Impact of biochar on plant productivity and soil properties under a maize soybean rotation on an Alfisol in Central Ohio

DISSERTATION

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ABSTRACT

Here we investigate the application of biochar to a maize (*Zea mays*)-soybeans (*Glycine max* L.) rotation in the U.S. Midwest in order to assess the agronomic impacts and changes to soil physical, chemical and biological properties. Biochar is a carbon-rich co-product of thermal degradation of biomass precursor material, a process called “pyrolysis,” intended for the use as a soil amendment as opposed to combusted for heat or energy. Biochar could offer a sustainable means of generating energy, sequestering atmospheric CO$_2$ (thereby mitigating climate change), and increasing agronomic productivity of crops through soil quality enhancement. At a global scale biochar could sequester >1 Pg C yr$^{-1}$, thereby substantially helping to mitigate climate change. At present, the majority of long-term field trials using biochar as a soil amendment have focused on highly weathered and degraded soils mainly in the tropics and subtropics. Very little long-term field trials have been conducted on agroecosystems in temperate parts of the world. Our research aimed to fill this void, by conducting a 4-year field experiment (2010-2013) with oak-derived biochar from a slow pyrolysis process at ~425°C at three rates (0 Mg ha$^{-1}$, 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$) with 100% and
50% of nitrogen fertilizer (146 kg ha$^{-1}$ N and 72 kg ha$^{-1}$ N, respectively) on a maize - soybean rotation on an Ohio alfisol soil. Variables analyzed included total above-ground biomass, grain yield, leaf and grain nutrient uptake; soil nutrient storage, moisture capacity, aggregate stability, and greenhouse gas emissions (CO$_2$, CH$_4$, and N$_2$O). Overall, our study revealed mixed results. Biochar did tend to increase above-ground biomass and grain yield in both maize and soybeans with the highest biochar treatment (25 Mg ha$^{-1}$) having the greatest benefit. The results were only significant in the second year, however, although a general positive trend was found in both the first and second year. In the third year, there was a significant drought which resulted in poor stand germination and highly heterogeneous results over all plots. No significant differences in above ground biomass were detected in 2010 or 2012 when soybeans were grown, although there was a significant increase in the total above-ground biomass and grain yield from maize in 2011. In the first year, total above-ground biomass of soybeans increased 8.2% and 12.8% with application of 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar, respectively, although the results were only significant (p<0.10) at the 25 Mg ha$^{-1}$ level. Maize grain yield decreased by -13 and -12% for the 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$, respectively, compared with control in the plots receiving 50% of recommended N fertilizer, but increased by 1% and 18% for the 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$, respectively, compared with control in plots receiving 100% N fertilizer. The specific surface area of the soil increased significantly with the application of biochar, while cation exchange capacity and pH did not significantly change. Increased available water content and increased plant uptake and assimilation of K and S are hypothesized to be contributing
factors to observed increases in production at the 100% fertilization level. N immobilization is attributed to decreased production in the treatments receiving 50% N fertilizer. The results indicate the importance of addition of adequate levels of N fertilizer with the application of biochar and reject the hypothesis that biochar may increase nitrogen fertilizer use efficiency at 50% of recommended N levels. The flux of CO$_2$ and CH$_4$ did not significantly differ with application of biochar although consistent trends were found for both gases. Cumulative CO$_2$ emissions tended to increase with the application of biochar. Within the 50% recommended N fertilizer plots, the cumulative CO$_2$ flux over the observation period increased 3.5% and 11.1% with the application of biochar at the 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ treatments, respectively, and 8.8% and 9.3%, respectively, within the 100% N fertilizer plots. CH$_4$ showed an opposite pattern—consumption (i.e. negative emissions) was correlated with application of biochar although the results were not significant. CH$_4$ consumption increased by 572.5% and 951.7% from the control within the 100% N fertilizer plots. N$_2$O emissions decreased significantly with the application of biochar (p>0.05). N$_2$O emissions decreased by 28.2% and 35.7% with 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar added, respectively, compared with the control within plots receiving 100% N fertilizer. Cumulative GWP was dominated by emissions of CO$_2$ followed by N$_2$O and, much less significantly, CH$_4$. The GWP was highest for plots receiving greater quantities of biochar. In the 100% N fertilizer plots GWP was 38,203, 39,778 and 39,560 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$, respectively, for the plots receiving 0, 5, and 25 Mg ha$^{-1}$ biochar application. Increased CO$_2$ emissions were hypothesized to be the result of an increase in labile C
from biochar or an increase in microbial decomposition of native C. Decreased N$_2$O emissions were hypothesized to be the result of increased NH$_4$ and NO$_3$ adsorption on biochar surfaces. The application of biochar at the highest rate decreased bulk density significantly by approximately 10%. Available water capacity also changed significantly with the application of biochar, increasing by approximately 8%. No significant differences were found in soil texture, hydraulic saturated conductivity, penetration resistance or infiltration rate. The specific surface area of the biochar was measured to be 58 m$^2$ g$^{-1}$. When added to soil, biochar was found to increase overall specific surface area by +12% and +34% with the addition of 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar, respectively. Measures of water stable aggregates were significantly different, however, such changes were likely to be the result of highly stable biochar fragments rather than actual soil aggregates although some characteristics of the biochar quasi-aggregates were likely to function much in the same way as naturally occurring soil aggregates. Generally, the results suggest that biochar may have significant benefits to soil quality particularly in regard to soil physical properties including reduced bulk density and increased moisture retention. Biochar may reduce emissions of N$_2$O and increase the consumption of CH$_4$, but this must be examined in terms of the entire emissions profile over time. Although not significant at a p<0.05 confidence level, there was an observed increase in CO$_2$ emissions among plots receiving biochar. This apparent increase in CO$_2$ emissions with biochar application offset total reductions in global warming potential (GWP) from both N$_2$O and CH$_4$. 

v
DEDICATION

Dedicated to my father—scientist, soccer coach, and political thinker—who taught me to think critically and never to give up in spite of the circumstances; my mother—social worker, wonderful parent and general goofster—who would be considered for sainthood if she were only Catholic; and my brother who, in addition to being my fiercest competitor, is also my best friend and partner in all things good. I love you guys.
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Major Field: Environmental Science
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................... ii
DEDICATION .......................................................................................................................... vi
ACKNOWLEDGEMENTS ......................................................................................................... vii
VITA ........................................................................................................................................ viii
TABLE OF CONTENTS .......................................................................................................... ix
LIST OF TABLES ........................................................................................................................ xiv
LIST OF FIGURES .................................................................................................................... xvii

Chapter 1: Fast-action and win-win strategies for mitigating climate change ............... 1
  1.0 Abstract .......................................................................................................................... 1
  1.1 Background .................................................................................................................... 2
  1.2 Fast-action strategies .................................................................................................... 7
      1.2.1 Methane ................................................................................................................ 10
      1.2.2 Nitrous oxide ....................................................................................................... 13
      1.2.3 Black carbon ........................................................................................................ 17
      1.2.4 Tropospheric ozone ............................................................................................ 22
      1.2.5 High GWP species ............................................................................................... 23
      1.2.6 Fast-action conclusion ......................................................................................... 26
  1.3 “Win-win” mitigation strategies .................................................................................. 27
      1.3.1 Energy conservation and efficiency .................................................................... 31
      1.3.2 Reducing deforestation ....................................................................................... 34
6.2 Background .............................................................................................................................................. 337
6.3 Materials and Methods ............................................................................................................................ 339
  6.3.1 Field Trial ............................................................................................................................................. 339
  6.3.2 Biochar Characterization ..................................................................................................................... 340
  6.3.3 Soil Analysis ........................................................................................................................................ 340
  6.3.4 Earthworm population ......................................................................................................................... 344
  6.3.5 Statistical Analysis ............................................................................................................................. 345
6.4 Results ........................................................................................................................................................ 345
  6.4.1 Biochar physical properties .................................................................................................................. 345
  6.4.2 Bulk density and total porosity ............................................................................................................ 345
  6.4.3 Soil moisture ...................................................................................................................................... 346
  6.4.4 Specific surface area ........................................................................................................................... 346
  6.4.5 Aggregation ...................................................................................................................................... 347
  6.4.6 Earthworm population ......................................................................................................................... 347
6.5 Discussion .................................................................................................................................................... 347
6.6 Conclusion .................................................................................................................................................. 351
6.7 References ................................................................................................................................................ 353
6.8 Tables and figures ..................................................................................................................................... 354
Chapter 7: Conclusion and synthesis ................................................................................................................ 371
Bibliography .................................................................................................................................................... 375
LIST OF TABLES

Table 1: Estimates of mitigation potential used to calculate fast-action and win-win strategies. .......................................................................................................................................................................................... 84

Table 2. Projected changes from 2005 through 2030 for key demographic, agronomic, environmental and public health indicators................................................................................................................................................................................ 152

Table 3: Projected impacts of select measures on food security, climate change, and public health with economic valuation. .............................................................................................................................................................................. 158

Table 4: Impact of increased SOC on crop yield (from Lal 2006)........................................................................................................................................................................................................... 159

Table 5: List of conventional methods (left) that can lead to net soil C loss and best management practices (right) that can enhance soil C storage (adopted from Lal, 2004). ................................................................................................................................................................................ 160

Table 6: Nutrient content of human excreta (data derived from Esrey, 2000)............................................................................................................................................................................................................. 161

Table 7: Global fertilizer use, and total potential nutrient availability from human excreta and fertilizer offset potential (Esrey, 2000; Heffer and Prud’homme, 2012)...................................................................................................................................................................................... 161

Table 8: GHG emissions from biochar amended soils from previous studies. ......................................................................................................................................................................................................... 205

Table 9: Chemical and physical properties of biochar and soil. Biochar was derived from oak (Quercus) feedstock produced in a “Missouri kiln” at ~425 °C. Biochar was incorporated into a Miamian soil (fine, mixed, active, mesic, Oxyaquic Hapludalfs). Unless otherwise noted, values were derived from 5 analytical replicates .................................................................................................................................................................................................................. 242

Table 10: Above-ground biomass (Mg ha⁻¹), grain yield (Mg ha⁻¹), and grain index (Mg ha⁻¹ grain: Mg ha⁻¹ above ground biomass). ........................................................................................................................................................................................................................................................................ 243

Table 11 (cont’d): Nutrient content (ug g⁻¹) and soil properties of Ohio Alfisol 1, 2, and 3 years after application of biochar in 2010. ........................................................................................................................................................................................................................................................................... 244

Table 12: Nutrient content (ug g⁻¹) and soil properties of Ohio Alfisol 1, 2, and 3 years after application of biochar in 2010. ........................................................................................................................................................................................................................................................................... 246
Table 13: Soil carbon (g kg$^{-1}$) in 2010, 2011, and 2012 at three depths (SE= standard error; Med = median).

Table 14: Soil carbon (g kg$^{-1}$) 2010, 2011, and 2012 at three depths (SE= standard error; Med = median).

Table 15: Rate of CO$_2$ flux (mg CO$_2$-C m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

Table 16: Rate of CO$_2$ flux (mg CO$_2$-C m$^{-2}$) by season as impacted by biochar and fertilizer treatments.

Table 17: Rate of CH$_4$ flux (mg CH$_4$-C m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

Table 18: Rate of CH$_4$ flux (mg CH$_4$-C m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

Table 19: Rate of N$_2$O flux (mg N$_2$O-N m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

Table 20: Rate of N$_2$O flux (mg N$_2$O-N m$^{-2}$) by season as impacted by biochar and fertilizer treatments.

Table 21: Greenhouse gas flux from soils as impacted by biochar and fertilizer treatments.

Table 22: Greenhouse gas flux from soils as impacted by biochar and fertilizer treatments.

Table 23: 20-yr global warming potential as impacted by biochar and fertilizer treatments.

Table 24: Total porosity ($f_t$), transmission porosity ($f_{trans}$), storage porosity ($f_{storage}$), and residual porosity ($f_{residual}$) in cm$^3$ cm$^{-3}$. SE = standard error, med.= median.

Table 25: Moisture retention at various pressures (kPa) expressed in terms of volumetric water content (cm$^3$ cm$^{-3}$).

Table 26: Pearson correlation matrix for biochar applied at 25 Mg ha$^{-1}$ rate (Biochar) for bulk density ($\rho_b$), available water capacity (AWC), total porosity ($f_t$), transmission porosity ($f_{trans}$), storage porosity ($f_{storage}$), residual porosity ($f_{residual}$), field capacity (FC), specific surface area (SSA), mean soybean biomass (S. Biomass), mean soybean grain yield (S. Grain), mean maize biomass (M. Biomass), and mean maize grain yield (M. Grain).
Table 27: Bulk density (g cm$^{-3}$) of plots with 0, 5 and 25 Mg ha$^{-1}$ biochar and two rates of N fertilizer at three depths (0-10 cm, 10-20 cm, and 20-30 cm). SE = standard error, med. = median.

Table 28: Soil moisture retention expressed in terms of volumetric water content (cm$^3$ H$_2$O cm$^{-3}$ soil) for each plot at the 0-10 cm depth level.

Table 29: Soil bulk density ($\rho_b$; g cm$^{-1}$) for each plot at the 0-10, 10-20, and 20-30 cm depth levels in 2011 and 2012.

Table 30: Specific surface area (SSA; m$^2$ g$^{-1}$) for each plot at the 0-10 depth level in 2010, 2011, and 2012.

Table 31: Pore size distribution for each plot at the 0-10 depth level where gravitational or transmission pores are >50 µm, storage pores are 0.5-50 µm, and residual or bonding pores are (<0.5 µm). The total volume of the pore space in each of these was calculate by differences in volumetric water content at specific matric potentials.

Table 32: Earthworm count (#) and mass (g) per plot.
LIST OF FIGURES

Figure 1: Conceptual warming estimates of (i) business as usual (BAU), (ii) fast action, (iii) CO2 mitigation exclusively, and (iii) fast-action and win-win strategies......................................................... 85

Figure 2: Global land use in 2005 (data from Lambina and Meyfroidt, 2011) .................................. 153

Figure 3: Schematic of population, food, water, energy, soil, and climate nexus (a) at present and (b) in 2050 under business as usual (BAU) conditions................................................................. 154

Figure 4: Major inputs, outputs, and feedbacks surrounding global food production at present (A) and as projected in 2050 (B). .......................................................................................... 155

Figure 5: Schematic of various strategies for increasing global food production.............................. 156

Figure 6: Impacts and strategies of conventional annual monoculture (A) and integrated sustainable intensification of food production (B) using novel methods................................. 157

Figure 7: Various estimates of carbon sequestration rates (Pg C yr-1) for biochar production compared with total fossil fuel emissions in 2008. ................................................................. 206

Figure 8: Schematic of biochar carbon sequestration strategy...................................................... 207

Figure 9: Experimental location. The field experiment is located at Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W, with elevation of 242 meters in the Olentangy River watershed and a soil type is Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the “Crosby” soil series. ........................................ 241

Figure 10: Total above-ground biomass for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years......................................................... 250

Figure 11: Total grain yield for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years................................................................. 251
Figure 12: Grain index (grain yield/total AGB) for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years. ...........................................252

Figure 13: Plant tissue nitrogen for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......253

Figure 14: Plant tissue phosphorus for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......254

Figure 15: Plant tissue potassium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......255

Figure 16: Plant tissue calcium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......256

Figure 17: Plant tissue magnesium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......257

Figure 18: Plant tissue sulfur for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......258

Figure 19: Plant tissue boron for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. .......259

Figure 20: Plant tissue molybdenum for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at
early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. ......260

Figure 21: Plant tissue zinc for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years. ........................................261

Figure 22: Results of the present experiment compared with results from other experiments (from Lehmann et al., 2006). ........................................................................................................262

Figure 23: Cation exchange capacity at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................263

Figure 24: Cation exchange capacity at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................264

Figure 25: pH at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................265

Figure 26: pH at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................266

Figure 27: Extractable phosphorus at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................267

Figure 28: Extractable phosphorus at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................268

Figure 29: Extractable potassium at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................269

Figure 30: Extractable potassium at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011. ........................................................................................................270

Figure 31: Plots planted in soybeans in 2010. ........................................................................................................271

Figure 32: Plots planted in maize in 2011 ........................................................................................................272

Figure 33: Meteorological data at the experimental location (Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W) over the observation period (May 2010 through September 2011). .................................................................314
Figure 34: CO\textsubscript{2} emissions rate (CO\textsubscript{2}-C g m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 50% recommended N fertilizer. ................................................................. 319

Figure 35: CO\textsubscript{2} emissions rate (CO\textsubscript{2}-C g m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 100% recommended N fertilizer. ................................................................. 320

Figure 36: Cumulative CO\textsubscript{2} emissions over the observational period (CO\textsubscript{2}-C g m\textsuperscript{-2}) from plots receiving 50% recommended N fertilizer. ................................................................. 321

Figure 37: Cumulative CO\textsubscript{2} emissions over the observational period (CO\textsubscript{2}-C g m\textsuperscript{-2}) from plots receiving 100% recommended N fertilizer. ................................................................. 322

Figure 38: CH\textsubscript{4} emissions rate (CH\textsubscript{4}-C mg m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 50% recommended N fertilizer. ................................................................. 323

Figure 39: CH\textsubscript{4} emissions rate (CH\textsubscript{4}-C mg m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 100% recommended N fertilizer. ................................................................. 324

Figure 40: Cumulative CH\textsubscript{4} emissions over the observational period (CH\textsubscript{4}-C mg m\textsuperscript{-2}) from plots receiving 50% recommended N fertilizer. ................................................................. 325

Figure 41: Cumulative CH\textsubscript{4} emissions over the observational period (CH\textsubscript{4}-C mg m\textsuperscript{-2}) from plots receiving 100% recommended N fertilizer. ................................................................. 326

