to 0-20 cm), with organic matter represented by two litter pools (metabolic and structural) and three SOM pools (one pool, termed ‘Active’, representing microbial biomass and associated microbial products with a rapid turnover rates), with the other two representing chemically/physically stabilized carbon, with decadal- (‘Slow’ pool) and century-scale (‘Passive’ pool) turnover times. N mineralization/immobilization rates for each pool are controlled max and min C:N ratios for each pool, soil temperature, soil moisture and microbial efficiency as a function of soil texture (Parton *et al.*, 1987). The soil nitrogen balance considers synthetic N fertilizer addition, manure and other organic N amendments, atmospheric deposition, volatilization, leaching, plant uptake, and N mineralization and immobilization associated with soil organic matter transformations. The model simulates nitrification of ammonium (NH_3^+) to nitrate (NO_3^-), including NO_X and N_2O fluxes derived from nitrification, as well as denitrification reactions to gaseous products (N_2O, NO_X, N_2). Nitrification is simulated by multiplying available soil NH_3^+ by a maximum potential nitrification rate adjusted based on soil temperature, water-filled pore space (WFPS), and pH limitations (Del Grosso *et al.*, 2000; Parton *et al.*, 2001). The overall rate of denitrification and the N_2O/N_2 ratio of its products are modeled based on the availability of nitrate and organic matter substrates as inferred from heterotrophic respiration rate, and local soil micropore redox state and gas diffusion rates as inferred from WFPS and heterotrophic respiration rate.

3.3.3. Model parameterization and validation

We undertook an extensive parameterization and validation of the DayCent switchgrass growth model to improve overall simulation accuracy and verify the capability to capture productivity variations across gradients of land quality and cultivation intensity. A large dataset of switchgrass field trials for the continental United States was assembled from the peer-reviewed literature. Studies were included in the dataset provided they a) specified the underlying soil in sufficient detail that a corresponding SSURGO map unit could be identified in the general area of the field trial using the Web Soil Survey (USDA NRCS); b) specified key management variables (switchgrass ecotype planted, N fertilizer application rate, harvest date) in sufficient detail to define DayCent management inputs; and c) reported disaggregated annual yield and GHG results (studies reporting results averaged across multiple sites or N treatments or cuttings were excluded). Parameterization and validation efforts were based on time-averaged yields across the multiple years of a given site and treatment, so studies that report either annual yield data or treatment-averaged data were included. If multiple cultivars of the same ecotype were included in a study, associated yields were averaged into a single representative value for the upland or lowland ecotype. Additional details are provided in Appendix A Section A.1.

A total of 25 appropriate studies were identified, covering 573 annual biomass yield points across 145 unique combinations of site (soil and/or climate) and management (N rate, harvest date, etc.), referred to as treatments. Initial exploratory analysis confirmed the need to exclude the first two seasons of yield data, before switchgrass yields stabilize (Lesur *et al.*, 2013; Arundale *et al.*, 2014b), and to filter out treatments for ecotypes grown outside their typical latitude range (up to 54° N for lowland varieties and down to 34° N for upland, as per Casler, 2012). The remaining dataset was then randomly split at the level of individual studies 70:30 into a parameterization dataset and an independent validation dataset (Table 3.1).

In addition to annual yields several of these field trials included more detailed information on biomass partitioning or nitrogen content (Frank *et al.*, 2004; Dohleman *et al.*, 2012; Anderson-Teixeira *et al.*, 2013), long-term changes in soil organic carbon based on either repeat measurements or paired sites (Ma *et al.*, 2001; Liebig *et al.*, 2008; Follett *et al.*, 2012; Anderson-Teixeira *et al.*, 2013; Bonin & Lal, 2014), and/or time-resolved nitrous oxide emissions (Nikièma *et al.*, 2011; Hong *et al.*, 2012; Schmer *et al.*, 2012; Smith *et al.*, 2013). There was insufficient data available to perform an independent validation of these model performance criteria, so all of these studies were included in the parameterization dataset. While the original SOC dataset was very noisy, eliminating individual data points that were not reported as statistically significant yielded a final reduced modeling dataset that behaved more predictably and was much more consistent with recent switchgrass SOC meta-analysis results (i.e., Qin *et al.*, 2014).

The combined parameterization and validation dataset covers a wide range of latitudes/longitudes (Figure 3.1) and temperature/precipitation regimes (Appendix A Fig. A.1) as well as a wide range of soil textures and Natural Resource Conservation Service land capability class (LCC) ratings (Helms, 1992; Appendix A Fig. A.2). Note that LCC ratings are reflective of a variety of land use limitations, some of which are explicitly considered in the DayCent model (e.g. dry climates, extreme textures, shallow soils) and some of which are not (e.g. erosion susceptibility, drainage class). Parameterization was further informed with data from switchgrass greenhouse or growth chamber experiments studying productivity across gradients of temperature (Balasko & Smith, 1971; Hsu *et al.*, 1985; Reddy *et al.*, 2008; Kandel *et al.*, 2013; Wagle & Kakani, 2014) or moisture (Xu *et al.*, 2006).

The parameterization process started with a default switchgrass crop parameter set based on previous work (Adler *et al.*, 2007; Davis *et al.*, 2012) and focused on refining parameters relating to productivity, temperature and moisture stress response, nitrogen management, shoot-versus-root partitioning, and tissue death and turnover rates, with separate parameterizations for both upland and lowland ecotypes as appropriate. Initial exploratory analysis suggested that differentiating the phenology of upland versus lowland switchgrass ecotypes was essential for accurate yield simulation, consistent with current understanding of maturation based on photoperiod as a strong determinant of yield differences between different cultivars grown at a given latitude (Casler *et al.*, 2004). We set green-up dates as function of latitude based on a variety of literature sources (Sanderson, 1992; Sanderson *et al.*, 1997; Wang *et al.*, 2013a) as illustrated in Appendix A Fig. A.5. Peak biomass dates were predicted as a function of both latitude and ecotype as inferred from a variety of sources (Sanderson, 1992; Hopkins *et al.*, 1995; Sanderson *et al.*, 1997; Vogel *et al.*, 2002; Frank *et al.*, 2004; Berdahl *et al.*, 2005; Casler *et al.*, 2007; Anderson-Teixeira *et al.*, 2013; see Appendix A Fig. A.6-A.7).

After crop phenology was set other parameter adjustments were implemented manually, but evaluation against the parameterization dataset was fully automated using the model execution and results analysis tools described in the next section. The parameterization process focused on maximizing measured-versus-modeled r-values for upland and lowland ecotype yields, changes in soil organic carbon, and growing season N_2O emissions, but also took into account time-resolved shoot:root and C:N ratio data where available for a multi-criteria parameterization (e.g., Appendix A Fig. A.11). Once the parameterization process was complete, independent validation of upland and lowland cultivar yield performance was conducted based on the data held in reserve (holdout validation method).

3.3.4. Spatial data inputs, model initialization, and automation

A variety of spatially-explicit data inputs are necessary to initialize and run the DayCent model for a large-scale parameterization or landscape analysis, including data on climate, soil type, and land use history. Data sources used in this analysis are summarized in Table 2. Soil input data was derived from the Natural Resource Conservation Service Soil Survey Geographic database (SSURGO, Ernstrom & Lytle, 1993). Soil texture, rock fraction, and pH for different soil profile layers of the dominant soil component for each map unit were taken directly from the SSURGO database, and bulk density, field capacity, wilting point, and saturated hydraulic conductivity were computed using the Saxton equations (Saxton *et al.*, 1986) and converted to DayCent input file format. Climate data on a 32 km grid was derived from the North American Regional Reanalysis database (NARR, Mesinger *et al.*, 2006).

Land use history and current land management practices were compiled from a variety of sources. Current land use was determined from the National Land Cover Database 2006 (NLCD, Wickham *et al.*, 2013), re-sampled from the native 30 m resolution to 240 m for ease of use, and re-classified into the simplified categories of annual agricultural lands (‘cultivated crops’, ‘pasture/hay’), rangeland (‘dwarf shrub’, ‘shrub/scrub’, ‘grassland/herbaceous’, ‘sedge/herbaceous’), and excluded (all other categories including forested and developed lands). Irrigated areas were identified using the MIrAD-US database (Pervez & Brown, 2010), and federally-owned lands were identified using the USGS Federal Lands of the United States data layer (USGS, 2014) and excluded from further analysis (3.4% of the landscape, most part of Cimarron National Grassland). These five GIS layers were then intersected and small slivers were eliminated by merging all polygons smaller than 1 ha into the neighbor with which they shared the longest border. This yielded 39,320 polygons of a variety of sizes across the Hugoton case study area (Appendix A Fig. A.15), representing 3,779 DayCent ‘strata’, i.e. unique combinations of inputs requiring individual simulation.

For each landscape strata, the DayCent model was pre-initialized using the same pre-settlement and historical land use assumptions in the EPA Inventory of U.S. Greenhouse Gas Emissions and Sinks (US EPA, 2014b) and described in detail by Ogle *et al.* (2010). Model initialization included an equilibration run of several thousand years duration reflecting the natural state of the land prior to conversion to agriculture in order for all soil C and N pools to achieve steady-state values. Historical management between initial plow-out and the modern period was simulated with crop rotations and management practices compiled at regional scale from a variety of historical and modern sources (Ogle *et al.*, 2010). The forward switchgrass simulations were then executed across part of a 29-node, 288-processor cluster computing system at the CSU Natural Resources Ecology Laboratory. Parallel execution was implemented in Python (https://www.python.org/) using forking operations to take advantage of multiple cores within each node.

3.3.5. Landscape analysis scenarios, results processing, and sensitivity analysis

For the landscape analysis case study we simulated conversion of all non-irrigated, non-federally owned polygons in the seven-county case study area to rain-fed lowland switchgrass cultivation. We conducted 30-year forward simulations to assess long-term productivity and soil C and N cycling averaged over the full range of the NARR historic weather record. In order to assess the response of crop productivity and GHG performance to management intensity, seven different rates of nitrogen fertilizer application were simulated for each strata (0-150 kgN/ha in 25 kgN/ha increments). We assumed replanting every 10 years with associated field preparation consisting of chisel plow and field cultivator operations. As per extension recommendations the crop was neither fertilized nor harvested the year of establishment in order to limit competition from weeds and ensure robust crop establishment. These assumptions are highly conservative, as switchgrass is often established in this region without tillage, the need for periodic replanting is widely debated, and first-year harvest can be possible if the crop achieves sufficient first year productivity.

Switchgrass harvest yields, changes in SOC levels, and annual N_2O emissions were then averaged over the 30-year simulation period for each strata. Annual average N_2O emission values were converted into CO_2 equivalents using a 100-year global warming potential (GWP_{100}) value of 298 (Forster *et al.*, 2007), then added to the net CO_2 flux values associated with SOC changes for an estimate of total direct biogenic emissions. Yields and biogenic GHG intensity as a function of nitrogen fertilizer application rate were interpolated for each strata by applying a cubic regression to the 30-year averaged simulation results for the different N rates. To determine the GHG intensity of production (Mg CO_2eq/Mg biomass harvested), total emissions per hectare were divided by the associated simulated switchgrass yield. The yield-maximizing and GHG balance-minimizing N rates for each strata were then re-associated with the appropriate landscape polygons and multiplied by their area in order to develop curves illustrating total potential landscape productivity and biogenic GHG emissions balance when managed based on these different goals. Sensitivity of these landscape results to key crop parameterization factors, landscape characterization, and switchgrass cultivation scenario assumptions was assessed as detailed in Table 4 in order to determine the overall robustness of our conclusions. All results analysis routines were automated in Python through a combination of SQLite database operations (https://sqlite.org/) via the ***sqlite3*** module (https://docs.python.org/2/library/sqlite3.html), data manipulation in the native Python list data type, and figure generation using the ***matplotlib.pyplot*** module (http://matplotlib.org/api/pyplot_api.html).

3.4. Results

3.4.1. Parameterization and validation

A total of 79 model parameter iterations were ultimately tested, and final upland and lowland ecotype parameter values that differ from the default DayCent switchgrass crop parameterization are detailed in Table 3.3. The most significant changes were:

- Increased plant potential NPP rate – The most recent version of DayCent explicitly models solar radiation atmospheric transmission losses, and the revised potential NPP parameter must be adjusted higher (relative to previously published DayCent applications to switchgrass) to reflect the new calculation on a canopy photosynthetically active radiation (PAR) level basis rather than a top-of-atmosphere PAR basis. Further adjustments were made to optimize the observed yield difference between the different ecotypes and to offset slightly increased belowground C partitioning.

- Adjusted temperature and moisture stress response curves – Crop temperature (Appendix A Fig. A.8) and moisture stress (Appendix A Fig. A.9) response curves were set based on the greenhouse and growth chamber studies listed in Table 3.1. In the case of temperature response, fine adjustments to the edges of the curve where direct empirical data were lacking were implemented based on changes in overall modeled-vs.-measured performance across the training dataset. The same curves were used for both ecotypes. Comparison of measured and modeled yield ranges binned by site average growing degree day accumulation (Appendix A Fig. A.10) or annual precipitation (Appendix A Fig. A.11) verifies that the model accurately captures increasing switchgrass productivity at warmer, wetter sites
- Increased belowground partitioning and root cycling – The default parameterization slightly underestimated belowground biomass, significantly underestimated observed SOC increases, and over-predicted N_2O emissions. A small increase in belowground partitioning coupled with a large increase in root turnover rates resulted in more carbon being cycled into the soil, more mineral N being taken up by the plant, reduced soil mineral N concentrations and hence reduced N_2O losses, thus, improving model performance on all three criteria.

Model parameterization and validation results for yields and soil GHG fluxes are shown in Figure 3.2. Sufficient data was available to perform holdout method independent validation of yield predictions for both the upland and lowland ecotypes (Fig. 3.2a). The out-of-sample validation root mean square errors (RMSE) are 3.7 and 4.1 Mg/ha for the upland and lowland ecotypes, respectively. For the combined dataset correlation coefficient r=0.66, suggesting that slightly less than half of observed yield variability across all sites is captured in our model.

When these data are binned by nitrogen fertilizer application rate (Fig. 3.2c) we see that the model is able to capture general trends in switchgrass productivity with increasing management intensity. In contrast, yield response to land quality was more ambiguous. Neither measured nor modeled yields exhibited a clear relationship with soil texture across the full parameterization and validation dataset (Fig. 3.2d), and the weak trend towards lower field trial yields at sites with higher NLCD land capability class rating was not replicated in our model (Appendix A Fig. A.12).

Field trial data on greenhouse gas balance were sparser, and the results presented in Fig. 3.2b reflect our parameterization dataset rather than an independent validation. Observed changes in SOC under switchgrass were much larger than measured growing season nitrous oxide emissions when compared in CO_2-equivalent terms. The within-sample RMSE for each type of GHG and the combined dataset are all < 0.5 $MgCO_2eq\ ha^{-1}\ y^{-1}$, and the combined correlation coefficient r=0.79 suggests that the model is capturing > 60% of the variation in these 19 GHG flux measurements covering a wide range of sites, climates, and nitrogen application rates (Figure 3.1). To the extent that the model tends to err in the direction of overestimating N_2O and underestimating SOC accumulation, resulting predictions of switchgrass GHG balance are somewhat conservative. Additional detail on SOC and N_2O performance is available in Appendix A Fig. A.14 and A.15.

3.4.2. Landscape analysis case study

Simulated lowland switchgrass yields as a function of nitrogen fertilizer application rate across the 3779 unique DayCent strata in the Hugoton case study area are shown in Fig. 3.3a (cropland conversion) and 3.3b (rangeland conversion). The maximum attainable yield under arbitrarily well-fertilized conditions shows significant variation with soil texture, ranging from >10 Mg/ha in certain clay and sandy soils down to ~6 Mg/ha in the more moderate texture silty soils. In this semi-arid climate of intermittent precipitation events, soil moisture levels are often near wilting point, and simulated average yields reflect a tension between the greater total water holding capacity of finer-textured soils (an advantage during relatively wet years) versus more effective infiltration and less surface soil evaporation in coarser soils (the so-called 'inverse texture effect', beneficial during dry years; Noy-Meir, 1973; Epstein *et al.*, 1997; Lane *et al.*, 1998). At low fertilizer application rates, switchgrass yields are higher on converted rangeland than they are on converted cropland, presumably due to higher nitrogen mineralization associated with greater transient soil organic matter turnover following conversion. Full yield potential is generally realized at N rates from 60-100 kgN/ha.

When examining landscape assessment results under different levels of management intensity it is important to note a discrepancy between the metrics of ***total*** biogenic GHG balance ($MgCO_2eq$ per hectare per year) and the GHG ***intensity*** of biomass production ($MgCO_2eq$ per Mg biomass grown). Biomass production GHG intensity results are shown as a function of nitrogen application rate across all simulation strata in Fig. 3.3c and 3.3d. For most strata at most nitrogen fertilizer rates, 30 year-average soil carbon sequestration outweighs nitrous oxide emissions on a CO_2-equivalent basis. Biomass has the lowest (most negative) direct biogenic GHG footprint when cultivated with no nitrogen fertilizer on previously cropped fine-textured soils due to their high carbon accumulation potential. This sequestration value is increasingly offset at higher N rates due to marginal soil N_2O emissions outpacing yield and SOC gains. In contrast, rangeland has higher initial SOC levels and thus less capacity for carbon sequestration after conversion to bioenergy feedstock cropping, which results in an overall GHG balance much closer to zero.

Total biogenic GHG balance is explored in relation to productivity in Figure 3.4. Since the landscape can be managed either to optimize yields or to optimize soil GHG balance, we selected a random 10% of the landscape polygons (evenly distributed by latitude), determined the nitrogen application rate that maximizes yield and the rate that maximizes GHG sequestration for each polygon, and aggregate the results for these different management strategies across our landscape sub-sample. The difference between the two curves indicates the degree to which system productivity and GHG performance can be modulated by adjusting management on the same limited land base. Converting 10% of the landscape to switchgrass managed under either strategy results in > 0.75 Mt biomass feedstock production annually, enough material to supply approximately two facilities of the same capacity as the Abengoa biorefinery, with the associated net GHG impact of sequestering > 0.06 Mt (60,000 Mg) of CO_2. Fig. 3.5 illustrates that the switchgrass management intensity associated with highest GHG mitigation is related to the distribution of soil types and current land use across the case study area, parameters that are also correlated with one another.

Our modeled landscape productivity and GHG balance are highly sensitive to certain key crop model parameters, particularly moisture sensitivity, optimal growth temperature, and potential NPP (Table 3.4), highlighting the importance of careful parameterization and validation. Landscape characteristics are important as well, with GHG mitigation particularly sensitive to past land use history. Interestingly, landscape simulation results were highly insensitive to crop agronomic management assumptions beyond the rate of N fertilizer applied, with changes to establishment tillage intensity and fertilizer timing impacting results < 1%.

3.5. Discussion and Conclusions

3.5.1. Challenges of data-intensive model parameterization

This modeling study was grounded in an extensive switchgrass model development and validation effort based on a data-rich multi-criteria approach and partial automation of the parameterization process. The diversity of studies included in our switchgrass field trial dataset was intended to provide a highly general test of model performance independent of a single study, environment, or management level, and the simultaneous consideration of different types of data (Table 3.1) was designed to ensure that accuracy of one model performance criteria was never improved at the expense of others. This approach proved very useful for sorting out interrelated model responses. For example, parameters relating the belowground partitioning and root turnover rate typically receive little attention during the model parameterization process, but have large effects on aboveground biomass yield, SOC changes, and N_2O rates that must be balanced in a systematic manner. Our resulting model explains approximately half of the observed variability in yields and GHG observations in our dataset, and accurately captures responses to climate and management intensity. While soil type has been observed to have an effect on bioenergy grass productivity in semi-arid climates (Evers & Parsons, 2003; Di Virgilio *et al.*, 2007; o Di Nasso *et al.*, 2015; Roncucci *et al.*, 2015), we did not observe a strong texture signal in our switchgrass productivity dataset, consistent with a similar previous large-scale model parameterization effort (Wullschleger *et al.*, 2010). Future modeling work on soil-climate interactions would greatly benefit from additional field trails like Wilson *et al.* (2014) that include paired trails across multiple soil types on a landscape.

While we believe the approach presented here represents an improvement over more limited model parameterization efforts, it is still possible to over-parameterize a model to a dataset of this size and achieve good fits via unrealistic mechanisms that do not translate well out-of-sample. In our experience, reliable yield performance was only achieved once crop phenology was adequately captured. This parameterization dependency is somewhat challenging, as there are a limited number of studies in the literature reporting detailed phenology in the form required for this type of generalized modeling effort (i.e., dates for green-up and peak biomass as a function of crop cultivar and site latitude). Additionally, since maturation dates can vary significantly even for cultivars within a single ecotype (Frank *et al.*, 2004), focusing on only two ecotype groupings introduces additional errors. Accurate representation of phenology can be superseded to a certain extent by narrowing crop temperature response curves to truncate early and late-season productivity (e.g., Necpálová *et al.*, 2015), but our initial parameterization efforts in this direction performed very poorly on validation.

After several dozen parameter set iterations we were approaching the limit of what could be accomplished with manual changes, as model responses became more subtle and antagonistic across the different performance criteria. This, coupled with the relatively large number of model parameters to be determined, suggests that the process could benefit greatly from systematic parameter optimization techniques such as inverse modeling and/or k-fold cross validation. Such techniques provide a more systematic and transparent approach, facilitate maximum extraction of information from a field trial dataset, and help to identify and avoid over-parameterization issues. While inverse modeling techniques have been demonstrated to improve model performance against small datasets (e.g., Necpálová *et al.*, 2015), they have yet to be applied at the scale of the parameterization effort in this study.

3.5.2. Case study interpretation and climate accounting issues

The Hugoton case study site was selected because it featured the most heterogeneity in soils and current land use among the first three commercial-scale cellulosic biorefinery sites in the US (the other two being located in prime agricultural areas in Iowa; Peplow, 2014). However, the dry climate at this site is challenging from a biogeochemical modeling perspective, with landscape simulation results showing high sensitivity to interactions between crop moisture stress parameterization and soil texture, and with N_2O response to increasing N rate muted relative to what might be expected in a wetter climate. Overall, our landscape simulation results are similar to others in the literature that find the greenhouse gas balance of perennial grasses dominated by soil carbon sequestration immediately post-establishment, with modest N_2O emissions (e.g., Gelfand *et al.*, 2013). In field trials where baseline N_2O emission rates are reported and an IPCC-style calculation is possible, observed N_2O emissions rates are often near or below the 0.3% lower bound of the IPCC Tier 1 emissions factor range (Appendix A Fig. A.15). This suggests that switchgrass is an efficient nitrogen cycler, and that the critique of biofuel GHG mitigation benefits being outweighed by direct and indirect N_2O emissions (Crutzen *et al.*, 2008b) is likely overstated for second-generation perennial grass feedstocks. Our predicted SOC sequestration rates after cropland conversion are very similar to median meta-analysis results, while the finding of a small net positive sequestration with the conversion of grassland is consistent with, but on the optimistic edge of, the observed range (Qin *et al.*, 2015a).

Full quantification of the confidence interval around this landscape assessment is highly challenging due to multiple levels of uncertainty in problem specification, landscape input data, model structure, and model parameterization (Walker *et al.*, 2003). While previous work has shown that uncertainty in DayCent-estimated changes in SOC is driven primarily by model structural uncertainty (Ogle *et al.*, 2010), extending this empirical uncertainty assessment approach to the problem of bioenergy landscape design is impractical as only one of the 145 treatments in our parameterization and validation dataset includes data for all three of the factors that determine biomass GHG intensity (yield, SOC change, and N_2O; Fig. 3.1). Here we rely on sensitivity analysis to identify priorities for future model improvement efforts. When discussing model sensitivity and uncertainty issues it is important to be cognizant of issues in the underlying field trial datasets. Field measurements of N_2O are very challenging due to emissions variability on extremely fine spatial (Li *et al.*, 2013) and temporal (Jørgensen *et al.*, 2012; van der Weerden *et al.*, 2013) scales, and studies based on sampling at weekly or every-other-week frequency (as were all N_2O studies in our dataset) are vulnerable to systematic biases of up to 20% and 60%, respectively (Parkin, 2008; Smemo *et al.*, 2011). Additionally, small-scale field trials do not necessarily reflect imperfections in agronomic management (e.g. uneven fertilizer application) and real-world harvest losses, possibly introducing a systematic over-estimation of switchgrass productivity (Searle & Malins, 2014).

Finally, there are several issues around climate impact accounting relevant to this landscape study. While soil carbon sequestration will eventually attenuate even though N_2O emissions will persist for as long as N fertilizer is being applied (Sheehan *et al.*, 2003; Adler *et al.*, 2007), our assessment for this semi-arid system suggests it will take 60-80 years for annual sequestration and N_2O rates to reach parity (SI Fig. 17). A more dynamic climate impact accounting approach that takes transient forcing benefits into account (Holtsmark, 2015) would tend to further weight near-term benefits against future emissions, though significant questions about how best to implement such accounting remain (United States Environmental Protection Agency, 2014). The current study is also somewhat limited in treating the climate impacts of biomass feedstock production from a purely biogeochemical perspective, ignoring potential biophysical impacts such as changes in surface albedo or feedbacks from changes in landscape-scale evapotranspiration and water dynamics that are likely significant in certain bioenergy production scenarios (Muñoz *et al.*, 2010; Georgescu *et al.*, 2011; Cherubini *et al.*, 2012; Caiazzo *et al.*, 2014). Additionally, future changes to atmospheric CO_2 concentrations and climate are not considered here, though they may have large repercussions for landscape design (Bryan *et al.*, 2010). The ability of current ecosystem models to accurately extrapolate to such future conditions is an active area of investigation (De Kauwe *et al.*, 2013). Additional sensitivity analysis on these points would improve our understanding of bioenergy landscape performance potential, and highlight priorities for future research efforts.

Table 3.1. DayCent switchgrass crop parameterization and validation and data sources

Parameter types	Data sources	# treatments
Parameterization		
Aboveground biomass yield	Ma *et al.*, 2001; Fuentes & Taliaferro, 2002; Vogel *et al.*, 2002; Pearson, 2004; Mulkey *et al.*, 2006; Schmer *et al.*, 2008, 2012; Nikièma *et al.*, 2011; Dohleman *et al.*, 2012; Follett *et al.*, 2012; Hong *et al.*, 2012; Kering *et al.*, 2012; Anderson-Teixeira *et al.*, 2013; Boyer *et al.*, 2013; Bonin & Lal, 2014; Pedroso *et al.*, 2014	98 (67 after filtering)
Soil organic carbon (SOC) changes	Ma *et al.*, 2001; Liebig *et al.*, 2008; Follett *et al.*, 2012; Anderson-Teixeira *et al.*, 2013; Bonin & Lal, 2014	18 (8 after filtering)
Soil nitrous oxide (N_2O) emissions	Nikièma *et al.*, 2011; Hong *et al.*, 2012; Schmer *et al.*, 2012; Smith *et al.*, 2013	9
Seasonal aboveground & belowground biomass accumulation, and/or C/N ratio	Frank *et al.*, 2004; Dohleman *et al.*, 2012; Anderson-Teixeira *et al.*, 2013	3
Phenology	Sanderson, 1992; Hopkins *et al.*, 1995; Sanderson *et al.*, 1997; Berdahl *et al.*, 2005; Casler *et al.*, 2007; Wang *et al.*, 2013a	NA
Productivity response to temperature	Balasko & Smith, 1971; Hsu *et al.*, 1985; Reddy *et al.*, 2008; Kandel *et al.*, 2013; Wagle & Kakani, 2014	NA
Productivity response to soil moisture	Xu *et al.*, 2006	NA
Independent validation		
Yield	Staley *et al.*, 1991; Muir *et al.*, 2001; Cassida *et al.*, 2005; Adler *et al.*, 2006; Fike *et al.*, 2006; Arundale *et al.*, 2014b; Wilson *et al.*, 2014	49 (44 after filtering

Table 3.2. Summary of spatial data inputs

Spatial database	**Data type**	**Year**	**Native resolution**	**URL**
SSURGO	Soils	2012	1:12,000 to 1:63,360	http://www.websoilsurvey.nrcs.usda.gov
NARR	Daily weather	1979-2010	32 km	www.emc.ncep.noaa.gov/mmb/rreanl
NLCD	Land use	2006	30 m	http://www.mrlc.gov/nlcd2006.php
MIrAD-US	Irrigation extent	2007	250 m	http://earlywarning.usgs.gov/USirrigation/
Federal Lands of the United States	Federal land ownership	2005	640 acres/ 1 mi^2/ 1:2,000,000	http://nationalmap.gov/small_scale/mld/fedlanp.html

Table 3.3. DayCent switchgrass crop parameter changes

Type of parameter change	Parameter name	Original value	Lowland value	Upland value
Productivity potential & temperature response: Increase in productivity to reflect updated solar radiation model and compensate for increased belowground partitioning; differentiation in productivity and temperature response between upland and lowland ecotypes	PRDX(1)	2.75	4*	3.5*
	PPDF(1)	30	30	
	PPDF(2)	45	44	
	PPDF(3)	1	0.75	
	PPDF(4)	2.5	2	
Growth response to moisture stress: Reduced sensitivity to soil moisture stress.	CWSCOEFF(1,1)	0.38	0.35	
	CWSCOEFF(1,2)	9	14	
Belowground partitioning: Reduction in baseline BG partitioning rate. BG partitioning in response to moisture stress reduced, but response to nutrient stress increased.	CFRTCN(1)	0.5	0.7	
	CFRTCN(2)	0.3	0.25	
	CFRTCW(1)	0.6	0.4	
	CFRTCW(2)	0.3	0.25	
Tissue N & lignin content: Root maximum allowable C:N ratio lowered slightly. Root lignin content reduced. Small amount of N fixation added to make growth under no-fertilizer conditions more realistic.	PRBMX(1,1)	55	50	
	FLIGNI(1,2)	0.26	0.06	
	FLIGNI(1,3)	0.26	0.13	
	SNFXMX(1)	0	0.005	
Tissue death rates: Death rate and fall rate for shoots increased. Root maturation rate increased, and turnover rate of both juvenile and mature roots increased.	FSDETH(3)	0.05	0.075	
	FALLRT	0.01	0.1	
	CMXTURN	0.12	0.3	
	RDRJ	0.4	0.72	
	RDRM	0.2	0.54	
N conservation: Increased translocation of nitrogen from shoots to roots during senescence.	CRPRTF(1)	0.15	0.43	

*change in the PRDX(1) values also reflects a recent change in the DayCent model to simulate atmospheric transmission losses of photosynthetically active radiation

Table 3.4. Sensitivity analysis

Parameter or assumption	**Change**	**Change in total landscape productivity**	**Change in total landscape GHG mitigation**
Baseline average landscape performance			
Yield = 6.90 Mg ha^{-1} $year^{-1}$ GHG mitigation = 1.29 Mg CO_2eq ha^{-1} $year^{-1}$			
DayCent crop parameterization			
Moisture sensitivity	Switch to the curve associated with the lowland ecotype	+59%	+94%
Optimal temperature	Increase PPDF(1) by 3 degrees	-20%	-31%
Productivity potential	Decrease PRDX(1) value by 10%	-9.4%	-14%
Root death rates	Decrease RDRJ and RDRM by 10%	+0.0012%	+0.14%
Site characterization			
Land use history	Assume a uniform cropped history rather than a mix of cropped & grazed (82)	+0.060%	+31%
Climate	Assume the NARR weather for Hugoton for the entire 7-county study area	-9.0%	11%
Agronomic management			
Fertilizer date	Assume fertilizer application one month earlier	-0.030%	-0.70%
Tillage intensity	Switch to no-till crop establishment	-0.032%	-0.60%

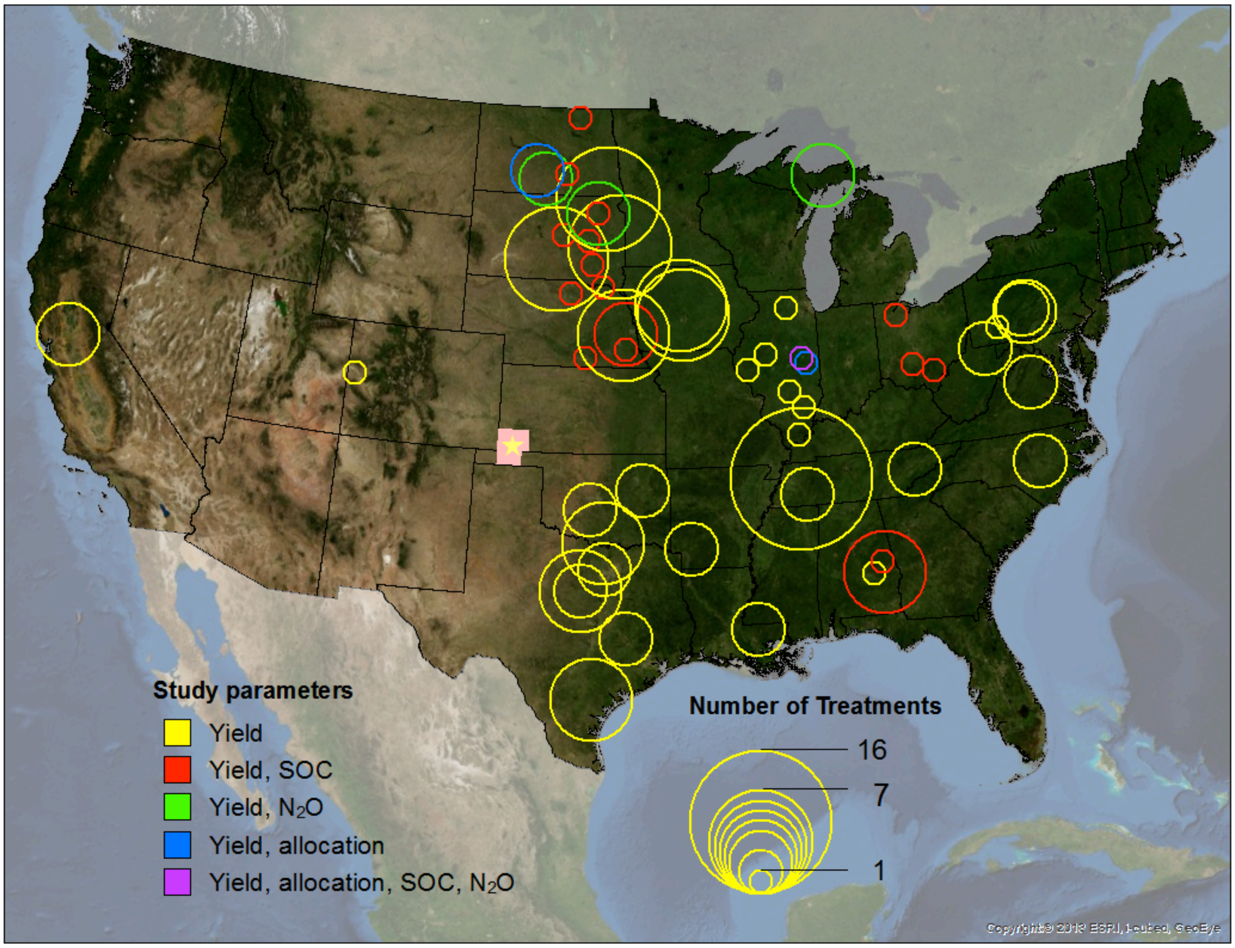

Figure 3.1. Map of all switchgrass field trial sites included in the full model parameterization and validation dataset prior to ecotype/latitude filtering. Ring size indicates the number of experimental treatments (e.g., different ecotypes or nitrogen fertilizer application rates) conducted at that site, and color represents the types of data available. The 7-county case study area is highlighted in pink, with a star designating the biorefinery location.

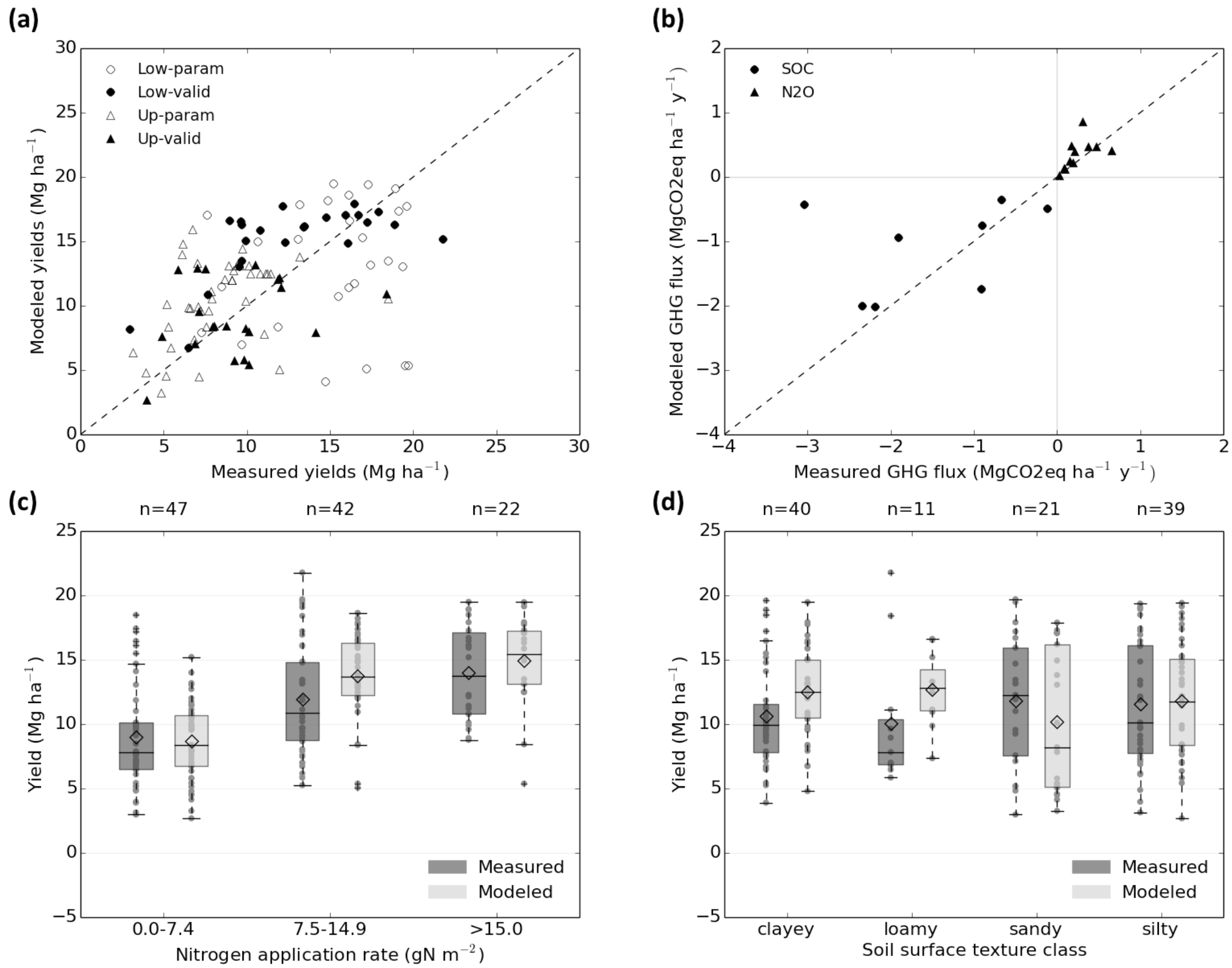

Figure 3.2. Parameterization and validation results: (a) modeled-versus-measured switchgrass biomass yield fits for lowland ecotype within-sample (‘Low-param’, r=0.10, root mean square error=6.2 Mg/ha) and out-of-sample (‘Low-valid’, r=0.66, RMSE=4.1) field trial results and upland ecotype within-sample (‘Up-param’, r=0.38, RMSE=4.0) and out-of-sample (‘Up-valid’, r=0.26, RMSE=3.7) results (combined r=0.46, RMSE=4.6); (b) modeled-versus-measured annualized changes in soil organic carbon (r=0.08, RMSE=0.43 $MgCO_2eq\ ha^{-1}\ y^{-1}$) and growing season N_2O emissions (r=0.54, RMSE=0.48) on a CO_2-equivalent basis (combined r=0.79, RMSE=0.46); (c) measured and modeled switchgrass yield ranges for different levels of nitrogen application rates across all parameterization and validation data points; and (d) measured and modeled switchgrass yield ranges for different soil surface texture classes across all parameterization and validation data points.

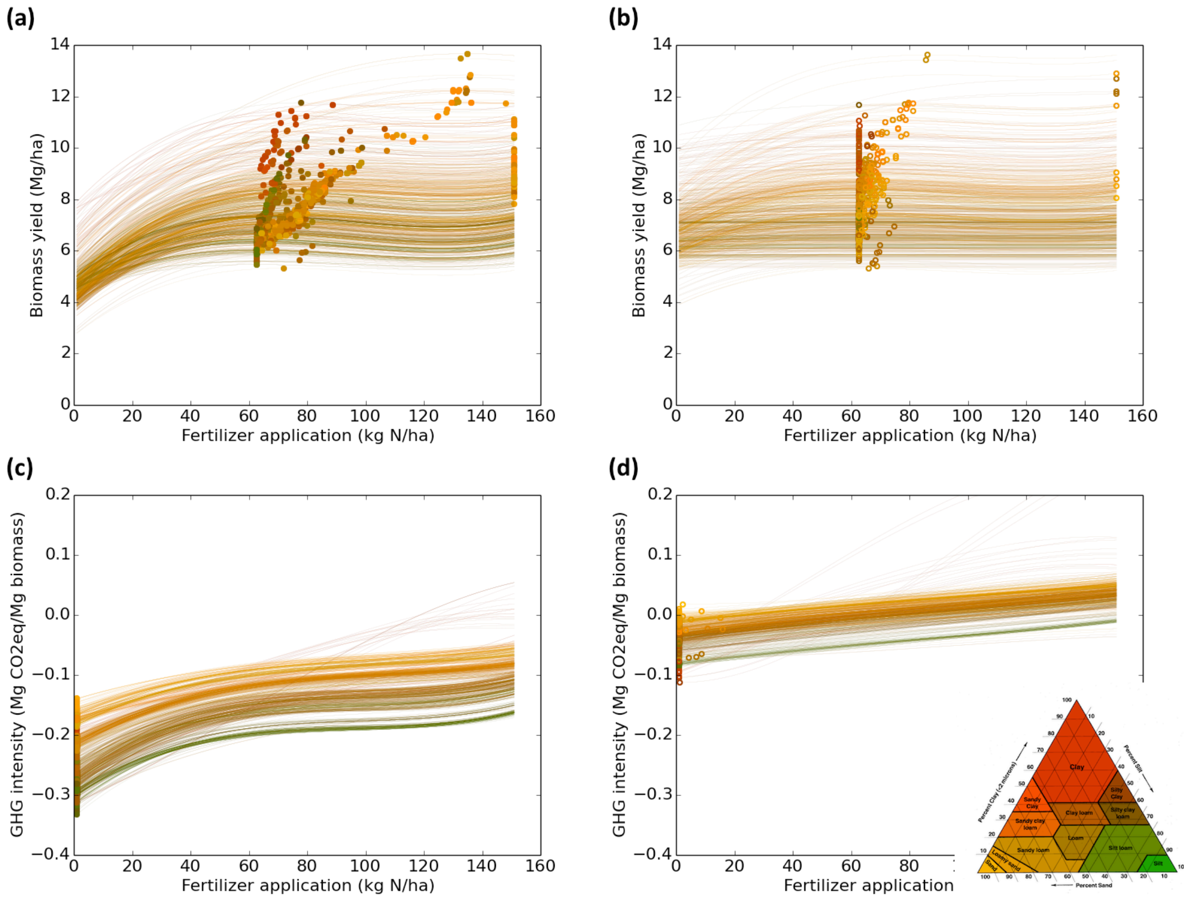

Figure 3.3. Simulated response to increasing nitrogen fertilizer rate of switchgrass yields with (a) crop land and (b) rangeland conversion as well as soil GHG flux intensity after crop land (c) and rangeland (d) conversion across the 3779 distinct DayCent strata in the case study landscape. Interpolated yield maxima and GHG intensity minima are marked with solid markers for cropland conversion and open markers for rangeland conversion. The color of the lines and markers indicates the soil surface texture of the strata as per the texture triangle key.

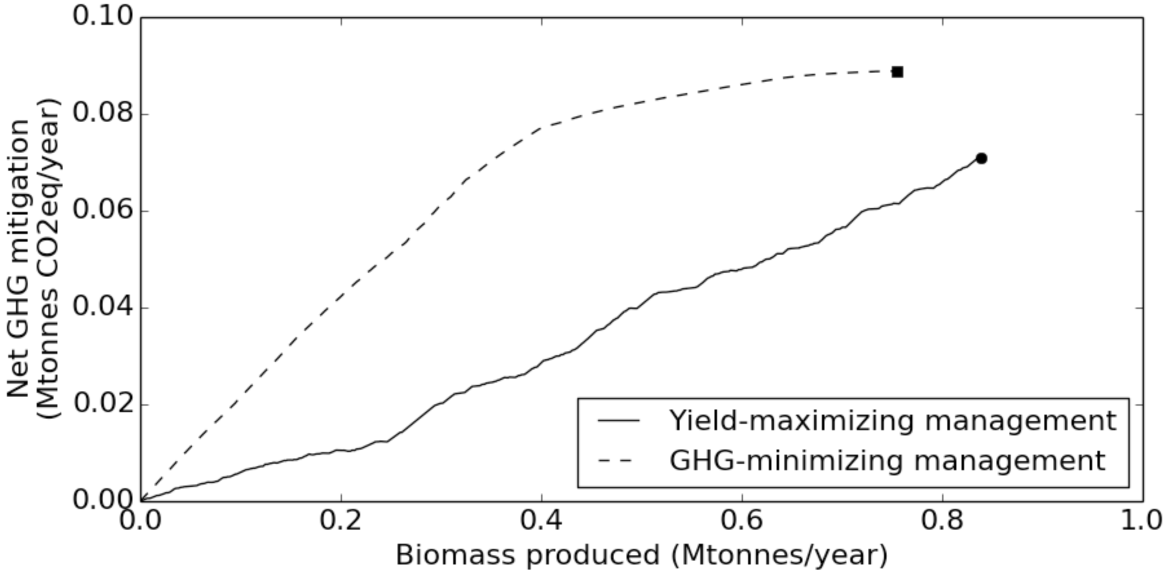

Figure 3.4. Cumulative total soil GHG mitigation versus cumulative switchgrass biomass production for a random 10% of the case study landscape under different management goals: managing each land parcel to maximize switchgrass yields (dashed line, highest-productivity sites aggregated first), or managing each land parcel to maximize ecosystem GHG mitigation (solid line, strongest mitigation sites aggregated first).

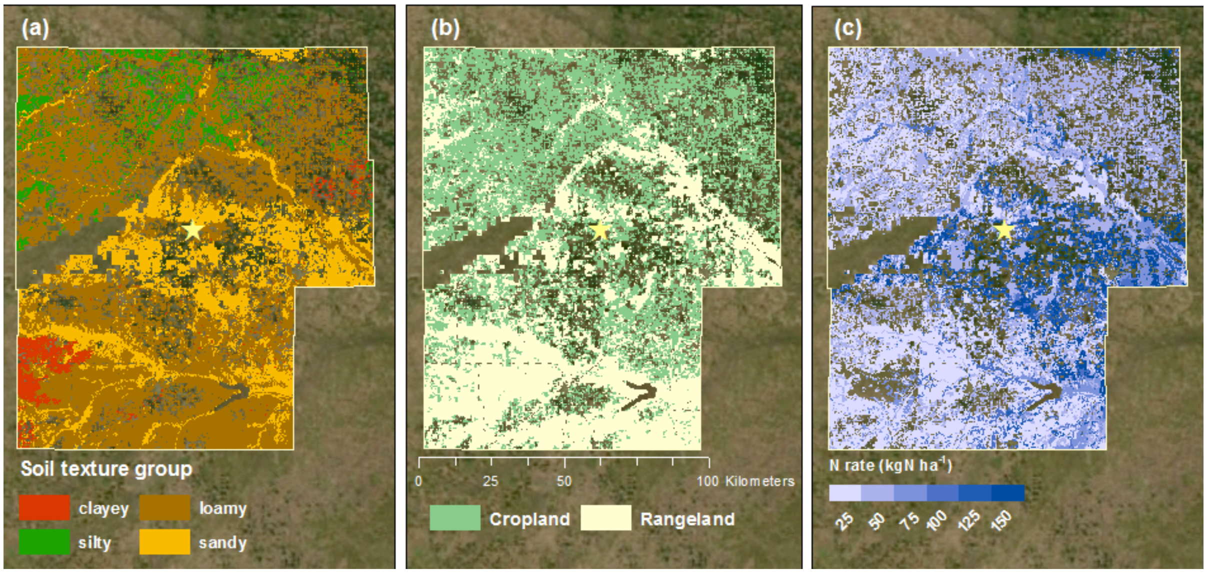

Figure 3.5. Map illustrating (a) soil texture distribution, (b) current land use, and (c) the switchgrass nitrogen fertilizer application rates associated with maximum soil GHG mitigation, for all non-federal non-irrigated cropland and rangeland across the Hugoton case study area. Aerial imagery is included as a background layer for scale, and the boundary of the 7-county case study area is shown in white with the biorefinery location marked with a yellow star.

CHAPTER 4

HIGH-RESOLUTION ASSESSMENT IDENTIFIES LOW COST MITIGATION OPPORTUNITIES IN BIOENERGY LANDSCAPES

4.1. Summary

Meeting current biofuel mandates or creating future carbon-negative biopower systems (Fuss et al., 2014; Sanchez et al., 2015) requires feedstocks be sourced in sufficient quantities at low cost and with minimal environmental impact. Cultivating perennial grasses on low-quality lands is a promising feedstock supply strategy minimizing on-site impacts and leakage effects (Robertson et al., 2008; Tilman et al., 2009; Perlack & Stokes, 2011), though questions remain around the identification of most suitable lands, the productivity potential on marginal sites (Shield et al., 2012), and the cultivation intensity that best balances non-linear yield responses and soil greenhouse gas (GHG) footprints (Anderson-Teixeira et al., 2012; Davis et al., 2013). In this work, fine-scale biogeochemical modeling was integrated with crop production budgets, a biomass transport model, a lifecycle assessment framework, and a multi-dimensional optimization routine in order to explore tradeoffs between production costs and GHG mitigation for switchgrass cultivation across a heterogeneous real-world bioenergy landscape. We find that biomass cost and GHG footprint are significantly affected by land use change and management intensity choices; that system design heuristics based on minimizing biomass collection radius have limited value; and that initial Biomass Crop Assistance Program-supported plantings in our case study area are likely located sub-optimally.

4.2. Introduction

4.2.1. Bioenergy landscape design considerations

The Renewable Fuel Standard (RFS2) established by the Energy Independence and Security Act of 2007 (110th Congress of the United States, 2007) established a variety of design priorities and constraints for future cellulosic biofuel production systems in the US. The high mandated blend levels imply that large amounts of biomass be sourced at low costs, for which the cultivation of dedicated bioenergy crops (DBC) will likely be required (Perlack *et al.*, 2005; Perlack & Stokes, 2011). The prohibition against feedstock production on previously uncultivated land removes agricultural extensification as a potential supply strategy, though still leaves the door open to production on otherwise marginal, degraded, or abandoned lands (Campbell *et al.*, 2008). Perhaps most novel, the imposition of lifecycle greenhouse gas emission reduction thresholds requires that supply chains be designed in such a way as to minimize emissions from supply chain energy use as well as biogenic emissions from feedstock cultivation. It is unclear where on existing agricultural landscapes DBC will best fit, or how intensively those crops might be managed (Davis *et al.*, 2013). While surveys can be useful in identifying the most promising candidate lands for conversion (Rizzo *et al.*, 2014), a variety of logistic, economic, and lifecycle assessment modeling tools are necessary to investigate the practical viability of potential system designs and their RFS2 compliance. These design tools highlight a variety of competing and contradictory system design priorities.

Since biomass is a relatively low density material and is subject to degradation without careful handling or pretreatment, minimizing transport distances and storage times is a priority in any biomass supply chain design (Hess *et al.*, 2009; Inman *et al.*, 2010). Intensive feedstock production on a limited land base in close proximity to the receiving biorefinery has the co-benefits of controlling per-unit-mass supply chain costs (Ebadian *et al.*, 2014) and emissions, and minimizing potential indirect land use change effects (Sheehan, 2009). Multiple studies in the literature attempt to identify biomass collection areas which balance the marginal costs of biomass transport against the economies of scale of conversion facilities, treating biomass productivity as uniform across the landscape, and resulting in the oft-cited system design heuristic of a 30-50 mile maximum biomass collection radius (Aden *et al.*, 2002; Kumar & Sokhansanj, 2007; Searcy & Flynn, 2009).

Crop production budgets must be developed for new DBC systems in order to understand associated biomass production costs. Keeping production costs low requires high area yields such that the fixed costs of tillage, seeding, pesticide application, etc. are spread out over a large amount of product. However, yields of even relatively hardy DBC such as switchgrass are sensitive to land quality (Mooney *et al.*, 2009; Shield *et al.*, 2012; Boyer *et al.*, 2013), yet the most productive prime agricultural lands carry high rental rates or opportunity costs of conversion associated with their potential for high-value food crop production. Thus, controlling biomass production costs requires identifying lands with limited value for conventional crops yet still capable of supporting reasonable DBC yields. Identification of such areas is often estimated using spatially-explicit biophysical models of crop performance, often ecosystem process models (Jain *et al.*, 2010, p. 201; Egbendewe-Mondzozo *et al.*, 2011; Yi *et al.*, 2011).

The biogeochemistry of feedstock production introduces an additional set of landscape design considerations (Robertson *et al.*, 2011). DBC systems based on perennial grasses are expected to out-perform first generation feedstock crops such as maize due to their longer growing season, high belowground carbon partitioning and sequestration potential (Anderson-Teixeira *et al.*, 2013; Qin *et al.*, 2015a), and efficient nitrogen cycling and low nitrous oxide emissions (Smith *et al.*, 2013). However, biogenic GHG emissions are highly sensitive to landscape factors, particularly soil type. While fine-textured soils have the greatest potential for carbon sequestration in soil organic matter (Six *et al.*, 2002), such soils are more prone to significant N_2O emissions, particularly via microbial-mediated denitrification in mesic and wet climates (Del Grosso *et al.*, 2000). Thus, feedstock production from the standpoint of GHG performance may be maximized on medium-textured (loamy) soils. Since productivity and ecosystem greenhouse gas balance vary strongly and non-linearly with ecosystem properties (climate, soil conditions, topography), ecosystem process models are typically used to extrapolate understanding of performance across the diversity of conditions encountered in a full commercial scale bioenergy system (Sheehan *et al.*, 2003; Thomas *et al.*, 2013; Robertson *et al.*, 2015).

Further complicating bioenergy landscape design is the strong interaction between land use choices and associated crop agronomic management requirements, the implications of which are so important to the GHG balance of bioenergy systems as to give rise to the term 'management swing potential' (Davis *et al.*, 2013). Nitrogen fertilizer application rate is an archetypical example. Adequate fertilizer rates are required to replace nutrient losses and maintain high area yields, but increasing N application leads to non-linear increases in nitrous oxide (N_2O) emissions through nitrification/denitrification processes (Hoben *et al.*, 2011; Shcherbak *et al.*, 2014) as well general air and water pollution through volatilization and leaching. The most economically rational application is likely higher than that which minimizes GHG footprint (Roth *et al.*, 2015), and both are highly sensitive to the underlying soil texture and climate.

4.2.2. Impact assessment for landscape optimization

The various system design imperatives summarized above imply that strategies or heuristics developed from a single disciplinary perspective or focused on a single performance criteria may have limited applicability. A more systematic approach to bioenergy landscape design requires integrated assessment studies in which various performance analysis tools are combined around a common set of biophysical assumptions or model results, and different system performance criteria balanced through a multi-objective optimization approach. This often involves determining system performance tradeoff curves or Pareto optimality frontiers, defined as the set of 'non-dominated' system designs for which performance on any criteria can only be improved at the expense of another criteria (You *et al.*, 2012; Herrmann *et al.*, 2014; Yu *et al.*, 2014). The curvature of such a frontier dictates whether meeting competing system performance goals is an 'either-or' proposition (a concave tradeoff curve), a 1-to-1 (linear) tradeoff, or whether there are synergies in which compromise solutions can achieve much of the maximum potential performance on each criteria simultaneously (convex curve).

There are several examples of such techniques being applied to balance productivity against various categories of environmental impacts in bioenergy landscape design. Zhang *et al.* (2010) used the EPIC biogeochemistry model to simulate productivity of first- and second-generation bioenergy feedstock crops in southwestern Michigan as well as associated biogenic GHG emissions and water quality impacts from nitrate leaching. Using a genetic algorithm optimization approach, they found a strong tradeoff wherein doubling total feedstock production on the landscape could completely erode the baseline GHG mitigation value from soil carbon sequestration. Similarly, Wu *et al.* (2012) used a combination of the SWAT hydrology and EPIC biogeochemistry models to assess productivity and water quality impacts of transitioning land in a large river drainage in the northern Great Plains to switchgrass production, ranking the most appropriate land parcels for conversion based under different system performance priorities. They found a high degree of convexity in the resulting tradeoff curve, i.e., that carefully backing off to only ~3/4 of total potential landscape production could reduce water quality impacts to only ~1/4 of what they would be at maximum production. Sims *et al.* (2014) take a similar analytic approach to a very different biomass system, using a mountain pine beetle dispersion model to estimate that proactively harvesting beetle-vulnerable pine stands could actually lead to a win-win outcome for northern Colorado in which both timber production and the number of surviving trees increase due to a reduced spread of beetle infestation.

When applied to assessments with both cost and GHG mitigation components, such tradeoff analysis and optimization techniques can help to quantify the lowest-cost opportunities for reducing GHG emissions through various supply chain modifications or substitutions. Dwivedi *et al.* (2015) pair county-level yield estimates for first- and second-generation bioenergy feedstock crops with GREET estimates of supply chain emissions and DayCent modeling of biogenic emissions, determining that the price premium of biofuels over conventional gasoline leads to GHG mitigation at an overall abatement cost equivalent of \$48/MgCO_2eq. Digging deeper into the design of individual biofuel supply chains, You *et al.* (2012) combined county-level feedstock yield estimates with detailed supply chain and conversion system models to determine the potential costs and GHG mitigation associated with cellulosic biofuel production in Illinois, using a mixed-integer linear programming approach to identify several areas for low-cost improvements in overall system GHG performance. Similarly, (Yu *et al.*, 2014) studied the siting of switchgrass biofuel facilities in Tennessee using county-level estimates of land productivity, DayCent simulations of CO_2 and N_2O emissions associated with different land use changes, and a detailed switchgrass harvest and transport logistics model. Their mixed-integer optimization approach generates a highly convex tradeoff frontier indicating great potential for low-cost GHG performance improvement based on careful selection of the type of land being converted to switchgrass.

In summary, a variety of studies have attempted to assess the potential environmental and economic tradeoffs encountered when large-scale DBC cultivation is integrated into existing agricultural landscapes, using combinations of different ecosystem, logistic, and economic models. Most identify significant system design tradeoffs at various points in the supply chain. In order to adequately address the different system design priorities outlined above, a landscape design study should, ideally: a) consider crop – land quality – management intensity interactions on yield and biogenic emissions at relevant spatial scales; b) integrate such results with estimates of crop production costs, biomass harvest and transport logistics, and lifecycle assessment tools in order to fully represent and ecosystem – supply chain tradeoffs; and c) include all relevant policy constraints.

4.3. Methods

4.3.1. Scenarios and crop simulation

We performed an integrated landscape assessment and optimization case study considering the establishment of switchgrass (*Panicum virgatum*) to supply feedstock for a newly-constructed 25 million gallon per year cellulosic ethanol biorefinery in southwestern Kansas (Peplow, 2014). The analysis area comprised 7 counties surrounding the facility, including Stanton, Grant, Haskell, Morton, Stevens, and Seward counties in southwestern Kansas and Texas County in the Oklahoma panhandle. We used the DayCent ecosystem model (Parton et al., 2001; Del Grosso et al., 2011) to perform point simulations of biomass productivity and net soil CO_2 and N_2O fluxes. The model was parameterized and validated against a large composite switchgrass field trial dataset as described in Chapter 3. Spatial databases used to initialize and run DayCent include the Natural Resource Conservation Service's Soil Survey Geographic database (Ernstrom & Lytle, 1993), the North American Regional Reanalysis climate database (Mesinger *et al.*, 2006), the National Land Cover Database 2006 (Wickham *et al.*, 2013), and the MIrAD-US irrigation database (Pervez & Brown, 2010), as well as proprietary coverages representing Conservation Reserve Program (CRP) and Biomass Crop Assistance Program (BCAP) enrollments. The landscape analysis considered the conversion of non-irrigated cultivated land, CRP areas, and uncultivated rangelands (shrub and herbaceous cover) to switchgrass; federally-owned areas and irrigated cropland were excluded from the analysis. The GIS intersection of these various input layers yielded 39,320 polygons of various sizes (Appendix B Fig. B.2) which encompass 3779 eligible unique DayCent simulation strata.

DayCent was initialized and historical land use simulated with the same methods used in the EPA Inventory of U.S. Greenhouse Gas Emissions and Sinks (US EPA, 2014b) as described in detail in Ogle *et al.*, (2010). We modeled all (non-irrigated) cultivated land with a winter wheat-fallow (WF) rotation and uncultivated areas as a 50:50 C3 & C4 temperate grass mix subject to continuous low-intensity livestock grazing. We assumed that CRP lands transitioned from WF to un-grazed grass in 1990. From 2015 we performed 30-year forward scenarios for each strata considering business-as-usual (BAU) land management versus conversion to switchgrass at seven different levels of nitrogen fertilizer rate (0-150 kgN/ha in the form of ammonium nitrate), re-using 30 years of NARR historic weather data and assuming tilled establishment. Simulations were executed in parallel across a 29-node, 288-processor cluster computing system at the CSU Natural Resources Ecology Laboratory, with model initiation and results processing automated in Python (https://www.python.org/). Yields and soil GHG fluxes were averaged across the duration of the forward simulation. Indirect nitrous oxide emissions (iN_2O) were estimated based on modeled leaching, nitric oxide emissions, and volatilization rates as per IPCC recommendations (Eggleston *et al.*, 2006). Landscape modeling details are described in detail in the previous chapter.

4.3.2. Farm production costs

Minimum break-even switchgrass farm-gate prices were estimated in the manner of Jain *et al.* (2010) considering the productivity-adjusted opportunity cost of land conversion from BAU uses (Appendix B Fig. B.4). For cropland, opportunity costs of land conversion were estimated as the net return calculated for WF using a local extension farm management guide (Dumler *et al.*, 2010) and DayCent-estimated BAU grain yield for each simulation strata. For rangeland, DayCent-estimated grazed biomass amounts were used to linearly adjust the average cash rental rate of pastureland in southwest Kansas (Dhuyvetter & Taylor, 2014) to generate a land conversion opportunity cost reflective of variations in land productivity. We estimated the opportunity cost of CRP conversion as the average county rental payment rate across the seven study area counties ($98.41/ha, United States Department of Agriculture, 2013) applied uniformly to all CRP areas. To estimate the enterprise costs of switchgrass production, the detailed switchgrass crop production budget from the USDA Future Agricultural Resources Model (Evans, 2012) was re-produced in Python. For each switchgrass management intensity scenario, the nitrogen rate, switchgrass yield, and opportunity cost of land conversion assumptions in FARM were updated, and farm-gate switchgrass break-even price estimated as the 30-year net present value of switchgrass production divided by the discounted switchgrass yields over the same period as per Jain *et al.* (2010), reflecting minimum supply cost to a biorefinery contracting with each individual supplier at a different price that reflects their unique production costs. As in Jain et al. 2010, all commodity prices besides switchgrass were treated as exogenous and static in the face of cropping changes within the case study area.