Figure 42: N\textsubscript{2}O emissions rate (N\textsubscript{2}O-N mg m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 50% recommended N fertilizer. ................................................................. 327

Figure 43: N\textsubscript{2}O emissions rate (N\textsubscript{2}O-N mg m\textsuperscript{-2} day\textsuperscript{-1}) from plots receiving 100% recommended N fertilizer. ................................................................. 328

Figure 44: Cumulative N\textsubscript{2}O emissions over the observational period (N\textsubscript{2}O-N mg m\textsuperscript{-2}) from plots receiving 50% recommended N fertilizer. ................................................................. 329

Figure 45: Cumulative N\textsubscript{2}O emissions over the observational period (N\textsubscript{2}O-N mg m\textsuperscript{-2}) from plots receiving 100% recommended N fertilizer. ................................................................. 330

Figure 46: Net annual CO\textsubscript{2} emissions (g CO\textsubscript{2}-C m\textsuperscript{-2} yr\textsuperscript{-1}) by season. ................................................................. 331

Figure 47: Net annual CH\textsubscript{4} emissions/consumption (g CH\textsubscript{4}-C m\textsuperscript{-2} yr\textsuperscript{-1}) by season. ................................................................. 331

Figure 48: Net annual N\textsubscript{2}O emissions (g N\textsubscript{2}O-N m\textsuperscript{-2} yr\textsuperscript{-1}) by season. ................................................................. 332

Figure 49: Annual GHG emissions (Mg CO\textsubscript{2}-eq ha\textsuperscript{-1} yr\textsuperscript{-1}) expressed in terms of 20-year global warming potential by gas as impacted by biochar and fertilizer treatment. ................................................................. 333
Figure 50: Annual GHG emissions (Mg CO$_2$-eq ha$^{-1}$ yr$^{-1}$) expressed in terms of 100-year global warming potential by gas as impacted by biochar and fertilizer treatment. .............................................. 334

Figure 51: Gas chambers in field (2011). ............................................................................................................................................................................. 335

Figure 52: Bulk density (g cm$^{-3}$) at three depths measured in 2011 using core technique (bars indicate standard error). .................................................................................................................................................. 359

Figure 53: Sieving of soil with 25 Mg ha$^{-1}$ biochar addition................................................................. 360

Figure 54: Soil-biochar complexed “quasi-aggregate.” ................................................................. 361

Figure 55: Two methods of bulk density determination showing biochar with 25 Mg ha$^{-1}$ treatment........................................................................................................................................ 362

Figure 56: Moisture characteristic curve at 0-10 cm depth expressed in terms of volumetric moisture content (cm$^3$ H$_2$O cm$^{-3}$ soil) (bars indicate standard error). ................................................................. 363

Figure 57: Field measurement of gravimetric moisture content (g H$_2$O g$^{-1}$ soil) bars indicate standard error of the mean. ........................................................................................................................................ 364

Figure 58: Earthworm (Oligochaeta) collection in May 2011................................................................. 370
Chapter 1:

Fast-action and win-win strategies for mitigating climate change

1.0 Abstract

Anthropogenic perturbations to Earth’s climate system are very likely the cause of recent increases in global surface temperature. Investigation of Earth’s paleoclimate has indicated the presence of “tipping points” within the climatic system which could trigger dangerous large-scale and potentially irreversible discontinuities. Despite large uncertainty, recent observations and modeling exercises suggest that Earth’s climate system may be near or at one or more of these tipping points. IMg has recently been suggested that 350 ppmv is the safe upper limit of atmospheric CO₂ levels. Atmospheric CO₂ levels are presently at ~394 ppmv and growing by 2.2 ppmv per year. Therefore there is need to investigate “fast-action” strategies that have significant impact over short periods of time. Generally, these include targeting of non-CO₂ forcing agents such as methane (CH₄), nitrous oxide (N₂O), black carbon (BC), tropospheric ozone (O₃-T), and high global warming potential (GWP) chemicals (HFCs, CFCs, HCFCs, etc.). This paper recommends concurrent investment in “win-win” mitigation strategies which have significant ancillary environmental and
humanitarian benefits. These include energy conservation and efficiency, reduced deforestation, reforestation, afforestation, agroforestry, soil carbon sequestration, wetland restoration and biochar production.

1.1 Background

Human beings have so utterly altered the state and processes of the Earth System that scientists now describe the current period of time as the “Anthropocene,” an epoch in which a single species—*Homo sapiens sapiens*—have influenced or taken control of the major aspects of the biogeochemical cycle (Crutzen, 2006). Worryingly, many researchers now predict that we are likely to cross multiple safe upper limits of planetary stability, which could potentially drive the Earth into a fundamentally dissimilar state of existence than has been the case since human evolution (Rockstrom, 2009). Many of these changes (e.g. alteration of the global nitrogen and phosphorus cycles, large-scale species extinction, depletion of the world’s fisheries, habitat destruction and fragmentation) are of pressing concern requiring immediate and sustained attention. Perturbation of the global climate system, however, is unique in that it represents the single greatest threat that faces or ever has faced the human species.

Atmospheric CO$_2$ concentration has increased from pre-Industrial levels of 280 parts per million by volume (ppmv) to present levels of ~390 ppmv, representing an increase of ~39% (Tans, 2010). Current CO$_2$ levels may be the highest atmospheric concentration since 15 million years ago when global
temperatures were 3-6 °C warmer and sea level was 25-40 meters higher than present levels (Tripati et al., 2009). According to the Intergovernmental Panel on Climate Change (IPCC, 2007), CO₂ levels rose an estimated 2 ppmv from 1995 to 2005, compared to 1.25 ppmv from 1960 to 1995. This increase in CO₂ has led to a warming of ~0.74 °C since 1900 (IPCC, 2007) and may have committed the Earth to a further warming of 1.4 – 4.3 °C over the 21st century (Ramanathan and Feng, 2008). Since 2000, the global energy imbalance has been 0.9 ± 0.5 watts per meter squared (W m²) (Trenberth, 2009).

The IPCC (2007) reported a 90% confidence level that human activities were the cause of climate change. Anthropogenic drivers include combustion of fossil fuels, biomass burning, cement production, land use change, deforestation, soil disturbance and drainage of wetlands. The increase in atmospheric C corresponds with anthropogenic emissions of ~400 petagrams (1 Pg = 10¹⁵ grams = 1 gigaton), ~270 Pg having resulted from fossil fuels combustion, and ~135±50 Pg from terrestrial ecosystems (IPCC, 2000). Approximately 78±12 Pg of terrestrial C loss has resulted from tillage and degradation of soils (Lal, 2004). Presently, deforestation in tropical countries, profligate fossil fuel consumption in wealthy mostly temperate countries, increased emissions in China and India, and poor soil management around the world are conspiring to rapidly increase atmospheric C levels over a relatively short period of time. Current anthropogenic C emissions are estimated to be ~10.5 Pg C yr⁻¹ of which ~9.1 Pg is from fossil fuel combustion and cement production with the
remainder ~0.6-1.5 from land use change—mainly deforestation and degradation of ecosystems.

Article II of the United Nations Framework Convention for Climate Change (UNFCCC) calls for the “stabilization of greenhouse gas [GHG] concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference [DAI] with the climate system,” and that this level, “should be achieved within a time-frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development proceed in a sustainable manner.” As such, determining the safe upper limit of anthropogenic interference is among the most important scientific questions of the 21st century with far-reaching implications for the future of humanity and the rest of biological life on the planet. Beyond this limit we may expect abrupt, irreversible, and/or uncontrollable changes to the climate system (Lenton et al., 2008; Smith et al., 2009). The evolution of the human species and the development of human civilization have occurred over a remarkably stable and short period of geologic time known as the “Holocene.” There is reason to believe that maintenance of this relatively stable climatic state is necessary for the continuation of agriculture and the protection of coastal infrastructure. Dangerous Anthropogenic Interference (DAI) of Earth’s atmospheric systems and the possibility of crossing irreversible tipping points may generate a qualitatively different climate system than that on which civilization has developed over the past 12,000 years (Hansen, 2008).
It is widely feared that climate change may be substantially underestimated by the recent IPCC assessment (2007), with an increased likelihood for rapid changes, higher emissions levels, and more severe potential consequences (Pittock, 2006; Rahmstorf et al., 2007; Hansen et al., 2008; Sokolov et al., 2009; Solomon et al., 2009; Smith et al., 2009). There are also many indications that the present anthropogenic perturbations are leading to destabilizing impacts around the world including extensive thinning of Greenland and Antarctic ice sheets (Pritchard et al., 2009), loss of volume and extent of Arctic summer sea ice (Kwok et al., 2009), and increased methane emissions associated with thawing permafrost (Shakhova et al., 2010). Determining a “safe upper limit” of human radiative forcing, a level that would reduce the likelihood of dangerous anthropogenic interference (DAI) with Earth’s climate system, is challenging due to the inherent complexity, uncertainty, and potential political ramifications of such a determination.

During the 1990s and 2000s, atmospheric CO₂ targets commonly ranged between 450 and 650 ppmv. Recent research, however, indicates that the safe upper limit could be substantially lower than these targets. Parties at the 2009 UNFCCC meetings in Copenhagen, Denmark agreed on limiting global warming to 2ºC (UNFCC, 2009), but no agreement was made on limiting emissions. Ramanathan and Xu (2010) estimated that staying within this agreed upon 2ºC warming maximum would require ensuring no more than +2.5 W m⁻² anthropogenic radiative forcing. However, the authors observed that 2005 forcing was 2.6-3.5 W m⁻², thereby already exceeding the agreed upon limit. In
contrast, the IPCC (2007) estimates positive anthropogenic forcing in 2005 to be +1.6 m² (+0.6 to 2.4 W m⁻²) (IPCC, 2007), although, certain human activities (e.g. aerosol emissions and land use change) can result in negative anthropogenic forcing.

Solomon et al. (2009) reported that a peaking of CO₂ levels at 450 to 600 ppmv in the 21st century will likely lead to irreversible and sustained drought conditions in many parts of the world thereby creating large challenges for basic food production and security. Hansen et al. (2008) suggest a limit of between 310 and 350 ppmv of atmospheric CO₂ (40 to 80 ppmv below present levels) based on current changes to the Earth System and indications of abrupt changes in the paleoclimatic record. One of the largest sources of uncertainties in predicting the sensitivity of Earth’s climate is “global dimming,” a negative forcing on Earth’s radiative budget caused by anthropogenic increase albedo mainly as the result of emissions of reflective aerosol pollutants into the atmosphere (Wild et al., 2007; Wild et al., 2009). Sulfur dioxide (SO₂), vapor trails left by aircrafts, and other pollutants are likely to decrease the total amount of irradiance reaching Earth’s surface thereby counteracting the full impact of climate change. Wild et al. (2007; 2009) and Pinker (2005), however, suggest that the total irradiance reaching Earth has been steadily increasing (a.k.a. global brightening) since the 1980’s in many parts of the world thereby diminishing this impact. The degree to which global dimming may be “masking” the full extent of anthropogenic perturbation is therefore difficult to estimate, but suggests Earth’s climate system may have higher sensitivity than is presently observed.
The “precautionary principle” advocates that even under circumstances of uncertainty, if there is risk for significant negative impacts, a careful and conservative approach is warranted in order to prevent undue harm. Whether or not the severity of climate change has been significantly underestimated is difficult to know due to inherent uncertainties and complexities of the climate system and due to the inability to precisely quantify thresholds for climatic tipping points. Nevertheless, the possibility that the Earth System could be near or at irreversible tipping points and DAI justifies investigation of fast-action mitigating strategies (Ramanathan and Feng, 2008; Molina et al., 2009). This paper will describe a novel approach for mitigating climate change based on implementation of “fast-action” measures that can swiftly reduce anthropogenic forcing while simultaneously investing in longer-term “win-win” mitigation strategies using technologically ready and cost-effective methods with significant ancillary benefits. These measures are likely to require extraordinary cooperation on a global scale. They are not, however, completely unprecedented. The 1987 Montreal Protocol halted the destruction of the ozone layer through a combined effort of solid science, international political cooperation, and fast-action on the part of countries across the world. The same approach is now needed to confront the climate change challenge.

1.2 Fast-action strategies

The term “fast-action” refers to strategies that can be implemented in a relatively short period of time with significant mitigation potential. Molina et al. (2009) define “fast-action” as those strategies that “can begin within 2-3 years
and be substantially implemented within 5-10 years, with the goal of producing desired climate response within decades.” Fast action strategies offer a means of quickly reducing anthropogenic forcing if evidence sufficiently indicates the Earth is at or near dangerous tipping points. This article excludes the so-called “geoengineering” options such as seeding the atmosphere with sulfate particles or ocean fertilization which are likely to have high risk, and tend to rely on more technically sophisticated means of altering Earth’s energy budget (e.g. Lenton et al., 2009).

Most important among fast action approaches is reduction of non-CO$_2$ climate forcing agents (NCCFAs) through a redrafting and expansion of the 1989 Montreal Protocol (IPCC-TEAP, 2005; Ramanathan and Feng, 2008; Molina et al., 2009). NCCFA refers to forcing agents other than CO$_2$ that make an appreciable contribution to positive radiative forcing. The term “climate forcing agent” is chosen in place of “greenhouse gas” as there are several anthropogenic agents that are not gases—the most prominent being black carbon (BC) soot, an aerosol—that also require consideration.

“Multi-gas” strategies have long been recognized as being a more effective and economic means of addressing climate change than exclusive-CO$_2$ strategies (e.g. Hayhoe et al., 1999; Hansen et al., 2000; Jensen and Thelle, 2001; Smith et al., 2000). However, these are often difficult to quantify using the conventional 100-yr GWP measuring stick (Shindell, 2009). The GWPs often ignore or underestimate chemical interactions, complex feedbacks, non-linear responses,
and spatial and temporal heterogeneity (Reilly et al., 1999). Furthermore, the conventional time horizon of 100 years is largely arbitrary and systematically undervalues short-lived NCCFAs. As such, a critical examination of the 100-yr GWP as the standard bearer for anthropogenic emissions is warranted (Reilly et al., 1999; Shindell, 2009). If tipping points are nearer to 20 or 50 years, as is likely, use of a 100-yr GWP may be inappropriate and imprudent, skewing mitigation efforts away from short-lived NCCFAs that would enable a more rapid response.

Many NCCFAs are short-lived (e.g. BC and methane) and/or have a much greater GWP than CO₂ (e.g. halofluorcarbons). This suggests that targeting certain NCCFAs species will provide stronger mitigation potential over a shorter period of time than focusing climate change mitigation efforts exclusively on CO₂. Furthermore, whereas CO₂ has proven technically, economically, and politically difficult to phase out and because it is a byproduct of nearly all fossil fuel use, there are strategies to rapidly phase out and reduce many NCCFAs that are comparatively simple, inexpensive and likely to garner greater political support in the near-term. Thus, while reducing CO₂ emissions is essential to long-term climatic stabilization and robust measures should be immediately implemented in order to do so, an exclusive focus on CO₂ without consideration of NCCFAs will likely lead to the formulation of incomplete and ineffective climate policy (Jackson, 2009) and would remove a powerful option for rapid mitigation.
1.2.1 Methane

Methane (CH\textsubscript{4}) is a powerful GHG that has a 20-yr GWP of 72, a 100-yr GWP of 25, a total radiative forcing of \(\sim+0.48\) W/m\(^2\) and a mean residence time (MRT) of \(\sim8.4\) yr (IPCC, 2007). Next to CO\textsubscript{2}, CH\textsubscript{4} is second most important anthropogenic forcing agent, 18.3\% of the total +2.63 W/m\(^2\) of the total positive anthropogenic forcing. Since the Industrial Revolution, global CH\textsubscript{4} concentration has risen from \(\sim700\) parts per billion by volume (ppbv) to \(\sim1775\) ppbv (IPCC, 2007), an increase of \(\sim153\%\). CH\textsubscript{4} is also a precursor gas in the formation of tropospheric ozone and stratospheric water vapor — two other powerful forcing agents. This “indirect effect” of CH\textsubscript{4} may be understated in prior assessments (IPCC, 2007) and therefore CH\textsubscript{4} may have a radiative impact 10\% - 40\% higher than the above stated 100-yr GWP of 25 (Shindell, 2009).

CH\textsubscript{4} acts as warming agent in the atmosphere in two ways. First, similar to CO\textsubscript{2}, CH\textsubscript{4} allows short-wave radiation from the sun to pass by, but absorbs a portion of the long-wave radiation being emitted from the Earth, and sends some of this energy back, causing a positive forcing effect. Second, CH\textsubscript{4} impacts the climate through a series of reactions with other chemical compounds in the atmosphere (NO\textsubscript{x}, carbon monoxide [CO], volatile organic compounds [VOCs]) and sunlight to produce additional GHGs—the most important of which is tropospheric ozone. CH\textsubscript{4} undergoes oxidation when it is exposed to NO\textsubscript{x} by the hydroxyl radical (OH) and sunlight, thereby creating tropospheric ozone (O\textsubscript{3}). Thus, reaction with OH is the dominant process by which CH\textsubscript{4} is removed from
the atmosphere, but it simultaneously lead to the formation of yet another powerful GHG.

There are many sources—both natural and anthropogenic—of atmospheric CH$_4$. Over two thirds (~71%) of CH$_4$ emissions are of anthropogenic. Augenbruan et al. (1997) calculated emissions sources as: coal and oil mining and natural gas (19%); enteric fermentation from livestock production (16%); rice cultivation (12%); biomass burning (8%); landfills (6%); sewage treatment (5%); and animal waste (5%) (Augenbraun et al., 1997). The remaining 29% come from natural sources: wetland (22%); termites (4%); and methane hydrates and oceans (3%). Ramanathan and Xu (2010) reported 230 to 300 megatons (Mt = 1,000,000,000 grams = 1 gigagram) annual global CH$_4$ emissions: 33-45% from agriculture and livestock, 30% from energy production, and 25% from waste treatment and disposal (Ramanathan and Xu quote IPCC 2007, IEA 2008, Rypdal et al., 2005).