4.3.3. Transport distances and costs

We intersected our 39,320 landscape polygons against a 4 km x 4 km square grid in order to reduce the number of biomass transport distance calculations required. The geographic distance (as the crow flies) between the centroid of each grid cell and the case study conversion facility location was computed using the Haversine equation, from which the actual driving distance was estimated by multiplying by a constant tortuosity factor. Actual driving distances are estimated by multiplying the geographic distance by an empirical correction factor (tortuosity factor) that accounts for the typical geometry and continuity of local road infrastructure. To estimate an appropriate tortuosity factor, a set of ten latitude & longitude pairs were generated randomly across the case study area, and Google Maps (https://www.google.com/maps) was manually used to compute the shortest driving distance to the facility, with a factor of 1.45 found to be most representative of the road network in this area (Appendix B Fig. B.1). Associated trucking costs were estimated using the Trucking Cost Model from the University of Tennessee, Knoxville Forest Product Center (Norris, 2009), a simple model that does not consider dispatch and routing of individual trucks. We assumed default dry van settings with mileage adjusted to 5.3 mi/gal and payload to 50,000 lbs for consistency with GREET, a loading and unloading times of 45 minutes, a 30 min dwell time, and a driver labor rate of $15/hr. Transport cost as a function of one-way transport distance was then mapped to an exponential function integrated within our Python code. Associated GHG emissions were estimated by increasing the truck transport share distance in GREET as described in the following section.

4.3.4. Lifecycle assessment

The 2014 GREET.net model (https://greet.es.anl.gov/greet/index.htm) was used to make GHG performance estimates for the full biomass supply chain through the biorefinery gate under a consequential lifecycle assessment accounting approach (Brander *et al.*, 2009). The default GREET switchgrass production pathway was updated for consistency with the USDA FARM model as described in Appendix B. GREET well-to-pump biomass lifecycle GHG footprint results were mapped into our Python code as a function of nitrogen fertilizer input rate and DayCent-simulated crop yield, soil CO_2 and direct and indirect N_2O flux as compared to the BAU scenario, and biomass transport distance. The resulting GHG footprint estimates for each management intensity level in each DayCent strata reflect embodied emissions associated with all farm operations and inputs, ecosystem emissions associated with local management changes, and transport emissions.

In addition to these effects, the indirect leakage effect associated with the displacement of crop and forage production is explored through a basic indirect land use change (iLUC) penalty calculation. While the downscaling of iLUC estimates for use in regulatory settings is widely recognized as being problematic for both practical and theoretical reasons and highly sensitive to model assumptions (Babcock, 2009; Zilberman *et al.*, 2010, 2011; Warner *et al.*, 2013), a conservative approach to consequential GHG impact accounting demand that some estimate be made (Fritsche *et al.*, 2010). Furthermore, the estimate should be based on the quantity of commodity displaced rather than the land area converted, reflecting that conversion of low-productivity marginal lands is less disruptive to commodity markets (Dwivedi *et al.*, 2015). We took a conservative high estimate of the iLUC effect (34 gCO_2eq/MJ ethanol) from Wang *et al.* (2011), and related this back to the amount of grain consumed to produce a megajoule of ethanol, for a penalty of 323 gCO_2eq/kg corn consumed. The corn-equivalents of all wheat and grass displaced relative to our BAU scenarios were then estimated by applying the appropriate cattle feed equivalence ratios (1.03 and 1.9, respectively; Gadberry & Beck; Lardy, 2002), as this is a primary market for all these commodities in this part of the country. While a more comprehensive accounting would require shocking the specific commodities in question within a partial or general equilibrium global trade model, we believe that the simplified approach adopted here provides a conservative first-order accounting of the effect that can be readily operationalized.

4.3.5. Results integration and optimization

The resulting feedstock production cost and GHG mitigation estimates for each parcel at each level of management intensity were then integrated to generate Pareto frontiers representing the highest GHG mitigation at lowest costs that could be achieve while meeting the annual feedstock requirements of the biorefinery under a given set of system design or land conversion constraints. The multi-criteria optimization problem was solved through a simple weighted solution approach in which GHG emissions or mitigation were valorized based on a particular carbon price, and the combination of biomass production financial costs and GHG mitigation value (termed the 'total social cost' of production) minimized across the landscape. The process is detailed schematically in Figure 4.1. Prior to optimization, 30% of the parcels on the landscape were randomly selected as potentially eligible for conversion to switchgrass based on willingness-to-grow survey results for western Kansas (Fewell *et al.*, 2011).

4.4. Results

4.4.1. Landscape characterization

The land in the case study area is currently devoted to a variety of uses as shown in Figure 4.2. Approximately one third of the landscape is classifiable as non-irrigated cultivated land (cropland & hayland). Additional analysis using the Cropland Data Layer (Boryan *et al.*, 2011) suggests that winter wheat - fallow (WF) is the dominant rotation in these areas, though with significant presence of more intensive rotations featuring one or more crops of grain sorghum (e.g., WSF or WSSF). An additional 13% of the landscape is covered by Conservation Reserve Program easements, much of which is located in the corners around center-pivot irrigated fields. Federally owned lands (3% of the landscape) and irrigated areas (21%) were excluded from the analysis as inaccessible and unlikely to be profitable for conversion, respectively. The remainder of the landscape is classified as shrubland or herbaceous vegetation, and was modeled as lightly grazed rangeland in this assessment.

As illustrated in Figure 4.3, the distribution of land use across the case study landscape mirrors patterns in the distribution of underlying soils. The case study area features a wide diversity of soil textures ranging from silt loams to sands, with small pockets of fine-textured clays. Figure 4.4 shows the area-weighted distribution of soil surface textures within the various land use classifications. Crop and hay production both predominantly take place on silty loams, whereas rangeland and CRP are much more evenly distributed across the full range of soil types encountered on this landscape. Interestingly, BCAP enrollments are heavily skewed towards the coarsest soils on the landscape. The distribution of Natural Resources Conservation Service Land Capability Class (LCC) ratings within the different land use classes is shown in Appendix B Fig. B.3.

4.4.2. System performance tradeoffs under current policy

Landscape optimization results are shown for a variety of system design and land use change scenarios in Figure 4.5. Each point along a given Pareto frontier represents an optimal landscape design across three dimensions (two spatial dimensions and an additional management intensity dimension) balancing biomass production costs and GHG footprint based on a particular valuation of greenhouse gas emissions. While estimates of the optimal valuation of GHG emissions relative to the marginal damages that they cause (the so-called 'social cost of carbon') vary widely (Newell *et al.*, 2014), landscape solutions that correspond to the \$12-63/$MgCO_2eq$ range recommended by the US Interagency Workgroup on the Social Cost of Carbon (United States Government Interagency Workgroup on Social Cost of Carbon, 2010) are illustrated with a thick band. Several individual solutions A-F are selected for more detailed description as included in Fig. 5 and Appendix B Fig. B.5.

Solutions for the base case of RFS2-compliant land use conversion (i.e., conversion of previously-cultivated land only) are shown in blue. A range of potential feedstock cost and mitigation outcomes are possible depending on how heavily GHG mitigation is valued. When only costs are considered, the optimal landscape design consists of cropland and CRP conversion to switchgrass managed at moderate fertilizer rates (30-60 kgN/ha, detail A). This results in a biorefinery-gate switchgrass breakeven price of \$78/Mg. While cultivation of switchgrass under these conditions sequesters ~0.17 Mg CO_2 as soil carbon for every metric ton of switchgrass produced, this sequestration is offset by the combination of upstream emissions from the production of fertilizer and other farm inputs, on-farm energy use, soil nitrous oxide emissions, and emissions associated with biomass transport to the biorefinery, for a net GHG emission of ~0.05 $MgCO_2eq$ per metric ton of switchgrass produced.

As GHG mitigation is valued more and more heavily (detail B and C), optimization results suggest that less intensive production across a larger area base of cropland results in best performance. At the high end carbon valuation of \$250/$MgCO_2$, reduced N_2O emissions (lower that the BAU case) and increased soil carbon sequestration are observed, resulting in a net GHG mitigation of ~0.12 $MgCO_2eq$ / Mg switchgrass, though at an increased biorefinery gate breakeven price of \$86/Mg. In all cases, the optimal switchgrass cultivation locations are widely distributed across the entire case study area, with productivity-weighted average collection distances in the range of 63-66 km (Appendix B Fig. B.5).

4.4.3. System design considerations and strategies

The range of potential landscape performance outcomes when crop management is fixed at 50 kgN/ha (Fig. 4.5, orange curve) is much narrower, and always results in a positive net feedstock lifecycle GHG footprint (emissions > sequestration). This is consistent with the notion of the management swing potential of bioenergy feedstock crops (Davis *et al.*, 2013) and a strong location – management interaction. In addition, the fact that this curve is 'dominated by' (i.e., lies to the lower left of) the base case curve suggests that these solutions are sub-optimal when costs and emissions are considered together, and that modulation of fertilizer rates is a tool that rational producers would likely use to maximize their profitability.

While a 50 km maximum biomass collection radius is an oft-cited landscape design heuristic, our simulation results (red curve, detail D) suggest that this strategy results in landscape designs that are strongly dominated relative to the unrestricted base case. The maximum collection radius limits the exploitation of favorable production sites along the edges of the case study area and forces more intensive switchgrass production on cropland and greater cultivation of CRP land in order to meet the biorefinery feedstock requirement. This results in a production price premium of up to ~\$5/Mg or a GHG footprint increase of ~0.1 $MgCO_2eq/Mg$.

The strong concentration of BCAP enrollments on sandy soils across the landscape (Fig. 4.3) suggests that the pioneer switchgrass producers in this region are engaging in a strategy targeting conversion of lands with the least suitability for conventional crop production. However, these coarse soils accumulate organic matter much more slowly and require greater fertilizer inputs for a given level of production (grey curve, detail F). Our simulations suggest this will likely result in a much higher net GHG footprint and higher overall production costs, despite the lower opportunity costs of land conversion due to the lower BAU wheat productivity in these areas.

4.4.4. Policy constraints

In this particular landscape, the inclusion of an iLUC penalty term leads to only a small erosion of system GHG mitigation value (green curve) due to the relatively low output of the wheat – fallow crop production system being replaced by switchgrass cultivation. While it is possible that a more detailed commodity-specific iLUC assessment (see Methods section above) or an expansion of the BAU scenario to include consideration of the higher-yielding WSF and WSSF rotations on the landscape in the BAU scenario might result in a greater estimated iLUC effect, at present the inclusion or exclusion of this effect exerts minimal influence on our case study landscape design and performance.

The Renewable Fuel Standard excludes biofuels derived from feedstocks produced on previously uncultivated lands from counting towards the mandate in an attempt to limit pressure for agricultural extensification. Our analysis suggests that this policy can impose an important and binding constraint in bioenergy landscape development. The low opportunity costs associated with rangeland conversion coupled with reduced nitrogen fertilizer requirements due to higher background soil N mineralization levels suggests that these areas could be mobilized to produce switchgrass at up to $10/Mg more cheaply than on former croplands (purple curve, detail E). However, these areas will not experience any significant net increase in soil organic matter, resulting in worse overall GHG performance. Thus, the prohibition should tend to limit conversion that would be economically profitable but have reduced GHG benefits, and could be problematic from a biodiversity perspective (e.g., Evans *et al.*, 2010).

4.5. Discussion

While feedstock productivity and associated biogenic emissions of cultivation are central to the sustainability of any bioenergy supply chain, strong interactions between crop type, climate, soils, land use history, agronomic management, and harvest and transport logistics preclude simple generalizations about the most cost effective and most environmentally-friendly feedstock cultivation strategies. The methodology presented here attempts to untangle these effects via high-resolution process based modeling, simulating feedstock productivity, management options, and environmental outcomes while simultaneously considering practical implications for the feedstock producer. To our knowledge this is the first analysis to examine carbon abatement costs associated with bioenergy landscape design that fully endogenizes crop management while synthesizing both ecosystem and supply chain emissions. Our results suggest that simply minimizing biomass collection radius or targeting the most marginal land on the landscape for feedstock production are poor bioenergy system design heuristics that can lead to sub-optimal cost and GHG mitigation performance, insights that contradict conventional wisdom in this area.

The conclusion that landscape performance can be widely tuned based on the performance criteria considered is consistent with what other emerging landscape optimization studies have found (Zhang *et al.*, 2010; Wu *et al.*, 2012; Yu *et al.*, 2014). While previous studies have focused on the implications of different land use change scenarios (Yu *et al.*, 2014), our consideration of variable crop management intensity suggests that this is an equally important landscape design consideration, consistent with the management swing potential observation (Davis *et al.*, 2013). The richness of bioenergy landscape design tradeoffs identified in this case study is partly attributable to the underlying heterogeneity in the landscape around Hugoton

Kansas. The commercial-scale cellulosic biofuel facility there is unique in this regard, as the other two commercial-scale biorefineries in the US are located in Iowa (Peplow, 2014), a region much more homogeneous in soils and land use. It is left as future work to determine how the degree of underlying landscape heterogeneity affects the range of possible bioenergy system performance outcomes, as assessed across multiple case studies in different regions with different regionally-appropriate feedstock crops.

This quantification of GHG mitigation opportunities and associated costs in the feedstock supply chain is complementary to other GHG assessment efforts focusing on different aspects of the full bioenergy supply chain, for example the fuel conversion process (Bernardi *et al.*, 2012; Eason & Cremaschi, 2014) or the management of conversion co-products (Anex *et al.*, 2007; Field *et al.*, 2013; Pourhashem *et al.*, 2013; Woolf *et al.*, 2014). The strong observed feedbacks between feedstock sourcing, conversion facility siting and capacity, and the potential use of low-value conversion co-products as carbon-sequestering soil amendments suggest that a true 'global' optimization of any given bioenergy system is only possible when the analysis scope is expanded to include all such effects in tandem. Additionally, while we focus on costs and GHG mitigation in this study, this weighted solution method to the multi-criteria landscape optimization problem could easily be extended to water use or nitrate leaching for subsequent analyses (e.g., Wu *et al.*, 2012).

There are a number of analytical challenges associated with different aspects of this integrated assessment. While the performance of our ecosystem model across a wide range of climates and nitrogen fertilizer rates is well validated, the secondary effects of climate-soil interactions on crop yield remain difficult to rigorously parameterize and validate (Chapter 3). While our efforts specifically targeted switchgrass field trials on marginal lands from the literature, our final model parameterization and validation dataset still skewed heavily towards field trials on lands with LCC ratings of 2-3, i.e. areas with moderate to severe use limitations for cropping, whereas other perennial grass modeling studies have focused on LCC 5-7, i.e. non-arable areas restricted to use as pasture or rangeland or left unexploited (Gelfand *et al.*, 2013).

While we simulated ecosystem productivity and emissions at a high level of detail using a process-based model, our assessment takes a relatively simplistic approach to switchgrass biomass logistics, coupling estimates of harvest, bailing, and stockpiling costs and emissions from the USDA FARM and GREET models, respectively, with a non-dispatch distance-based transport model. Another recent switchgrass integrated assessment and optimization effort takes the opposite strategy, coupling a detailed custom model of switchgrass production logistics with a lower-resolution productivity estimates and ecosystem assessment (Wang *et al.*, 2013b; Yu *et al.*, 2014). Their results suggest that existing simpler approaches may underestimate the true costs and emissions associated with switchgrass biomass logistics. However, our conclusion that biomass collection radius is a relatively weak control on system cost and GHG performance is consistent with previous work suggesting that transport emissions are small in magnitude relative to biogenic emissions fluxes (Smith & Smith, 2000), and that total logistics costs and emissions are a weak function of system capacity for both conventional and depot-based feedstock supply chains (Argo *et al.*, 2013).

Our production cost estimates are highly detailed in considering land conversion opportunity costs as a function of simulated productivity at high spatial resolution. However, we assume a static cost model in which all input and commodity prices are fixed exogenous factors. While this is a reasonable assumption when considering a single biorefinery facility in isolation, the emergence of a more extensive bioenergy or biomaterials sector in the future would require a more dynamic economic assessment approach in order to estimate feedbacks on agricultural input and commodity prices as feedstock production extends to a greater share of the agricultural landscape. Economic partial equilibrium models can be integrated with spatially explicit ecosystem modeling efforts in order to make estimates of such market feedbacks (e.g., Cohn *et al.*, 2014), though this introduces a new range of challenges and uncertainties to the assessment effort (Warner *et al.*, 2013).

Finally, while the current analysis thoroughly investigated feedstock price - GHG mitigation tradeoffs, a next logical step would be to determine how much of the landscape could be devoted to bioenergy feedstock production before the impacts of increasingly intensive feedstock production offset the fossil fuel displacement value of the resulting biofuel. In order to make a credible estimate of the maximum GHG mitigation potential of a bioenergy production landscape our analytic approach would likely have to be expanded to consider: a) a more detailed biomass logistics model; b) conversion facility economies of scale and associated effects on facility energy use; c) a more dynamic economic model capability of assessing market price feedbacks; d) an estimate of the displacement ratio of gasoline by the finished biofuel (rebound effect); and e) tradeoffs on other system impact criteria such as biodiversity.

Table 4.1. Sensitivity analysis for total landscape GHG mitigation associated with a 25 MGY facility at a carbon valuation of $39/MgCO_2$

Parameter or assumption	**Change**	**Mitigation response**	**Delivered cost response**
Default values	-	0.041 Mg CO_2 / Mg biomass	$79.29 / Mg biomass
Ecosystem modeling			
Yield (switchgrass, wheat, grass) average	Uniform 10% increase	-7.3%	-3.4%
Soil GHG flux (CO_2, N_2O) average value	Uniform 10% increase	+120%	+0.34%
Crop production budget			
Farm input (chemicals, fuel, labor) prices	Uniform 10% increase	-4.9%	+7.5%
Wheat price	10% increase	-29%	+3.3%
Transport model			
Tortuosity factor	10% increase	-7.3%	+0.4%

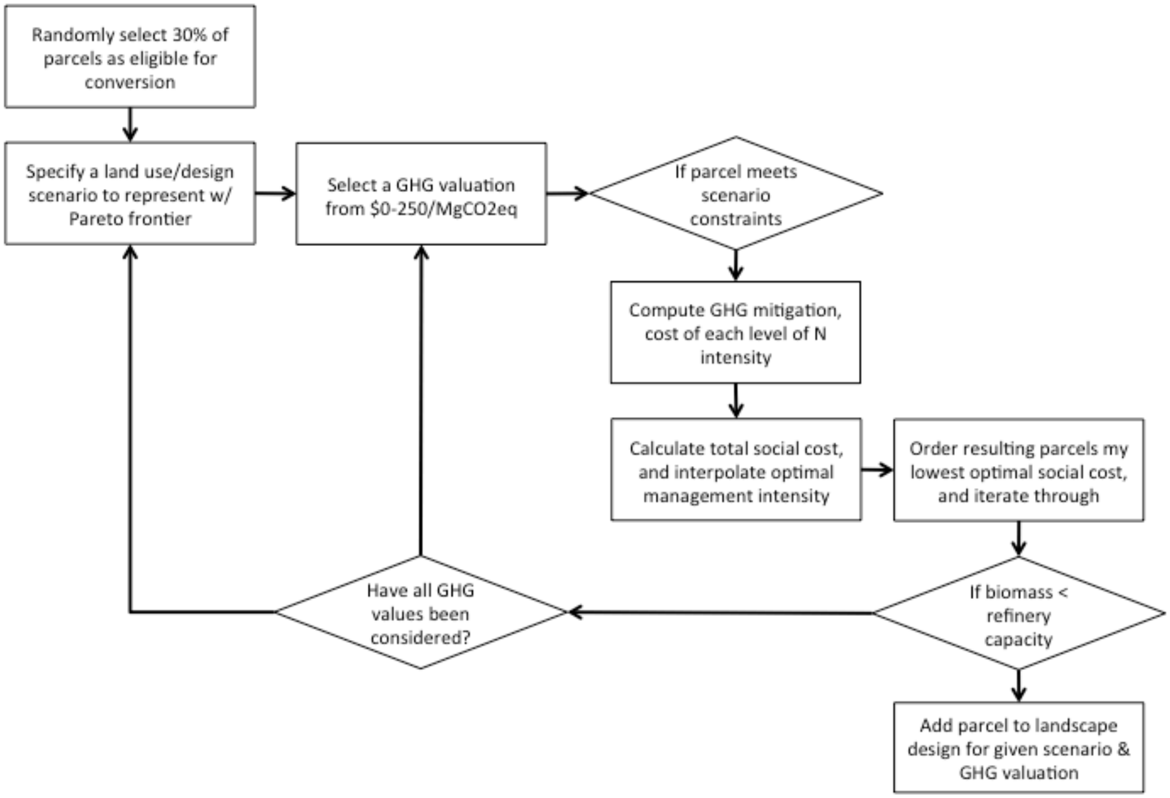

Figure 4.1. Landscape optimization sequence.

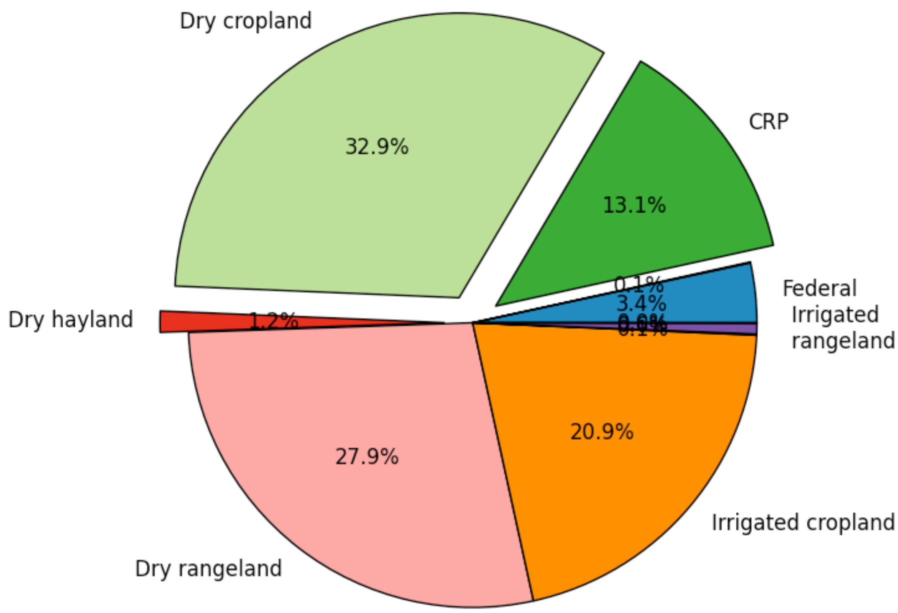

Figure 4.2. Current land use distribution across the 7 county case study area. Land types shown with exploded view are the primary focus of the assessment due to their RFS2 compliance and/or likelihood of conversion.

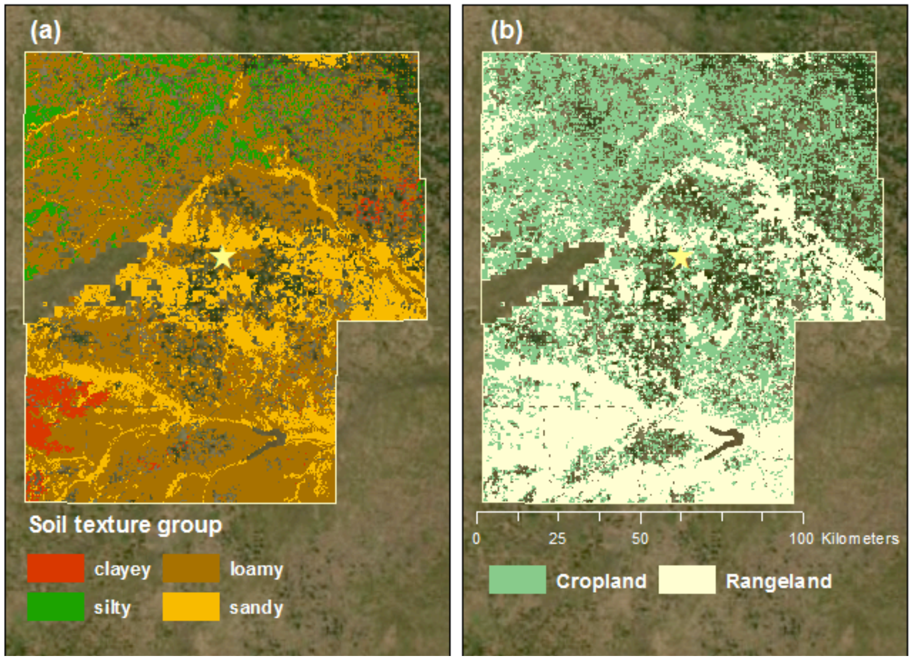

Figure 4.3. Case study area showing a) soil surface texture and b) current land use, with federal and irrigated land excluded. Case study cellulosic biorefinery location is marked at center.

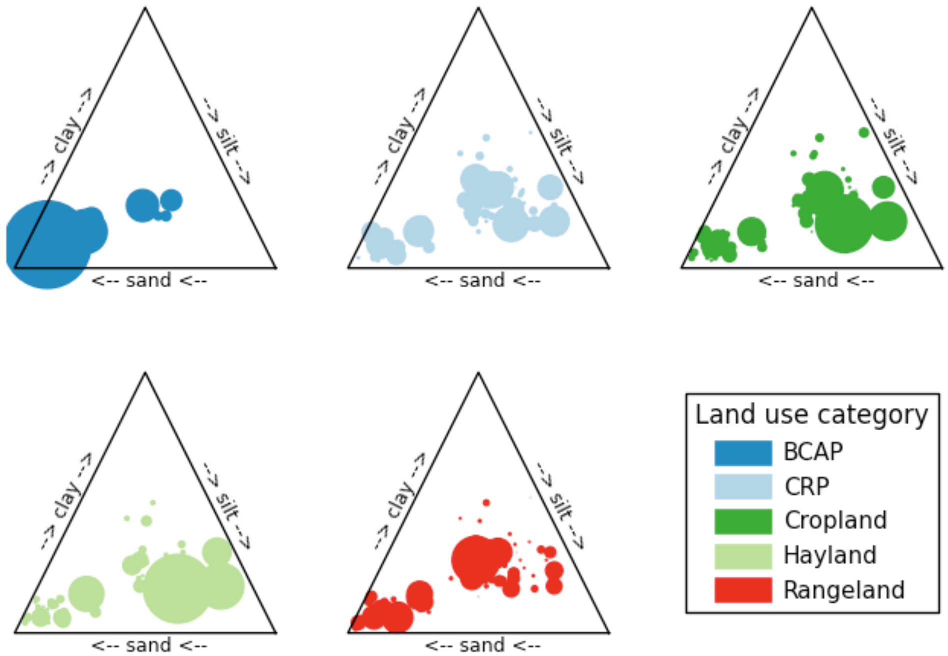

Figure 4.4. Area-weighted soil surface texture distribution by land use class, including land enrolled in Conservation Reserve Program (CRP) easements or the Biomass Crop Assistance Program (BCAP).

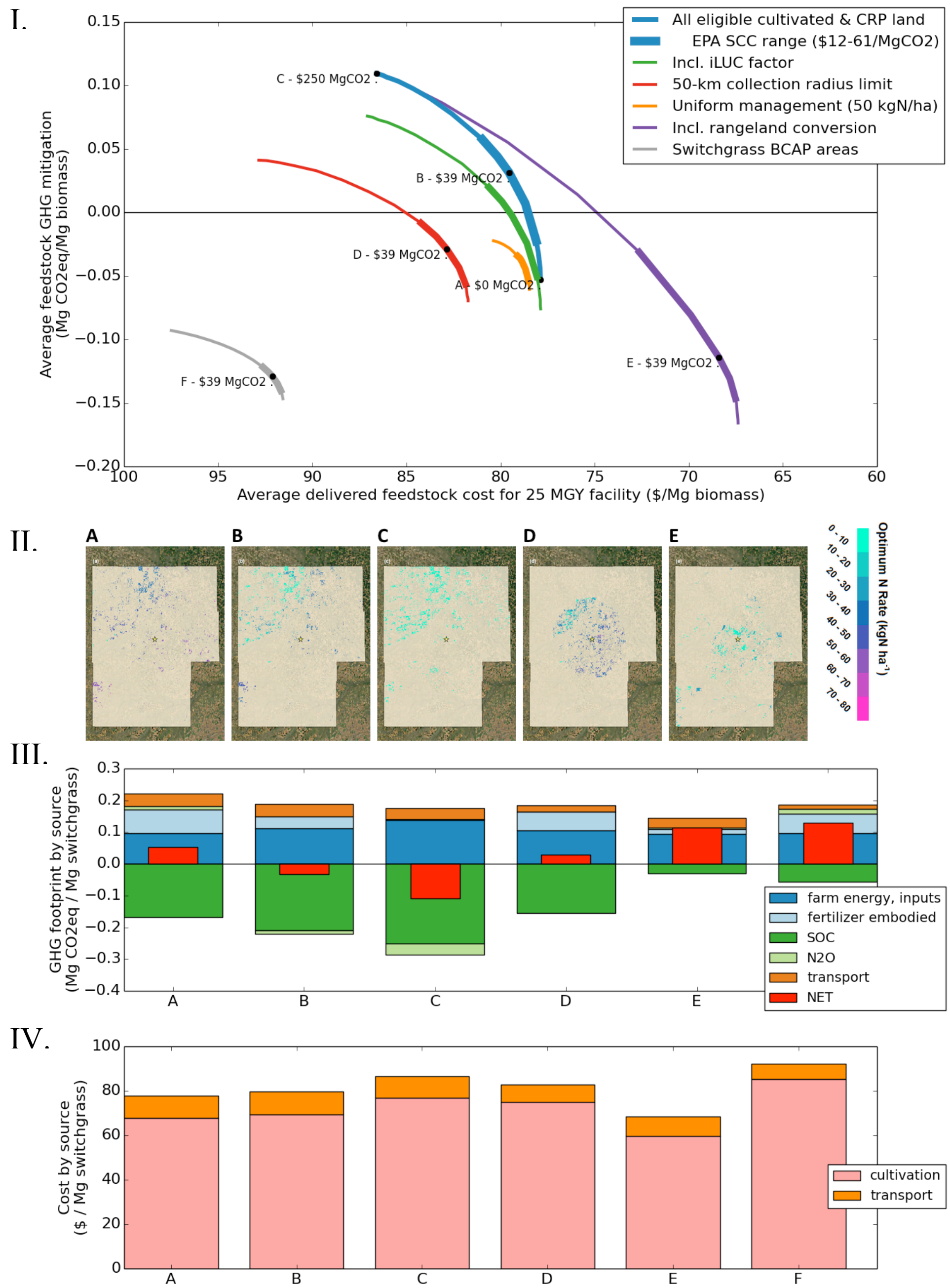

Figure 4.5. Optimal landscape performance under different design strategies and policy constraints. I. Pareto frontiers showing maximum landscape GHG mitigation and minimum average delivered feedstock cost to supply a 25 MGY facility, with landscape design solutions A-F highlighted for additional detail; II. Maps showing optimal cultivation locations and management intensities for landscape solutions A-E (solution F not shown, as BCAP locations are confidential); and associated feedstock GHG footprint (III) and delivered cost (IV) breakdowns.

CHAPTER 5

DISTRIBUTED BIOCHAR AND BIOENERGY CO-PRODUCTION: A REGIONALLY-SPECIFIC CASE STUDY OF ENVIRONMENTAL BENEFITS AND ECONOMIC IMPACTS[1]

5.1. Summary

Biochar has been advocated as a method of sequestering carbon while simultaneously improving crop yields and agro-ecosystem sustainability. It can be produced from a wide variety of biomass feedstocks using different thermochemical conversion technologies with or without the recovery of energy co-products, resulting in chars of differing quality and a range of overall system greenhouse gas (GHG) mitigation outcomes. This analysis expands on previous sustainability studies by proposing a mechanistic lifecycle GHG and economic operating cost assessment model for the co-production of biochar and bioenergy from biomass residue feedstocks, with a case study for north-central Colorado presented. Production is modeled as a continuous function of temperature for slow pyrolysis, fast pyrolysis, and gasification systems. Biochar environmental benefits (C sequestration, N_2O suppression, crop yield improvements) are predicted in terms of expected liming value and recalcitrance. System-level net GHG mitigation is computed, and net returns are estimated that reflect the variable economic costs of production, the agronomic value of biochar based on agricultural limestone or fertilizer displacement, and the value of GHG mitigation, with results compared to the alternate use of char for energy

[1] Field JL, Keske CMH, Birch GL, DeFoort MW, Cotrufo MF (2013) Distributed biochar and bioenergy coproduction: a regionally specific case study of environmental benefits and economic impacts. *GCB Bioenergy*, **5**, 177–191.

production. Case study results indicate that slow pyrolysis systems can mitigate up to 1.4 Mg CO_2eq/Mg feedstock consumed, provided a favorable feedstock is utilized, production air pollutant emissions are mitigated, and energy co-products are recovered. The model suggests that while financial returns are generally greater when char is consumed for energy (biocoal) than when used as a soil amendment (biochar), chars produced through high-temperature conversion processes will have greater GHG mitigation value as biochar. The biochar scenario reaches economic parity at carbon prices as low as $50/Mg CO_2eq for optimal scenarios, despite conservative modeling assumptions. This model is a step toward spatially-explicit assessment and optimization of biochar system design across different feedstocks, conversion technologies, and agricultural soils.

5.2. Introduction

Biochar is the carbon-rich solid co-product of thermochemical biomass conversion technologies. Its production and application to agricultural soils has been advocated as a greenhouse gas (GHG) mitigation strategy capable of rapid deployment, substantial total annual abatement potential, and significant co-benefits for agricultural system sustainability (Lehmann 2007b; Molina *et al.* 2009; Woolf *et al.* 2010). Biochar is characterized by stable aromatic C structures, low O and H to C ratios, low bulk density, moderate cation exchange capacity (CEC), and high ash content, pH, and surface area (Lehmann, 2007a). Because the C in biochar is derived from atmospheric CO_2 fixed in biomass via photosynthesis, the stable storage of biochar in soils represents a long-term removal of atmospheric C, i.e. terrestrial C sequestration. Additionally, when applied as a soil amendment in agricultural systems, biochar has been shown, in many cases, to suppress N_2O emissions (a byproduct of the microbial metabolism of nitrogen fertilizer that dominates the GHG balance of many modern agricultural systems) (Clough & Condron 2010; Singh *et al.* 2010; Zheng *et al.* 2012) and improve crop yields (Atkinson *et al.* 2010; Jeffery *et al.* 2011). Like any other organic matter addition to soil, biochar application affects a multitude of soil properties including bulk density, water-holding capacity, drainage, CEC, and pH, resulting in a substantial re-engineering of the soil environment (Atkinson *et al.* 2010) with respect to basic physical (Busscher *et al.* 2010) and chemical properties (Gaskin *et al.* 2010), water dynamics (Gaskin *et al.* 2007), and macro- and micro-fauna viability (Liesch *et al.* 2010; Lehmann *et al.* 2011).

Biochar can be made from a variety of feedstock materials via several different thermochemical conversion pathways (Goyal *et al.* 2008; Meyer *et al.* 2011), resulting in chars with different chemical properties (Brewer *et al.* 2009; Keiluweit *et al.* 2010) and associated differences in recalcitrance (Spokas, 2010), agronomic performance (Atkinson *et al.* 2010; Deal *et al.* 2012), and overall economic value (Lin & Hwang 2009; Yoder *et al.* 2011). Thermochemical conversion involves the heating of biomass feedstocks in oxygen-restricted environments, causing the biomass to undergo a series of de-polymerization, volatilization, and reorganization processes resulting in a mixture of low-molecular weight gases, high-molecular weight condensable liquid vapors, and solid char (Laird *et al.* 2009). A range of thermochemical conversion technologies exist, with process conditions such as temperature, heating rate, and atmosphere optimized to favor either solid, liquid, or gas yields (Goyal *et al.* 2008; Laird *et al.* 2009; Brown *et al.* 2011; Meyer *et al.* 2011). Slow pyrolysis typically involves the low-temperature (300-550 °C) conversion of biomass with long residence times (e.g. hours), favoring yields of char (Gaunt & Lehmann 2008; Laird *et al.* 2009; Brown *et al.* 2011). Fast pyrolysis is characterized by much faster heating rates, shorter residence times (e.g. seconds) and potentially higher temperatures (350-900 °C), and has been explored as a method of generating high yields of stable, energy-dense pyrolysis oils (Wright & Brown 2007; Coleman *et al.* 2010). Gasification implies the high temperature (600-1200°C) intermediate-duration (10s of seconds) auto-thermal conversion of biomass, at less than stoichiometric air-fuel ratios, into a primarily gaseous product rich in H_2, CO, and CH_4 that can be used for power generation (Alauddin *et al.* 2010; Mai Thao *et al.* 2011; Dasappa *et al.* 2011). While each of these thermochemical conversion technologies have been used in the past for the production of fuels or feedstock chemicals, only gasification is typically employed for energy production today, and only in certain niche markets. However, pyrolysis technologies with the potential to co-produce fuels and biochar are currently the subject of intensive research efforts (Bridgwater *et al.* 2002; Ringer *et al.* 2006) and numerous commercial ventures (Butler *et al.* 2011; Kauffman *et al.* 2011; Solantausta *et al.* 2012; US Biochar Initiative 2012).

Though all of these processes will produce a solid, liquid, and gaseous product fraction, the yields and chemical composition of each fraction will vary considerably. As a result, the derived char can display a wide range in properties such as pH and CEC that will affect its function as a soil amendment (Spokas & Reicosky 2009), and likewise the liquid and gas fractions will exhibit a range of different heating values that will dictate their value as energy products (Tsai *et al.* 2007). In real-world thermochemical bioenergy systems not all product fractions are necessarily recovered for productive use, particularly in distributed small-scale systems where potential revenues from the smaller fractions are insufficient to justify capital investments in the required separation, filtration and other cleanup equipment. Many slow and fast pyrolysis systems may in practice lack the capacity for pyrolysis gas recovery (Brick & Lyutse 2010), while many gasification systems make no provision for generating energy from the pyrolysis oils filtered from the gas stream. Pyrolysis gas management is particularly important for system sustainability, as the CH_4 it contains is a potent GHG. While not typically included in quantitative sustainability assessment studies, improper management (e.g. venting or incomplete flaring) of these gases has been hypothesized as a potentially significant source of GHGs and other air pollutants (Laird *et al.* 2009; Brick & Lyutse 2010).

Several aspects of biochar production system sustainability can be quantified scientifically. Lifecycle assessment (LCA) is the systematic study of input and output flows of materials and energy across a given production chain in order to determine its full cradle-to-grave impact on areas such as anthropogenic GHG emissions, environmental quality, or human health (Finnveden *et al.* 2009). LCA techniques have been widely applied to biofuel and bioenergy systems (Farrell 2006; Bai *et al.* 2010; Wang *et al.* 2011). Several recent LCA studies and less formalized GHG mitigation assessments have analyzed the co-production of biochar and bioenergy from slow pyrolysis of various biomass feedstocks, considering GHG emissions associated with feedstock sourcing, bioenergy co-production, and agronomic effects of biochar, in addition to the direct C sequestration effect (Gaunt & Lehmann 2008; Roberts *et al.* 2010; Woolf *et al.* 2010; Hammond *et al.* 2011). These studies conclude that such systems will mitigate 0.7-1.4 Mg CO_2eq per Mg of feedstock consumed. It is also recognized that there exists an inherent tradeoff between bioenergy and biochar production (Fowles, 2007). Char produced through the thermochemical conversion of biomass has significant heating value and can be used as a fuel, or alternately the conversion system can be configured for the complete combustion of the feedstock for maximum energy generation with no char production. These biochar GHG mitigation studies generally conclude that biochar-producing systems can have greater GHG mitigation value than systems configured for maximum bioenergy production, though the underlying analysis typically relies upon coarse estimates of crop yield increases and N_2O suppression based on extrapolations of small numbers of greenhouse or field trials.

Significant work has also been conducted in the area of economic assessment of biochar systems (Islam & Ani 2000; McCarl *et al.* 2009; Lin & Hwang 2009; Roberts *et al.* 2010; Pratt & Moran 2010; Yoder *et al.* 2011; Galinato *et al.* 2011; Shackley *et al.* 2011). These studies typically find that the potential economic profitability of biochar production systems varies depending on the feedstock used (Lin & Hwang 2009; Roberts *et al.* 2010), the conversion technology employed (Pratt & Moran 2010; Brown *et al.* 2011), or the inclusion of carbon credits reflecting the social value of GHG mitigation (Roberts *et al.* 2010; Pratt & Moran 2010; Galinato *et al.* 2011; Shackley *et al.* 2011). One study has explored the implications of different production techniques and resulting variations in biochar properties for overall system performance, modeling the tradeoff between product yield and product quality as conversion temperature increases (Yoder *et al.* 2011). Taken together, most of the existing biochar sustainability literature tends to focus on a somewhat narrow and idealized case of dedicated biochar production in modern, efficient slow pyrolysis systems. However, practically speaking, much of the biochar available today or expected to be available soon will be either a) produced in small-scale carbonization systems that lack the capacity for air pollutant mitigation and energy co-product recovery; or b) a by-product from fast pyrolysis or gasification systems optimized for energy production rather than biochar production (e.g. Brick & Lyutse 2010; Deal *et al.* 2012).

The purpose of this study is to construct an integrated lifecycle GHG and economic operating cost assessment tool around a detailed thermochemical biomass conversion dataset coupled with a mechanistic model of agronomic responses in order to assess the GHG mitigation and variable costs of systems that co-produce bioenergy and biochar, and to apply that tool to a biochar production case study. Yields and product qualities are compiled for slow pyrolysis, fast pyrolysis, and gasification across a range of reaction temperatures, with the recovery of individual product fractions adjusted as appropriate for the type of system modeled. Biochar recalcitrance is estimated as a function of production temperature, and agronomic response is modeled based on the biochar liming effect. While biochar addition affects a variety of physical, chemical, and biological soil properties, this analysis focuses exclusively on the liming effect because a) pH increases have been observed across a wide variety of biochar trials (Blackwell *et al.* 2009; Streubel *et al.* 2011); b) liming effects are relatively straightforward to simulate quantitatively (Galinato *et al.* 2011); and c) meta-analyses show agronomic reposes to be better correlated with pH changes than other biochar effects (Verheijen *et al.* 2009; Jeffery *et al.* 2011). Several aspects of the sustainability of biochar systems will vary regionally, including the availability of different feedstocks, the prices of system inputs and outputs, and the agronomic response to amendment of a specific soil type. A regional case study is presented in order to ground the analysis for a specific production case with realistic feedstock materials, transportation distances, energy pricing, and agronomic conditions. Following the presentation of the case study, the analysis is generalized to investigate sustainability in systems based on different conversion technologies and feedstocks, and with different transportation distances and native soil qualities, in order to enrich the analysis and bound the range of scenarios that are likely to achieve positive results.

Overall this analysis expands on previous LCA and economic assessment methods in the literature to elucidate: a) how system configuration and production-phase air pollutant management affect net environmental benefits and economic returns; b) how the quality, agronomic performance, and associated value of biochar changes across a range of thermochemical conversion conditions; and c) under what circumstances system optimization for environmental versus economic outcomes are in competition.

5.3. Methods

An integrated lifecycle GHG and economic operating cost assessment tool is developed to examine the feasibility of establishing a biochar and bioenergy co-production facility in north-central Colorado. This tool considers a variety of feedstocks and thermochemical conversion technologies, and models biochar properties, recalcitrance, and agronomic responses in a continuous, mechanistic manner. An LCA approach is employed, and the assessment is consequential in that it focus on marginal emissions associated with a specific case study, the principle of system expansion is used to value the GHG impact of energy co-products, and indirect effects are included where appropriate (specifically, indirect N_2O) (Brander *et al.* 2008; Kauffman *et al.* 2011). The functional unit considered is the management of 1 dry Mg of biomass residue. The lifecycle inventory is constructed from a variety of sources, with many of the upstream embodied emissions and system expansion factors derived from the Argonne National Laboratory GREET model (Wang, 1999) version 1.8d. The impact assessment considers climate change impact using the metric of global warming potential (GWP).

The model follows the convention of treating CO_2 emissions from harvested biomass as neutral (e.g. assuming rapid biomass regrowth), but includes emissions of non-CO_2 GHGs such as CH_4 from the uncontrolled open burning of those feedstocks or from pyrolysis in scenarios where pyrolysis gas emissions are not captured or flared. Both CO_2 and non-CO_2 GHG emissions associated with lifecycle fossil energy use are included where necessary. Capital embodied emissions are assumed to be similar across the different scenarios investigated and small enough relative to other lifecycle emissions (Hill *et al.* 2006) that they could be considered negligible. Likewise, the economic model specifically focuses on operating costs, otherwise known as variable costs, associated with the co-production of energy and biochar, and does not include capital costs. Capital costs are not negligible for determining the overall feasibility of commercial systems; a recent economic analysis found that they contribute 27-31% to total biochar production costs from forestry residues, depending on system scale (Shackley *et al.* 2011). However, focusing exclusively on operating costs is a reasonable approach for the first-order estimate of design tradeoffs investigated in this study, and a fully developed enterprise budget-based profitability assessment of biochar production systems is outside the scope of the current analysis. An overview of the integrated analysis methods is presented below, while some of the more technical details are given in Appendix C.

5.3.1. Case study scenarios

A case study is conducted for locating a thermochemical biomass conversion facility in Larimer County, Colorado, operating on one of two different locally-available biomass residue feedstocks. The case study lifecycle inventory includes: 1) operations associated with sourcing feedstock material; 2) feedstock transport to a centralized conversion facility; 3) processing and thermochemical conversion into biochar and energy co-products with associated air pollutant emissions; 4) transport of the resulting biochar to appropriate agricultural regions; and 5) biochar application to agricultural soils with associated direct sequestration of C, as well as displacement of agricultural inputs and suppression of N_2O emissions due to the liming effect (Figure 5.1). Agronomic benefits are evaluated in the context of winter wheat production under two different sets of assumptions: a) an initially-limed system in which biochar application displaces an equivalent amount of agricultural limestone (aglime) application (Galinato *et al.* 2011) while soil pH, nitrogen fertilizer inputs, and crop yield remain constant; and b) an initially non-limed system in which biochar application increases soil pH, reducing the amount of N fertilizer required to maintain a given crop yield and partially suppressing N_2O emissions (Gaunt & Lehmann 2008; Roberts *et al.* 2010; Woolf *et al.* 2010).

The case study evaluates the use of pine wood and slash sourced from Jackson County, Colorado (Figure 5.2), as a waste biomass feedstock material. Forests in Jackson County have been devastated by an outbreak of the Mountain Pine Beetle (US Forest Service, 2012), and dead pine trees in proximity to roads, homes, and recreational area are being cleared to reduce the risks of wildfire and falling trees. The material is typically piled and open-burned for disposal, with significant associated air pollutant emissions. In this analysis the feedstock is transported via diesel truck to Larimer County, Colorado, where it is then ground prior to thermochemical conversion. The second biomass residue feedstock is spent grains produced at one of the many breweries in Larimer County. Similar to distillers grains and solids (DGS) derived from corn ethanol production, these spent grains have value as animal feed capable of offsetting corn and soy consumption (Arora *et al.* 2008). In this case the spent grains are assumed to be dried in a natural gas-fired drier and consumed in a thermochemical conversion facility co-located with the brewery. Forgone emissions-avoidance and revenues associated with alternate management of the biomass residue feedstocks are treated as opportunity costs or credits (Woolf *et al.* 2010).

The analysis considers the conversion of these biomass feedstocks to char and energy co-products through traditional charcoal production methods (carbonization), slow pyrolysis, fast pyrolysis, or gasification, as these are the most well-developed thermochemical conversion technologies (Meyer *et al.* 2011). It is assumed that char is recovered for each technology and consumed locally as a substitute for coal (biocoal) in industrial boilers or power plants, or transported to Hall County, Nebraska and used as a soil amendment in winter wheat farms, applied a single time in the course of normal tillage operations at a rate of 25 Mg biochar per hectare. This particular site is selected since it is one of the closest areas with agriculture on native low-pH soils, specifically a Corzad loam of pH 5.6 and CEC of 15 $cmol_e$/kg (Soil Survey Staff, 2012). In the same manner, other recovered product fractions are assumed to be used for energy generation locally, displacing the use of fossil fuels.

5.3.2. GHG accounting

Standard UN Intergovernmental Panel on Climate Change values for the GWP of CH_4 and N_2O on a 100-year analytical time horizon are used for this analysis (Solomon *et al.* 2007), and values for CO, non-methane hydrocarbons, and particulate matter emissions are taken from Grieshop *et al.* (2011) (Appendix C section C.1). The direct C sequestration value of biochar is estimated as a carbon stability factor (Hammond *et al.* 2011) in CO_2-equivalent terms according to the equation

$$CO_{2,sequest} = -3.66\left(1 - e^{(t_{1/2} \cdot \ln(0.5))/TH}\right)$$

where 3.66 is the ratio of the molecular weight of CO_2 to that of C, $t_{1/2}$ the half-life of biochar in soil, and *TH* the analytical time horizon, in this case 100 years. The sequestration value of the char varies from zero to -3.66 Mg CO_2eq/Mg biochar-C as recalcitrance increases.

5.3.3. Feedstock sourcing

Harvest costs for beetle-kill pine are estimated from local US Forest Service studies (Lynch & Mackes 2003; Duda 2008), and associated GHG emissions are estimated by applying a general emissions intensity term for the US forestry sector (US Department of Commerce, 2010). The authors have made a conservative assumption of attributing these costs and emissions fully to the biochar lifecycle, even though large quantities of beetle-killed pine wood and slash will continue to be collected and piled for disposal via open burning in Jackson County regardless of the existence of a local biochar industry. Since the alternate disposal method is uncontrolled open burning with high associated emissions of CH_4, particulate matter, and other products of incomplete production, an emissions credit based on data from McMeeking *et al.* (2009) is applied to the biochar production scenario for the avoidance of those emissions. It is assumed that the material will air dry to a moisture content of 10% after harvest but prior to transport, which is described in the next section. Feedstock handling and grinding costs at the conversion facility are estimated from Hess *et al.* (2009), and associated GHG emissions are computed using the same emissions intensity factor for the US forestry sector employed previously. Modeling of the spent grains feedstock sourcing is described in Appendix C Section C.2.

5.3.4. Transport

Diesel fuel consumption and associated emissions are modeled for the transport of pine feedstock 100 miles (160 km) from Jackson County to Larimer County, Colorado, and for the transport of biochar to Hall County, Nebraska (400 mi/645 km, Figure 2). The analysis models transport in heavy trucks using default payload capacity and fuel economy values from a trucking cost model (Norris, 2009) and from the GREET model. The full lifecycle emissions associated with consuming a unit of diesel fuel is calculated by combining tailpipe CO_2 emissions along with an estimate of the embodied emissions associated with the upstream extraction, refining, and distribution of the fuel. Both estimates are derived from the GREET model (detailed in Appendix C Section C.3).

5.3.5. Thermochemical conversion

Thermochemical conversion product yields and associated heating values, as well as char C content, are modeled continuously as a function of temperature based on bench-top scale analyses from the literature specific to pine wood and spent grains feedstocks. A composite dataset simulating the slow pyrolysis of pine is assembled with data from Şensöz & Can (2002), Şensöz (2003), and DeSisto *et al.* (2010) for temperatures from 350-500 °C. Likewise, fast pyrolysis of pine is modeled from 400-600 °C with data from DeSisto *et al.* (2010), and gasification from 650-775 °C with data from Herguido *et al.* (1992) and Brewer *et al.* (2009). Note that the slow pyrolysis and gasification datasets are composites assembled from across multiple studies (the assumptions underlying which are detailed in Appendix C Section C.4) and are thus somewhat more speculative than the fast pyrolysis dataset. No scaling factors are applied to bench-top scale results, and there is uncertainty around achieving these exact product distributions in a large-scale system. This is particularly true in the case of fast pyrolysis, where the ability to match bench-top scale heat transfer rates at commercial scale is the subject of considerable research (Ringer *et al.* 2006), and as a result this scenario should be viewed more as a bound than an expected value. However, it is not uncommon for assessment studies to assume bench-top scale product distributions directly for large-scale systems (Bridgwater *et al.* 2002; Ringer *et al.* 2006). In addition to these continuous process models, point estimates for other technologies and feedstocks are included in the model for comparison. The production of char from wood via carbonization in a more traditional batch charcoal kiln design is modeled with data from Pennise *et al.* (2001) in order to contrast traditional char production processes with modern ones. While the authors are unable to identify continuous data or slow pyrolysis data for the spent grains feedstock in the literature, fast pyrolysis of spent grains at a single temperature (500 °C) is modeled for barley DGS as per Mullen *et al.* (2009). Details of the studies underlying these datasets are given in Table 5.1.

These product fractions are then corrected to reflect a) the consumption of energy co-products on-site to drive the endothermic pyrolysis process; or b) those that are not typically recovered in a useable form. It is assumed that the energy equivalent of 0.21 kg of pyrolysis gas is required to drive the pyrolysis (fast or slow) of 1 kg of dry biomass (Brown *et al.* 2011), and that the higher energy requirements of higher-temperature pyrolysis is compensated by the increased heating value of the gas produced under these conditions. In production regimes where gas yields are insufficient to meet this requirement, a fraction of one of the other products (pyrolysis oil for slow pyrolysis and char for fast pyrolysis) is consumed to fulfill the requirement. Gasification is auto-thermal and thus no products are consumed externally to drive the process, but it is assumed that the liquid fraction (tar) produced is not recovered for energy generation due to the relatively small yield and low quality. In the traditional charcoal kiln scenario it is assumed that pyrolysis oil and gas are not recovered for energy production but rather are vented to the atmosphere or flared.

Recovered pyrolysis oils are modeled as being consumed locally to displace heavy fuel oil use on an energy-equivalent basis. Pyrolysis gases are modeled as being converted to electricity to offset grid electricity demand on-site. For biocoal scenarios, the char is assumed to displace local coal consumption on an energy-equivalent basis. It is assumed that non-CO_2 GHG emissions rates are similar between heavy fuel oil and bio-oil (Solantausta *et al.* 2012) and between coal and biocoal, so no additional GHG burden is calculated at this step. The details of these calculations are described in Appendix C Section C.4.

5.3.6. Biochar amendment to agricultural soils

Biochar recalcitrance to biotic and abiotic mineralization after its application to soil is modeled as per Spokas (2010), which compiles data from a number of studies and maps biochar half-life estimates ranging over several orders of magnitude to char production temperature using char O:C ratio as proxy. A conservative fit of half-life versus O:C is used here, as detailed in Appendix C Section C.5. Biochar half-life estimates are then converted to CO_2-equivalent sequestration terms using Equation 1. The potential for a biochar 'priming effect' leading to changes in native soil organic matter dynamics is ignored in this analysis. While some previous LCA studies attempt to include such an effect (e.g. Woolf *et al.* 2010), recent studies suggest that the direction of the effect varies among soils and its magnitude is small (e.g. Stewart *et al.* 2012).

Several sources in the literature report the liming value of various biochars in terms of calcium carbonate equivalence (CCE), along with their elemental makeup (Van Zwieten *et al.* 2009; Van Zwieten, Kimber, Downie, *et al.* 2010; Van Zwieten, Kimber, Morris, *et al.* 2010). The authors compile a composite dataset from these sources and supplement the analysis with additional biochar samples (see Appendix C Table C.1 for additional details). The measured CCE is regressed against biochar elemental composition including C, ash, and base element content using JMP Pro 9 (SAS Institute Inc.). It is found that CCE is well-predicted based on the final base and ash content of the biochar (adjusted R^2=0.78, p=0.0047) according to the empirically-derived regression:

$$CCE\ (\%) = 5.378 + 1.582 \cdot B - 0.2136 \cdot A$$

where *CCE* is the acid-neutralizing capacity of material relative to that of pure $CaCO_3$, *B* the percentage of base elements (Ca, Mg, K, and Na) in the biochar, and *A* the total ash content, all on a mass basis. The base and total ash content of the pine feedstock are estimated from Bramryd & Fransman (1995), and those of spent grains using data on DGS from Spiehs *et al.* (2002). These mineral fractions are not perfectly conserved during the thermochemical conversion (Gaskin *et al.* 2008; Novak *et al.* 2009) and a uniform recovery factor of 80% is assumed for both base and total ash content of the feedstocks across all scenarios.

The liming effect is then evaluated in the context of a previously-limed scenario in which aglime consumption is displaced, and a previously-unlimed scenario in which fertilizer is displaced. In the first case, biochar displaces an equivalent amount of aglime of 100% CCE value (pure calcitic limestone). A fraction of the C in aglime is released as CO_2 during the re-acidification of the soil over time (West & McBride, 2005), and this avoided emission is credited to the biochar in addition to the embodied emissions from the manufacture and distribution of the displaced aglime as estimated in GREET. Final soil pH and associated crop yields are assumed uniform in this scenario. In the second case it is assumed that soil is not initially being limed, and any biochar additions will result in an increase in soil pH, computed based on the initial soil CEC (a proxy for soil buffering capacity) according to the Adams-Evans method (Evans & Adams, 1962) and comparable in duration to that encountered with an application of aglime as reported in Lukin & Epplin (2003). In an acid soil this pH increase can result in an improvement in crop productivity and associated reduction in the amount of nitrogen fertilizer needed to maintain a given yield (assuming a baseline fertilizer rate below that of maximum yield response), as well a reduction in N_2O emissions based on the decreased fertilizer application rate combined with a pH-mediated reduction in the N-to-N_2O emissions factor (Clough & Condron 2010; Zheng *et al.* 2012). The associated calculations are detailed in Appendix C Section C.5.

5.3.7. Economic assessment

An economic assessment of system operating costs is performed by applying prices to all lifecycle model inputs of material and labor, and all system outputs, as detailed in Appendix C Section C.6 and Table C.2. In the case of the spent grains feedstock, DGS prices reflect the opportunity cost of using the material as a feedstock rather than as animal feed. Prices for commodities subject to high price volatility (e.g. some fuels and energy-intensive products such as nitrogen fertilizer) are computed based on multi-year averages. The value of biochar is inferred from the cost of aglime or nitrogen fertilizer displaced, depending on the scenario. All prices are adjusted for inflation to 2012 US dollars.

Complex non-market valuation models can be conducted for a variety of environmental externalities associated with the energy and agricultural sectors (e.g. air and water pollutant emissions) (Keske, 2011). However, the non-market valuation in the current analysis is limited to the pricing of GHG emissions in order to quantify the social benefit of systems that mitigate GHGs relative to the fossil fuel *status quo*. Marginal damage estimates are taken from the United States Government Interagency Workgroup on Social Cost of Carbon (2010), with a median estimate of the social cost of carbon (SCC) of \$23.09/Mg CO_2eq when adjusted for inflation. Note that while most carbon emissions trading systems focus on a narrow set of GHGs (CO_2, CH_4, and N_2O as per the Kyoto protocol) and approved mitigation technologies, CO_2-equivalent forcings from particulate matter emissions and direct sequestration of CO_2 as biochar-

C are monetized here as well in order to reflect the best estimate of total system climate impact. Conversely, the price of carbon necessary to achieve parity of returns between a low-financial return, high GHG-mitigation biochar scenario and a higher return but lower GHG-mitigation biocoal scenario can be calculated as follows:

$$P_C = \frac{R_{coal} - R_{char}}{GHG_{char} - GHG_{coal}}$$

where *R* denotes financial returns ($/Mg feedstock) in the absence of non-market or social costs of carbon, *GHG* denotes the net greenhouse gas mitigation of the scenario (Mg CO2eq/Mg feedstock), and the subscripts *coal* and *char* correspond to the biocoal and biochar scenarios, respectively.

5.4. Results

5.4.1. Slow pyrolysis: effects of technology configuration

The analysis suggests substantial GHG mitigation but weak economic performance for the slow pyrolysis case study scenario assessed. The net mitigation of 1.41 Mg CO_2eq (100-y time horizon) and a net revenue of -$78 (i.e. unprofitable operation) are predicted for every metric ton of dry pine feedstock processed through this system (Figure 3), assuming slow pyrolysis at 500 °C with pyrolysis oil recovery, biochar application at a rate of 25 Mg/ha (~2% by mass at an incorporation depth of 10 cm), and biochar valuation based on fertilizer displacement (note the sign convention of showing GHG avoidance and revenues as positive, and GHG emissions and costs as negative). The largest positive contributor to GHG mitigation is the direct sequestration of carbon in soil as biochar-C. Under these conversion conditions the model predicts a char mass yield of 29% with a C concentration of 89% and an O:C ratio of 0.21, corresponding to a conservative soil half-life estimate of 240 years and a resulting C sequestration value of 0.76 Mg CO_2eq/Mg feedstock processed. System economic returns are dominated by pyrolysis oil production at a 21% yield and a higher heating value of 34.1 MJ/kg. This results in a heavy fuel oil displacement rate of 0.8:1 that contributes 0.61 Mg CO_2eq/Mg and $61/Mg to the system GHG mitigation and financial returns, respectively. Significant costs are incurred to harvest the pine feedstock (-$109/Mg) and from lifecycle energy use associated with transport, handling, and grinding of the feedstock and transport and field incorporation of the derived char (-$63/Mg), though the GHG burden associated with these operations (-0.03 and -0.05 Mg CO_2eq/Mg) is relatively small. Smaller GHG benefits are accumulated from the avoidance of open burning of the pine residue material (0.10 Mg CO_2eq/Mg) and the displacement of fertilizer and N_2O emissions suppression (0.03 Mg CO_2eq/Mg). Finally, monetizing total system GHG mitigation at a SCC of $23/Mg CO_2eq contributes a further $33/Mg of revenue. When all of these terms are combined the system shows a strong GHG mitigation potential, though production costs are so high that it would operate at a net loss even before capital costs are considered.

These GHG mitigation and economic return estimates are highly dependent on the configuration of the char production system (Figure 5.4). For the same scenario relying on a traditional batch carbonization method with uncontrolled air pollutant emissions and no energy co-product recovery, net system GHG mitigation value drops to virtually zero; this is primarily the result of losing the mitigation value of pyrolysis oils displacing heavy fuel oil use and the accumulation of an additional GHG burden of -0.72 Mg CO_2eq/Mg feedstock from the uncontrolled release of high-GWP pyrolysis gases. Associated net economic returns drop to a deficit of -$171/Mg feedstock processed. System GHG performance is improved somewhat with the addition of pyrolysis gas flaring, though performance is better still for modern slow pyrolysis systems that completely combust excess pyrolysis gases in the course of electricity generation. Net economic returns are particularly poor across all system configurations that do not include recovery of the pyrolysis oil fraction. For both traditional kilns and slow pyrolysis systems the char produced has relatively high heating value (~31 MJ/kg). As a result, the biocoal scenario leads to better GHG and economic results from the displacement of coal than the biochar scenario does through the direct sequestration of C and displacement of fertilizer and suppression of N_2O in agricultural soils. GHG mitigation and economic returns are reasonably well-correlated across all of the scenarios plotted in Figure 4 (Spearman $\rho=0.70$, $p=0.05$), suggesting that optimizing the system configuration to maximize profitability will also tend to maximize GHG performance even in the absence of carbon social cost valuation. Monetizing system GHG mitigation increases net returns, but even the best-performing scenario still operates at loss.