Various measures to reduce the output of CH$_4$ from enteric fermentation, which accounts for ~16% of CH$_4$ (radiative forcing) have been examined. The most effective means of reducing CH$_4$ emissions from livestock is by reducing demand of meat and dairy products from ruminants animals mainly cattle, goats, and sheep of the genus Artiodactyla (McMichael et al., 2007). Such an approach would also help avoid land clearing for pasture production of cattle, which in the Amazon accounts for ~80% of deforestation (Nepstad et al., 2009). Other benefits of reducing meat consumption and beef consumption in particular are
those for human health (McMichael et al., 2007). Reducing CH$_4$ production in the “rumination” process involves researching alternative feed strategies, various supplements, methanogen and protozoa inhibitors, and genetic selection of breeds of ruminants which tend to produce less CH$_4$ (see, for instance, Boadi et al., 2004). CH$_4$ capture from animal manure, human sewage, and landfills is critical and often provides negative costs (i.e. net profit). Oxidizing CH$_4$ to CO$_2$ through capture and combustion provides both energy to offset fossil fuel use and avoids additional radiative forcing of CH$_4$ vis-à-vis CO$_2$ emissions.

Reducing CH$_4$ emissions from rice (Oryza sativa L.) production (~12% of global emissions) is considered to be a viable strategy because of preexisting intensive management on these agricultural lands. Methods include: (i) direct seeding of rice; (ii) infrequent/intermittent irrigation and improved drainage strategies; (iii) amendment of rice paddies with sulfate containing fertilizer which reduces CH$_4$ due to inhibitory effect of SO$_4$-ions; and (iv) compost or biochar addition in place of fresh organic matter (Dubey, 2001). Additionally, transitioning from flood irrigation rice production to aerobic rice cultivars offers opportunity for reducing CH$_4$ emissions substantially in addition to conserving water which is likely to be of increasing importance under conditions of increasing freshwater scarcity (Bouwman et al., 2002).

The maximum technically feasible reduction (MTFR) for CH$_4$ emissions has been estimated to be between 20% and 40% over various timeframes ranging between 20 and 40 years. Cole et al. (1997) estimated total MTFR of CH$_4$ to be
West et al. (2006) estimate that 65 Mt yr\(^{-1}\) reduction (~20% of annual global CH\(_4\) emissions) at $12 \text{CO}_2\text{-e}$ which would result in a decrease of radiative forcing by 0.14 W m\(^{-2}\) (~5.3% of total forcing) when accounting for reductions in both CH\(_4\) and resulting tropospheric ozone (O\(_3\)-T) with substantially ancillary benefits for air quality, human health, energy production, and agriculture. Cofala et al. (2007) estimated MTFR of 30% by 2030 for CH\(_4\) emissions. Molina et al. (2009) estimated that robust CH\(_4\) mitigation efforts could lower emissions by 40% at relatively low costs of $40 \text{ton}^{-1} \text{CO}_2\text{-eq}$ and approximately 15% of these projects would generate more money than expended.

### 1.2.2 Nitrous oxide

Nitrous oxide (N\(_2\)O) is a potent GHG with a 20yr-GWP of 289 and a 100yr-GWP of 298, a net radiate forcing of +0.16 (~8% of total anthropogenic radiative forcing) and a MRT of 114 years (IPCC 2007). The concentration of N\(_2\)O in the atmosphere has increased from ~270 ppbv to ~320 ppbv since the Industrial Revolution (IPCC, 2007), an increase of ~19%. N\(_2\)O is among the most harmful substances, contributing to the deterioration of the stratospheric ozone layer (Ravishankara, 2009).

Approximately 70-80% of anthropogenic N\(_2\)O emissions are from agriculture (primarily due to application of synthetic N fertilizers and, to a lesser extent, livestock), ~20% from industrial processes (Galloway, 2008), and ~10% from deforestation (Bouwman et al. 1995). Biomass burning, sewage treatment,
waste incineration, disturbance of natural ecosystems, and fossil fuel combustion are all contributors, though the magnitude of these sources and sinks remains poorly understood (Bouwman et al., 1995). Uncertain but substantial N₂O emissions are associated with industrial processes including manufacture of plastics, nylon, glues, resins, melamine, explosives and livestock feed supplements (Galloway, 2008).

Nitrogen fertilizer application is the primary anthropogenic source of N₂O being released into the atmosphere and is also responsible for the emissions of NOₓ which is a precursor gas to the formation of tropospheric ozone (Smith et al., 2007). Lack of plant available N is often the most limiting factor for crop production (LaBauer and Treseder, 2008; Robertson and Vitousek, 2009) and synthetic inorganic N fertilizer is the most widely used farm input. The vast majority of N fertilizer is derived from H₂ via oxidation of natural gas through the Haber-Bosch process. Through a series of chemical reactions, highly stable triple-bonded atmospheric N₂ (which comprises 78% of the atmosphere by volume) is fixed into reactive/biologically-available ammoniacal compounds including ammonium nitrate (NH₄NO₃), ammonium sulfate ((NH₄)₂SO₄), anhydrous ammonia (NH₃), and urea ((NH₂)₂CO) (Smil, 2001).

Since 1930, use of synthetic N fertilizer has increased 40–fold (Mosier et al. 1999) with global synthetic N use growing from 11.6 teragrams (Tg = 10¹² grams) in 1961 to 104 Tg in 2006 (FAO, 2009). Over-application of N fertilizer is a problem common throughout the world (Millar et al., 2010) although it is
particularly prevalent in many developing countries such as China where reductions in N fertilizer use would have minimal to neutral impacts on crop yield (Hvistendahl, 2010). Maximum N fertilizer uptake efficiency (FNUE) is low—only 18 to 49% of synthetic N fertilizer applied is taken up by crops (Raun and Johnson, 1999; Cassman et al., 2002; Ladha et al., 2005) with the remainder being lost due to leaching or volatilization. In spite of large potential benefits, relatively little work has been done to provide farmers with accurate, regionally appropriate and soil specific guidelines for N fertilizer application.

A significant portion of unutilized N is lost to downward leaching which can have toxicological impacts for humans (e.g. methemoglobinemia, a fatal condition for infants) (Knobeloch et al., 2000) and for other animals (Camargo and Alonso, 2006; Powlson et al., 2006); is the leading driver of eutrophication of coastal habitat causing large-scale hypoxic “dead zones” around the world (Diaz, 2001; Donner and Kucharik, 2008); and is largely responsible for depletion of the ozone layer (Hahn and Crutzen, 1982; Ravishankara, 2009). Approximately 3% to 5% of applied synthetic N is volatilized into the atmosphere in the form of N₂O-N (Cassman et al., 2002; Crutzen et al. 2008) with the percentage of N₂O emissions increasing disproportionately with higher rates of N application (Schlesinger, 2008). Furthermore, use of synthetic N may also contribute to decline in native soil N and C through the “priming” effect whereby microbial decomposition of organic matter is stimulated by N that has been added to the soil system (Mulvaney, 2009). This impact is additional to increased radiative forcing through N₂O emissions alone. Recent policy
decisions pushing the development of biofuels as an alternative for fossil fuel energy may be reason for concern as proposed C offset by biofuel production may be negated by increased emissions of N₂O (Crutzen et al., 2008).

The primary means of reducing global N₂O emissions is a focus on the agricultural sector which produces >75% of N₂O emissions (Tubeillo, 2009), although reductions in emissions from fossil fuel combustion, industrial sources, biomass burning, and deforestation are also important. The most effective means of reducing N₂O emissions from agriculture is by increasing N fertilizer efficiency by applying the proper rate at the proper time with the proper type of N fertilizer (Roberts, 2007); adoption of “precision agriculture” approaches (Bongiovanni et al., 2005); decreasing cultivation of crops requiring high N fertilizer application; use of slow-release N fertilizers (Alexanders et al., 1997) such as polyolefin-coated ammonium nitrate/sulfate; side-dressing crops at appropriate times once the planMg has been established instead of single large N application; optimizing irrigation and drainage management; use of nitrification inhibitors e.g. nitrapyrin (Besler and Schmidt, 1981), dicyandiamide (Merino et al., 2002) and encapsulated calcium carbide (Bronson and Mossier, 1991); application of soil amendments such as biochar (e.g. Singh et al., 2010); root-zone proximate and subsurface N application; use of cover crops that scavenge residual N can be incorporated into crop rotations in order to reduce leftover N bank at the end of growing seasons (Follet, 2005).
Cole et al. (1997) estimated global MTFR of 0.71 Tg N$_2$O yr$^{-1}$, ~17% of emissions. Similarly, Mosier et al. (1998) suggest N$_2$O emission reduction from agriculture of 20%. Assuming 75% of N$_2$O emissions to be from agriculture, this would lead to a net reduction of global N$_2$O emissions by ~15% which would be equivalent to reduced radiative forcing of ~0.023 W m$^{-2}$.

1.2.3 Black carbon

Black carbon (BC) comprises a range of carbonaceous soot particle that results from incomplete combustion of fossil fuel and biomass burning. BC has a large but uncertain impact on Earth’s climate systems with a 100-yr GWP of 680 and a 20-yr GWP of 2200 (Bond and Sun, 2005), a radiative forcing variously estimated to be +0.2± 0.15 W m$^{-2}$ (IPCC, 2007), ~+0.8 W m$^{-2}$ (Hansen et al., 2005), and ~+0.9 W m$^{-2}$ (Ramanathan, 2007) and an atmospheric residence time of days to weeks (Ramanathan and Xu, 2010.)

Unlike GHGs, it is difficult to quantify the role of BC as a climate forcing agent due to extreme heterogeneity over temporal and spatial scales (IPCC, 2007). It is not well mixed and can vary seasonally, thus it often affects certain regions of the world to a greater degree than others (e.g. the “Asian Brown Cloud”) and is generally hard to quantify on a global basis. BC causes warming in three distinct ways: (i) airborne BC particles absorb incoming short-wave radiation from the sun, thereby warming the upper troposphere; (ii) BC can accelerate melting of snow and ice when it is deposited, causing substantial decrease in albedo; (iii) depending on chemical composition and location within
Earth’s atmosphere, BC can cause increase or decrease of cloud cover thereby resulting in changes to Earth’s albedo and to the global energy budget (Koch and Del Genio, 2010).

The impact of BC emissions on land and sea ice is highly damaging. Shindell and Faluvegi (2009) estimated BC to have led to increased warming in the Arctic by ~0.4 to 1.5 °C since 1890, and BC is considered to be a large contributor to melting of the Greenland Ice Sheet and the Hindu-Kush-Himalaya-Tibetan (HKHT) glacier system (Ramanathan and Carmichael, 2008). At the current melt rate the HKHT glacier complex, which supplies 500 million people or more with fresh water resources, is predicted to become 75% deglaciated by 2050 (Ramanathan, 2008). Due to the short lifetime of the aerosol and the uncertain but likely large forcing effect, targeting BC has often been proposed as a fast-action strategy for mitigating climate change (see, for instance, Jacobson, 2002; Bond and Sun, 2005; Ramanthan and Carmichael, 2008; Ramanathan and Xu, 2010).

Because BC also has adverse effects on human health (particularly pulmonary-cardiovascular systems), there is strong need to reduce BC emissions for reasons other than climate change. One study, for example, found that premature deaths could be reduced by 17% annually in India with adoption of clean-burning cook-stove technologies (Wilkinson et al., 2009). While reducing BC emissions has been widely recognized as being beneficial both to human and climatic health (Bice et al., 2009; Montgomery et al., 2009), some researchers
have disputed the efficacy and economics of targeting BC as a strategy to reduce radiative forcing (Kandikar et al., 2009). Because BC emissions are generally accompanied by emissions of other compounds such as organic matter and sulfate which can have net cooling effect, disentangling impacts and predicting net radiative reductions from BC emissions reductions is inherently difficult (Kandikar et al., 2009).

Globally, 35% of BC emissions are the result of fossil fuel burning and 65% from biomass burning, with the majority of biomass burning occurring in the tropics (Bond et al., 2004; Bond et al., 2007). Bond (2007) estimated the sources of BC emissions as being 42% from open biomass burning (e.g. slash-and-burn agriculture and combustion of crop residues), 18% from traditional household biofuel use, 14% from diesel for transport, 10% from diesel for industry and 6% from residential coal use.

Fossil fuel combustion has been regarded as a more viable target for BC reductions versus biomass burning as controlling emissions can be dealt with through legal and regulatory measures on manufacturers of combustion appliances. Reducing BC emissions from fossil fuel combustion include state regulations requiring transition from diesel to gasoline; mandates for diesel engines to be fitted with particulate traps; and improved capture of BC soot particulate from coal combustion and jet engines (Jacobson, 2002). Switching from diesel to gasoline, while reducing BC emissions, can also reduce energy efficiencies.
Regulating biomass burning may be more difficult than fossil fuels, however, reducing biomass burning is essential due to concurrent benefits of lowering CH$_4$, N$_2$O, O$_3$-T, and non-methane volatile organic compounds (NMVOCs) as well as protecting natural C sinks. Forest and agricultural fires, particularly in eastern Asia, Siberia and northern Europe, are a significant source of BC and NMVOCs in the arctic (Klonecki et al., 2003; Generoso et al., 2007; Stohl et al., 2006). Targeting open biomass burning of crop residues, dung and forest biomass—particularly in Eastern Europe where BC emissions have a disproportionate impact on Arctic ice melt and in East India where BC emissions have a disproportionate impact on the Himalayan glacial complex—is critical for reducing radiative forcing (Ramanathan and Carmichael, 2008).

Improved cookstove technologies in developing countries is an important part in reducing BC emissions as traditional biomass burning accounts for ~18% of emissions. Efficient cookstove technologies have additional benefits of reducing pressures on natural ecosystems for fuelwood, improving human health, and preventing drudgery associated with fuelwood collection which primarily impacts women and children. Cookstoves technologies include solar cookers, gasification units, and various other devices (Bailis, et al., 2005). Of particular interest are pyrolytic cookstoves capable of producing biochar as a byproduct which could be used to increase agricultural production of subsistence agriculturalists (Joseph, 2009). Pyrolysis can also be used as an improved charcoal production technique, and distributed farm or community scale pyrolyzers offers a strategy for targeted BC emissions reductions.
A large-scale comprehensive strategy to reduce BC emissions should include finding alternatives to slash and burn (ASB) (e.g. mulching, cover cropping, agroforestry etc.) (Palm et al., 2005); eliminating combustion of crop residues (potentially through pyrolysis as well as by use of residues as mulches and compost); and reducing traditional biomass burning (through improved high-efficiency cookstove and charcoal production systems). A multi-faceted strategy of this nature could substantially reduce emissions from forest degradation and land use change, which is approximated at 0.5-2.4 Pg C yr$^{-1}$, while increasing C cycling and sequestration in biological systems.

Strategies for reducing BC must also take note of and prepare for likely future emissions sources. Prevention of large-scale forest fires through prescribed burns and other fodder management strategies may be required to decrease the risk of catastrophic fires and associated BC emissions (Bowman et al., 2009). Second, as continued melting of the arctic continues, increased activity in sea vessel transport is likely. Ensuring low BC emissions from sea fleets will therefore be increasingly necessary in order to protect Artic sea ice and the Greenland ice sheet from melting both of which have been identified as tipping points within Earth’s climate system (Lenton et al., 2009).

1.2.4 Tropospheric ozone

Tropospheric ozone (O\textsubscript{3}-T), contained within the 10-18 kilometers of Earth’s surface, is a highly reactive, potent GHG and a highly destructive oxidizing agent that negatively impacts human health (Bell et al., 2004), infrastructure, crop yields, and natural ecosystems (Tubiello and Howden, 2007; Wittig et al., 2009). The global concentration of O\textsubscript{3}-Mg has increased from \(~\)10-15 ppbv in 1860 to \(~\)20-30 ppbv in 2010 (Lelieveld and Dentener, 2000; West and Fiore, 2005) with a total radiative forcing of \(+0.35 \pm 0.15 \text{ W m}^{-2}\) (IPCC, 2007) and an atmospheric lifetime of \(~\)1 month (Ramanathan and Xu, 2010). Background levels of O\textsubscript{3}-T are superimposed by higher O\textsubscript{3}-T levels in urbanized and industrial areas with greater health risks. Higher O\textsubscript{3}-T concentrations reduce global net primary productivity and are predicted to reduce C cycling and storage in soil organic C pools (Loya et al., 2003). O\textsubscript{3}-T is created through a complex series of oxidation reactions wherein precursor constituents (nitrogen oxides [NO\textsubscript{x}], carbon monoxide [CO], CH\textsubscript{4}, and NMVOCs) undergo various physio-chemical reactions to create O\textsubscript{3}-T. CO reacts to create hydroxyl radicals (OH), which reacts with O\textsubscript{2} to produce peroxy radicals (HO\textsubscript{2}). HO\textsubscript{2}, in turn, react with NO to produce NO\textsubscript{2} which are then phyto-dissassocited by incoming short wave solar electromagnetic radiation to produce O which bonds with ambient O\textsubscript{2} to produce O\textsubscript{3}.