5.4.2. Fast pyrolysis: effects of feedstock choice

The choice of feedstock can significantly affect system GHG balance and profitability. Pine and spent grains feedstocks are contrasted directly for a fast pyrolysis process at 500 °C in Figure 5, and spent grains system performance is characterized by lower net GHG mitigation value (0.97 versus 1.58 Mg CO_2eq/Mg feedstock) but higher economic returns (-\$8 versus -\$45/Mg feedstock, again both net losses) than pine. The difference in GHG performance is driven primarily by the emissions associated with sourcing the feedstock itself. While in the case of pine the avoidance of air pollution from open burning more than offsets emissions from feedstock harvest, the spent grain carries a large opportunity emissions burden (-0.44 Mg CO_2eq/Mg) associated with diverting the feedstock away from use as an animal feed replacing corn and soy consumption, as well as significant emissions associated with drying the material down to 10% moisture content (-0.19 Mg CO_2eq/Mg). The spent grain scenario is also characterized by lower biochar-C concentration (51%) and higher pyrolysis oil heating value (32.9 MJ/kg) as compared to the pine scenario (76% and 24.7 MJ/kg). However, the resulting effects of less direct soil C sequestration and greater heavy fuel oil displacement roughly cancel each other out on a GHG basis. While the spent grain feedstock carries a large opportunity cost (-$91/Mg), it is still somewhat lower than the harvest cost of pine (-$109/Mg). This, in addition to larger revenues associated with the greater heavy fuel oil replacement rate, makes the spent grains scenario more profitable than the pine feedstock, though net returns are still negative.

5.4.3. Biochar valuation

This analysis includes the valuation of biochar by two different methods (aglime displacement and fertilizer displacement), the results of which are shown in Table 5.2 for the scenario of modern slow pyrolysis of pine at 500 °C described above. When this biochar is used in place of aglime it results in the displacement of 61 kg lime per Mg char (based on the predicted CCE value), which is associated with the avoidance of 53 kg CO_2eq/Mg biochar and a value of $0.53/Mg. In the alternate scenario where the biochar is introduced into a non-limed system, it is predicted to increase soil pH by 0.13 units, improving fertility by approximately 2% and allowing a reduction in fertilizer application rate of 11 kg ammonia per hectare for the duration of the liming effect. The combined effect of N_2O reduction and nitrogen fertilizer embodied emissions avoidance in this case is 87 kg CO_2eq/Mg biochar, and the fertilizer savings is valued at $1.48/Mg biochar. For the remainder of the analysis the fertilizer displacement method is used for biochar valuation.

However, additional emissions and costs are incurred for the transport of biochar from the thermochemical conversion facility to the farm and for soil application, detracting from its overall value. This effect can be bounded in terms of the maximum transport distance possible before transport and application emissions or costs outweigh agricultural GHG mitigation benefits (not including the direct C sequestration value of the biochar) or revenues with or without carbon social cost valuation, given a farm soil buffering capacity. For scenarios where fertilizer displacement is considered, positive GHG mitigation is the least-binding criteria, and maximum transport distances of 1640 and 520 km can be tolerated for biochar that will be applied to soils with a CEC of 5 and 20 $cmol_e/kg$, respectively (assuming an initial pH of 5). Achieving positive revenues is more constraining, with maximum transport distances of 50 and 125 km with and without carbon valuation, respectively, for low buffering-capacity soils (CEC of 5 $cmol_e/kg$). When aglime displacement is considered, incorporation costs will always outweigh biochar revenues, even at transport distances of zero. Note that the case study scenario includes a biochar transport distance of 645 km and application to a native soil of CEC of 15 $cmol_e/kg$. In this case, the costs associated with biochar transport and incorporation outweigh the agronomic value of the char, even when the non-market values of agronomic GHG mitigation are calculated. The associated emissions value is negative when biochar is valuated as displacing aglime but positive when displacing fertilizer.

5.4.4. Biochar versus biocoal across conversion technologies

This analysis finds that financial returns from using char as biocoal are higher than that of using it as biochar across all of the production technologies, conversion temperatures, and agricultural soil properties explored. However, the net GHG mitigation value of biochar does exceed that of biocoal under certain conditions, as plotted for three different production technologies as a function of conversion temperature and soil CEC in Figure 5.6. Regions shaded bright red and purple represent regimes for which biochar GHG mitigation outperforms that of biocoal by up to 0.11 Mg CO_2eq/Mg feedstock consumed. This occurs for fast pyrolysis scenarios at high conversion temperatures and low soil CEC values, and across all gasification scenarios investigated. These conversion conditions are associated with relatively high char C-concentration, recalcitrance, and liming values, and relatively low heating values. Since biochar is shown to outperform biocoal on a GHG basis but underperform on a revenue basis, Equation 3 can be applied to compute the price of carbon necessary to make up the revenue deficit (P_C). These results are shown for gasification in Figure 5.7, indicating that biochar will be more valuable than biocoal at carbon prices as low as \$49/Mg CO_2eq when produced at high conversion temperatures and used in soils with low buffering capacity, to as high as \$155/Mg CO_2eq under the opposite conditions.

5.4.5. Sensitivity analysis

Sensitivity analysis is performed on the price of carbon for biochar-biocoal parity (P_C), since this parameter encompasses both the GHG and revenue aspects of the assessment into a single metric. Sensitivity of results is evaluated in response to a standardized perturbation to key input parameters, as is commonly done for speculative assessment scenarios where rigorous bounding of total uncertainties is problematic (e.g. Bridgwater *et al.* 2002; Bergqvist *et al.* 2008). The analysis of pine gasification at 700 °C and biochar application in soils of pH 5 and 10 $cmol_e$/kg CEC (see Figure 5.7) is perturbed by increasing or decreasing the value of key model input parameters by 1%, and the resulting response in P_C is plotted in Figure 5.8. This analysis shows that results are driven primarily by the physical properties of the char; a 1% reduction in biochar C-content increases P_C by 9%, while a 1% increase in char heating value increases P_C by 8%. Input parameters of intermediate influence (0.2-0.9% response to a 1% perturbation) include labor and energy prices and variables describing the duration of the char liming effect and the stability of biochar in soil, as well as the magnitude of the baseline farm soil N_2O emission rate. The char CCE regression coefficient and the price of fertilizer exert minimal influence on overall results (~0.1% response to a 1% perturbation). The model is even less sensitive to changes in biochar incorporation costs.

5.5. Discussion

The goal of this analysis is to develop an integrated lifecycle GHG and economic operating cost assessment tool applicable to biochar production in north-central Colorado. The model captures some of the diversity in biochar production technologies encountered in the real world, models the C sequestration and agronomic value of biochar in a mechanistic manner, and estimates the value of biochar based on its displacement of other agricultural inputs. Overall, the analysis suggests that: a) slow pyrolysis biochar systems based around modern conversion technologies can mitigate up to 1.4 Mg CO_2eq/Mg pine wood feedstock in Colorado, but this performance depends on air pollutant management and energy co-product recovery; b) the locally-available biomass residue feedstocks considered are generally too expensive for system profitability; c) the agronomic value of biochar makes only a very small contribution to total system GHG mitigation and profitability; and d) that using char as biochar only unambiguously outperforms using it as biocoal when it is produced via high-temperature fast pyrolysis or gasification and when GHG mitigation is valued above \$50/Mg CO_2eq.

The net GHG mitigation estimate for the biochar-producing slow pyrolysis system assessed in this case study is very comparable to that estimated by other assessment studies in the literature, which typically report mitigation values between 0.6 and 1.4 Mg CO_2eq/Mg depending on the details of the scenario (Gaunt & Lehmann 2008; Roberts *et al.* 2010; Woolf *et al.* 2010; Hammond *et al.* 2011; Kauffman *et al.* 2011), as summarized in section S7 of the SI. The relatively low GHG footprint of sourcing the pine feedstock considered here contributes to the positive overall results. Also, the assumption of pyrolysis oils being used to displace heavy fuel oil locally rather than being combusted directly for electricity generation further improves the GHG balance relative to other studies, since fuel oil always has a high GHG footprint whereas the footprint of electricity generation being displaced can vary regionally. This analysis implicitly assumes that total regional biochar production is sufficiently low that local fuel oil demand will fully consume the associated pyrolysis oil co-product.

The lack of profitability of the slow pyrolysis scenario modeled in this case study is somewhat unexpected, though not inconsistent with other economic assessment studies that report both positive and negative net returns depending on the feedstock used (Roberts *et al.* 2010), conversion technology employed (Pratt & Moran, 2010), and price of carbon (Galinato *et al.* 2011). This result is primarily driven by the cost of feedstock sourcing; spent grains have a significant opportunity cost stemming from their value as animal feed, and the harvest of beetle-killed pine is very costly. Studies suggest that large quantities of cellulosic biomass will be available at the national level for the future bioenergy industry at prices starting as low as \$25-60/Mg (Jain *et al.* 2010; U.S. Department of Energy 2011; Egbendewe-Mondzozo *et al.* 2011), a range low enough to move some of the scenarios analyzed here into profitability if located in appropriate regions.

The finding that biocoal will be more profitable across all scenarios analyzed and will mitigate more GHG emissions when char is produced by slow pyrolysis and under most fast pyrolysis conditions also runs counter to the conventional wisdom. While previous studies typically make assumptions about crop yield response and N_2O suppression that are largely independent of specific biochar physical and chemical properties, those authors find that biochar outperforms energy-maximizing scenarios on a GHG basis. There is, however, wide disagreement as to whether that result is sensitive or insensitive to factors such as biochar recalcitrance in soil (Gaunt & Lehmann 2008; Hammond *et al.* 2011), displaced electricity GHG footprint (Woolf *et al.* 2010), or even system analytical boundaries (Roberts *et al.* 2010). This study is similar in that it reports a nuanced result in which biochar will only outperform an energy-maximizing scenario within certain limits of production temperature and application rate, outside of which the recalcitrance level and liming effect are too low to produce GHG mitigation in excess of what would be achieved from displacing fossil coal emissions. However, both the biochar and biocoal scenarios lead to significant GHG mitigation, and the difference between these two values is relatively small and thus highly sensitive to certain modeling assumptions, as illustrated in the sensitivity analysis.

The approach of this study to estimate the GHG benefits and economic value of biochar based solely on its liming potential is very conservative, in that it neglects other potential benefits from biochar application in agricultural systems. In addition to liming effects, evidence suggests that biochar can have agronomic value with respect to water dynamics, nutrient retention, and microbial activity. In some cases the underlying drivers (CEC, surface area) of these effects will show the same positive relationship with production temperature (Lehmann, 2007a) that liming capacity is predicted to have here. It is effects such as these, rather than a transient liming effect, that underlie the long-term improved fertility of the Terra Preta soils that inspired the biochar concept (Glaser *et al.* 2001; Laird *et al.* 2009). However, such effects have been neglected here due an incomplete understanding of their mechanism that makes assessment extremely challenging. While it is debatable whether or not the biochar market is sufficiently well-developed that current prices accurately reflect the underlying agronomic value of biochar, the fact that there are a diversity of niche markets willing to pay several orders of magnitude more for biochar (Keske & Lohman 2012) than the valuation estimated here strongly suggests that char has additional benefits beyond what can be explained through the liming effect alone. The analysis is also conservative to the extent that no attempt is made to correct for the decreasing value of the biocoal alternative as char ash concentration increases with production temperature, resulting in a fuel with greater propensity for slagging (Vamvuka *et al.* 2010).

Finally, it is also likely that the true GHG-mitigation value of biochar is under-estimated with the carbon stability factor approach used here and in most other biochar LCA studies. While this analysis only considers the GHG-mitigation impact of the fraction of biochar-C remaining in the soil at the end of 100-year analytical time horizon, a more dynamic accounting approach would consider the CO_2-equivalent value of the transient sequestration of the char volatile fraction. Dynamic accounting of changes in carbon sinks is becoming more common in bioenergy LCA studies (O'Hare *et al.* 2009; Cherubini *et al.* 2011), and it is conceivable that it might significantly raise the GHG mitigation value of biochars, particularly those with relatively low soil half-lives relative to the analytical time horizon.

These limitations notwithstanding, the authors believe this study makes an important step in improving the methodology of sustainability assessment in biochar systems. It expands the scope of analysis beyond slow pyrolysis systems to account for the diversity of thermochemical technologies that are currently producing biochar around the world, and includes effects such as conversion air pollutant emissions that are neglected in other studies. The transition to continuous, mechanistic estimates of thermochemical conversion product yields and biochar recalcitrance and agronomic benefits has the potential to improve assessment accuracy and address the tradeoffs inherent in the design of such systems. This is consistent with the increasingly-common use of biophysical models of feedstock production and soil management in bioenergy LCA (Zhang *et al.* 2010) and economic assessment studies (Jain *et al.* 2010), allowing for the regionally-specific assessment of system performance and sustainability that reflects variance in climate, soil type, and land use history. Further development of such mechanistic assessment methods will enable spatially-explicit assessments of biochar systems in the context of feedstock availability, energy co-product demand, and agricultural needs, facilitating the design and siting of biochar production facilities to maximize both profitability and environmental benefits.

Table 5.1. Thermochemical conversion studies used in model

Conversion scenario	Charcoal kiln (pine)	Slow pyrolysis (pine)	Fast pyrolysis (pine)	Fast pyrolysis (spent grain)	Gasification (pine)
Primary data source(s)	Pennise et al. 2001	Şensöz & Can 2002, Şensöz 2003	DeSisto et al. 2010	Mullen et al. 2009	Herguido et al., 1992, Brewer et al. 2009
Temperature range[1] (°C)	-	350-500	400-600	500	650-775
Feedstock	Eucalyptus	Pine, pine bark		Barley DDGS	Pine chips
Max particle size (mm)	-	10, 0.60	0.4	2	10
Atmosphere	Air	Pyrolysis gas	N_2	N_2	Steam/N_2, Air/N_2
Reactor type	Circular Brazilian kiln	Fixed bed	Fluidized bed	Fluidized bed	Fluidized bed

[1]Temperature range used in this model; may be a subset of the full temperature range reported in the source study

Table 5.2. Different biochar valuation results calculated over the lifetime of the liming effect

		ΔpH	Displacement rate (kg/Mg char)	GHG mitigation (kg CO_2eq/Mg char)	Value ($/Mg char)[2]
Case 1	Aglime displacement	0	61	Avoided emissions (embodied & field): 53	0.53
Case 2	N fertilizer displacement	0.13	3.9	Avoided emissions (embodied & field): 28	1.48
				Additional pH-mediated N_2O suppression: 58	

[2]Does not include valuation of GHG mitigation

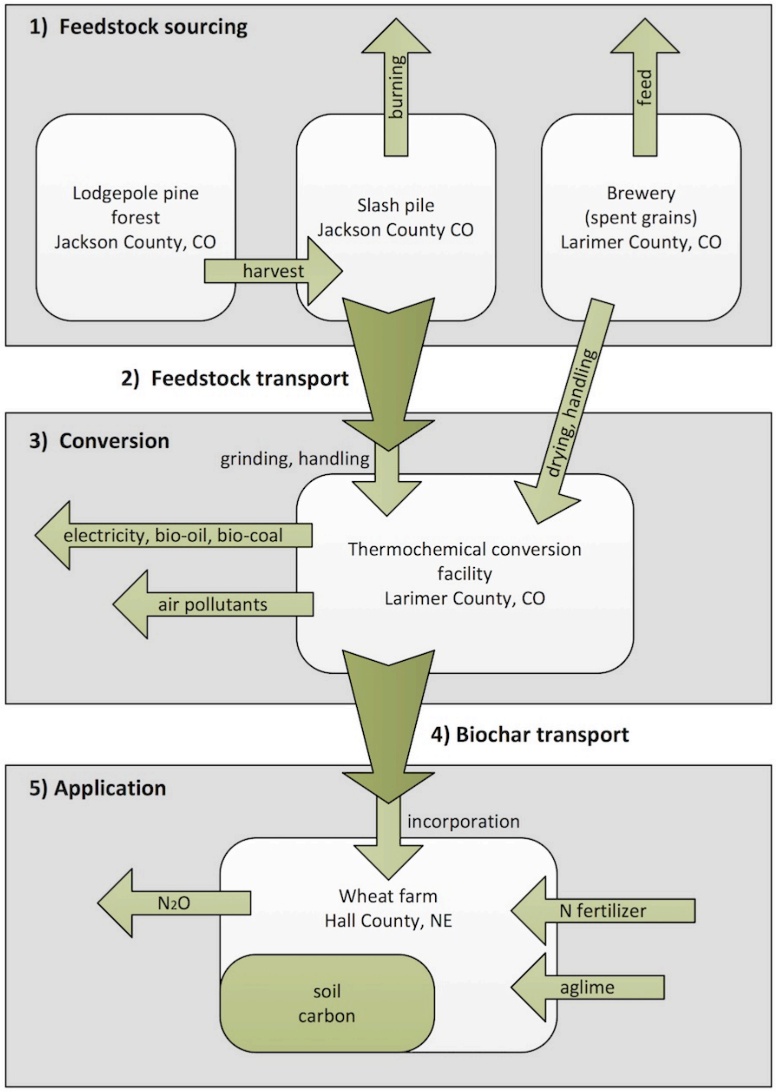

Figure 5.1. System schematic illustrating the different lifecycles phases and processes included in the assessment

Figure 5.2. Map showing the locations of feedstock sourcing (Jackson County, Colorado for pine and Larimer County, Colorado for spent grains), thermochemical conversion (Larimer County, Colorado) and agricultural soil incorporation (Hall County, Nebraska), and the highway network (US-14, I-25, and I-90) connecting them, for the hypothetical case study assessed

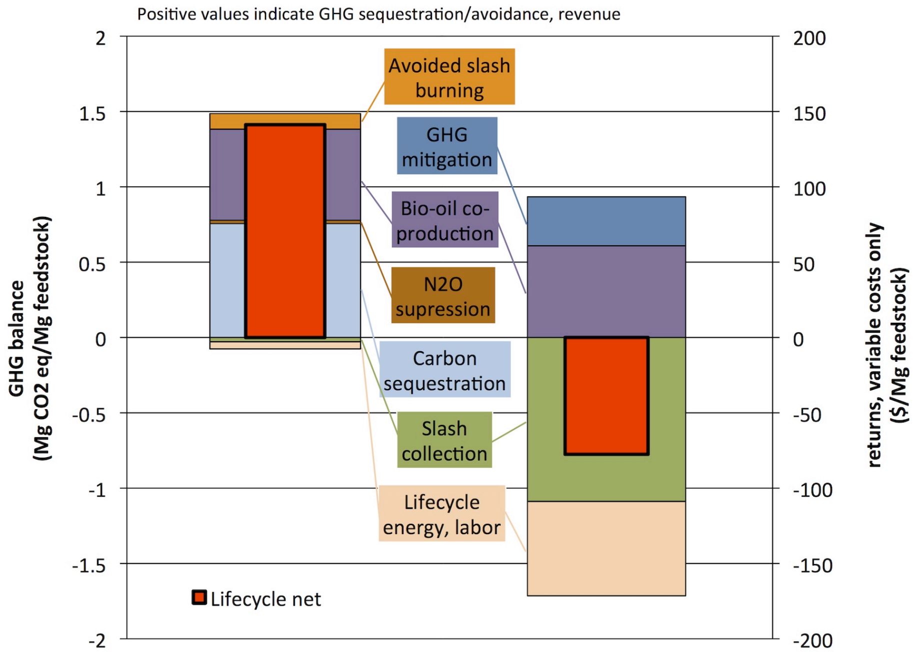

Figure 5.3. Detail of the GHG balance and economic returns for the slow pyrolysis of pine feedstock at 500 °C, assuming biochar application at 25 Mg/ha to a Corzad loam soil of pH 5.6 and CEC 15 $cmol_c$/kg. Valuation of GHG mitigation is based on a \$23/Mg CO_2eq estimate of the social cost of carbon using a 100 year analytical time frame for the calculation of CO_2 equivalence.

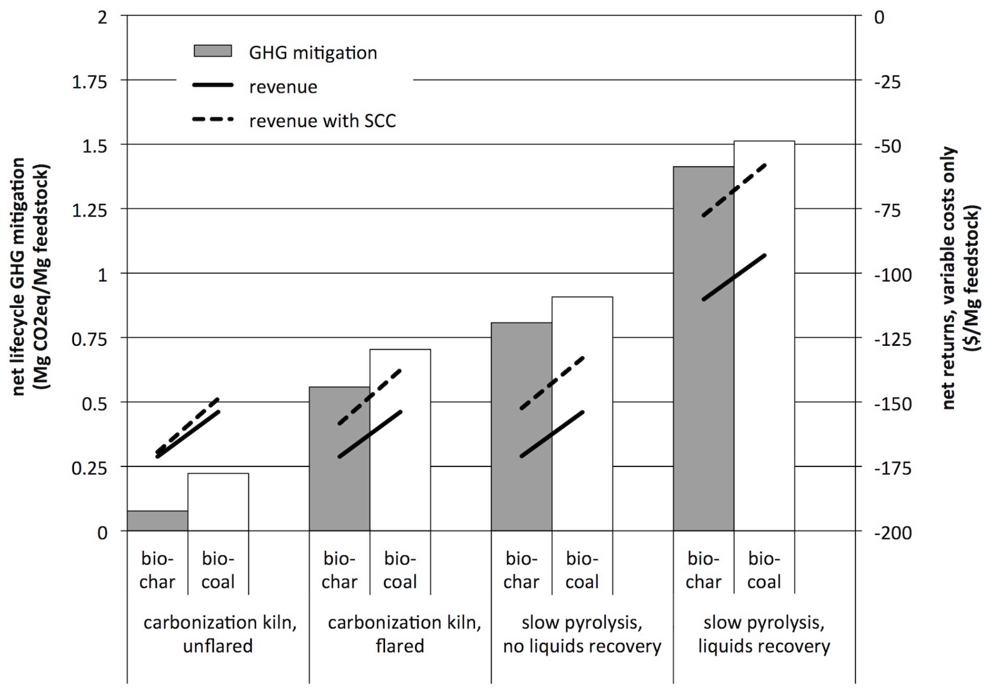

Figure 5.4. Net GHG mitigation and economic returns for different conversion technology configurations, with the resulting char used either as biochar or biocoal

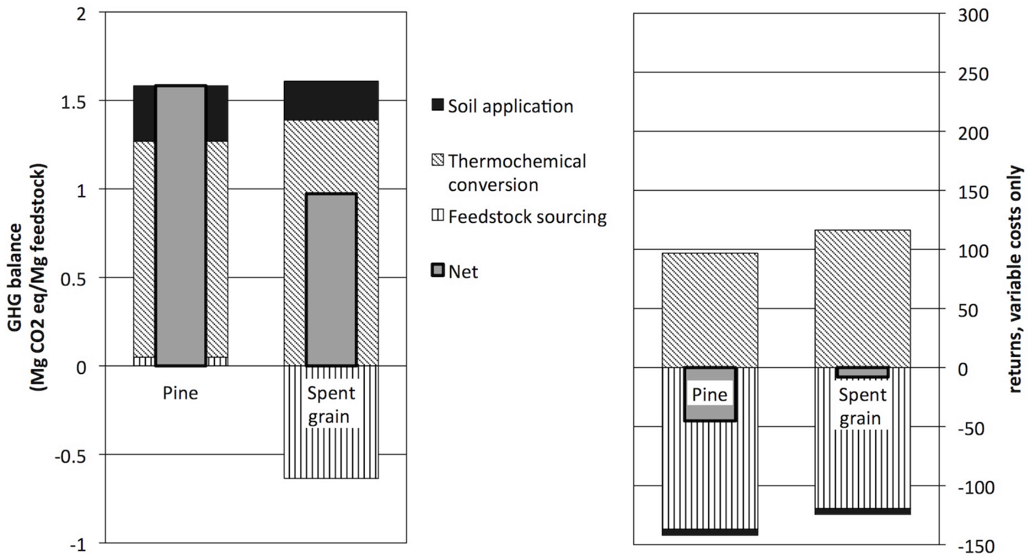

Figure 5.5. Simplified detail of the GHG balance and economic returns for the fast pyrolysis of pine and spent grains feedstocks at 500 °C

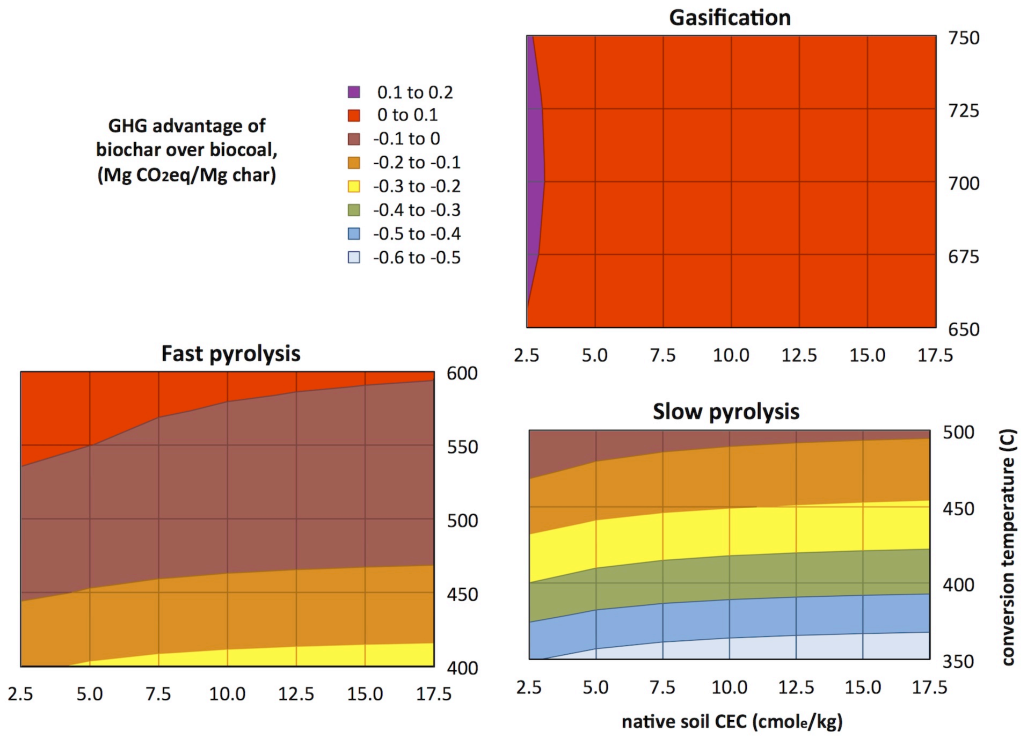

Figure 5.6. The relative GHG mitigation advantage of biochar over that of biocoal, plotted for char produced from multiple conversion technologies as a function of production temperature and soil CEC. Regions in which biochar outperforms biocoal are plotted in red and purple.

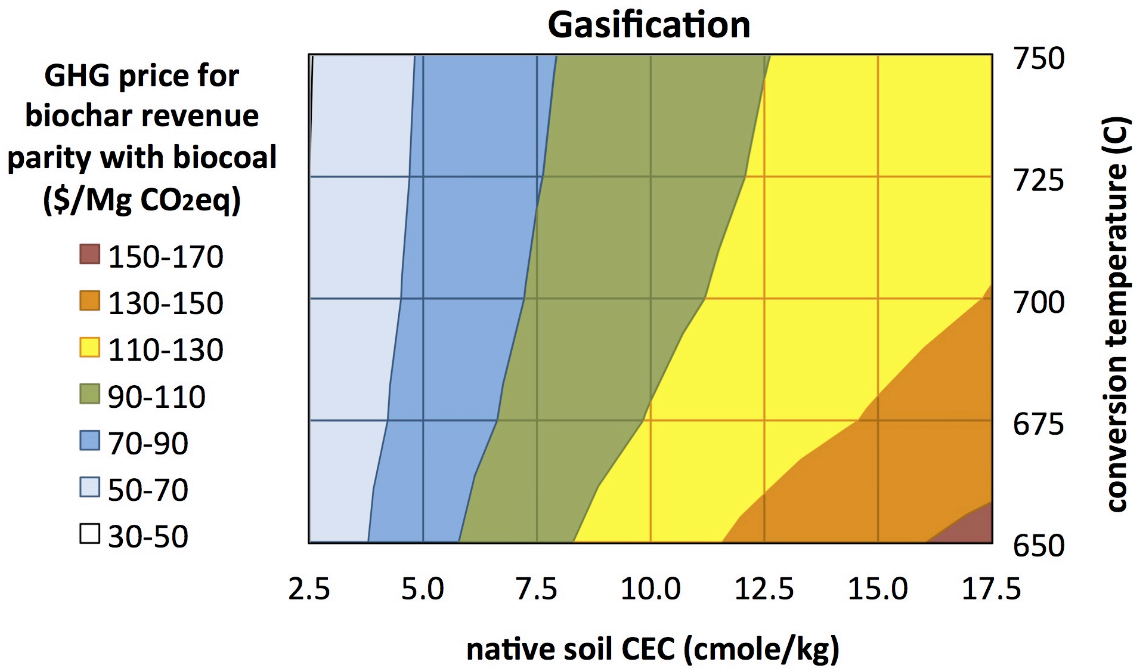

Figure 5.7. The price of carbon valuation necessary for biochar revenue to equal biocoal revenue (P_C), for char produced from the gasification of pine, as a function of production temperature and farm soil CEC

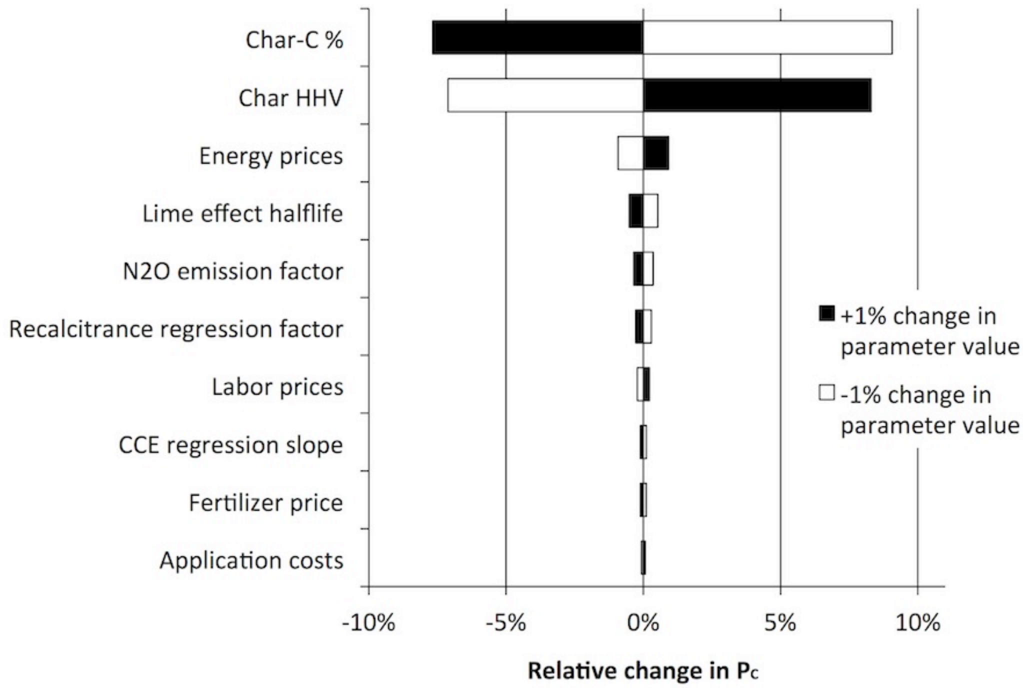

Figure 5.8. Sensitivity analysis for the carbon price for biochar-biocoal parity (P_C) for char produced from pine gasification at 700 °C and applied to soil of pH 5.0 and CEC of 10 $cmol_e$/kg

CHAPTER 6

CONCLUSIONS AND ONGOING WORK

Bioenergy is a widely-scalable renewable energy technology with significant climate mitigation potential through displacement of fossil energy use (Creutzig *et al.*, 2015). Bioenergy technologies are particularly attractive relative to other renewable energy sources for their potential to produce high-value liquid fuels that can integrate with present transport infrastructure, and potential for carbon sequestration in soils or geological reservoirs (Tilman *et al.*, 2006b; Fuss *et al.*, 2014). While lifecycle assessment (LCA) techniques have been applied for the study of bioenergy system environmental performance for several decades, agroecosystem management for feedstock provisioning introduces a variety of highly challenging conceptual and methodological issues around bioenergy supply chain climate impact accounting (as explored in detail in Chapter 2), many of which are still being resolved. Refining existing LCA tools and coupling them with economic analyses is critical for understanding the practical feasibility of bioenergy systems as a climate mitigation tool relative to other renewable energy technologies and land management interventions. The resulting integrated assessments are useful for producing estimates of system carbon abatement cost (CAC), i.e., putting a price tag on GHG mitigation associated with specific bioenergy supply chain substitutions or modifications. Table 6.1 shows the CAC estimates resulting from the two case studies of this dissertation in the context of several other bioenergy CAC estimates for various different bioenergy supply chains. Several of these studies include consideration of enhanced carbon sequestration through the addition of Carbon Capture and Storage technology or through ecosystem-mediated carbon sequestration in agricultural soils.

The case study results suggest that a) any valuation of climate mitigation will significantly affect optimal bioenergy landscape design, with a majority of potential mitigation benefits achieved at valuations as low as \$60/MgCO_2eq (Chapter 4); and b) use of thermochemical conversion co-products as soil amendments rather than low-quality process fuels becomes attractive when climate mitigation is valued at \$50/MgCO_2eq or greater (Chapter 5). Both results are well within the range of CAC values reported in the literature for different supply chain interventions, estimates ranging from slightly negative CAC values for some fossil-to-bioenergy transitions (i.e., bioenergy slightly cheaper than the fossil-fueled Business-As-Usual case; Bo, 1998; Ravindranath *et al.*, 2006), all the way up to \$500/MgCO_2eq or greater associated with some switches in conversion technology (Eason & Cremaschi, 2014) or land use change scenarios for perennial grass feedstock cultivation (Yu *et al.*, 2014). The latter study is similar in scope to the landscape design work presented here, but our much lower CAC estimate is likely the result of a more detailed biogeochemical assessment that considers correlation between land quality and land use history, and endogenizes crop management intensity. One might hypothesize that optimization studies with higher assessment resolution or wider scope will tend to identify lower-cost mitigation options that more limited studies might miss, though the number of studies present in the literature to date is insufficient to offer much empirical support on that point. The CAC value range predicted in the biochar case study is consistent with that from a previous biochar study in the literature (Clare *et al.*, 2015), but both of those are much higher than a recent CAC estimate range for the analogous case of lignin management in a biochemical conversion system (Pourhashem *et al.*, 2013). However, all of these studies are very sensitive to the potential agronomic benefits of these soil amendments, benefits that are not yet well characterized.

Pairing estimates of the carbon abatement costs of various technologies with estimates of their maximum scale of deployment allows for the development sector-wide (MacLeod *et al.*, 2010) or economy-wide (Enkvist *et al.*, 2007) carbon abatement curves. While the two case studies presented here each advance the state-of-the-art in bioenergy supply chain integrated assessment, additional work is necessary to prior to scaling these results up and generating credible estimates of regional or national bioenergy carbon abatement potential. This might include:

1. Conducting additional landscape design case studies to determine how maximum ecosystem-mediated carbon sequestration potential is controlled by climate and other environmental variables over greater spatial scales. To the extent that such a study would require the consideration of different regionally-appropriate feedstock crops, it implies the need for additional model parameterization and validation work, likely benefitting from automated tools as discussed in Chapter 3.

2. Introduction of more detailed spatial models of harvest logistics, biomass transport networks, and markets for finished biofuels. This need is probably best met through collaborations with other groups already developing such tools; to that end, a collaboration has been initiated with researchers at the Department of Transportation to link the landscape biogeochemical assessment capabilities developed here with an existing national-scale transport logistics and fuel demand model.

3. Enhancing the level of simulation detail around business-as-usual cropping systems, and considering their sustainable intensification as a strategy for increasing overall landscape productivity. These ideas are developed further in a recent response submitted to a

Department of Energy Request For Proposals on the topic of sustainable bioenergy landscape design.

4. Direct integration of non-conventional soil amendments such as biochar and pure by-product lignin into the DayCent biogeochemistry model, introducing environmental controls on amendment degradation dynamics and improving understanding around their agronomic effects, as discussed in Chapter 5. Preliminary work in this area is planned through the Bioenergy Alliance Network of the Rockies.

5. Development of more sophisticated biorefinery models and landscape optimization approaches beyond the weighted-solution approach presented in Chapter 4, in order to consider landscape cost-mitigation tradeoffs as a function of bioenergy system size.

Such additional work will be essential for determining the maximum potential scale of bioenergy deployment before limits on agroecosystem sustainable production are reached, and the total regional or global potential for bioenergy system carbon sequestration and climate mitigation.

Table 6.1. Recent estimates of carbon abatement costs associated with bioenergy supply chain modifications or substitutions. All cost estimates adjusted to 2015 USD values.

Study	**Scenario**	**Considers carbon sequestration?**	**Carbon abatement cost estimate ($ / Mg CO_2eq)**
Full supply chain			
Bo, (1998)	Replacement of fossil fuels in Swedish district heating systems with woody biomass	No[1]	$-16 to 52, depending on biomass source, fuel displaced
Ravindranath *et al.* (2006)	Replacement of coal consumption in Indian grid generation with various biopower technologies	No	$-27 to 51, depending on conversion technology
Dwivedi *et al. (*2015)	Replacement of gasoline with cellulosic ethanol from various feedstocks	Yes (soil carbon)	$52 to 405, depending on feedstock crop and land quality
Feedstock production			
Yu *et al.* (2014)	Optimized switchgrass land conversion for enhanced soil carbon sequestration	Yes (soil carbon)	Tradeoff frontier, half of mitigation achieved between $250 and 500
Dissertation chapter 4	Optimized switchgrass location and management for soil carbon sequestration	Yes (soil carbon)	Tradeoff frontier, half of mitigation potential achieved at ~$60
Conversion to fuels			
Möllersten *et al.* (2003)	BECCS addition to sugarcane biorefineries or pulp mills	Yes (BECCS)	$29 to 68, depending on the system type
Eason & Cremaschi (2014)	Changing from anaerobic digestion to gasification	No	~$800
Coproduct management			
Pourhashem *et al.* (2013)	Use of biochemical conversion lignin byproduct as soil amendment	Yes (soil carbon)	$-110 to 41, depending on exact agronomic benefits of lignin application
Clare *et al.* (2015)	Pyrolysis of agricultural residues for biochar production	Yes (soil carbon)	$50 to 70, depending on biochar agricultural performance
Dissertation chapter 5	Management of biochar as a soil amendment rather than a process fuel	Yes (soil carbon)	$50 to 150, depending on biochar synthesis temp. and target soil type

[1]Study considers sequestration in a separate reforestation scenario, but not within the bioenergy scenario

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APPENDIX A

A.1. Switchgrass Parameterization and Validation Dataset Development

In order to generate the largest parameterization and validation dataset possible, study requirements for inclusion were kept to a minimum level, with specifications required for each study focusing only on parameters to which the DayCent model is most sensitive: underlying soil type, total seasonal nitrogen application, supplemental irrigation, and ecotype being cultivated. Other parameters such as field preparation details, planting dates, nitrogen application dates, etc. still must be specified in order to complete a DayCent simulation, though they have much less effect on overall simulated yields, and average values were used as necessary to complete the simulations specification. Model initialization procedures and soil and climate data inputs are as described in the main text. It was assumed that all field trial sites had a generic non-irrigated cropped history, and that conversion to switchgrass required chisel tilling followed by a cultivator/planter.

Figures A.1 and A.2 show additional metadata associated with the US switchgrass parameterization and validation dataset. Note that there is little correlation between soil texture and land capability class rating, illustrating that high LCC ratings are driven by climate, topography, and soil profile depth in addition to extreme soil textures.

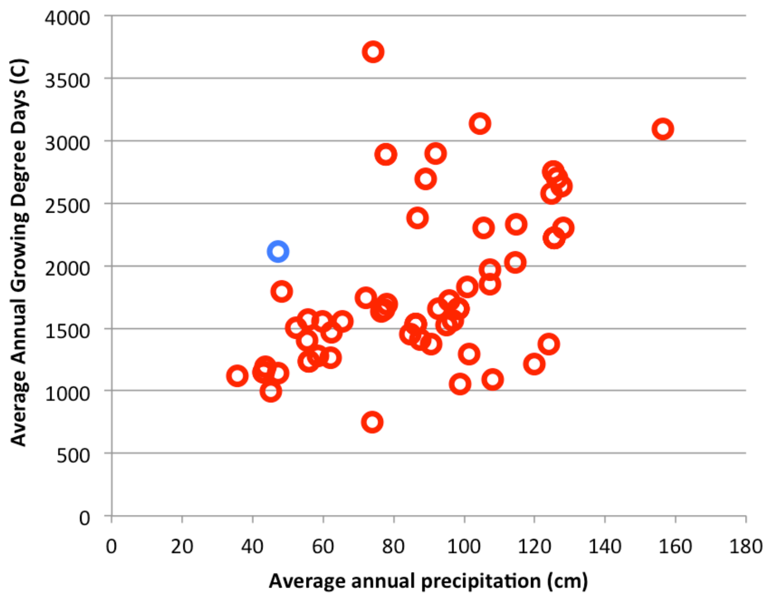

Figure A.1. Climate range covered in the full switchgrass calibration & validation dataset as per the NARR database. The blue point indicates the climate of Hugoton, KS.

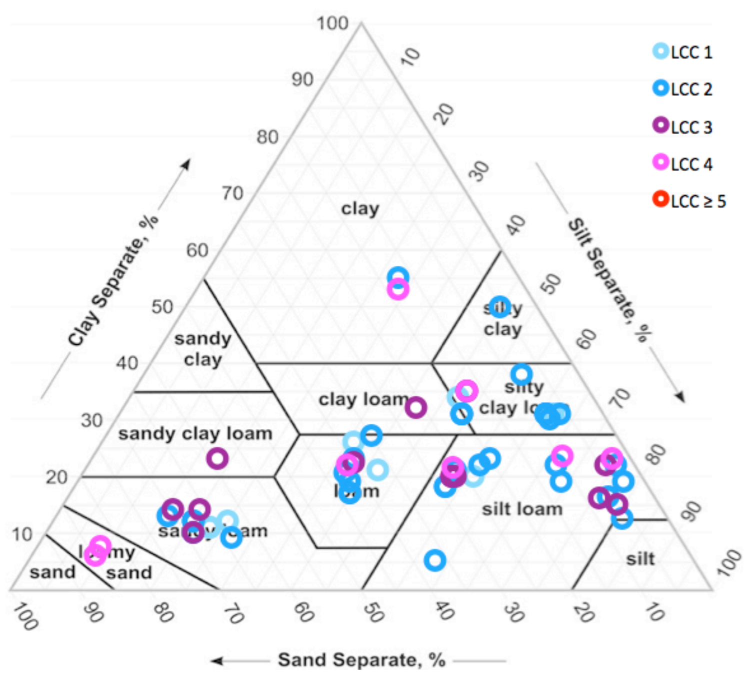

Figure A.2. Classification of calibration and validation dataset field trial sites by soil surface texture and NRCS land capability class (LCC) rating.

Scatter matrices for field trial site parameters (Fig. A.3) and soil parameters (Fig. A.4) are useful for understanding correlations in model inputs and looking for outliers indicative of dataset coding errors.

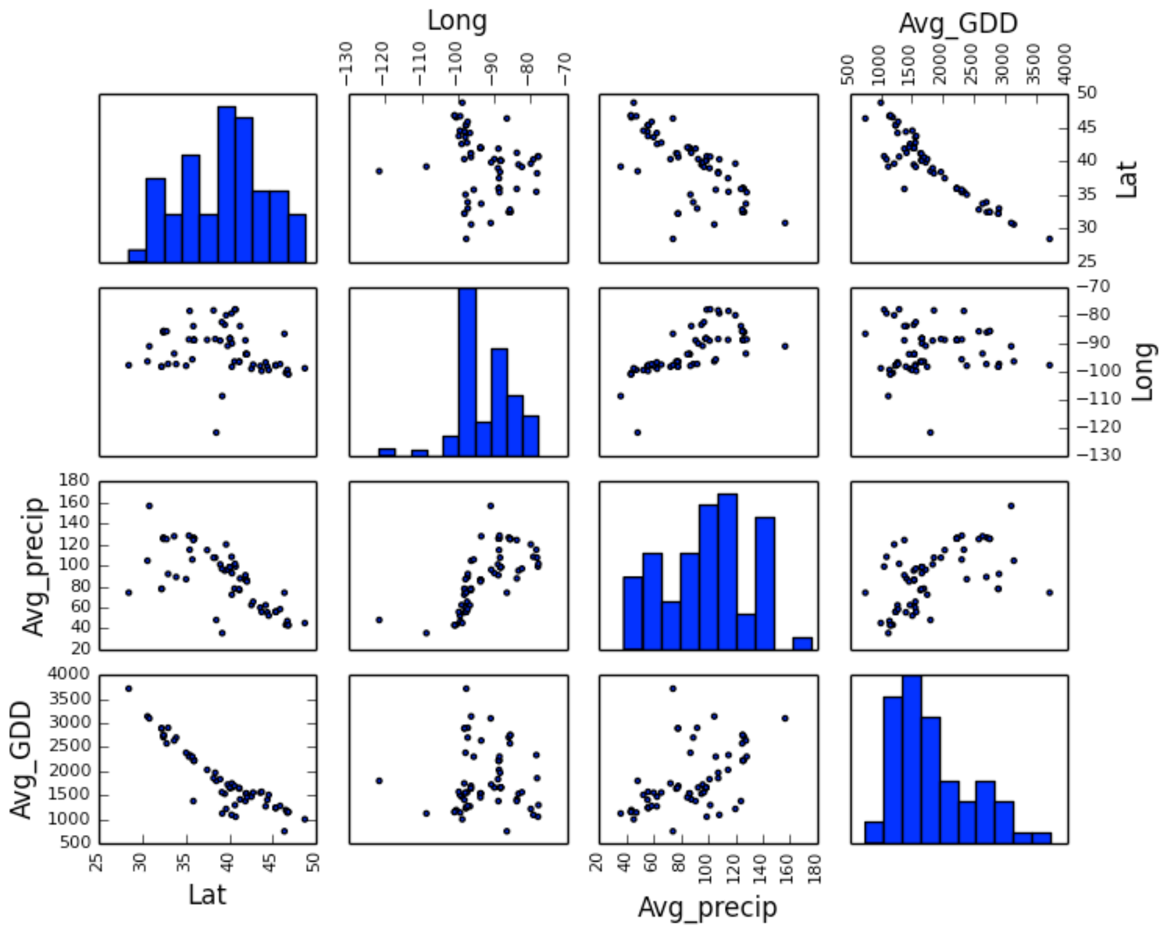

Figure A.3. Scatter matrix of site location and climate parameters in the switchgrass parameterization & validation dataset.

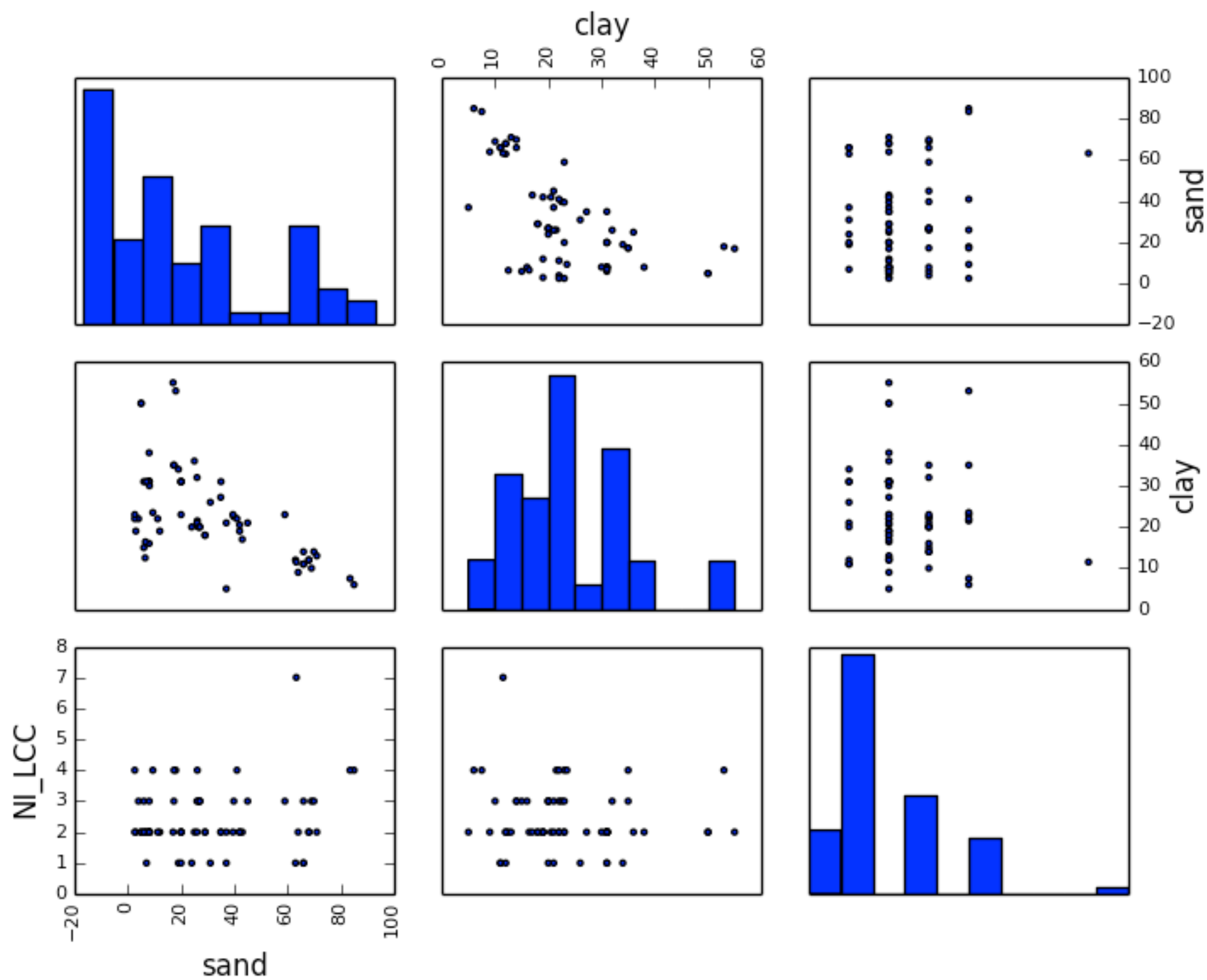

Figure A.4. Scatter matrix of soil parameters in the switchgrass parameterization & validation dataset.

A.2. Parameterization and Validation Detail

For both the parameterization and landscape simulation model runs we use DayCent in the mode where phenological events are pre-scheduled for a specific day of the year, rather than determined annually based on accumulated growing degree day thresholds. Green-up, heading, and peak biomass were estimated as a function of ecotype and/or site latitude as described in the main text, and illustrated in Fig. A.5 to A.7 below. The patterns of later heading for lowland ecotypes within a given site and later heading for both ecotypes at higher latitudes were across all of the studies we reviewed. Note that implementation often required minor adjustments to avoid conflicts with fertilizer application or harvest events.

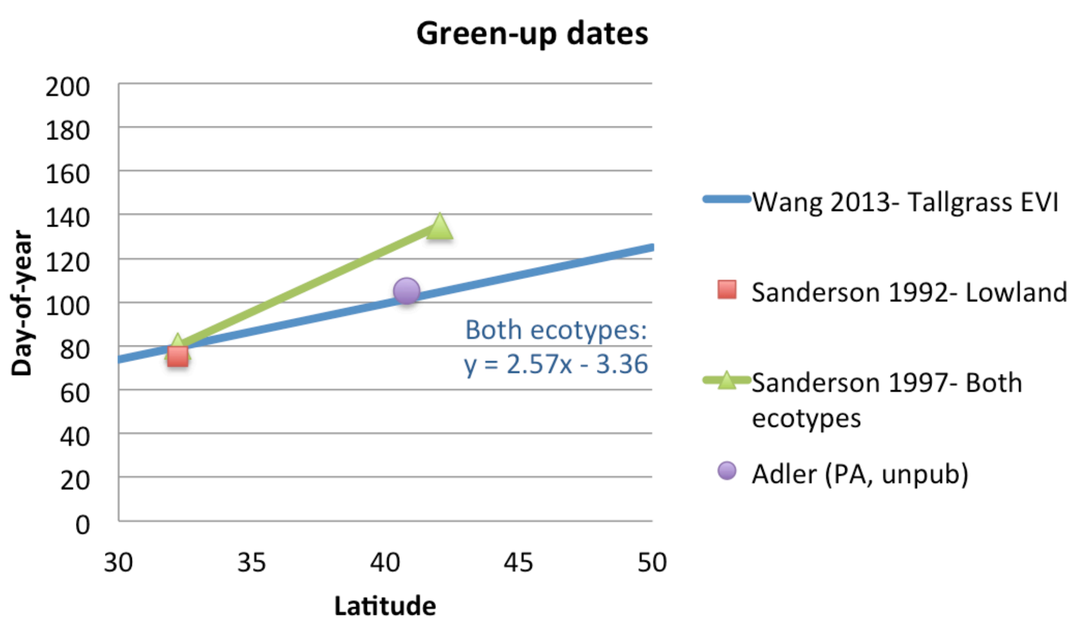

Figure A.5. Switchgrass green-up as a function of latitude only. The regression fit corresponds to the scheduling of FRST events in DayCent that define the first day of the year the simulated plant can perform photosynthesis and accumulate biomass.

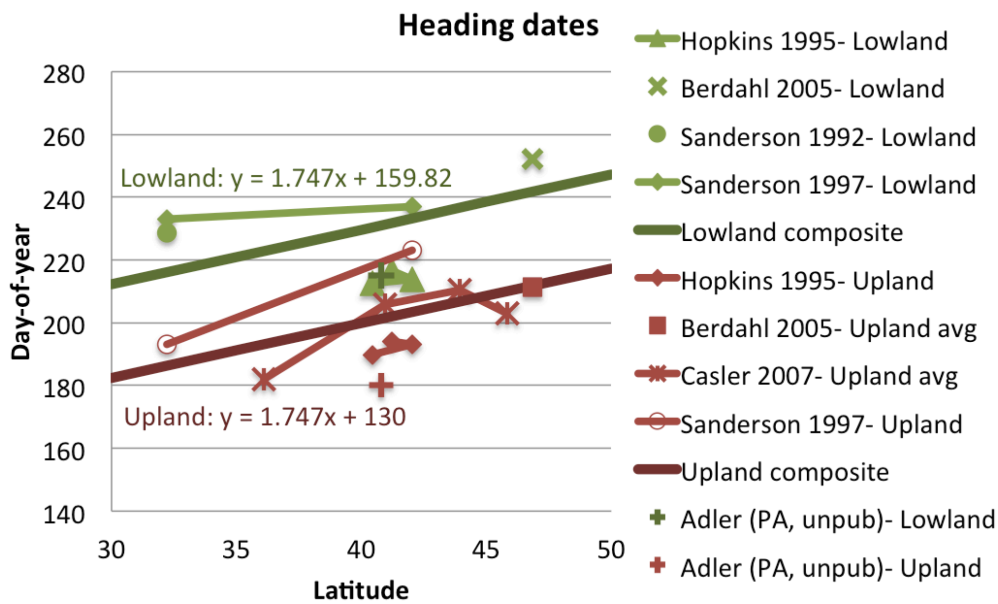

Figure A.6. Heading dates estimated as a function of ecotype and site latitude.

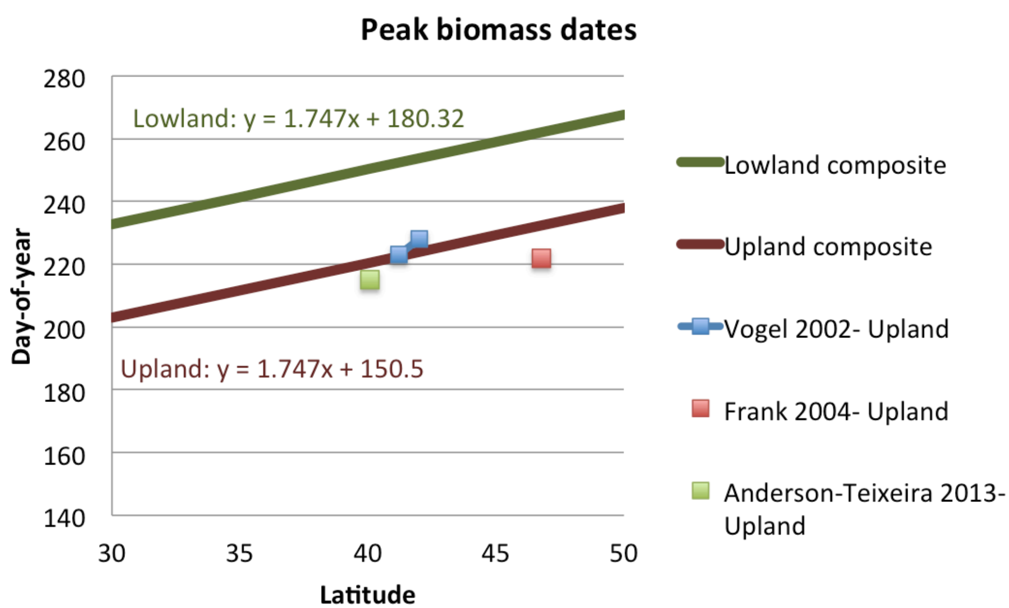

Figure A.7. Peak biomass as estimated to occur three weeks after heading, as compared to observations for upland switchgrass at multiple sites. These were used to set senescence SENM events in DayCent.

The same temperature and soil moisture response curves were used for both switchgrass ecotypes (Fig. A.8 to A.9). Curves were set based on the sources cited, with fine-tuning as necessary to improve modeled-vs.-measured yield fits (Fig. 3.2a).

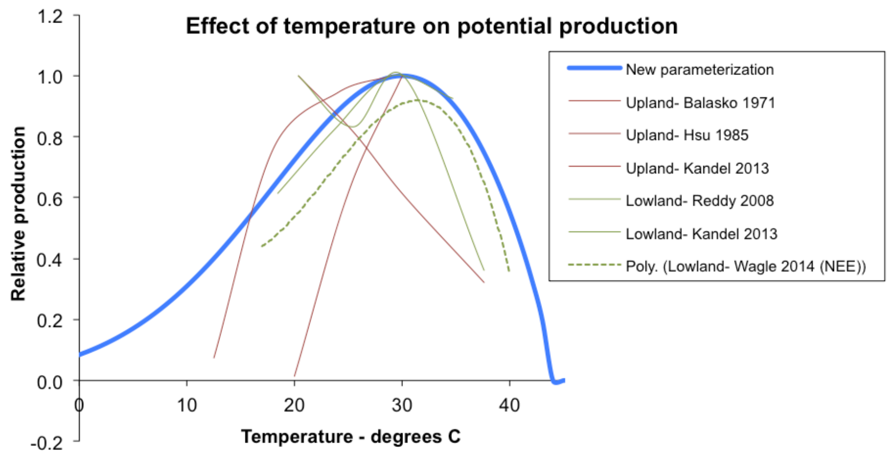

Figure A.8. Temperature stress response curve based on experimental data from a variety of sources (Balasko & Smith, 1971; Hsu *et al.*, 1985; Reddy *et al.*, 2008; Kandel *et al.*, 2013; Wagle & Kakani, 2014)

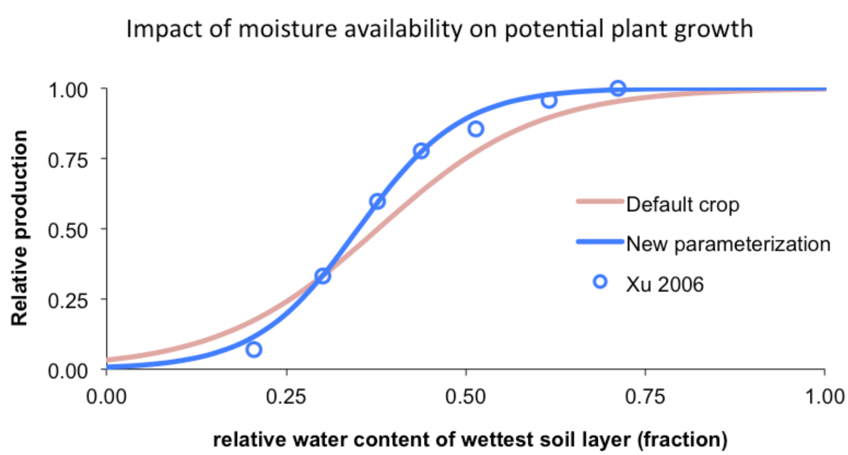

Figure A.9. Moisture stress response curve compared to normalized experimental data from Xu *et al.*, (2006) and model defaults.

Temperature and moisture stress response can also be inferred from measured and model yield plotted across a gradient of average annual site growing degree day (GDD) accumulation and precipitation levels, respectively.

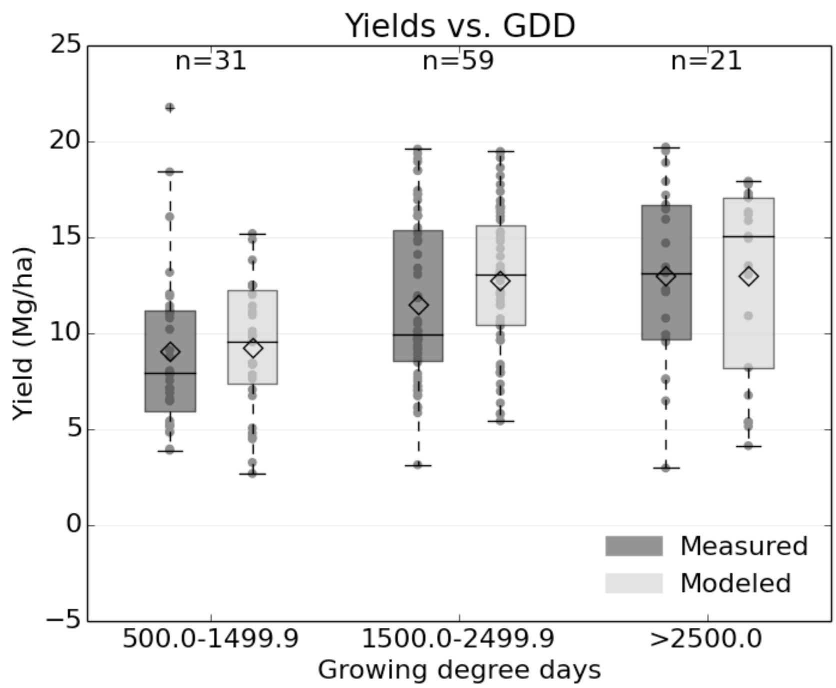

Figure A.10. Modeled and measured yield ranges binned by site average annual growing degree day accumulation (calculated for the range 12-30 C).

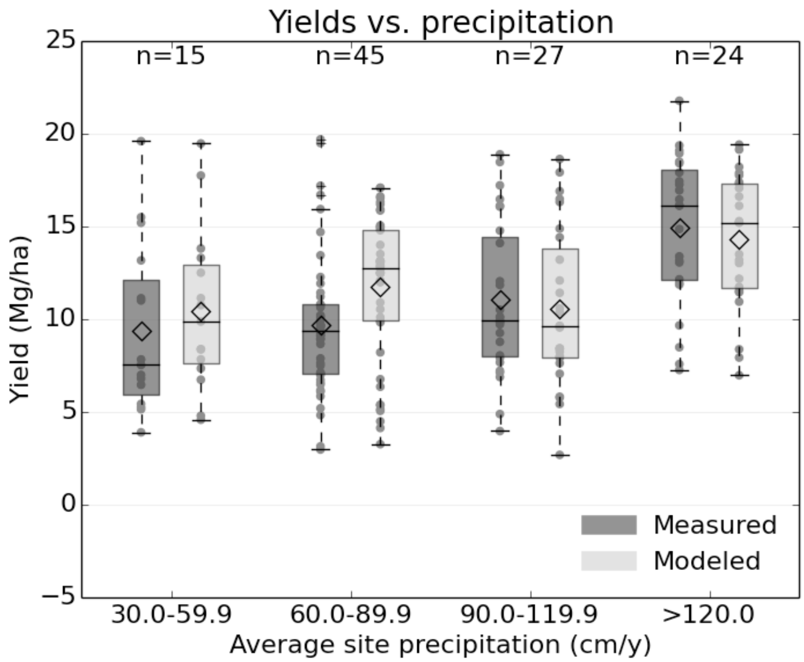

Figure A.11. Modeled and measured yield ranges binned by site average annual precipitation.