Because formation of anthropogenic O\textsubscript{3}-T is caused primarily through emissions of other pollutants and not through direct emissions, targeting leading
precursor gases (CH$_4$, NO$_x$, and NMVOC) is widely accepted as the most effective means for mitigation. NO$_x$ is responsible for the majority of O$_3$-T in polluted areas, but CH$_4$ may have a more powerful impact globally (West and Fiore, 2005). Debate continues regarding the best species to target in order to reduce O$_3$-T concentrations. Anthropogenic NO$_x$ results primarily from combustion of fossil fuels in internal combustion engines and power plants, biofuel combustion, open biomass burning pulp mills and N fertilizer application. Using a 3-d global chemistry model, Fiore et al. (2002) observed that reducing CH$_4$ by 50% had a greater impact on O$_3$-T production efficiency (OPE) than did a 50% reduction of NO$_x$, with decrease in surface ozone by 1-6 ppb, and that CH$_4$ has approximately 7 times the impact of anthropogenic NMVOCs. Thus, Fiore et al. (2002) refer to CH$_4$ emissions abatement as a “powerful lever” for reducing anthropogenic forcing.

1.2.5 High GWP species

There are several classes of chemicals that have extremely high GWPs that disproportionately impact anthropogenic radiative forcing. These include chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and other long-lived organic hydrocarbons which are commonly used as refrigerants, propellants, solvents, foam-blowing agents, and fire protection agents. The total radiative forcing of CFCs, HCFCs, and other Kyoto gases (HFCs, PFCs and SF6) are +0.268, +0.039, and +0.017
W/m$^2$, respectively (IPCC, 2007). The MRT of the various species is typically relatively long—persisting for decades to millennia.

In 1975, Rowland and Molina provided a clarion warning of the possible impact of CFCs on Earth’s stratospheric ozone layer. This eventually led to the 1987 Montreal Protocol which phased-out production and emissions of CFC-11, CFC-12, CFC-113, and methyl chloroform compounds. Because, many gases with high ozone depletion potential (ODP) also tend to have high GWPs, targeting these species can significantly reduce radiative forcing on Earth’s climate system. The Montreal Protocol has led to estimated emissions reductions of ~3 Pg C-e yr$^{-1}$ from 1990-2010 (Velders et al. 2007) which has been alternatively assessed by the UN Millennium Development Goals Report (2010) to have avoided ~36.8 Pg C during the same time period. By contrast, the Kyoto protocol contributed to emissions reductions of ~0.55 Pg Pg C-e yr$^{-1}$ (Velders et al. 2007). The comparison is striking considering that the Montreal Protocol was not designed in order to mitigate climate change—it was aimed at reducing depletion of the Earth’s stratospheric ozone layer. In contrast, the very purpose of the Kyoto Protocol was climate change mitigation.

While replacement of CFCs with HFCs and HCFCs has lead to a partial stabilization of the ozone layer, the mitigative impact on climate change has been less successful due to the relatively high radiative forcing of the alternatives. For instance, replacement of CFC-12 (ODP= 1 , 100yr-GWP = ~10,000) commonly used in mobile air conditioning units found in passenger
vehicles with HFC-134a (ODP= 0 , 100yr-GWP= ~1,300) benefited the ozone layer due to negligible ODP, but still has a detrimental effects on Earth’s climate system. Recently, a climate-friendly alternative, HFO, which has a 100yr-GWP of 4 and an atmospheric MRT of 11 days has been developed to replace HFC-134a (IGSD, 2010). Ensuring low-cost and high market accessibility of HFOs while duly compensating manufacturers will (similar to development of low-cost drug treatments for developing countries) present hurdles but none that are insurmountable.

In 2007, Parties to the Montreal Protocol agreed to an accelerated phase-out of HCFCs with developed countries pledging to a 75% reduction by 2010, 90% reduction by 2015 and 100% by 2020, and developing countries agreeing to a 10% reduction by 2015, 25% reduction by 2020, 67.5% reduction by 2025, and 100% by 2030 (UNEP, 2008; Velders, 2009).

Building on the success of the Montreal Protocol and the 2007 agreement for accelerated HCFC phase-out, strategies for furthering RF of high GWP chemicals include: (i) research and development of low-GWP alternative chemicals (particularly low-GWP refrigerants [e.g. HFOs], ammonia, hydrocarbons and CO₂ for refrigeration) (Devotta et al., 2001; Velders et al., 2009) (ii) identification, monitoring, and destruction of ODS stockpiles from refrigeration units, air conditioning equipment, fire suppression systems and insulating foam (IPCC-TEAP, 2005, 2007), (iii) heightened regulations on sale and distribution of high GWP refrigerants and chemicals, and (iv) reduced need
for air-conditioning and refrigeration systems through improved building technologies and use, (v), decreased dependence on personal vehicle transportation, and (iv) food production, processing, and storage facilities that decrease refrigeration needs. Velders et al. (2007) estimated a mitigation potential of 0.24 to 0.3 Pg C-e yr\(^{-1}\) based on CFC and HCFC emissions reductions, better containment and storage of refrigerants and destruction of ODS banks, and HFC reductions.

1.2.6 Fast-action conclusion

There are likely to be additional non-geoengineering “fast-action” approaches not considered here that are worth attention. Increasing albedo through use of reflective roofing, for instance, could be another important fast-action strategy. Menon et al. (2010) report that ~15.4 Pg of C-eq could be avoided globally if urban areas uniformly adopted “cool roof” programs that simultaneously increase reflectivity and decrease energy loads by air-conditioning units. So-called “carbon negative” cement production, presently being non-commercially developed by several private companies, could also be part of a fast-action portfolio (Biello, 2008).

In summary, reducing the emissions and concentration of NCCFA in the atmosphere through an update and extension of the 1989 Montreal Protocol to include CH\(_4\), BC, tropospheric ozone, and the full suite of halocarbons including HFCs is arguably the most effective, rapid, and politically feasible mitigation
effort that can be taken to immediately reduce anthropogenic forcing on the
global climate system.

1.3 “Win-win” mitigation strategies

Numerous climate change mitigation strategies exist which are likely to have positive impacts on ecological health, human wellbeing, and global security—these we refer to as “win-win” strategies as they often have significant ancillary benefits beyond climate change mitigation alone (Lal, 2004; UNEP, 2009). Among the win-win options, reducing energy waste through conservation and efficiency in “developed countries” is likely to bring about some of the largest opportunities at low or even negative costs (Enkvist et al., 2008). Also of great potential are biological approaches to C management which seek to protect and enhance natural C pools. In contrast to current forest and agricultural management practices, which are largely based on extraction and degradation of biological C pools, we suggest a regenerative. Forests, soils and wetland—the Earth’s systems major terrestrial C pools—are essential for much of biological life on the planet and collectively provide humanity with invaluable ecosystem services far beyond C sequestration alone (Costanza, 1997; Chazdon, 2008). The threat of global climate change provides impetus for more urgent action to save, protect and indeed expand these biologic systems while sustainably providing for human needs.

Approximately 120 Pg C is sequestered from the atmosphere on an annual basis through the photosynthetic process—a full order of magnitude
greater than all annual anthropogenic emissions estimated to be ~10 Pg yr$^{-1}$. Of the 120 Pg captured, ~60 Pg C is returned to the atmosphere through respiration and C oxidation. The remaining ~60 Pg returns to the soil as coarse organic residues, detritus, hemicellulose-lignin compounds, and soil humus. The soil, in turn, nourishes and provides habitat to microbial communities and plants which live within and on top of the soil. Through erosion, decomposition, methanogenesis, and oxidation the soil eventually gives back ~60 Pg C to the atmosphere. Thus, in the end (and without anthropogenic interference in the natural system) the terrestrial C cycle is largely balanced. The amount of C from the atmosphere going into the plants and soils is roughly equal to the amount of C exiting back into the atmosphere.

Current practices of deforestation, forest degradation, soil tillage and mismanagement, peatland burning, and wetland drainage and destruction, however, have largely unbalanced the system so that the terrestrial C pools are losing >1.5 Pg yr$^{-1}$ (greater than 15% of annual C emissions). The opportunity therefore lies in restoring the C balance, or perhaps even tipping the systems toward net C sequestration while simultaneously protecting biological diversity, indigenous communities, food security, hydrological functioning and as well as other important ecosystem services (UNEP, 2009).

The U.S. Department of Energy defines C sequestration as, “…the provision of long-term storage of carbon in the terrestrial biosphere, underground, or the oceans so that the buildup of CO$_2$ (the principal GHG)
concentration in the atmosphere will reduce or slow." C sequestration can be suitably divided into two categories: (i) capture of the CO$_2$ and (ii) stable and long-term storage in natural or human-made repositories. Various methods for capturing C include photosynthetic/biotic capture, humification capture (i.e. soil organic C stabilization), post-combustion capture, carbonate mineral capture, and air-capture using chemical scrubbers which remove ambient CO$_2$ directly from the atmosphere. Options for storing C include terrestrial biota, soils, geologic reservoirs, oceanic biota deposition, deep ocean reservoirs, deep ocean sea floor, and mineral deposits.

Each C capture and storage technique has its own set of opportunities, risks, costs, and potential benefits. Although beyond the scope of this paper, a full accounting is essential for assessing the usefulness of each C sequestration and storage pathway through, for example, lifecycle assessments (LCA) and cost-benefit analyses (CBA). Most discussion of C sequestration has heretofore narrowly focused on “C capture and storage” or CCS which involves post-combustion gas streams from stationary fossil fuel energy generation plants with subsequent geologic storage. While significant and sustained resources are warranted for CCS, such a narrow focus tends to restrict consideration of a wider range of potential mitigation solutions. Furthermore, research and development thus far suggests that CCS, at present, may not be scalable for decades (MIT, 2007; Haszeldine, 2009), is not economically viable without dramatic increases in the price of C emissions (Al-Juaied and Whitmore, 2009), and even if successfully scaled-up would be able to address only ~20% of global C
emissions (Haszeldine, 2009). Conversely, many biological C sequestration platforms (primarily forests, soils, and wetlands) are proven, shovel-ready, cost-effective, and, in many circumstances, able to provide significant ancillary benefits such as increased food security and protection of ecosystem services (Lal, 2004). Unlike CCS from fossil fuel emissions, biological systems are capable of directly drawing down atmospheric C levels as opposed to only reducing emissions. This distinction becomes particularly important if we are indeed beyond safe upper limits for C in the atmosphere and there is need for direct drawdown technologies (Hansen, 2008). However, C alone should not be the exclusive measuring stick of progress and ecosystem health—other ecological measures are necessary to making informed decisions. Importantly, complex feedbacks need to be considered and potential unintended consequences and conflicts properly identified and mitigated where possible. There are technical challenges with biological C sequestration such as quantifying C sequestration stocks, rates, and potentials which vary strongly from region to region. Thus, assessing biological C sequestration platforms requires intimate knowledge about local C cycling and storage dynamics and best management practices specific to regional biomes and agroecosystems (UNEP, 2009).

Tradeoffs also exist. For example, implementation of policies that encourage planting of forest plantations may reduce pressure on natural systems by limiting the land area harvested, but may also negatively impact biologic diversity and local communities (Harrison, 2000).
1.3.1 Energy conservation and efficiency

Energy and resource conservation and efficiency (C&E) is likely to be among the most cost-effective and rapidly implementable strategies for reducing global C emissions (Levine, 2007). Reducing C emissions through C&E is likely to be a more effective strategy than C sequestration due to lower and often net negative removal costs and greater reductions in radiative forcing per unit of C avoided (Cao and Caldiera, 2010). C&E strategies are made increasingly necessary in light of rapid depletion of fossil fuels that are expected to be exhausted within ~100 years (Shafiee and Topal, 2009) and by emerging evidence that we are at or approaching near-term “peaking” of global conventional oil resources (Hirsch et al., 2006; Karecha and Hansen, 2008; Lloyd and Subarraro, 2008).

Global energy use in 2008 was ~474 exajoules (EJ, 474 x 10^{18} J or 449 Quads [10^{15} British thermal units]) with ~80-90% of this coming from fossil fuels (IEA, 2009). Sources of global energy break down accordingly: oil (~37%), coal (~25%) natural gas (~23%), nuclear (~6%), biomass (~4%), hydro (3%), solar heating (~0.5%), wind (~0.3%), geothermal (~0.2%), biofuels (~0.2%), and solar photovoltaics (~0.04%) (IEA, 2009). Plans to exploit “unconventional” energy sources such as the tar sands and oil shale could have significant human health and environmental costs (Timoney and Lee, 2009) and would likely drive Earth’s climate system past safe upper limits (Kharecha, 2010).
Energy use and concomitant C emissions are extremely disparate among countries. Approximately 50% of energy consumption occurs in “developed countries” (e.g. the U.S., E.U., Japan, etc.), 50% in “developing countries” (e.g. the former Soviet Union, China, India, etc.) and negligible amounts (<0.01%) in “least developed countries” (e.g. Afghanistan, Angola, Bangladesh, etc.) (Raupach, 2007). The United States presently uses ~25% of the global energy but makes up only ~4% of world population (Pimentel, 2009) with annual per capita C emissions of ~5.21 tons C in 2003. China, India and Malawi were 1.25, 0.33, and 0.03 tons C person\(^{-1}\) year\(^{-1}\), respectively, in 2003 (UN Millennium Development Indicators).

Energy use in LDCs and in much of the “developing” world could be allowed to rise to allow for sustainable development, while proactive measures should be aimed at reducing per capita consumption in developed countries as well as the so-called “BRIC” countries (Brazil, Russia, India and China). Such allowances for increased C emissions in LDCs and in energy-poor countries could allow for substantial global net C emissions reductions so long as developed countries reduce energy consumption levels to be at parity with the rest of the world in terms of per capita energy use.

C&E measures mainly target developed countries in which profligate consumption patterns are common and in which the most dramatic improvements can be made. Pimentel et al. (2009) have estimated that the average U.S. homeowner could save ~50% on home heating costs with cost
reductions of ~$US 1,000 yr\(^{-1}\) with improved efficiency measures such as improved windows, added insulation, air sealing, decreased heating and cooling use, and improved heating ventilation and air-conditioning equipment. Similar reductions in energy use can be made in appliances, transport, commerce, and food production and consumption patterns (Pimentel et al., 2009). Implementation of “deep retrofits,” robust and comprehensive energy reduction strategies, and “passive-house” techniques which make use of passive solar heating on buildings could offer even greater gains in efficiency potentially reducing energy use in homes by >70% (Wigington, 2008).

A recent assessment (McKinsey & Co, 2009) found that the US economy could save ~$USD 2.1 trillion over 10 years with an initial investment of $520 billion with a resulting decrease in net energy consumption by 23%. Similar improvements in energy conservation and efficiency are likely to be possible in other developed countries. With robust lifestyle changes and converging global per capita energy use, it may be possible to reduce consumption in developing countries by 50% or more. So-called deep retrofits combined with significant behavioral changes (e.g. driving less, backyard gardening, and reducing non-essential consumption) toward more sustainable and energy efficient lifestyles could dramatically lower energy consumption in developing countries. The IPCC (2007) estimated that 3% to 4% of baseline emissions could be avoided based on prices of $USD 20 ton CO\(_2\)-eq and $USD 100 ton CO\(_2\)-eq, respectively, however, it is noted by the authors that this is likely to be an underestimate of maximum potential.
1.3.2 Reducing deforestation

Deforestation is the full or partial removal of above-ground biomass through human activity typically for conversion to agriculture, pasture or urban development. C emissions from deforestation is an large but uncertain C source accounting for 0.5 to 2.4 Pg C yr\(^{-1}\) (Fearnside, 2000; Houghton, 2000; Fearnside, 2004FAO, 2006) contributing roughly 10-20% of total annual anthropogenic C emissions and ~10% of total annual anthropogenic N\(_2\)O emissions (Bouman et al., 1995). In addition to loss of above-ground biomass C, significant losses of belowground C and emissions of N\(_2\)O, CH\(_4\), and BC can also accompany deforestation processes—particularly when fire is employed as the land clearing technique. Future emissions due to deforestation are estimated to be 87 to 130 Pg C by 2100 (Houghton, 2005; Gullison et al. 2007). Reducing deforestation is widely agreed to be a low-cost, high-return mitigation option thatMg has and can be deployed successfully in many countries throughout the world (Stern, 2006) and which could be essential for limiting the increase in average global temperatures to 2°C above preindustrial levels (Warren et al., 2009).

Terrestrial biomass C sequestration takes place constantly through the photosynthetic process as plants convert CO\(_2\) to relatively stable compounds such as lignin and cellulose. The accumulation of living and dead organic matter constitutes a large pool of 560 Pg C with the estimated net uptake of C by forests systems of 1.7±0.5 Pg C yr\(^{-1}\) (Fan et al., 1998). Deforestation reduces net primary productivity (NPP), thereby causing a decrease in terrestrial systems to cycle and sequester C. Recent studies indicate that old-growth forests,
previously considered to be C neutral, actual provide a substantial sink for C on the order of \(~1.36\, \text{Pg C yr}^{-1}\) (Lyssaert, 2008).

Vital connections exist between forests, soils, hydrology, nutrient cycling and ecosystem services. Conversion of forest to agricultural fields or pasture, for example, can result in a 20% to 40% decline in soil C (Archard, 2004; Guo, 2002). Changes in the global climate system may increase the vulnerability of forests with amplified incidence of fire (Flannigan, 2000) and pests (Kurz, 2009). The cause and magnitude of deforestation is difficult to quantify and can vary significantly on an annual basis. The bulk of deforestation, \(~1.1\, \text{Pg C yr}^{-1}\), is from tropical countries (Archard, 2004) where strong pressure exists from the cattle industry, soy and palm production, and slash-and-burn agriculturalists. Nepstad et al. (2009) estimated that \(~80\%\) of deforestation in the Amazon rainforest (\(~19,500\, \text{km}^2\) cleared annually from 1996-2005) is the result of the cattle production industry in Brazil with resulting emissions of 0.19 to 0.38 Pg C-eq yr\(^{-1}\).

Slash-and-burn (otherwise known as assarting, swidden, or shifting cultivation) accounts for the majority of biomass burning in the tropics. Globally, \(~410\, \text{million ha or } ~30\%\) of total arable land is presently under slash-and-burn management (Brady, 1996). Alternatives to slash-and-burn (ASB) are central to reducing deforestation and lowering global C emissions (Brady, 1996). Pervading economic and social conditions present formidable challenges particularly for small holders and subsistence agriculturalists to have the
necessary means for implementing ASB (Palm et al., 2005). Strategies to reduce deforestation include: protection of indigenous lands and conservation reserves (Ricketts et al., 2010); enforcement of existing anti-logging laws by governments (Tacconi, 2007); community owned forestry cooperatives (Klooster and Masera, 2000); sustainable timber harvesting methods (Putz et al., 2009); alternatives to slash-and-burn (Palm et al., 2005); rapid soil enhancement methods for tropical countries including biochar production (Lehmann, 2006); and payment of ecosystem services and C sequestration to landowners through REDD (Heal, 2000).

The total amount of C emissions that can be avoided is highly dependent on adopted policies and the price of C. Gullison et al. (2007) suggested that halting deforestation in countries once 50% of the land area has been deforested and slowing present rates of deforestation by 50% will prevent emissions of ~50 Pg C by 2050. Nabuurs et al. (2007) using bottom-up models suggested that the mitigation potential of forestry options could lead to emissions reductions of 0.44 to 0.74 Pg C-e yr\(^{-1}\) at prices of 20 to 100 US$/tCO\(_2\)-eq, respectively, by 2030. Top-down models suggested much larger mitigation potential of 3.76 Pg C yr\(^{-1}\) at prices US$/tCO\(_2\)-eq of 100 by 2030 (Nabuurs et al., 2007).

1.3.3 Reforestation and afforestation

Reforestation and afforestation are strategies to increase terrestrial C sequestration through the planting of trees on deforested and previously non-forested sites, respectively. The percent of land occupied by plantations in 2005
was ~4% of global forest area (FAO, 2006) and is growing by ~2% annually (van Dijk et al., 2007).

Reforestation and afforestation are likely to provide the largest C sequestration potential on degraded lands (Lal, 2004). Forests plan significant role in stabilizing or enhancing ecosystem services including hydrologic and nutrient cycling and protection of biodiversity. Poorly sited or managed reforestation and afforestation projects, however, can lead to nutrient depletion (Berthrong et al., 2009), soil salinization, reduced stream flow and/or groundwater recharge (Jackson et al., 2005), and reduction of biodiversity. Careful site selection and sustainable management are therefore necessary for sequestering C in forests while preserving ecological health and replenishment of natural resources.

In contrast to native forests, reforested and afforested lands typically have lower C storage. Based on a synthesis of 86 studies, Liao et al. (2010) found plantations to have 28% lower C stock per unit of land area than forests and similarly reduced levels of N, P and K. Many of the system studied were plantation monocultures, i.e. single specie systems planted over large areas. C stock density, nutrient cycling, and gains for biodiversity may be enhanced through diversifying tree species (Jandl et al., 2007). Particular sites may also afford C storage capacity. High clay soils, for example, can increase the soil C storage in reforested and afforested sites (Laganiere et al., 2010). Careful selection of tree species is also important. Deciduous broadleaf trees, for
example, are likely to contribute to greater soil organic C build up as compared with coniferous species (Laganiere et al., 2010). As we shall examine in the next section, use of agroforestry may provide a more productive and diverse alternative than monoculture plantations.

The tradeoffs between water and afforestation projects (particularly in semi-arid and arid climates) have been clearly recognized (Jackson et al., 2005; Bates et al. 2008). There may, however, be positive, synergistic effects between forests and water availability for the case of large-scale reforestation and afforestation projects. The connection between vegetation and meteorology is highly uncertain, but the impact of forests on surface roughness, wind speed and direction, and net evapotranspiration are expected to have some impact of weather phenomenon. A single tropical tree can transpire hundreds of liters of water per day through their stomata (Goldstein et al. 1998). In the Amazon, 5.4 billion hectares of forest collectively transpire on the order of 8 trillion tons of water (Nepstad, 2008). Thus, large forested areas are generally thought to be able to “recycle” water through evapotranspiration-precipitation events. Importantly, a new hypothesis by Makarieva and Gorshokov suggested that forests are able to control regional climate patterns by “pulling in” moist oceanic air as a result of differential heating and evaporative processes of forests vis-à-vis oceans (Makarieva and Gorshokov, 2007). The authors suggest that large-scale, contiguous afforestation within proximity to oceans can act as a large-scale biological water pumps that can increase regional precipitation (Makarieva et al., 2006; Makarieva and Gorshokov, 2007) and indirect evidence exists that
Deforestation of Australia’s coastal forests may have decreased inland precipitation thereby leading to widespread desertification event, although an anthropogenic signal to changes in precipitation patterns is difficult to prove (Bowman, 2002).

Ornstein et al. (2009) suggest a novel concept for C sequestration via afforestation of large portions of the Saharan Desert and Australian Outback with *Eucalyptus* irrigated with desalinated ocean water. Based on previous studies and climate modeling simulation the authors suggest sequestration potentials of 6-12 Pg C yr\(^{-1}\). Using global climate models, the authors find that biophysically-induced rainfall eventually reduces or eliminates the need for irrigation in many afforested regions. Thus, the results of Ornstein et al. at least superficially corroborate the Makarieva and Gorshokov hypothesis of “forests attracting rain.” The validity and extent of the hypothesis remains under serious scientific debate (Meesters, et al., 2007), nevertheless this potentially important phenomenon warrants advanced studies using interlinked GCMs, remote sensing, forest and hydrologic models. If modeling exercise do indeed indicate large land areas that i) could potential induce higher rainfall under afforested conditions, and ii) are technologically and economically feasible for tree plantings, this might be of grave importance for large-scale climate stabilization.

Ornstein et al.’s conceptMg has significant practical problems: (i) the use of a single tree species could have negative impacts on biodiversity; (ii) the energy requirements for desalinating and pumping water at the required scale are
enormous; and (iii) the sheer physical requirements for planting trees at the scale required would be massive. A “win-win” agroforestry approach would likely be more viable. For instance, use of diverse multi-function tree species that also provide food, fodder, construction materials fuelwood etc., in addition to C sequestration would encourage greater local buy-in, successful implementation, and regional economic benefits. Instead of large-scale desalinization, more appropriate rainwater harvesting, storage and delivery systems could be utilized (e.g. swales and sand dams) (Dillon, 2005).

Beyond C sequestration, of great interest is the impact of reforestation and afforestation on Earth’s hydrological processes, cloud cover and radiative budget (Jackson et al., 2008). Forested areas can change biogeophysical processes including the way in which energy is partitioned as either sensible or latent heat, surface roughness, and land-surface albedo (Pitman, 2005). Generally, reforestation and afforestation in the tropics and sub-tropics is predicted to decrease radiative forcing whereas in temperate and boreal climates the impacts are likely to have less cooling potential and potentially could even increase warming under some circumstances (Feddema, 2005; Bala et al., 2006). Beyond C sequestration, deliberate attempts to mitigate climate change with forests (e.g. by increasing cloud cover) is worth investigation but requires careful consideration of all potential biogeophysical feedbacks (Jackson et al., 2008).
Land area that would qualify under existing Clean Development Mechanism afforestation and reforestation criteria is 749 Mha (Zomer et al., 2008). Benitez-Ponce et al. (2007) estimated that at 13.6 US$/t CO₂, reforestation and afforestation could sequester 0.51 Pg C yr⁻¹ for the first 20 years. Canadell and Raupach (2008) estimated that reforestation C sequestration rates of 0.16 to 1.10 Pg C yr⁻¹ to 2100. Nilsson and Schopfhauser (1995) predicted total land area available for afforestation to be 345 million ha with associated C sequestration values of 1.48 Pg C yr⁻¹ achievable after 60 years.

1.3.4 Agroforestry and perennial cropping

Agroforestry is “a dynamic, ecologically based, natural resources management system that, through the integration of trees on farms and in the agricultural landscape, diversifies and sustains production for increased social, economic and environmental benefits for land users at all levels” (ICRAF, 2010). Agroforestry systems can include a wide variety of tree utilization techniques including food forests, orcharding, alley cropping, riparian buffer strips, silvopasture, and windbreaks (Nair, 2009).

Over time, agroforestry systems can lead to the net accrual of biomass 5 to 10 times the biomass of conventional cropping systems (Watson et al., 2000) although this is highly dependent on conditions such as climate, tree species, planting density, soil type, and management strategies (Nair, 1993). Small-scale agroforestry systems in the tropics can sequester 1.5-3.5 t C ha⁻¹ yr⁻¹ (Montagnini and Nair, 2004). Total C storage has been estimated to be 9 Mg C
ha$^{-1}$ in semi-arid, 21 in subhumid, 50 in humid and 63 in temperate agroforestry systems (Montagnini and Nair, 2004). Depending on end-use, products made from wood such as construction materials may create a substantial C sink of $\sim$0.3 Pg C yr$^{-1}$ (Watson et al., 2000), however, due to relatively short (~30 year) use period, C sequestration for construction material is considered to be small or negligible.

The use of trees on farms as well as perennial cropping systems offer a paradigm shift from C-positive to C-neutral and C-negative farming. The synergistic use of trees with grain and vegetable cropping systems has the potential for increasing C storage and increasing food production in developing countries (Sanchez and Swaminathan, 2005). Trees greatly enhance C cycling and storage compared to annual cropping systems and therefore can offer a powerful pathway for C sequestration and climate mitigation in addition to REDD, reforestation, and afforestation (Schroeder, 1993; Batjes and Sombroek, 1997; Watson, 2000; Montagnini and Nair, 2004; Mutuo et. al, 2005; Nair et al., 2009). Agroforestry systems increase above- and below-ground C stocks vis-à-vis cropland and pastures, protect and enhance soil quality by reducing erosion and fixing N, and decrease atmospheric C concentrations (Palm et al., 2004; Mutuo et al., 2005). Similarly, non-tree perennial crops are more beneficial than annual crops in terms of protecting soil, sequestering C, and adapting to potential changes in regional climates (Cox et al., 2006).
Data from the tropics suggests that CO$_2$, CH$_4$, and N$_2$O emissions from agroforestry systems are often considerably less than those from high-input agricultural systems (Palm et al., 2002). Because tillage is often reduced or altogether unnecessary in perennial cropping systems, C emissions as a result of mineralization and erosion associated with soil disturbance is minimized or eliminated. Reduced fuel usage associated with tree and perennial crop farming systems may provide additional mitigative benefits as annual tillage, planting, and fertilization are reduced.

In addition to cycling and storing greater amounts of C than traditional annual monoculture row crops, agroforestry systems are also capable of producing diverse outputs, including highly nutritious fruit and nut crops, medicines, edible fungi, saps and resins such as latex, timber and raw materials for craft and construction, and many other non-timber forest products (NTFP). They fix atmospheric N thereby offsetting cost of, dependence on, and GHG emissions of manufactured N fertilizers, and provide important habitat for wildlife as well as aesthetic beauty to people.

Returning organic C from trees in the form of litterfall, prunings, and fine and coarse roots can enhance SOC levels far beyond what cropland alone is capable of, thereby increasing the potential productivity of the given piece of land. Difficulty extracting and quantifying root biomass presents significant uncertainties, yet, it is well understood that root systems (which make up 30% or more of total tree biomass) likely contribute large quantities of C to deep soil
Biochar production offers a robust synergy with agroforestry and perennial cropping systems (Blackwell, 2009). Pruning, cutting and processing of wood is common in agroforestry systems and unused residues, otherwise combusted or discarded, may provide low cost feedstock materials. Resulting biochar can subsequently be returned to the soil from which the feedstock was produced thereby providing an important return of nutrients to the system while sequestering atmospheric C.

In many developing countries where fertility inputs are limited, growing trees (particularly species that fix atmospheric N) can lead to greater biological productivity. For instance, in Malawi the leguminous N-fixing Acacia Albida (Faidherbia albida) has been found to greatly enhance production of maize (Zea mays) upwards of 280% around the base of the trees from 1.3 to 4.1 Mg ha⁻¹ yr⁻¹ (World Agroforestry Council, 2009). The tree can also provide fuel wood, construction material and medicinal products from its bark (World Agroforestry Centre, 2009).

Agroforestry systems may also provide a hedge against effects of climate change as tree crops are often more resilient to extreme weather conditions including droughts and flooding (Syampungani et al., 2010; Neufeldt et al., 2009). Because trees have deeper root structures, they are often able to extract nutrients and water from lower layers of the soil thereby decreasing competition with shorter rooted annual crops (Nair, 1993). Conversely, tree crops can be subject to substantially reduced yields if there are wide variations in temperature.
at important developmental stages such as flowering (Tubiello, 2007) or if biological pollinator species undergo population declines or asynchronistic phenological changes due to changes in global climate patterns.

More than 66% of global cropland is dedicated to the cultivation of annual species (Cox et al., 2006), whereas natural terrestrial ecosystems are dominated by perennial plant communities (Chiras and Reganold 2004). Perennial plants are more effective than annual crops in protecting soil from erosion, resisting pests, and managing water, nutrients and soil C (Cox et al., 2006). Robertson et al. (2000), for example, reported perennial crops providing greater SOC storage (320 to 440 kg ha\(^{-1}\) yr\(^{-1}\)) as compared to annual crops (0-330 Kg ha\(^{-1}\) yr\(^{-1}\)) (Robertson et al. 2000). However, perennial grain crops have largely been ignored for human production due to small seed size and challenges associated with breeding productive cultivars (Cox et al., 2006). Transitioning from annual to perennial cropping systems could, theoretically, greatly increase soil C storage while reducing need for annual planting and tillage operation thereby conserving C emissions associated with soil disturbance. Quantifying this potential is difficult at present, however, and perennialized crops have yet to be adequately developed for commercial production.

A large-scale transition from annual cropping to perennial cropping and agroforestry systems will help conserve soil and water, and buffer agricultural communities from the impacts of climate change in addition to providing an important sink for atmospheric C. Agroforestry also makes more efficient use of
space and time than one-dimensional, seasonally-fallowed annual agricultural systems. Thus, agroforestry approaches may be able to increase the global NPP from an estimated 59.22 Pg C yr\(^{-1}\) closer to the potential productivity of 65.51 Pg C yr\(^{-1}\) annual systems with multi-dimensional, long-season, biomass-rich perennial agroecosystems (Haberl, 2007). Challenges to adopting agroforestry practices include the lag-time in productivity and revenue generation (Palm et al., 2003), higher initial labor requirements (Vosti et al., 2001), and resistance or hesitation to adopt new practices by farmers. In developing countries, the struggle to simply produce enough food and money for a single season and land ownership/tenure rights are often obstacles to promoting long-term investment in land and sustainable management practices. Watson et al. (2000) estimated that agroforestry practices could sequester ~0.4 Pg C yr\(^{-1}\) by 2010 and 0.59 Pg C yr\(^{-1}\) by 2040 on 630 million ha of marginal or degraded crop and pasture land. The C sequestration potential of agroforestry systems remains uncertain with a large range of estimates.

1.3.5 Soil carbon sequestration

The global soil layer, the “pedosphere,” constitutes a large but labile source of C with ~1500 Pg of soil organic C at a depth of 2 m and ~2500 Pg C at a depth of 3 m (Batjes, 1996; Batjes and Sombroek, 1997). Of the total soil C pool, ~1550 Pg is comprised of soil organic carbon (SOC) and ~950 Pg soil inorganic carbon (SIC) (Lal, 2004). Thus, the total soil C pool is > 3 times larger than the ~800 Pg C contained in Earth’s atmosphere. Historically, soils have lost 78±12 Pg C due to anthropogenic impacts—forest clearing, tillage, and erosion
corresponding to ~27% of historic anthropogenic emissions since 1750 (Lal, 2004). MMg has been suggested that at least of portion of this is recoverable through prudent land management and agricultural practices. Fundamentally, agricultural practices which remove greater C and nutrients (i.e. N, P, K, Ca, Mg, S, etc.) than are returned to the system are inherently unsustainable (Lal, 2009). For this reason, recent proposals to produce biofuels from crop residues could very likely come at heavy costs to maintaining SOC levels if urgent care is not taken to use only sustainable feedstock sources (Lal and Pimentel, 2007). On the other hand, positive C and nutrient budgets replenish and restore degraded soils while having potential benefits for climate change mitigation.

Soil restoration and C sequestration often leads to increased food productivity and on-farm income; concomitant reduction in poverty; improved soil aggregate stability, root penetration and soil tilth; reduced bulk density and soil erosion; improved ecosystem services such as infiltration; increased nutrient cycling and biodiversity; enhanced net primary biological productivity; and greater capacity for detoxification of environmental contaminants (Lal, 2004; Reid and Swiderska 2008). Thus, soil C has significant multidimensional ancillary benefits. The ability to simultaneously remove C from the atmosphere and buffer human populations from likely effects of climate change by has been widely understood as a “win-win,” “no-regrets” strategy (Lal, 2004).

At its roots, human civilization is deeply dependent on the health of soil as it provides the foundation for human agriculture, sustenance and survival.
Historically the fate of many civilizations has ultimately been determined by the management and care of soil (McNeill and Winiwarter, 2004). In the 21st century, this dependence is perhaps even more decisive than ever before due to the diminishment of natural resources and the exponential increase in the human population (Hillel, 2009). While continued degradation of the soil may ultimately lead to catastrophic consequence for human societies, regeneration of soils may provide important solutions for addressing the significant challenges that face humanity in the 21st century—particularly anthropogenic climate change and global food security (Lal, 2004).