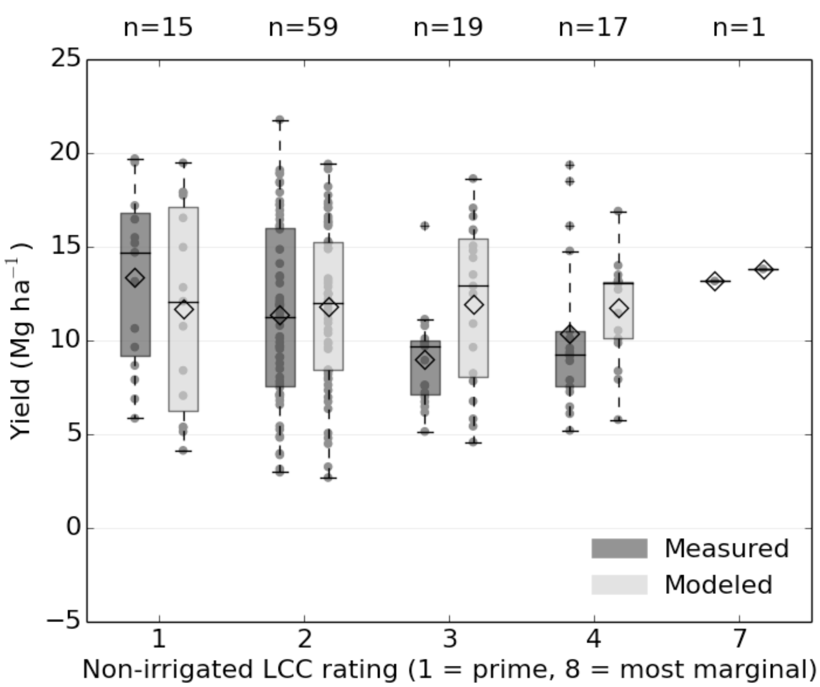

Figure A.12. Modeled and measured yield ranges binned by site NLCD land capability classification.

Likewise, the accuracy of our assumptions about crop phenology can be validated against field trials that report aboveground and belowground biomass accumulation over time, for example:

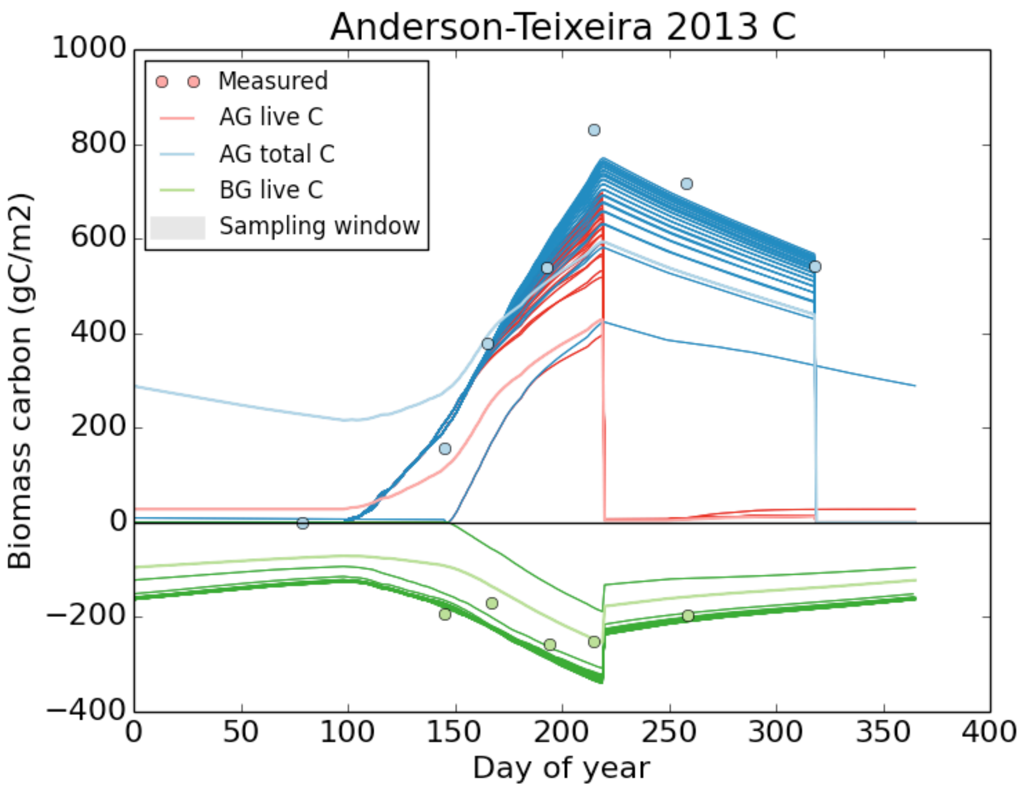

Figure A.13. Example of an observed-modeled comparison for a study (Anderson-Teixeira *et al.*, 2013) where time-resolved data is available for more detailed comparison, in this case for total aboveground carbon and belowground live carbon.

More detailed views of model soil greenhouse gas flux validation results are shown below for change in soil organic carbon (Fig. A.14) and growing season cumulative nitrous oxide emissions (Fig. A.15) for individual studies.

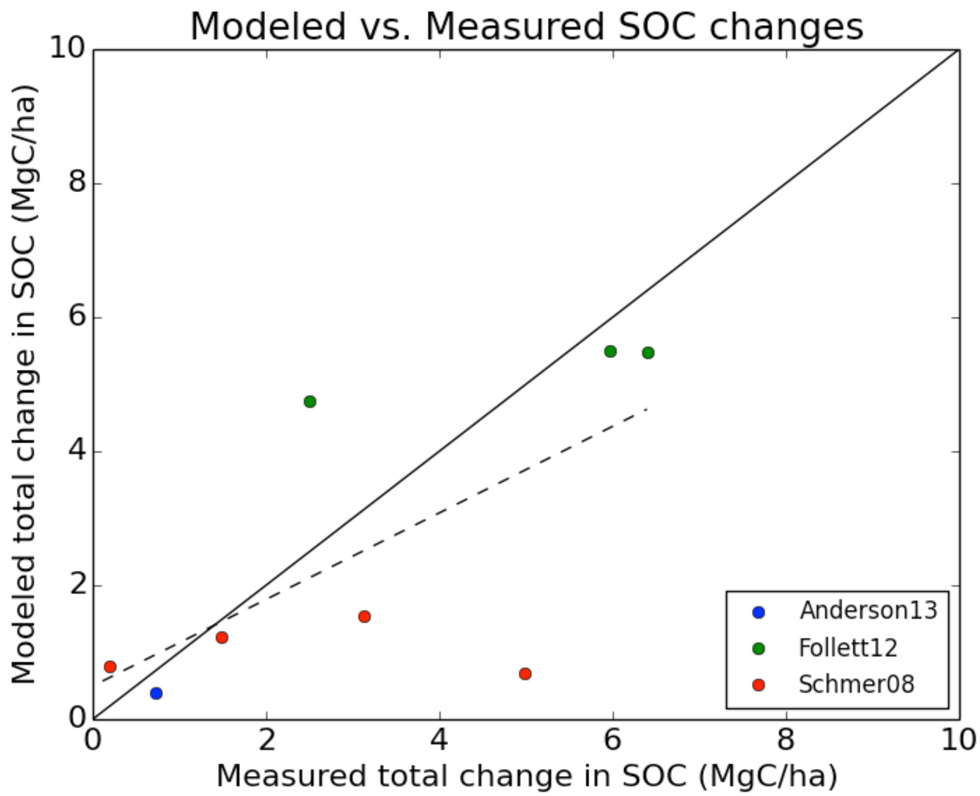

Figure A.14. Modeled-versus-measured changes in soil organic carbon by study for all studies in the parameterization & validation dataset that include usable SOC measurements.

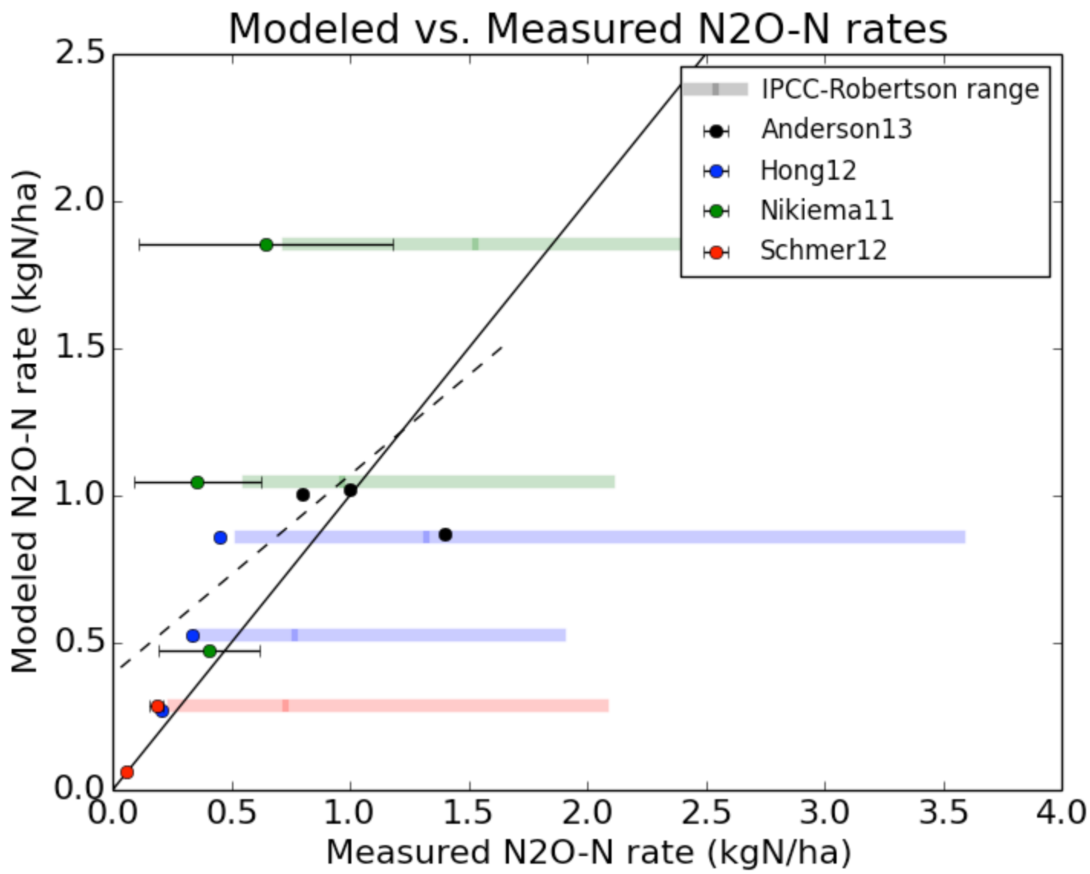

Figure A.15. Modeled-versus-measured cumulative annual emissions of nitrous oxide by study for all studies in the parameterization & validation dataset that include usable N_2O measurements. For studies that include background N_2O rates in unfertilized control treatments, a band of N_2O emissions based on the default IPCC emission factor as per Hoben *et al.*, 2011 (i.e., background N_2O rate plus 0.3-3% N_2O-N per mass of fertilizer N applied) is included for reference.

A.3. Landscape Analysis Detail

Fig. A.16 below shows the relative distribution of areas for the different polygons resulting from the intersection of the different input spatial data layers described in the main text and summarized in Table 3.2, and merging any resulting slivers of <1 ha in area into their neighbors.

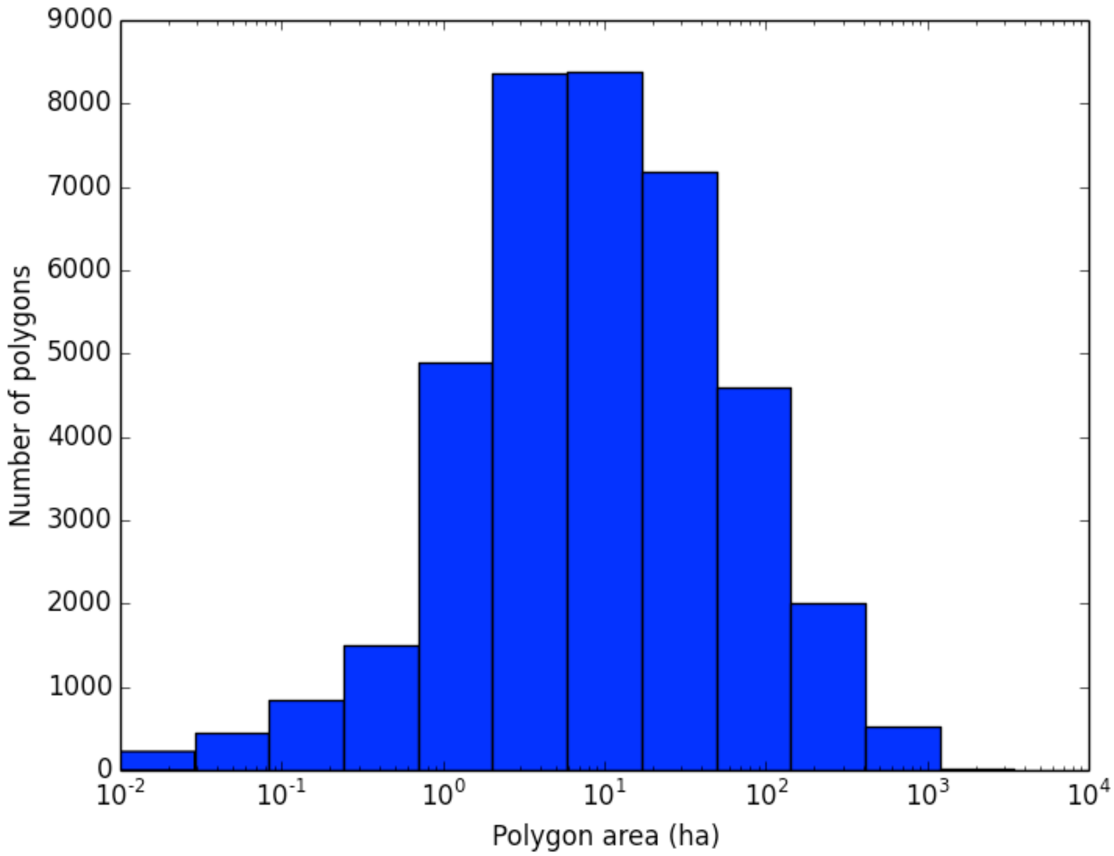

Figure A.16. Histogram showing the area distribution of the polygons generated during the GIS intersect operation.

A.4. Dynamics of SOC Changes and N_2O Emissions

While the average biogenic greenhouse gas footprint of switchgrass cultivation is a function of both soil carbon sequestration and nitrous oxide emissions, these two phenomena have different trends over time, as soil carbon storage potential is finite and sequestration rates will asymptotically return to zero over time, whereas N_2O emissions will continue as long as the crop is being fertilized with nitrogen-containing fertilizers. In this representative example from the Hugoton case study, soil carbon sequestration rates are very high for the first 15 years after establishment, but decline towards zero in the long-term. N_2O emissions also start high, presumably due to additional mineral nitrogen release associated with tillage and soil carbon pool turnover during establishment, but stabilize within ~10 years. However, it takes 60-80 years for carbon sequestration to fall to levels where annual sequestration is counterbalanced or exceeded by N_2O emissions, and the time-averaged biogenic greenhouse gas footprint of cultivation is strictly negative (net sequestration) a century after establishment. A more advanced approach to dynamics of GHG emissions accounting would tend to discount future emissions of N_2O relative to near-term sequestrations of soil carbon, further reinforcing the positive performance observed here.

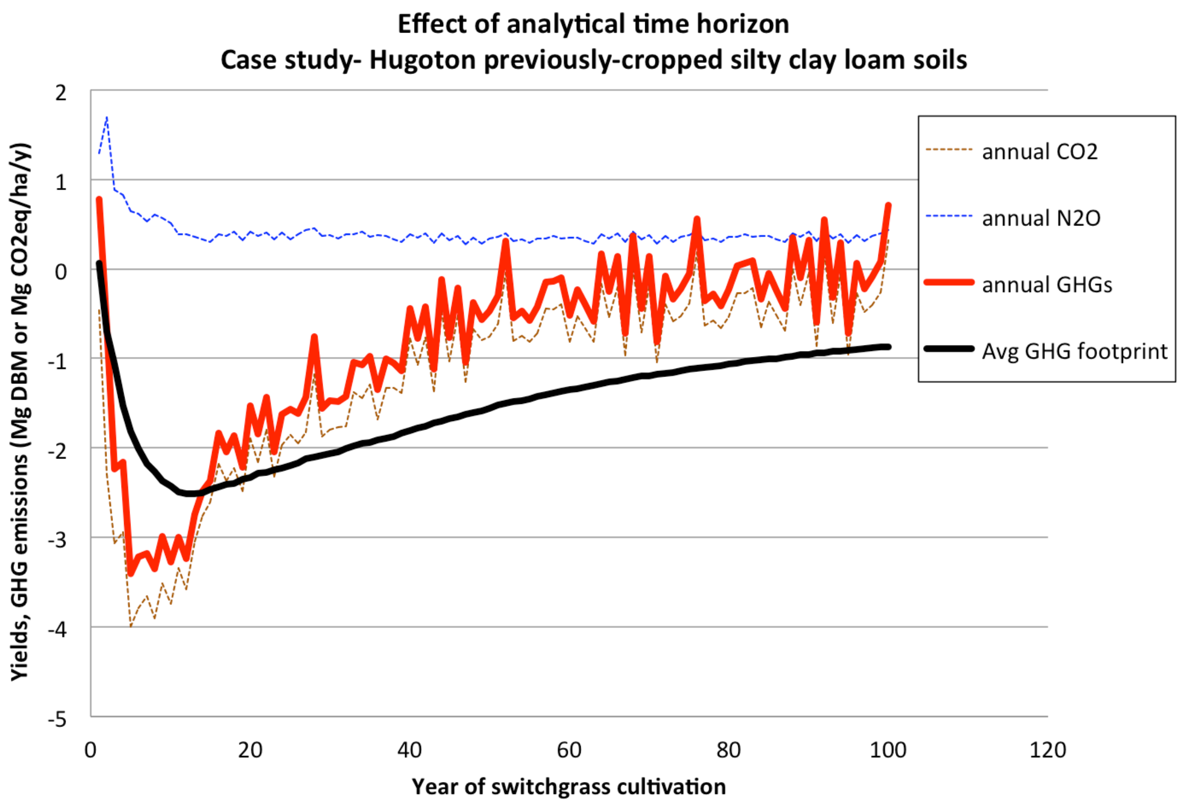

Figure A.17. Annual fluxes, assuming moderate tilling during field preparation for initial switchgrass crop establishment and every 8 years when the crop is replanted.

APPENDIX B

B.1. Cost Calculations

Net present value is useful for judging the desirability of projects that require up-front costs to secure future revenues. The NPV of a cash or material flow time series X_t over a time period T is given by:

$$NPV(X_t) = \sum_{t=0}^{T} \frac{X_t}{(1+d)^t}$$

where d is the annual discount rate, which reflects the opportunity cost of committing resources to the project. As per (Jain *et al.*, 2010), the break-even farm gate cost of biomass production that involves inputs and outputs that change from year to year can be represented as the NPV of the net cost of biomass cultivation divided by the discounted amount of biomass produced:

$$P_B = \frac{NPV(C_{tot,t})}{NPV(Y_t)}$$

where $C_{tot,t}$ is the total net cost of biomass cultivation each year t, and Y_t are the associated annual biomass yields. The farming costs considered in the USDA FARM switchgrass production budget include some (e.g., tillage, herbicide application) as a pure function of area (), and others as a function of biomass yield (e.g., P and K replacement, biomass baling). The net cost of biomass cultivation is generally estimated based on the amount of agricultural inputs and the field operations required to cultivate the biomass crop, minus the opportunity cost of land conversion per hectare C_{opp}:

$$P_B = \frac{\sum NPV(C_{area,t}) + \sum NPV(C_{yield,t} \cdot Y_t) - NPV(C_{opp,t})}{NPV(Y_t)}$$

B.2. Farm Model Harmonization

In the interest of a self-consistent assessment it is essential to harmonize assumptions around farm inputs and operations across the switchgrass production budget from the USDA FARM model, and the switchgrass production pathway in the GREET LCA model. The GREET model lacks detail on switchgrass cultivation requirements, and uses conservative numbers taken from Miscanthus instead (Wang *et al.*, 2013c). For this analysis, we use the very detailed set of switchgrass inputs and non-harvest farm operations in the USDA FARM model, based on a composite review of multiple previous assessments in the literature. In order to translate the farm operations into diesel fuel consumption rates in GREET we use operation fuel requirement estimates from the University of Iowa Extension (Hanna, 2005). This results in a non-harvest diesel energy intensity of 28,961 BTU/ton at the standard GREET yield level of 15 Mg/ha (Dunn *et al.*, 2011), compared to the default assumption of 50,000 BTU/ton. Since all of these operations are defined on area terms, we correct for DayCent-estimated area yield for each polygon. In contrast, the default GREET estimate of harvest energy use is much more detailed, and we lack a strong basis for translating the USDA FARM assumptions to diesel rates. In this case, we assume the default GREET harvest energy use assumption of 127,700 BTU/ton, invariant with yield. As our production is non-irrigated we delete the GREET default value for on-farm electricity consumption.

Both the DayCent simulations and the crop production budget are adjusted to reflect a 10-year replanting rate assumption, and NPV calculations are done on the same 30 year period as the bioenergy yield & biogenic GHG simulations.

B.3. Transport Model

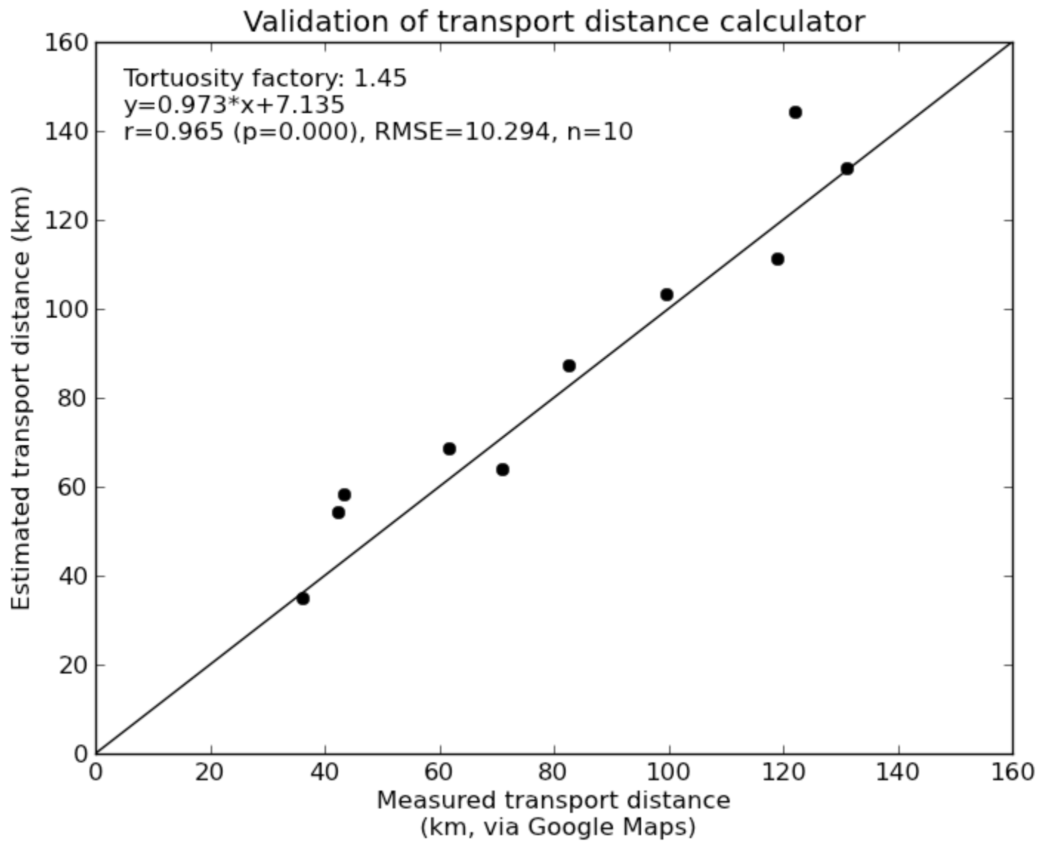

Figure B.1. Validation of the simplified transport distance estimate based on a calculation of geographic distance and application of a constant tortuosity factor representative of the area road network.

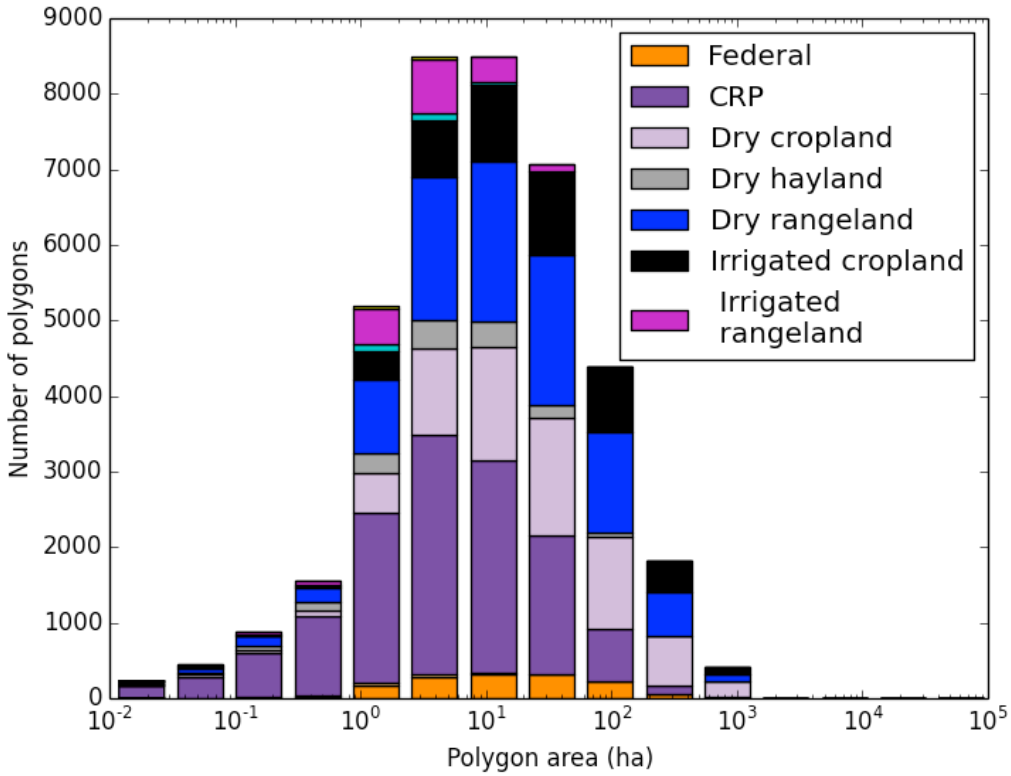

Figure B.2. Distribution of landscape GIS intersect polygon sizes, detailed by land use classification.

Results are included here based on NRCS Land Capability Classification rating. The DayCent model is able to represent this classification to the extent that the ratings are based on climate/texture combinations, or other factors such as topography that correlate strongly with texture in our case study landscape.

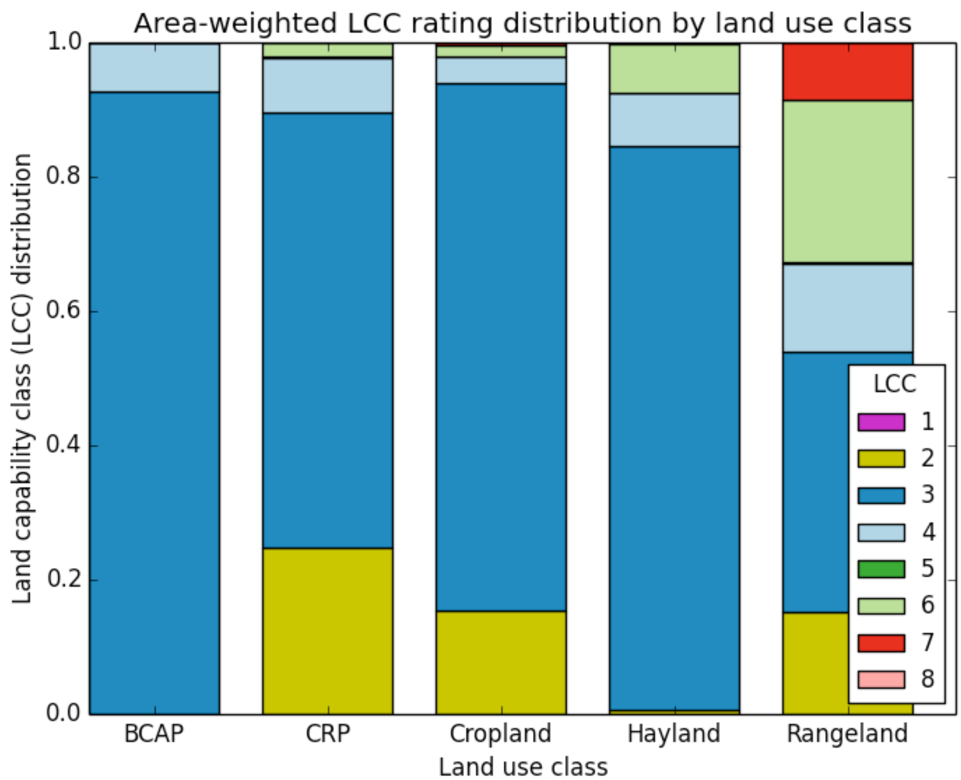

Figure B.3. Distribution of NRCS Land Capability Class ratings underlying the different land use classifications of the case study area. An LCC rating of 1 indicates prime cropland with no limitations on agricultural use, whereas LCC=8 indicates extremely marginal land unsuitable for cultivation.

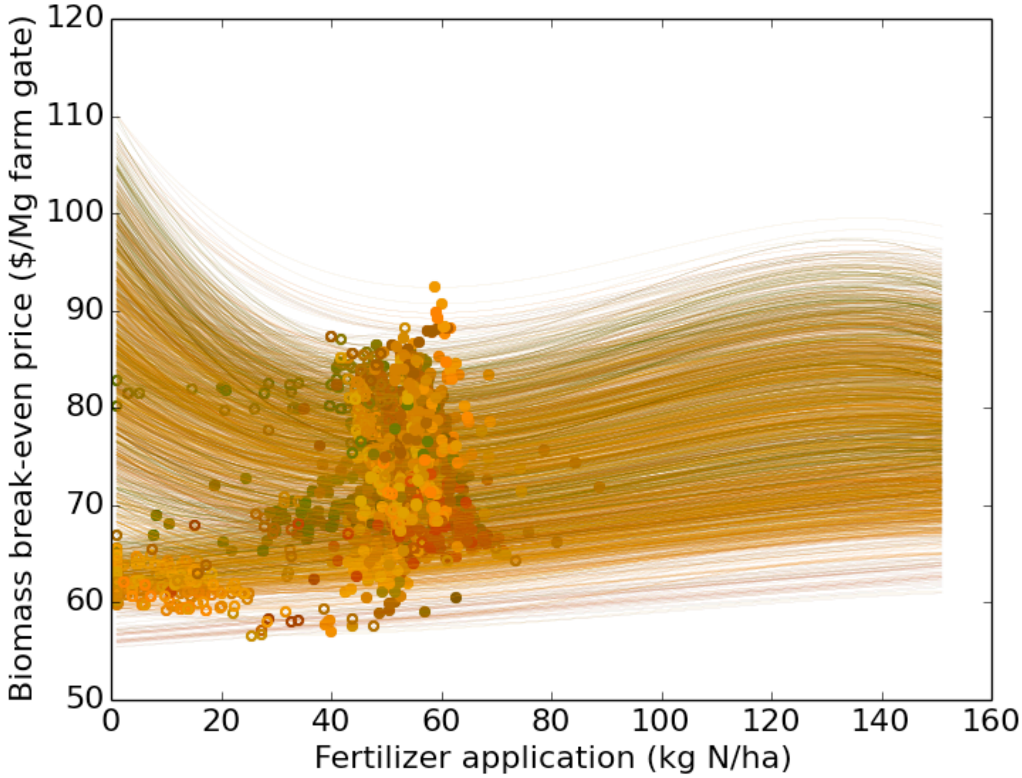

Figure B.4. Estimates of the farm-gate break-even price of switchgrass production as a function of nitrogen application rate across the 3779 DayCent simulation strata. Open markers represent price minima for rangeland conversion, closed markers for cropland conversion. The color of the markers and traces represents soil surface texture, with yellow=sand, red=clay, green=silt, and brown=loam.