Techniques employed to increase soil C include use of no-till and conservation tillage, reduced bare fallows, cover cropping and use of perennial crops, incorporation of manure and other carbonaceous materials, mulching, promotion of below-ground biodiversity, intensive-grazing pasture management, sustainable agroforestry practices, integrated nutrient and pest management, precision fertilizer and irrigation, proper drainage, and restoration of marginal farmland back to forest, savannah or wetlands. Soil C sequestration takes place through deposition of crop residues and translocation of root biomass which is subsequently transformed into more recalcitrant through the process of humification. In semi-arid and arid regions SIC occurs through the formation of bicarbonate mineral compounds. The rate of soil C sequestration depends primarily upon the quantity and quality of biomass residues being returned to the field and upon existing edaphic and climatic conditions. Lal (2006) compiled data from published studies demonstrating a correlation between food
productivity and SOC. For every 1 Mg SOC ha\(^{-1}\) in the root zone, crop yields for wheat, rice, and maize due increased 20-70 kg ha\(^{-1}\), 10-50 kg ha\(^{-1}\), 30-300 kg ha\(^{-1}\), respectively (Lal, 2006).

Drylands soil C sequestration make up a large proportion of potential C sequestration in soils as they make up >47% of global land surface area and could theoretically sequester ~1 Pg C yr\(^{-1}\) (Lal, 2004). Wohlfahrt et al. (2008) suggested that deserts may have much larger C cycling and storage capabilities than previously appreciated. Schlesinger et al. (2009), however, suggest caution is warranted in sequestration rates in dryland ecosystems suggesting that methodological issues have led to overestimates of soil C sequestration rates. Nevertheless, efforts to increase SOC in arid and semi-arid drylands by, for example, increasing residue incorporation of biomass via subsurface drip irrigation and/or fertigation, the practice of applying soluble fertilizer while irrigating (Ayars et al., 1999) and other technologies warrant investigation. Bainbridge (2007) provides excellent overview of existing technologies for desert restoration.

Soil C sequestration has both limitations and drawbacks. First, soil C can be relatively slow to accumulate in agricultural systems depending on climatic and edaphic conditions, and C sequestration rates can vary significantly according to local conditions. Second, soils can become “C saturated,” the point at which the soil reaches maximum C storage capacity and no further C sequestration gains can be made (Six et al., 2002) which places an upper limit on
the total amount of C which could be potentially sequestered in an area and globally. Third, soil C can be quickly lost if poor management practices are reinstated (Rasmussen et al., 1998). Fourth, addition of C can under particular conditions immobilize plant nutrients such as N thereby increasing need for N fertilizer and associated N\textsubscript{2}O emissions. Fifth, some data suggests increased levels of SOC can lead to increased soil N\textsubscript{2}O emissions.

In terrestrial systems, a tight coupling between C and N geochemical cycles exists wherein addition of C to soils may increase the turnover of N and increased emissions of N\textsubscript{2}O (Li et al., 2005). Using modeling of C-N dynamics for agroecosystems in the US, China and Germany, Li et al. (2005) found that over a 20-yr period using a 100-yr GWP of 296, increased emissions of N\textsubscript{2}O offset C sequestration gains by 75-310%. Thus, increasing SOC may be accompanied with higher N\textsubscript{2}O emissions which offset or exacerbate anthropogenic forcings. Conversely, Six et al. (2004) found that on average and over longer time periods practices such as no-till, which increase SOC, reduced net radiative forcing in comparison to conventional cropping systems although results are highly variable and often complex (Marland et al., 2001). Because soils are extremely complex and variable both spatially and temporally, quantifying C sequestration for the purpose of C trading is challenging. Technologies such as remote sensing, predictive mapping, and near-infrared and laser-induced breakdown spectroscopy (Martin et al., 2009) may allow for more rapid C monitoring in order to facilitate emergence of soil C sequestration to play a larger role in trading and offset protocols.
The various impacts of climate change on soil C are highly uncertain. CO₂ enrichment and increasing temperature is likely to create more favorable growing conditions in some parts of the world thereby increasing the potential amount of carbonaceous biomass being inputted into the soil and subsequent humification processes (Allard et al., 2005). On the other hand, increased temperatures also accelerate decomposition of soil C which could lead to net loss of soil C (Davidson and Janssens, 2006). At present it appears that soil C emissions have been increasing but it is not known whether this is the result of net C loss from soil systems or due to an overall acceleration of the terrestrial C cycle in which neutral or even positive C storage is possible (Bond-Lamberty and Thomson, 2010).

The MTFR of soil C sequestration has been estimated to be between 0.4 and 1.2 Pg yr⁻¹. Watson et al. (1995) estimated that 0.4-0.8 Pg C yr⁻¹ could be sequestered globally in agricultural soils. The IPCC (1995) predicted that 60-75% of C lost from agricultural systems is potentially recoverable. Assuming 78 Pg C to be the historic global soil C loss (Lal, 2004), this would be equivalent to a total C sequestration potential of ~47-58 Pg. Cole et al. (1997) estimated MTFR for soil C sequestration to be 0.44 to 0.88 Pg C yr⁻¹. More recent IPCC estimates (Smith et al. 2007) predicted global agricultural mitigation potential to be 0.41 Pg C yr⁻¹ to 1.09 Pg C yr⁻¹ with prices of $20 to $100 $/t CO₂-eq with 89% of this mitigation associated with increasing C stock in soils. Lal (2004) estimated soil C sequestration rates of 0.4 to 1.2 Pg C yr⁻¹ over 20 to 50 years.
1.3.6 Wetlands and permafrost ecosystems

Wetlands and permafrost biomes contain large amounts of C, ~550 Pg C (Parish, 2008) and ~1672 Pg C (Schuur, 2009), respectively, despite occupying a relatively small portion of Earth’s total land area. Human activities are currently leading to widespread disturbance and destruction of wetland and permafrost regions and these systems may be highly vulnerable to climate change. Draining and cultivation of tropical peatlands, for example, may be responsible for emissions of 0.5-0.8 Pg C yr\(^{-1}\) (UNEP, 2009). The saturated condition of wetland and permafrost ecosystems permits high levels of net primary productivity while restricting oxidation and decomposition. Large amounts of C can be stored under such reduced conditions, however these conditions are also favorable for CH\(_4\) production (Whiting and Chanton, 1993) a powerful GHG which has a 25 yr-GWP of 72 and a 100yr-GWP of 25 (IPCC, 2007). Collectively, wetlands and peatlands are responsible for ~20% of total global CH\(_4\) emissions. Protection of extant threatened wetlands and peatlands is essential for mitigating climate change (Mitra et al., 2005; UNEP, 2009), however, creation of new wetlands is unlikely to attenuate climate change under all but special circumstances.

Peatlands are a special type of wetland ecosystem particularly relevant to climate policy and the global C budget. Peatlands occupy ~4 million km\(^2\) (~3% of terrestrial land area) but contain ~550 Pg C (~22% of SOC) (Parish et al., 2008) and are widely considered to be the most C dense ecosystem in the world. Approximately 50% of C emissions from peatlands occurs in tropical countries.
particularly in Indonesia and Malaysia where there exists strong pressure for production of rice, oil palm (*Elaeis guineensis* Jacq.), and pulpwood (UNEP, 2009). Parish et al. (2008) have estimated that peatland fires may be responsible for as much as 50% of the 0.5-0.8 Pg C yr$^{-1}$ of tropical peatland emissions. In 1997, a “perfect storm” for peatland fires in Indonesia and Malaysia resulted from poor management practices including massive drainage of wetlands, use of slash-and-burn land clearing techniques, and extreme drought as the result of the anomalously powerful El Nino Southern Oscillation (ENSO) conditions. Page et al. (2002) have estimated the release of 0.81-2.57 Pg C from soils and aboveground biomass, representing ~7-30% of global C emissions over a one year period. Like most wetland ecosystems, peatlands are likely to be highly vulnerable to change in the global climate system (Bridgham et al., 2008).

Mitigation options for reducing wetland emissions include rigorous protection enforcement mechanisms (UNEP, 2009); restoration, reducing drainage and “rewetting” of drained wetlands (Gorham and Rochefort, 2003), and ending of perverse counterproductive biofuel subsidies which lead to destruction of wetland ecosystems (Fairgone et al., 2008). Permafrost biomes are similarly prone to perturbations of Earth’s climate system with expected increases in emissions of CH$_4$ and CO$_2$ that, if released, will lead to a potentially massive warming feedback to Earth’s climate system. Schuur et al. (2008) suggest permafrost thawing could contribute ~11 Pg C within a 40 year period and ~27 Pg C within a 90 year period, thereby exacerbating the impacts of climate change. Mitigation options for directly confronting permafrost thawing
are challenging due to the harsh, remote and expansive nature of these ecosystems. One idea proposed has been to restore natural permafrost ecosystems by reintroducing grazing megafauna which would effectively increase winter soil temperatures through compaction of the insulating snow area by trampling (Mascarelli, 2009). Reduction of forest extent and maintenance of grasslands in permafrost ecosystems may also have the advantage of increasing planetary albedo as well as increasing SOC storage.

Construction of new wetlands may also provide an opportunity for long-term atmospheric C removal and storage; however, emissions of CH$_4$ are likely to offset a large portion of any mitigation potential. IMg has been suggested that wetlands provide a safer long-term C sink than do forests due to the permanency of C within wetland ecosystems as compared forests which can be subject to pest infestation, fire and other disturbance regimes (Gorham, 1991). Under most conditions in most of the world, however, wetland creation is not likely to have favorable climatic impacts due to high wetland production of methane, which has a strong GWP.

Attention should be paid to wetland ecosystems thaMg have lower CH$_4$ emissions as these can provide targets for conservation efforts and models for reconstruction projects. Tidal marshes, mangrove swamps, and freshwater fens may represent particularly good candidates as CH$_4$ emissions tend to be lower in these systems (Chmura, 2003…need source for fens). Tidal marshes and mangrove swamps account for >44.6 Tg C globally while sequestering on the
order of 57 g C m$^2$ yr$^{-1}$, an order of magnitude greater than C sequestration by peatlands (5.5–8.2 g C m$^2$ yr$^{-1}$) (Roulet, 2000; Chmura, 2003). Prevailing saline conditions greatly reduce CH$_4$ emissions as high sulfate levels substitute for CO$_2$ as an electron receptor. Freshwater “fens” tend to have much higher oxygen levels as the result of a constant recharge from groundwater, may also be worthy of investigation, although C storage tends to be less due to oxidation of C deposits and subsequent release of C as CO$_2$. Location of created wetland is likely to be important. Boreal wetlands, for instance, have been found to have higher CH$_4$ as compared to lower latitude wetlands (Matthews and Fung, 1987).

A thought-provoking mitigation concept is to harness likely sea level rise (SLR) due to climate change in order to irrigate large swaths of coastal land through a series of channels and swales. In essence, it would be a mega-project to create large artificial wetland ecosystems that would subsequently sequester C and protect inland areas from storm surges. The IPCC (2007) predict SLR, the result of both thermal expansion of oceans and of melting land ice, to be between 0.18 and 0.59 meters (IPCC, 2007) by 2090-2099 as compared to the time period between 1980 and 1999. Recent modeling attempts and empirical data suggest the IPCC’s estimate could significantly underestimate potential SLR (Rahmstorf, 2010). In spite of uncertain magnitude, utilizing anticipated SLR in order to sequester C may provide unique opportunity for creating a negative feedback mechanism that would dampen the impacts of climate change. Best locations would likely be semi-arid regions in which biomass production is presently limited by water availability. Many halophytic plants with high salinity
tolerance have been identified that can be variously used for livestock forage and fodder, and, indeed, some research has been conducted on using sea water irrigation for agricultural production (O’Leary, 1985;). Use of low-cost desalinization for water treatment may also be worthy of investigation (Shannon et al., 2008).

Restoration of wetlands may also be advantageous on farms when integrated with irrigation/drainage systems that filter and trap nutrients and sediments (Fausey et al., 2003). Such systems would reduce nutrient loading of water bodies thereby reducing risk of downstream hypoxia. Farm-scale wetlands could be used to trap, use, and produce biological N. Crops such as the genus *Azolla*, an aquatic fern plant that Mg has a special relationship with a N-fixing algae (*Anabaena azollae*), can double in mass every 3-5 days and has been investigated as N fertilizer in the past (Riemer, 1983). On farm production of N would offset emissions with manufacture of inorganic N fertilizer products. Like forest and soils, wetland ecosystems are prone to human degradation and climate change and could potentially move from sinks to sources of atmospheric C.

1.3.7 Biochar production

Biochar production has recently been proposed as a novel means for sequestering C, generating energy, and improving soils (Sombroek et al., 2003; Lehmann et al., 2006; Glaser, 2007; Laird, 2008; and Hansen et al., 2008;). Biochar is a C-rich, fine-grained, highly-porous, charcoal-like product of a
biomass-to-energy process called “pyrolysis.” When incorporated into soils, biochar has been observed to enhance soil quality and plant productivity while effectively sequestering atmospheric C for centennial to millennial time scales. Pyrolysis is the thermal degradation of C-rich materials under oxygen limited conditions leading to the formation of polyaromatic C structures. The remaining uncombusted biochar is a highly recalcitrant material comprised of 65% to 95% C with residual amounts of mineral ash and volatile matter (Antal and Gronli, 2003).

Biochar production occurs under natural conditions from fire activity. Estimates of global biochar production via natural processes are estimated to be 40-600 Tg yr⁻¹ (Schmidt and Noack, 2000) with estimates of biochar extent being 5-30% of the soil C stock in grassland ecosystems around the world (Rodionov et al., 2010). Increasing this natural rate of biochar production through human processes is essential to substantially sequestering C from the atmosphere.

Global net primary productivity (NPP) is estimated to be 120 Pg C yr⁻¹, of which 60 Pg C yr⁻¹ is invested by plants into semi-stable hemi-cellulose, cellulose, and lignin products. Human appropriated net primary productivity (HANPP) is estimated to be 22% (Haberl, 2006) to 39% (Vitousek, 1986). This provides a total potentially usable biomass pool of ~14.7 to 29.5 Pg C yr⁻¹ in the form of crop residues, forestry debris, and other carbonaceous materials (Haberl, 2007), however a much smaller percentage is realistically available due to
limited feedstock suitability and economic constraints. Assuming 10% of HANPP to be realistically available for use and a biomass-to-biochar C efficiency of 30%, this would provide a “ballpark” estimate of ~0.44 to 0.89 Pg C yr\(^{-1}\) or 4.4 to 8.9% of the 10 Pg C emitted annually on a global basis.

The C contained within the biochar typically constitutes anywhere between 10-70% of the originally biomass C depending upon pyrolytic processes with the remainder being liberated as CO\(_2\) into the atmosphere. Approximately 80-90% of C added in the form of uncharred biomass can be mineralized in 5-10 years in tropical environments (Jenkison and Ayanaba, 1977), whereas biochar has been found to persist 1-2 orders of magnitude longer (Lehmann et al., 2006; Cheng et al., 2008). Thus, the mechanism for C sequestration is the transformation of biomass through pyrolysis into highly recalcitrant biochar with mean residence times ranging from hundreds to thousands of years (Skjemstad et al., 1998; Krull et al., 2003). Additional potential benefits from a biochar C sequestration platform include greater food security, and reduced pressure on forests and other ecosystems from which fuel wood is currently being harvested. Thus biochar likely offers significant win-win opportunities. Additional mitigative potential from a biochar strategy beyond enhanced C storage in soil include avoided fossil fuel use; possible reduced emissions of N\(_2\)O and CH\(_4\) from soils; and increased global NPP (Woolf et al., 2010).

Biochar soil C sequestration may be able to overcome some the limitations of other soil C sequestration strategies. First, biochar does not appear
to be subject to a C saturation point as has been often observed within other C inputs (Sohi et al., 2009). IMg has been generally assumed that only 60-75% of C lost from agricultural systems due to tillage, erosion and other C extractive processes (IPCC, 2005), however biochar is not likely to subject to this constraint thereby making it theoretically possible to increase C storage in soils above preindustrial levels. Second, application of labile forms of C to soils generally requires additional nutrients due to nutrient immobilization (particularly of N), however, there is evidence that biochar, in many cases, may not lead to large nutrient immobilization because of its physiochemical stability (Chan and Xu, 2009) although N immobilization has been observed in some experiments (Lehmann et al. 2003). Third, the recalcitrant nature of biochar in soils prevents rapid mineralization as can occur, for example, when no-till is converted back to tillage. Fourth, biochar is likely to be easier to quantify in soils for purposes of verifying C sequestration.

These advantages of biochar do not suggest that it is mutually exclusive to other soil C management strategies or sustainable agricultural practices. For instance, the use of crop residues in no-till (NT) allow for the creation of a protective top-layer that prevents wind and water erosion—an important function that biochar alone would not be able to achieve. Best management would likely consist of combining the two strategies by taking only the percent of crop residue that can be harvested without detrimental effects and to use that as the feedstock with which to make biochar that would be incorporated back into the soil. Similar arguments can be made for the use of leguminous cover crops,
manure applications, and mulching. Thus, biochar, if eventually adopted as an agricultural and climate mitigation strategy, should work in synergy with other best management practices (BMPs) not in exclusion of them.

Numerous potential negative impacts could result from improper use of biochar. Application of biochars containing contaminants such as heavy metals; excessive transport distances; application of improper biochar types to particular soils (e.g. high pH biochar applied to alkaline soil); food-to-fuel concerns; and unsustainable harvesting of biochar feedstock material are among the most important considerations. Clearly, biochar should proceed carefully and within a sound regulatory or certification framework that ensures sustainable biochar production with maximized humanitarian and environmental benefits. Biochar production must be accomplished in a judicious, energy efficient and environmentally sustainable manner lest potential benefits are offset by increased C emissions in the form of leakage and disturbance of environmentally sensitive ecosystems.

Development of robust biochar technologies has not been forthcoming from the commercial sector despite recent interest. This suggests significant hurdles to scaling-up biochar to significant levels within short periods of time. Biochar production technologies are not incredibly technologically sophisticated and short-term progress is likely to be fairly rapid, however, getting to the Pg C yr\(^{-1}\) level within a decadal timeframe will likely require significant incentives, or
C payments in order to spur research, development, and adoption of the technology.

Amonette et al. (2007) have estimated biochar C sequestration rates to be 1.50 to 3.0 Pg C-eq yr\(^{-1}\) (assuming NPP=60.6 Pg C yr\(^{-1}\); 10% appropriation of NPP; 50% carbonization efficiency) with additional mitigation from fossil fuels offsets to result in total reductions of 2.4 to 4.8 Pg C yr\(^{-1}\). Hansen et al. (2008) estimated maximum C sequestration from “waste derived” biochar production to be 0.16 Pg C yr\(^{-1}\). The International Biochar Initiative (2009) estimated biochar C sequestration rates to be 0.25 to 0.75 Pg C yr\(^{-1}\) (assuming NPP=61.5 Pg C yr\(^{-1}\); 1.2 to 3.4% appropriation of NPP; and 40% carbonization efficiency).

Additional biochar mitigation from fossil fuel offsets, N\(_2\)O emissions reductions, increases in NPP, and combined use of CCS technologies result in total reductions of 0.70 to 2.6 Pg C-eq yr\(^{-1}\). Woolf et al. (2010) estimated biochar “maximum sustainable technical potential” of 1.8 Pg C yr\(^{-1}\) achieved within half a century (12% of current anthropogenic C emissions), with a total of 130 Pg C over a 100-year period (assuming no land-use change from food to fuel or from forest to fuels; biomass extraction below levels that would cause soil erosion or degradation; no feedstock materials that would introduce contaminants in the soil; and some dedicated energy crops on abandoned and degraded lands.)

Woolf et al. define maximum sustainable technical potential to be “what can be achieved when the portion of the global biomass resource that can be harvested sustainably (i.e., without endangering food security, habitat, or soil conservation) is converted to biochar by modern high-yield, low-emission, pyrolysis methods”.

61
Importantly Woolf et al. find that utilization of biochar in soils produced 22-27% greater mitigation potential than the same biochar combusted to offset fossil fuels.

1. **3.8 Win-win conclusion**

There are likely to be other strategies which could be used to mitigate climate change that have not received adequate attention. For example, use of bioenergy with carbon capture and storage (BECCS) provides opportunity for C-negative energy production similar to that of biochar (Kraxner, 2003) although it would have nearly identical economic and technical challenges as CCS. Mineral C sequestration via carbonization of ultramafic rocks such as peridotite may be able to sequester >0.27 Pg C yr\(^{-1}\) (Keleman and Matter, 2008), however, data for this method is scant and it would offer few if any ancillary benefits.

It is important to note that all three biologic C sequestration platforms—forests, soils, and wetlands—are incredibly vulnerable to changes in the Earth System brought about by climate change. As Earth’s surface temperature rises many biological systems could move from sinks to sources of atmospheric C thereby exacerbating climate change (Schaphoff, 2006). Such predictions reemphasize the need for comprehensive mitigation strategies which include aggressive reduction of C emissions through conservation and efficiency, fast-action approaches that target the “other half” of anthropogenic forcing agents, and biological C sequestration.
1.4 Conclusion

Climate change has emerged as perhaps the most significant of the challenges facing humanity today, although certainly not the only. Solving this seemingly intractable problem will likely require significant transformations on nearly every front of global society, economics, politics, and individuals’ daily lives. Among the most important steps are establishing an accurate price of C emissions that adequately quantifies heretofore externalized costs to societies and ecosystems. Stabilizing and/or reducing the human population to sustainable levels through voluntary and ethical national and international policies may be among the most important and most difficult problems human society is likely going to have to confront (Ehrlich and Ehrlich, 1997; Kippen et al., 2010). Also needed are proactive measures to monitor and reduce risk of crossing potentially catastrophic tipping points.

Here we have presented a combination of “fast-action” and “win-win” approaches which collectively may be able to shift the Earth away from potentially catastrophic tipping points without the use of geoengineering or CCS technologies. Such geoengineering and CCS technologies may be necessary if observational data suggest we are indeed at or near tipping points which could drive the Earth’s climate system beyond dangerous threshold points. Nonetheless, investment in fast-action and win-win approaches deserves greater investigation and investment due to high mitigative potential, technological readiness, economic feasibility, and large potential ancillary benefits. When
combined with fast-action measures, biologic mitigation options could provide a robust means of reducing anthropogenic forcing on Earth’s climate system.
1.5 References


Bond, T. (2007). Testimony for the hearing on black carbon and climate change. *House Committee on Oversight and Government Reform, Pg, 2*


### 1.6 Tables and figures

<table>
<thead>
<tr>
<th><strong>FAST-ACTION</strong></th>
<th>GWP (100-yr)</th>
<th>MRT (yrs.)</th>
<th>Avoided Warming by 2050 (°C)</th>
<th>Reference</th>
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<td>Methane (CH$_4$)</td>
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<th>Max. Net C Seq. in 2050 (Pg C)</th>
<th>Avoided Warming by 2050 (°C)</th>
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**Table 1:** Estimates of mitigation potential used to calculate fast-action and win-win strategies.
Figure 1: Conceptual warming estimates of (i) business as usual (BAU), (ii) fast action, (iii) CO$_2$ mitigation exclusively, and (iii) fast-action and win-win strategies.
Chapter 2:

Food security, climate change, ecosystem services and public health: A review of “win-win” climate smart agricultural practices

2.0 Abstract

Food security has emerged as one of the most critical challenges of the 21st century with a clear ethical imperative. The world population is projected to increase from 7.1 billion in 2012 to 9.3 billion by 2050 requiring an estimated 50-70% increase in global food production. Concurrently, the impact of climate change, declining per capita energy and water availability, soil degradation and other factors will further jeopardize the global harvest. The world’s poorest populations with the least ability to adapt are likely to be the most adversely impacted. This article reviews a range of “win-win” strategies to increase global food security with a focus on developing countries. Improvements in soil, air, and water quality could increase global food production by >85 million metric tons annually while preventing ~7.5 million premature deaths annually, and avoiding warming of ~0.63°C by 2050 with a total economic valuation of greater than US $6.0 trillion per year.
2.1 The Food Security Challenge

Humanity in the 21st century faces a set of converging challenges revolving around the nexus of population, food, water, energy, soil, and climate. All these elements impact global food security making it a complex challenge without simple solutions. Food security is defined as the “situation that exists when all people, at all times, have physical, social, and economic access to sufficient, safe, and nutritious food that meets their dietary needs and food preferences for an active and healthy life” (FAO, 1996). This definition requires addressing multiple dimensions of food security and its full lifecycle including production, access, utilization, stability and retention (Pinstrup-Andersen, 2009; Ravi and Swaminathan, 2012).

The objective of this review is to identify several “win-win” strategies which can both increase food production and have important ancillary co-benefits such as: i) mitigating climate change, ii) increasing ecosystem services, and iii) improving public health. This review specifically focuses on strategies which have the most direct benefits for people in developing countries who are most at risk from food insecurity. Many of the strategies examined herein can be readily deployed in developing countries, as they rely upon practical and low-cost appropriate technologies.

2.1.1 Global Food Production, Present and Projected

At present, the world produces ~3.9 billion metric tons of food (FAOSTAT, 2010) for a population of ~7.1 billion people (UN ESA, 2011). The
number of people in the world is projected to reach 9.3 billion by 2050 (UN
SEA, 2011). In order to keep pace with rising demand for calories and protein, it
is estimated that grain production will need to increase at least 50% to 70% by
2050 (Wild, 2003; Bruinsma, 2009; Godray, 2010; Tilman et al., 2011).
Achieving this will require expanding food production by 1.35% to 1.95%
annually for a total annual global food grain production of ~6.2 billion metric
tons by 2050. Practically all of the projected population growth will occur in
developing countries where food insecurity is already the highest. More than
98% of population growth is projected to occur in developing countries
including Africa, South America and Asia (excluding Australia, New Zealand
and Japan), with the population projected to increase from 5.3 billion in 2005 to
7.9 billion by 2050 (Bongaarts, 2009).

Presently, ~850 million people (15% of the global population) live in a
state of hunger (FAO, 2012) with the majority living in India, Africa, East Asia,
and parts of Latin America. A much larger number of people, >3 billion, suffer
from dietary nutrient deficiencies (e.g. vitamin A, protein, zinc, and iron) which
are key risk factors for many of the global burden of diseases (Welch and
Graham, 2004; de Onis et al., 2003; Lal, 2009). Even if the amount of food
currently being produced is sufficient to feed the global population, issues of
distribution, access, stability and nutritional quality remain critical barriers to
nutritious and adequate food reaching all people at all times (Barrett, 2010).
First, food is not necessarily grown where it is most needed, yet most
populations in developing countries still rely on local food production as the
source of year-round food security (Funk and Brown, 2009). Second, systems and infrastructure for storing, preserving, and transporting food are lacking in many developing countries. The amount of food wasted globally is estimated at 30-40% of the global harvest (Fox et al., 2013). Lastly, many of the poorest people cannot acquire sufficient calories simply because they are too poor to purchase food, i.e. they lack “purchasing power” (Funk and Brown, 2009; Godfray et al., 2010). Agriculture and agriculturally-related jobs make up >50% of the workforce in developing countries (UN-DESA, 2007). People in many developing countries often spend >60-70% of their income on food (FAO, 2011). Increasing crop yield in developing countries can therefore addresses two key problems which drive food insecurity: lack of production and access.

Although food grain production has increased over the past several decades, the rate of increase in many areas of the world has slowed, stagnated, or collapsed (Hatner, 2003; Ray et al., 2012). Between 1960 and 2008, 24-39% of croplands have either experienced no significant increase or declining yields in major grain crops, maize (Zea mays), soybeans (Glycine max), rice (Oryza sativa L.) and wheat (Triticum spp.) (Ray et al., 2012). Per capita food grain production in sub-Saharan Africa (SSA), among the most food-insecure regions of the world, is either stagnant or declining (Godfray et al., 2010). The causes are likely to include environmental, climatic, social, economic and political issues that vary by region. Declining per capita energy and water availability, the rising cost of mineral fertilizers, declining soil fertility, growing demand for
biofuels and a warming climate are likely to be strong contributing factors for observed declines.

2.1.2 Rethinking agriculture

Addressing food security will require “radically rethinking agriculture in the 21st century” (Fedoroff et al., 2010). Many experts and development organizations advocate increased access of mineral fertilizers to resource-poor farmers (Quiñones et al., 1997; Denning et al., 2011). While judicious use of mineral fertilizers could substantially increase crop yields in many regions of the world (Sánchez, 2010), there are risks from relying exclusively on this approach. First, the price of fertilizer is often much higher in developing countries due to lack of transportation infrastructure. In Africa, the delivered cost of fertilizer is often 2-6 times that in a developed country (Sánchez and Swaminathan, 2005). Second, large investments in fertilizer can hurt resource-poor farmers in years of low productivity, when they are unable to recoup input costs (Glover et al., 2012). Moreover, the cost of nitrogen (N) and phosphorus (P) fertilizers could substantially increase in coming decades with rising energy costs for producing N fertilizers and peaking of world rock phosphate production (Cordell et al., 2009; Craswell et al., 2010). Third, the over-application of N fertilizers without input of carbon (C)-rich organic amendments can diminish soil quality and decrease soil organic carbon (SOC) levels (Bationo et al., 2007).

Others advocate increasing access to genetically-modified and improved crop varieties to improve food security (Tester and Langridge, 2010). Access to
genetically-modified or improved crop varieties, however, is not the key limiting factor to food production (Sánchez and Swaminathan, 2005). Instead, the decisive limiting factor is low and declining soil fertility and lack of water availability (Sánchez and Swaminathan, 2005). Concurrently, tropospheric ozone and black carbon soot, decrease food production by as much as 2-15% annually and contribute significantly to climate change (Shindell et al., 2012; Wilkinson et al., 2012). An integrated approach to “climate smart” agriculture which focuses not only on increasing agricultural inputs such as fertilizer and genetics, but also on improvements to soil, water, and air quality is needed to ensure that safe and nutritious food is accessible to “all people at all times.”

2.1.3 Constraints to agricultural growth

In order to assess effective means of increasing global food production, the following constrains must be considered: (i) the remaining area of land available for crops and livestock, (ii) water availability for irrigation; (iii) soil quality and the rate of soil degradation; iv) the availability of critical plant nutrients; and v) predicted changes to the global climate system that could impact agricultural productivity.

2.1.3.1 Land

Over the history of agriculture, humans increased food production by expanding the land area under production—this strategy is no longer possible due to rapidly diminishing land availability. Of the ~13 billion hectares of terrestrial surfaces on Earth, humans use 32% to 41% with pastureland
accounting for 19-26% (2,500-3410 Mha), croplands 12% (1,510-1,611 Mha), and human settlements 1% to 3% (66-351 Mha) (Lambin and Meyfroidt, 2011). Globally, the amount of land available for food production not currently in use is 356-445 Mha (Lambin and Meyfroidt, 2011) which represents a mere 9% of the total 4,515 Mha crop and pasture land. The remaining land is either too environmentally sensitive, infertile, degraded, steep, cold or otherwise unsuited for food production.

Land degradation and competition from biofuels and urban development will claim land that could otherwise be used to feed people. In the U.S., the amount of maize that went to biofuel production was only 3% of the total supply in 1993 which increased to 37% by 2010 (Wallington et al., 2012). By 2030, it is projected that biofuels and urban development will claim an additional 92 to 218 Mha. An additional 60 Mha will be too degraded for productive use (Lambin and Meyfriedt, 2011). Without including deforestation, an 85-Mha deficit of productive land is projected by 2050 (Lambin and Meyfriedt, 2011). With only 9% more arable land available, it is clear that simply expanding land under cultivation cannot increase the global harvest by the required 50-70%. Instead it will be necessary to intensify food production on existing land through sustainable intensification and adoption of best management practices or BMPs (Tilman et al., 2011).

2.1.3.2 Water
Globally humans use ~4430 km$^3$ of fresh water each year, 70% of which is used for agriculture (UNWATER, 2011). The 20% of croplands (~277 Mha) which are irrigated produce 40% of the world’s food (FAO, 2012). The remaining 80% of croplands, being rain-fed, require sufficient seasonal precipitation. Global water use for croplands must increase by 70-90% by 2050 to keep pace with projected food demand (Ercin and Hoekstra, 2012). This rate of water withdrawal may be unsustainable, however (Gleick and Palaniappan, 2010).

Groundwater resources are being withdrawn faster than recharged in some critical regions (Wada et al., 2010). Many of the largest grain producers—U.S., China and India—are “mining” water at unsustainable rates (Scanlon et al., 2012; Qui, 2010; Rodell et al., 2009) as is evidenced by rapidly depleting aquifers such as the Ogallala in US, the Indo-Gangetic Plains in India and Pakistan, and the Huang-Huai-Hai (HHH) plains in China (Lal and Stewart, 2012). “Fossil water” aquifers, which are not recharged, could be completely depleted within decades to centuries (Taylor et al., 2012; Scanlon et al., 2012). As much as 15% of India’s irrigation water may come from unsustainably mined groundwater aquifers (particularly in the states of Rajasthan, Punjab, and Haryana) which could severely impact more than 115 million people (Rodell et al., 2009).

Climate change is likely to exacerbate water scarcity by changing precipitation patterns, expanding deserts, increasing evapotranspiration, shrinking mountain glaciers, increasing intrusion of salt water into fresh
groundwater, and increasing frequency and severity of droughts (Parry et al., 2007; Bates et al., 2008; Romm, 2011; Taylor et al., 2012). Projected warming is likely to decrease precipitation in the sub-tropics (15° to 40° latitude) as Hadley cells shift pole-ward causing an expansion of global deserts (Held and Soden, 2006). An 8-10% decrease in dry-season precipitation over large parts of Europe, Australia, and Africa is likely under business-as-usual CO₂ emissions scenarios (Solomon et al., 2009). This decreased precipitation could result in widespread and long-lasting drought conditions over many parts of the world. Large, even continental-scale droughts such as those experienced during the “Dustbowl” in the U.S. southwest in the 1930’s and 40’s and in 2012 throughout the U.S. could become more frequent with increasing global temperatures (Solomon et al., 2009; Dai et al., 2010; Romm, 2011). Food security and water security are tightly coupled; solving either requires addressing both (Rockström et al., 2007).

2.1.3.3 Soil

Maintaining soil quality is critical to ensuring future food security and to the long term sustainability of agriculture. Soil quality is "the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation" (Karlen et al., 1997). Top soil, the nutrient- and C-rich upper most layer of soil where most biological activity takes place, requires centuries to millennia to form (Miller et al., 1998) and yet can be destroyed or eroded away in a matter of years under poor
management. Erosion, nutrient depletion, contamination, salinization, compaction, and desertification of soils are pervasive around the world (Oldeman, 1994; Scherr, 1999; Feddema and Freire, 2001; Stocking, 2003). Such practices which disturb and degrade soils must be mitigated to maintain soil quality.