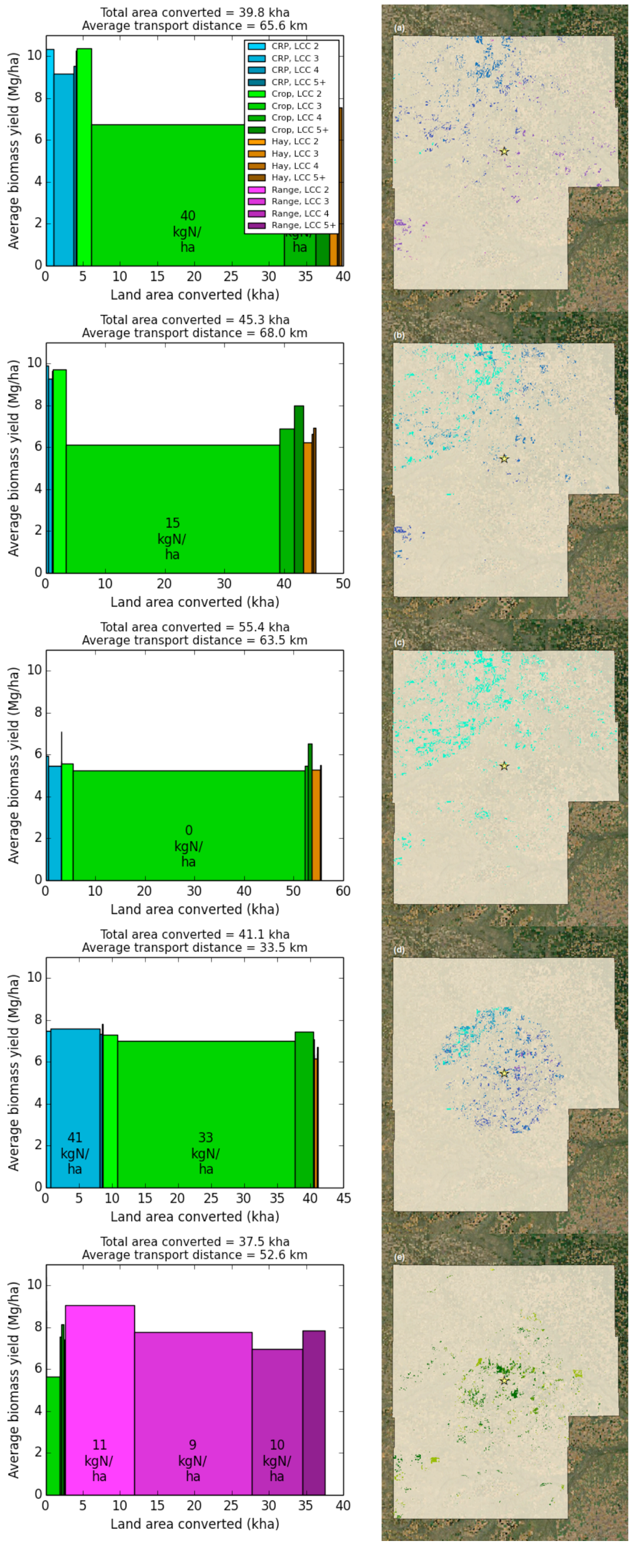

Figure B.5. Landscape optimization detail scenarios, showing total areas of land converted and associated average management intensity and yield, broken down by land use and LCC rating.

APPENDIX C

C.1. GHG Accounting

The calculation of global warming potentials (GWP) allows for the direct comparison of the long-term warming impact of different climate-forcing agents relative to a pulse emission of CO_2 on a mass basis, accounting for both the forcing magnitude and atmospheric lifetime of a pulse emission (Solomon et al., 2007). Since a fraction of the reference CO_2 pulse will remain in the atmosphere for geological time periods, it is necessary to evaluate the relative impact of the other emission over a finite analytical time horizon, with 20-, 100-, and 500-year time horizons commonly used. The choice of time horizon is arbitrary but representative of the time frame over which climate-change damages and policy responses are assessed; the choice of longer time horizons effectively de-weights the impact of short-lived forcing agents. A 100-year analytical time frame was used throughout this analysis. GWP-100 values for pulse emissions of CH_4 and N_2O are given by the IPCC as 25 and 298, respectively. Carbon monoxide and non-methane hydrocarbons were assigned GWP values of 1.9 and 3.4 to reflect the relative rapid oxidation of their C to CO_2 after release (Grieshop et al., 2011). Aerosols such as particulate matter (PM) emissions have a strong climate forcing value and are emitted in considerable quantity in uncontrolled or poorly-controlled combustion processes (Molina et al., 2009). Grieshop et al. 2011 suggest that the 100-year equivalent GWP of particulate matter emissions from biomass combustion can be calculated as

$$GWP_{PM-100} = 455 \cdot BC - 35 \cdot OC$$

where BC is the fraction of the total PM emission that exists in the form of black (elemental) carbon, OC the fraction as organic carbon, and 455 and -35 are literature-averaged global mean

GWP estimates. Calculation of the carbon stability factor of biochar is detailed in the main document, and Figure III.1 shows biochar carbon sequestration value plotted as a function of char soil half-life as evaluated over various common analytical timeframes.

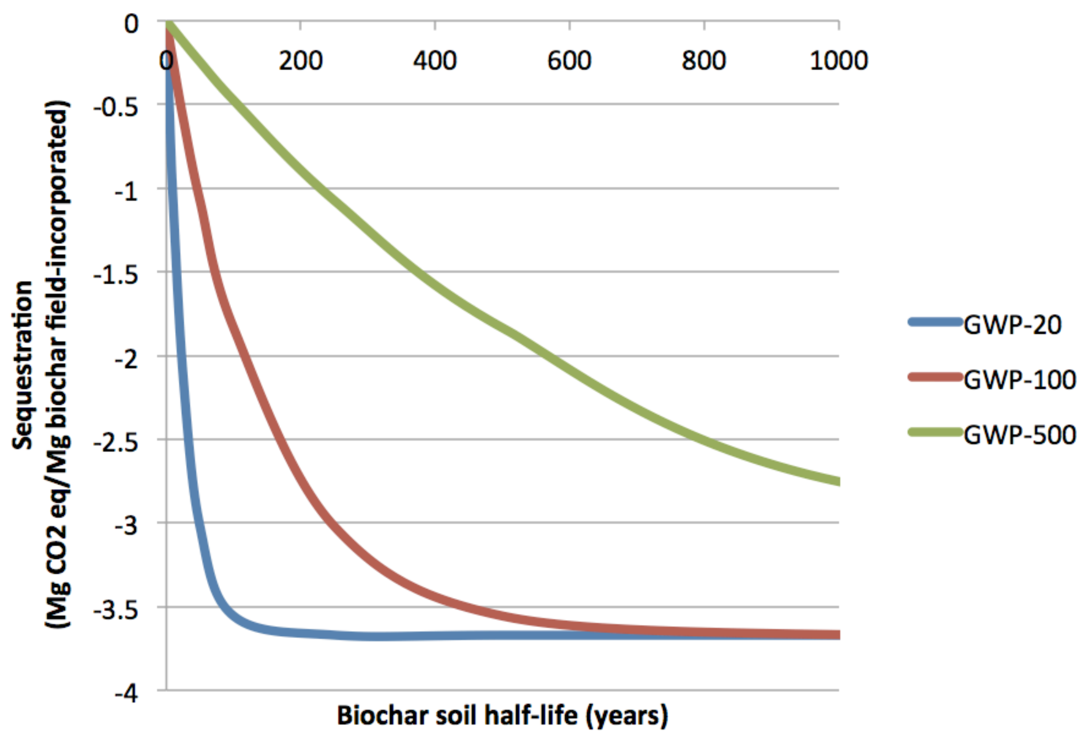

Figure C.1. Carbon sequestration value of biochar as a function of its half-life in soil

C.2. Feedstock Sourcing

An overview of the calculations associated with the pine biomass feedstock is given in the main article. An emissions intensity term of 0.26 mmton CO_2eq/$billion for the US forestry sector (US Department of Commerce, 2010) was used in the analysis to estimate the GHG footprint of pine feedstock sourcing operations for which price estimates are readily available in the literature but energy and emissions data are not. Estimates of emission factors for CO, CH_4, NMHC, N_2O, and PM (both EC and OC) from the open burning of lodgepole pine were taken from McMeeking *et al.* (2009), and a mixture GWP of 103 g CO_2eq/kg dry pine waste burned was computed.

In the spent grain feedstock scenario the thermochemical conversion facility was assumed to be co-located at the brewery where the spent grain is produced at a moisture content of 40%. Since the alternate use of spent grain is as animal feed which substitutes for corn and soybean products, an estimate of the forgone mitigation of corn and soy cultivation emissions that would have been avoided had the material not been used as a feedstock must be included. It was assumed that the spent grain is functionally equivalent to distillers grains and solubles (DGS) and a co-product emissions penalty of 0.44 kg CO_2eq/kg dry DGS was derived from the Argonne National Laboratory GREET 1.8d model (Wang, 1999; Arora et al., 2008), based on the displacement method (Kendall and Chang, 2009). The spent grain was assumed to be dried down to 10% moisture content with associated consumption of energy in the form of natural gas as per Wright *et al.* (2010). On-site receiving and handling costs ($2.10/dry ton) were taken from Hess *et al.* (2009) and used to estimate GHG emissions using the forestry sector emissions intensity factor.

C.3. Transport

The analysis modeled transport of pine feedstock and biochar in heavy trucks with 50,000 lb. (22 Mg) capacity and fuel efficiency of 5.5 and 6.5 mpg (2.3 and 2.8 km/L) loaded and unloaded, respectively, based on default values from a trucking cost model (Norris, 2009). It was assumed that the bulk density of all material being transported is high enough such that full truck weight capacity is met, i.e. that vehicle volumetric capacity is not limiting.

C.4. Thermochemical Conversion Product Yields and Qualities

Thermochemical conversion product fractions and associated carbon concentrations and higher heating values used in the model are plotted as a function of production temperature for the main technologies analyzed in figures C.2-C.4. While the entire fast pyrolysis dataset (including product yields and qualities) is derived from a single study, the limited studies available in the literature for the slow pyrolysis and gasification of pine necessitated that data from multiple similar (but not identical) studies be combined to form composite datasets representing these technologies. Data on slow pyrolysis yields for pine wood (Şensöz & Can 2002) and pine bark (Şensöz 2003) were combined in a weighted average based on their relative proportion in the stems of pine trees as reported by Peichl & Arain (2007). Data on the associated quality of those products is taken from Şensöz (2003) for production at 450 °C, and adjusted as a function of production temperature based on the curve fits for the DeSisto *et al.* (2010) fast pyrolysis dataset. For the pine gasification dataset, continuous product yield and gas composition data for the steam gasification of pine wood chips were taken from Herguido *et al.* (1992) and paired with static estimates of char carbon content and heating value from air-blown gasification as reported in Brewer *et al.* (2009).

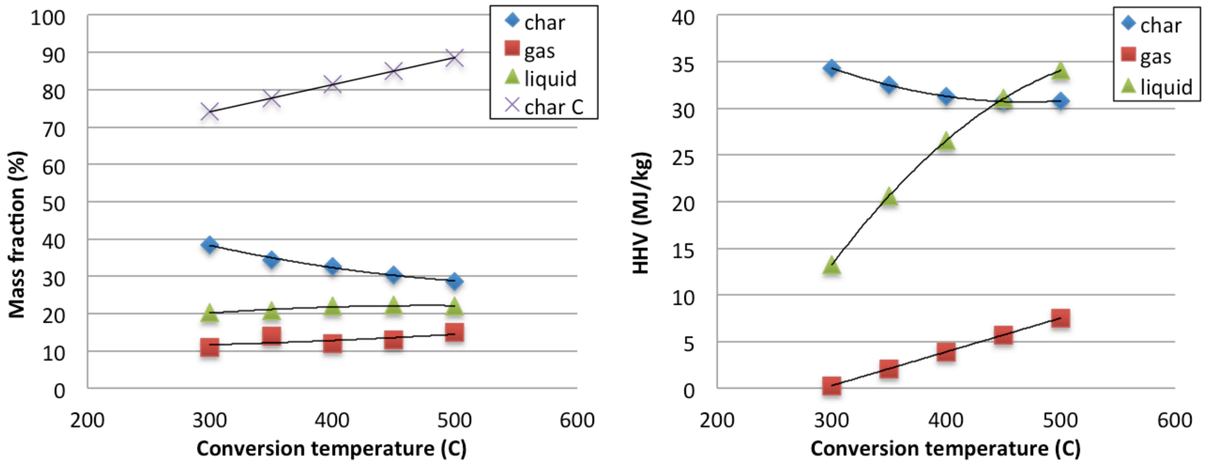

Figure C.2. Estimated product yields and qualities from the slow pyrolysis of pine

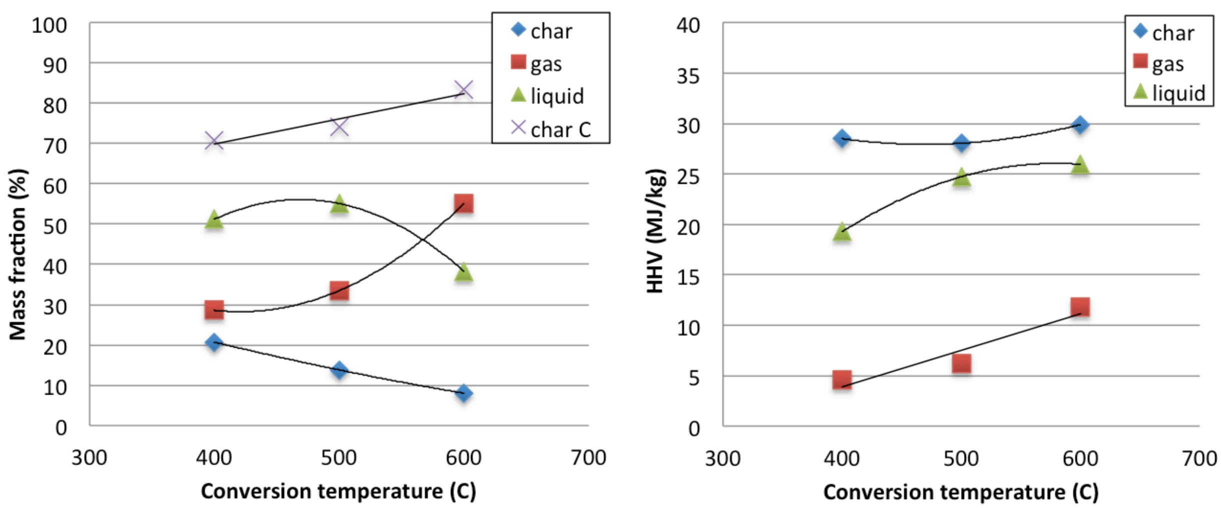

Figure C.3. Estimated product yields and qualities from the fast pyrolysis of pine

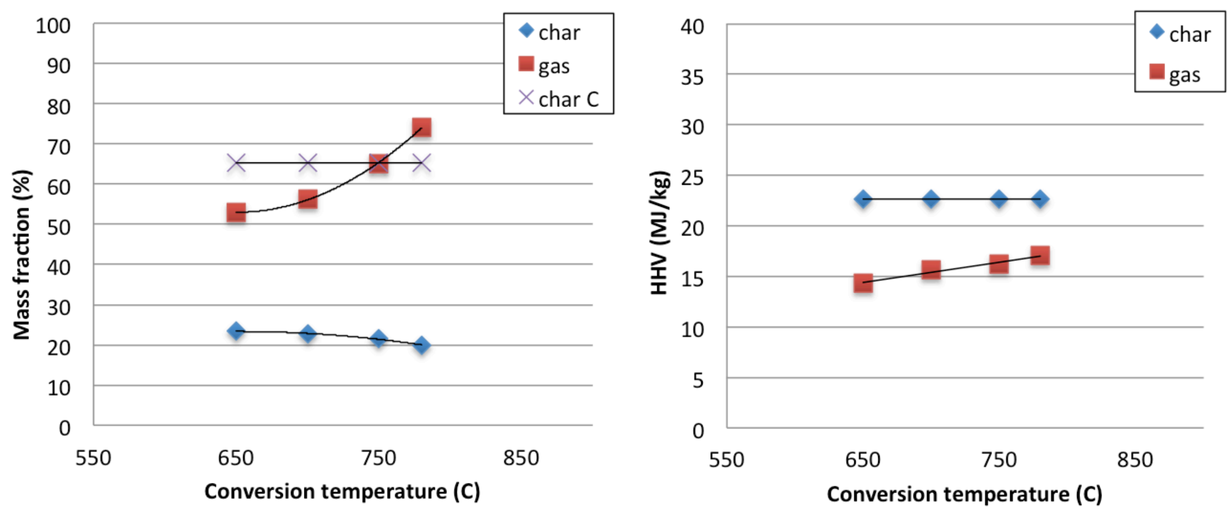

Figure C.4. Estimated product yields and qualities from the gasification of pine

In scenarios where the char produced is used locally as biocoal in boilers or power stations it was assumed to displace 8,800 BTU/lb (20.5 MJ/kg) Powder River Basin coal from Wyoming on an energy equivalent basis, with an associated emissions footprint of 1.98 kg CO_2eq/kg based on GREET data. Recovered pyrolysis oils were modeled as being used locally as fuel for industrial boilers (Oasmaa and Czernik, 1999; Laird et al., 2009) displacing the consumption of heavy fuel oil with a footprint of 3.64 kg CO_2eq/kg (GREET). Recovered pyrolysis gas was assumed converted to electricity, modeled conservatively based on a small-scale compression ignition engine using data from Uma *et al.* (2004) and Bond *et al.* (2004) for thermal efficiency (22.5%) and associated tailpipe non-CO_2 pollutant estimates (46 g CO_2eq/kWh). The GHG emissions embodied in the grid electricity displaced in this scenario were estimated at 0.83 kg CO_2eq/kWh for the WECC Rockies sub-grid using the US EPA eGRID2012 database (US EPA, 2011). In the charcoal kiln scenario estimates of charcoal mass yields (29%) and gaseous air pollutant emissions (2.45 kg CO_2eq/kg charcoal) were taken from Pennise *et al.* (2001) for an improved round Brazilian kiln of intermediate performance, supplemented with generic estimates of BC (0.21 g/kg feedstock) and OC (1.43 g/kg feedstock) emissions for charcoal-making from Bond *et al.* (2004). In scenarios where the pyrolysis gases are flared, a conversion efficiency estimate of 67% based on values measured for the Canadian gas industry (Strosher, 2000; Leahey et al., 2001) was applied uniformly to all air pollutant species.

C.5. Biochar Amendment to Agricultural Soils

Biochar was modeled as being incorporated into farm soils to a depth of 10 cm using conventional tillage techniques and assuming negligible additional disturbance of the soil beyond what would normally occur in the conventional cultivation of winter wheat. Tractor diesel fuel use was assumed to increase by 20% over a baseline estimate of 13.6 gal/ha from GREET for the cultivation of maize, and the associated additional labor requirement of 0.19 man-hours/Mg char was estimated from Williams & Arnott (2010). Biochar recalcitrance was modeled as a function of production temperature by fitting a conservative response function to the dataset developed in Spokas (2010), equivalent to the lower 10th percentile of the data range:

$$O:C = max\begin{cases} 0.6 - 0.00079T \\ 0 \end{cases}$$

$$t_{\frac{1}{2}bc} = 1000e^{-7(O:C)}$$

where T is the thermochemical conversion process temperature and $t_{1/2bc}$ the half-life of the biochar in soil. Data used in the regression of char calcium carbonate equivalence (CCE) are detailed in Table C.1. For the three new data points included in that dataset, CCE was measured using a back-titration method (Williams, 1984, Method 1), and base element and total ash content were evaluated at Hazen Research (Golden, Colorado).

Table C.1. Biochar liming potential prediction dataset

Data source	Biochar description	CCE (%)	C content (%)	Base (Ca, Mg, K, Na) (%)	Total ash (%)
(Van Zwieten, Kimber, Morris, et al., 2010)	Green waste feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 350 °C	8.4	62	0.538	3.055
"	Green waste feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 550 °C	7.5	75	0.242	1.483
"	Biosolids feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 550 °C	1.7	21	7.17	65.71
"	Poultry litter feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 550 °C	8.8	42	8.1	35.53
"	Papermill waste feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 550 °C	18	38	11.86	23.04
(Van Zwieten, Kimber, Downie, et al., 2010)	Green waste feedstock, converted by Pacific Pyrolysis via slow pyrolysis at 600 °C	0.5	78	0.272	1.771
(Van Zwieten et al., 2009)	Paper mill waste feedstock, converted by BEST Energies Australia[1] via slow pyrolysis at 550 °C	33	50	19.56	-
"	"	29	52	43.88	-
This study	Pine feedstock, converted by Biochar Engineering Corporation[2] via char-optimized gasification in the B-1000 system	6.88	93.04	0.744	1.864
"	Wheat straw feedstock, converted by Biochar Engineering Corporation[2] via char-optimized gasification in a TLUD[3] device	14.05	51.56	9.380	41.74
"	Corn stover feedstock, converted by the National Renewable Energy Laboratory via an unspecified fast pyrolysis method	16.93	37.07	15.77	65.39

[1]Now Pacific Pyrolysis
[2]Now Biochar Solutions Inc.
[3]TLUD = Top-lit updraft

Data on the yield response of winter wheat to changes in soil pH were compiled from multiple sources (James & Jackson 1984; Rhoads & Manning 1989; Slattery & Coventry 1993; Tsadilas et al., 1997; Adhikari et al., 2006; Kovacevic et al., 2010) and regressed to generate the following liming response function:

$$Y = -0.09224 \cdot pH^2 + 1.197 \cdot pH - 2.9318$$

where Y is the relative yield expected (adjusted R^2=0.44, p=0.001), shown in Figure C.5. The resulting reduction in nitrogen fertilizer that can be tolerated to maintain the same yield was then back-calculated from a nitrogen response curve given in Halvorson *et al.* (2004).

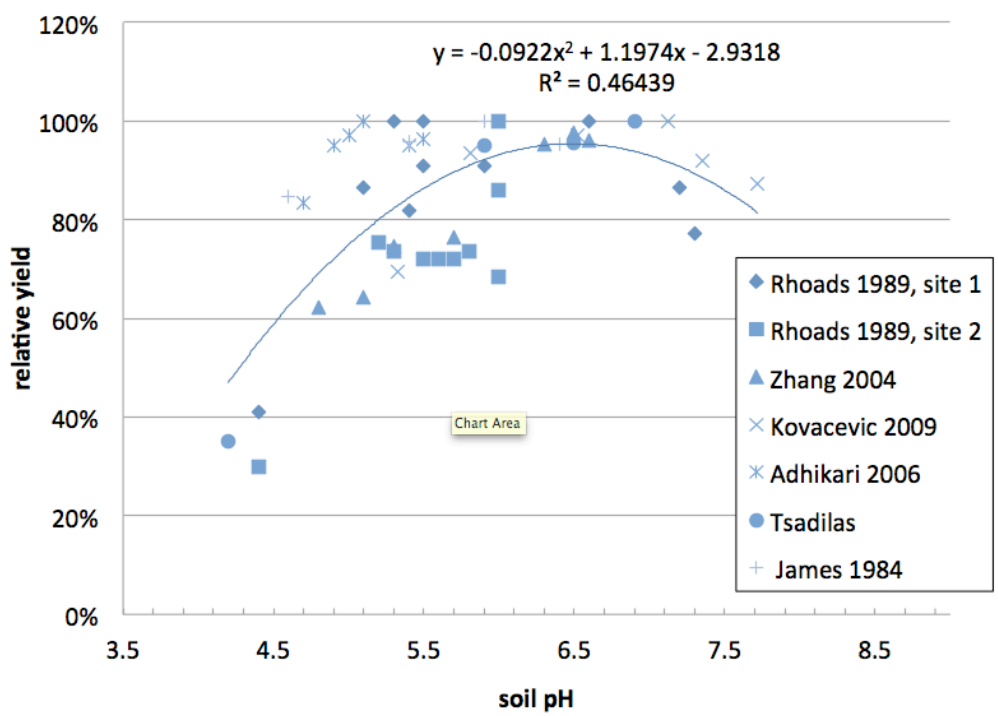

Figure C.5. Relative winter wheat yield response to changes in soil pH

Biochar application has been hypothesized to reduce N_2O emissions by sorbing some of the nitrate substrates of the denitrification process, as well as through increases in soil pH which tend to shift denitrification products away from N_2O and towards N_2 (Van Zwieten, Kimber, Morris, et al., 2010). This assessment used the results of a biochar incubation experiment (Zheng et al., 2012) that give N_2O suppression as a function of final soil pH:

$$f_{N2O} = e^{-1.92(\Delta pH)}$$

where f_{N2O} is the fraction of baseline N_2O emissions persisting after biochar application and ΔpH is the increase in soil pH from the biochar liming effect. These correction factors for reduced fertilizer use and reduced N_2O emissions rate were then applied to compute GHG avoidance assuming a baseline scenario of 150 kg ammonia applied per hectare, fertilizer embodied emissions (2.18 kg CO_2eq/kg NH_3) from GREET, and an IPCC Tier I emission factor of 1.3% N_2O-N/N applied that includes both direct N_2O emissions as well as downstream N_2O emissions associated with fertilizer volatilization and leaching (Eggleston et al., 2006).

C.6. Economic Assessment

Estimates for all prices used in the model are detailed in Table C.2. Labor use for transport operations was based on an assumed average truck speed of 45 miles per hour, plus one hour of material loading and one hour unloading per trip. Labor requirements at the conversion facility of 0.8 man-hours per dry Mg of feedstock processed were estimated from Badger *et al.* (2011) and assumed uniform across all conversion technologies. While CO_2 emissions have been linked to global climate change (Denning et al., 2003), the financial impact and social costs of carbon emissions have been the source of diverse opinions and spirited debate. Social cost of carbon (SCC) estimates vary widely because climate change impacts are highly uncertain and may be geographically diffuse. Although previous researchers have reviewed the impact of carbon prices on profitability of biochar systems (Pratt and Moran, 2010; Galinato et al., 2011), the U.S. carbon market is not considered stable at this time. The Interagency Workgroup estimate of SCC used in this analysis reflects annual monetized damages associated with an incremental increase in anthropogenic GHG emissions in a given year, including changes in net agricultural productivity, human health effects, property damages from increased flood risk, and loss of ecosystem services due to climate change. The values are based upon different climate scenarios of three scientifically accepted integrated assessment models: FUND (Tol, 2009), DICE (Nordhaus, 2008), and PAGE (Hope, 2008).

Table C.2. Prices for all operating costs, displaced fuels & products, and non-market variables

Parameter	Unit	Value(s)[1]	Detail	Reference
Operating Costs:				
Pine waste harvest	($/wet ton)	88.85	Average value across several field studies	Lynch and Mackes, 2003
Pine handling & grinding	($/dry ton)	14.38	Point estimate	Hess et al., 2009[2]
Spent grain opportunity cost	($/wet ton)	36.01, 54.42, 115.64	Mean values, Feb 2006-June 2007	Tonsor, 2009[3]
Spent grain handling	($/dry ton)	2.10	Point estimate	Hess et al., 2009[2]
Transport labor	($/hr)	19.74	Mean national wage, 2011	US BLS, 2011[4]
Conversion labor	($/hr)	26.46	Mean national wage, 2011	US BLS, 2011[5]
Farm labor	($/hr)	13.06	Mean national wage, 2011	US BLS, 2011[6]
Diesel fuel	($/gallon)	3.58	Average of 2006-2012 mean national values	US EIA, 2012a
Natural gas	($/tCF)[7]	9.29	Average of 2001-2010 mean Colorado values	US EIA, 2012b
Displaced Fuels & Products:				
Electricity	($/kWh)	0.0349	2012 City of Fort Collins utility price	City of Fort Collins, 2012[8]
Coal	($/ton delivered)	19.38	2010 price for Powder River Basin coal	US EIA, 2011a, 2011b)[9]
Heavy fuel oil	($/ton)	331.92	Average of 2001-2008 mean national value	US EIA, 2010
Nitrogen fertilizer[10]	($/ton)	420.91	Average of 2006-2012 mean national value	Apodaca, 2012
Crushed limestone	($/Mg)	8.72	2010 mean national value	Willet, 2010
Non-Market Variables:				
Greenhouse gases	($/Mg CO_2eq)	23.09	Median marginal damage cost estimate	Keske, 2011

[1]All values adjusted to 2012 dollars
[2]Based on an estimate for switchgrass feedstock
[3]Range based on DGS moisture content, 65-70%, 50-55%, and 10% moisture content, respectively
[4]Tractor-trailer driver rate
[5]Boiler operator rate
[6]General farm labor rate
[7]tCF = thousand cubic feet

[8]Range reflects the Schedule GS750 Industrial non-summer prices
[9]Price reflects mine gate price plus rail transport to Fort Collins
[10]Ammonia as the nitrogen fertilizer source

C.7. Results of Other Biochar Assessment Studies

Several other studies in the literature have estimated the GHG mitigation value of biochar-producing slow pyrolysis systems. Gaunt & Lehmann (2008) found that bioenergy/biochar systems using dedicated energy crop (DEC) and crop waste feedstocks mitigate 2-19 Mg CO_2/ha annually when the biochar is applied to croplands at a moderate rate of 5 Mg-C/ha, corresponding to 1.4 Mg CO_2eq/Mg feedstock in the DEC case. Woolf *et al.* (2010) showed that an aggressive worldwide strategy of pyrolyzing crop wastes and DEC grown on marginal or abandoned lands could result in the mitigation of 1.8 Gt CO_2-C eq annually, which averaged across all feedstocks and all scenarios (at the maximum rate of emissions mitigation prior to the adoption of alternate biochar disposal options) corresponds to 1.4 Mg CO_2eq/Mg feedstock. Hammond *et al.* (2011) predicted 0.7-1.3 Mg CO_2eq/Mg feedstock mitigation across a wide range of different feedstocks (crop wastes, forestry residues, and DEC including short rotation woody crops) and facility scales, with the best performance coming from the large-scale conversion of forestry residues. The only negative GHG outcome was reported by Roberts *et al.* (2010) who found that, while bioenergy/biochar from crop waste and municipal waste feedstocks mitigate 0.8-0.9 Mg CO_2eq/Mg, this system might actually be a slight net GHG source for DEC feedstocks when a high estimate of indirect land use change is included (Searchinger *et al.*, 2008). Additionally, one study (Kauffman *et al.*, 2011) examined the effect of producing bio-oil via fast pyrolysis from corn stover from the same corn crops used for first-generation ethanol production. That study estimates a mitigation of ~0.6 Mg CO_2eq per Mg of corn stover for the thermochemical part of the system, though note that the assessment boundary is somewhat different from that of the other studies included due to the more complex scenario investigated. Thus, the range of GHG mitigation estimates encountered across all of these biochar-bioenergy studies (including a variety of diverse feedstocks and at least two different conversion technologies) is 0.6-1.4 Mg CO_2eq/Mg feedstock.