Agricultural practices that remove greater quantities of C and nutrients than are returned to the soil are fundamentally unsustainable (Lal, 2009b). In industrialized agriculture practiced in developed countries, excessive fertilizer application is common, while developing countries often lack access to fertilizers. As a result, nutrients in soils of many developing countries are currently being “mined” without replenishment. The loss of soil fertility in SSA has been well documented. Over the past 30 years, nutrients have been lost at the rate of 22 kg N, 2.5 kg P, and 15 kg K ha\(^{-1}\) yr\(^{-1}\) in 37 African countries (Sánchez, 2002). Approximately 95 Mha of farmland in Africa has reached degradation levels that would require significant investment simply to replenish to baseline conditions (Henao and Baanante, 2006). The amount of nutrients exported from depleting soils in SSA alone represents billions of dollars’ worth of fertilizers (Henao and Baanante, 2006). Achieving food security requires more than simply intensifying yield; it also requires that soil quality be maintained or improved by replenishing nutrients and increasing SOC levels.

**2.1.3.3.1 Nitrogen**

Nitrogen (N) is often the most limiting plant nutrient in agricultural systems (LeBauer and Treseder, 2008). The success of the Green Revolution
was largely achieved by increasing N availability to crops (Smil, 2004). From 1860 to 2005 the amount of N introduced into the environment has increased from 15 teragrams (Tg = 10^{12} grams or million tonnes) N yr^{-1} to 187 Tg N yr^{-1} (Galloway et al., 2008). By contrast, the amount of N made available by N-fixing crops in 2005 only accounted for ~40 Tg N yr^{-1} (Galloway et al., 2008).

While developed countries including China often use N fertilizers far in excess of what is required (Millar et al., 2010), many food-insecure regions face extreme N deficiencies. Many farmers could substantially reduce N fertilizer use without reducing crop yields (Hvistendahl, 2010; Chen et al., 2011). Unused N is readily lost to the environment by runoff, leaching, or volatilization. This loss of N has detrimental effects on the environment, human health, the ozone layer, and the global climate system. At the global level, excess N introduced into the environment is causing large-scale perturbations to the planet’s geochemical cycles (Rockström et al., 2010) including depletion the stratospheric ozone layer (Hahn and Crutzen, 1982; Ravishankara, 2009), pollution of aquatic ecosystems and drinking water (Camargo and Alonso, 2006; Powlson et al., 2006) and eutrophication of coastal habitat leading to large-scale hypoxic “dead zones” around the world (Diaz, 2001; Donner and Kucharik, 2008).

Only 18 to 49% of applied N fertilizer is actually absorbed by crops (Raun and Johnson, 1999; Cassman et al., 2002; Ladha et al., 2005). Approximately 3% to 5% of applied synthetic N fertilizer is volatilized in the
form of N\textsubscript{2}O (Cassman et al., 2002; Crutzen et al., 2008) which has a global warming potential (GWP) of 298 and 289 over 100 and 20 year periods, respectively (IPCC, 2007). Globally, N\textsubscript{2}O emissions are responsible for \(~6.2\%\) of observed warming (WMO, 2010). The percentage of N\textsubscript{2}O emissions increases almost exponentially with higher rates of N application (Schlesinger, 2009). The vast majority of N fertilizer is manufactured from fossil fuels via the Haber-Bosch process whereby atmospheric N\textsubscript{2} is fixed into biologically available forms including anhydrous ammonia, ammonium nitrate and urea (Smil, 2004). Globally, 1-2\% of world energy supply and 3-5\% of natural gas supply is used to produce N fertilizers (Smil, 2004). Because N fertilizers are derived almost exclusively from fossil fuels, fertilizer cost and access are closely tied to energy prices (Naylor et al., 2007). Volatility in global energy markets can therefore increase the price of fertilizers and, in turn, that of food.

Increasing N use efficiency in developed countries can free up N for use in developing counties in addition to strategies to increase biologically derived N.

2.1.3.3.2 Phosphorus

Addressing the future of world rock phosphate supplies is critical to maintaining global food production, yet the issue of peak phosphorus (P) production have remained largely overlooked (Cordell et al., 2009; Craswell et al., 2010). P, like N, is a critical plant nutrient essential for crop growth. Unlike N, P is mined, not synthesized. Annually, 148 million tons (Tg) yr of rock phosphate is mined, crushed, and transformed into phosphoric acid and elemental P which are used to produce triple superphosphate, ammonium
phosphate and other soluble, plant available forms. A significant proportion of applied P is lost through runoff and leaching into groundwater which can diminish water quality and harm aquatic ecosystems, particularly inland freshwater systems which are generally more P-limited than coastal ecosystems (Conley et al., 2009).

Demand for rock phosphate is expected to increase 50% to 100% by 2050. Yet, the world could be facing “peak” global P production as soon as 2030 and complete depletion within 50-100 years (Sibbesen and Runge-Metzger, 1995; Steen, 1998; Cordell, 2009). Rock phosphate reserves are unequally distributed around the world with the vast majority in China, U.S., and Morocco. With limited future access and unequal distribution, there is potential for geopolitical conflict over access to future rock phosphate reserves (Cordell et al., 2009). Increasing P use efficiency and findings means of recycling and reusing P is critical to ensuring future global food security.

2.1.3.3.3 Soil Organic Carbon

Soil organic carbon (SOC) is a vital indicator of soil quality. The concentration of SOC has been strongly correlated with increases in crop yield (Lal, 2006) and key indicators of soil quality (Mulumba and Lal, 2008). However, as agricultural land use has expanded, SOC levels have fallen. Conversion of forests, prairies and other ecosystems to agriculture decreases SOC by 60-75% (Lal, 2004) mainly as a result of tillage which promotes microbial decomposition and increases the susceptibility of soil to erosion via
wind and water. It has been estimated that, in total, soils have lost 78±12 Pg C since the pre-Industrial era, equivalent to ~20% of anthropogenic CO₂ emissions (Lal, 1999). Depletion of SOC can result in permanent decrease in net primary productivity (NPP) and significant reductions in crop yields. Without human activity, it is estimated that NPP would be ~10% greater, ~65.5 Pg C yr⁻¹ (Haberl et al., 2007). Increasing C cycling and storage in agricultural systems through practices which sequester C in soils and biomass such as reduced tillage, agroforestry and increased soil fertility could potentially restore some of the lost NPP. Restoring SOC has been identified as an important means of increasing global food production while also removing atmospheric CO₂ through photosynthesis and soil C storage (Lal, 2010).

2.1.3.4 Climate change and air quality

Anthropogenic warming of the climate system is unequivocal (Solomon et al., 2007). Mean surface temperature has increased >0.8°C since 1900 (Vose et al., 2012) corresponding to a rapid increase in the concentration of greenhouse gases (GHGs) in the atmosphere, widespread deforestation and soil disturbance. Atmospheric concentrations of CO₂ have increased from ~278 ppmv in the pre-Industrial era to 394 ppmv today (WMO, 2012; Tans, 2013) causing an increase in radiative forcing of ~1.87 W m⁻². In 2010, anthropogenic activities released ~10.6 Pg C yr⁻¹ (equivalent to ~36.7 Pg CO₂ yr⁻¹). Of this, 9.1 Pg C yr⁻¹ are the result of fossil fuels combustion and cement production with the remaining 1.5 Pg C yr⁻¹ are from deforestation, soils and peatlands (Van Der Woolf et al., 2009; Peters et al., 2012).
With the business as usual (BAU) pathway, temperatures could increase 3-6°C by the end of the century (Solomon et al., 2007) causing significant challenges to basic food production. Article II of the United Nations Framework Convention for Climate Change (UNFCCC) calls for the “stabilization of GHG concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference [DAI] with the climate system,” and that this level, “should be achieved within a time-frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development proceed in a sustainable manner” (UNFCCC, 1992).

Food production is both a major contributor to climate change and is severely vulnerable to such changes (Parry and Rosenzweig, 1990). At present, agriculture is responsible for 10-12% of all GHG emissions including 47% of global anthropogenic CH\textsubscript{4} emissions, and 58% of global anthropogenic N\textsubscript{2}O emissions (Smith et al., 2008). Agriculture and livestock is a major driver of deforestation which accounts for 6 to 17% of global CO\textsubscript{2} emissions annually (Baccini et al., 2012). The impacts of climate change are still uncertain, but are likely to have an overall negative impact on global food production (Long et al., 2006; Schmidhuber and Tubiello, 2007; Brown and Funk, 2008; Lobell et al., 2011). Increasing temperature, changing precipitation patterns, increasing frequency and magnitude of extreme weather events including droughts and floods (Rosenzweig et al., 2001), spread of pests and disease (Chakraborty and Newton, 2011), asynchronistic changes in pollinator-host communities
Tylianakis, 2010), shrinking mountain glacier water supply (Beniston, 2003) and other changes are likely to have complex and interactive impacts. There may be limited benefits to crop yields from “CO₂ fertilization” and warming in northern climates. Since 1980, CO₂ fertilization has increased crop yields by ~3.0% for C3 crops (wheat, rice, soybeans) and 0% for C4 crops (e.g. maize, which are not responsive to increases in CO₂ levels) (Lobell et al., 2011). By 2050, CO₂ levels are projected to be >500 ppmv CO₂ which is projected to increase crop yield by 10-13% for C3 crops and 0% for C4 crops (Long et al., 2006).

The impacts of climate change could outweigh benefits, however. Already, anthropogenic climate change has decreased the global yield of maize and wheat by 3.8% and 5.5%, respectively (Lobell et al., 2011). It is projected that without adaptation, crop yields will decline by ~1.5% per decade (Lobell and Gourdji, 2012) or by ~5.6% by 2050. Poor people in developing countries, which are predominantly located in the tropics and subtropics, are likely to be most adversely impacted by climate change due to lack of resources and adaptive capacity (IPCC, 2007). Many of these regions are already at the maximum threshold for crop heat stress—increasing temperatures in these regions are likely to have negative impacts on crop production (Lobell et al., 2008). Recent studies have found that higher growing season temperatures could lead to dramatic non-linear decreases in global food production (Battissi and Naylor, 2009; Schlenker and Roberts, 2009). Increased temperature at night and during critical periods of plant reproduction can have disproportionately
deleterious impacts on crop yields (Teixeira et al., 2011). By 2030, food insecurity in Africa is projected to increase by 43% as a result of climate change and population growth (Funk and Brown, 2009). Crop yields of maize, sorghum (*Sorghum bicolor*), millet (e.g. *Pанicoideae* and *Chloridoideae*), groundnut (*Arachis hypogaea*), and cassava (*Manihot esculenta*) in Africa are projected to decrease by 11%, 17%, 17%, 18%, and 8%, respectively, by 2050 (Schlenker and Lobell, 2010). By 2080 it is estimated that 5 to 170 million more people may face chronic hunger as the result of climate change (Schmidhuber and Tubiello, 2011).

In 2009, members countries of the UNFCCC agreed to limit warming to no more than 2°C which corresponds to ~450 parts per million by volume (ppmv) of CO$_2$ in the atmosphere (Meinshausen et al., 2009). More pessimistic assessments suggest that warming should be limited to <1.5°C corresponding to ~350 ppmv CO$_2$ (Hansen et al., 2008). The target level of 350 ppmv implies that we will not merely have to find means of drastically reducing CO$_2$ emissions, but that CO$_2$ may have to be directly removed from the atmosphere via C sequestration. Regardless of the precise safe level, food security rests categorically on humanity’s ability to effectively mitigate climate change in a timely manner. Without substantial mitigation it is very unlikely that humanity will be able to adapt in time to ensure food security for “all people at all times.”

### 2.2 Win-Win Strategies for Increasing Food Security
“Win-win” strategies refer to actions or policies which have two or more positive effects. Parry and Rosenzweig (1990) suggested the importance win-win approaches to anthropogenic climate change by, for example, increasing the resilience of farming operations which would both increase current food security and would safeguard against future changes due to climate change. Similarly, Lal (2004) described soil C sequestration as a “win-win” strategy for increasing food security while simultaneously providing mitigative and adaptive capacity. Since then the use of the term “win-win” has spread to describe various strategies for dealing with global challenges including agroforestry systems (Syampungani et al., 2010), clean cookstoves (Simon et al., 2012), biochar production (Laird, 2008), water management (Kundzewicz et al., 2008), black carbon emissions reductions (Sato et al., 2003), and ecological sanitation (Gensch, 2008).

The following description is of a subset of win-win strategies that focus on enhancing global food security and that have potentially large ancillary benefits for climate change mitigation, soil restoration and protection of ecosystem services. Strategies examined here include: i) soil C sequestration; ii) agroforestry; iii) ecological sanitation; iv) enhanced fertilizer use efficiency; v) improved water use efficiency; vi) sustainable biochar production; vii) CH$_4$ emissions reductions; and viii) BC emissions reductions. In aggregate, the above strategies are predicted to increase global food production by >85 million metric tons annually while preventing ~7.5 million premature deaths annually,
and avoiding warming of ~0.62°C by 2050 with a total economic valuation of greater than US $6.0 trillion per year by 2030.

2.2.1 Soil Carbon Sequestration

The strategy of increasing the SOC concentration beyond the critical limit, particularly in degraded soils, in order to mitigate climate change and increase food security, has been widely recommended (Lal and Kimble, 1997; Batjes, 1998; Schlesinger, 1999; Bruce et al., 1999; Lal, 2004). Soil C sequestration is one process of “recarbonizing” the global biosphere and pedosphere (Lal et al., 2012) involving anthropogenic strategies to increase the C storage of forests, prairies, savannahs, wetlands, permafrost, and soils under pasture, cropland, and agroforestry systems. The total maximum technical potential, the amount attainable without practical or economic constraints, for C sequestration in these systems is estimated at ~2.6 to 5.0 Pg C yr\(^{-1}\) (Lal, 2009) with a technical potential of 0.4 to 1.2 Pg C yr\(^{-1}\) for agricultural systems. The actual economically attainable is contingent on the future price, if any, on C sequestration (Metz et al., 2007).

Recarbonization of soils used to grow food can increase food security by increasing soil quality, plant nutrient uptake and crop yield especially in poor and degraded soils that are common in many developing countries including SSA. Lal (2006) compiled data from published literature finding that an increase in SOC by 1 megagram (Mg=10^6 g) ha\(^{-1}\) could increase grain production in developing countries by 31.6 (±11.1) million tons yr\(^{-1}\), or 0.8% of total current
global food production. Recarbonization of the biosphere and pedosphere can increase adaptive capacity and resilience of agroecosystems coping with and adapting to climate change. Lastly, recarbonization can enhance ecosystem services such as storm water management, filtration and removal of pollutants, C and N cycling and storage, net primary productivity, above- and below-ground biodiversity and ecosystem resilience (Lal et al., 2012; 2013).

While anthropogenic emissions of CO$_2$ and resulting increases in atmospheric C concentrations (~840 Pg C) is the leading driver of climate change; increasing the SOC concentration in degraded soils to above the critical limit can improve soil quality and crop yield (Doran et al., 1996). Higher SOC levels have been found to impact key indicators of soil quality including porosity, root penetration, aggregate stability, moisture retention, nutrient cycling and retention, microbial density and diversity as well as other key soil characteristics used to quantify soil quality (Mulumba and Lal, 2008). A strong but not universal positive correlation between SOC levels and crop yields has been documented (Qui, 2009; Lal, 2010a;b).

Soils contain roughly three times the amount of C to 1-m depth than is in the atmosphere with an estimated 1550 Pg of SOC and 950 Pg of soil inorganic carbon (SIC) (Batjes, 1993; Lal, 2004). Fluxes from atmosphere-biosphere-pedosphere complex can vary on an annual basis, but remain remarkably well balanced (Schlesinger, 1997). Globally, the biosphere absorbs ~123 Pg C yr$^{-1}$ from the atmosphere as gross primary productivity (GPP). Approximately 60 Pg
C yr\(^{-1}\) of the GPP is lost through plant respiration and decomposition. Thus ~63 Pg C yr\(^{-1}\) remains as NPP (Haberl et al., 2007; Jansson et al., 2010). Anthropogenic CO\(_2\) emissions from fossil fuel burning and deforestation, in comparison, are six times less than the amount of C transferred between the atmosphere, biosphere and pedosphere on an annual basis. Small changes in the rate of biotic and soil C emissions and sequestration can therefore have profound effects on the net atmospheric CO\(_2\) balance, either exacerbating or mitigating climate change (Lal et al., 1995; 2009d).

Increasing global SOC first requires reducing practices which decrease SOC such as drainage of wetlands, excessive tillage, bare fallows, residue removal, residue burning, and slash-and-burn agriculture. Second, BMPs should be identified and implemented. While BMPs are specific to climate, soil type, cropping system, and other environmental and socioeconomic factors, general principles for maintaining and enhancing soil quality can nevertheless be established (Pretty et al., 2003). These include no-till (NT) and conservation agriculture (CA), cover cropping and green manures (particularly N-fixing plants), application of C-rich mulches, windbreaks and alley cropping systems, application of manures, and judicious application of inorganic mineral fertilizers.

If BMPs were adapted on a global scale, \(1\) Mg has been estimated that cropland soils could sequester between 0.4 and 1.2 Pg C yr\(^{-1}\) with a maximum sequestration potential of ~40-60 Pg C, equivalent to ~10 to 15 ppmv CO\(_2\) by 2050 (Lal, 2004). The ultimate amount of C that can be sequestered in soils may
have an upper limit. Eventually soils are likely to reach a “saturation point” wherein any additional C that is added to the system is not transformed into recalcitrant humic compounds, but instead is respired back to the atmosphere (Six et al, 2002; Stewart et al., 2007). A possibly important exception to the saturation limitation is “biochar,” discussed below, which is extremely recalcitrant (Lehmann and Joseph, 2009). Not all soil types or climatic conditions favor C sequestration in soils. Generally, the higher the temperature, the more C will be respired away by microbial decomposition of organic matter. High clay soils can increase the soil C storage in reforested and afforested sites (Laganiere et al., 2010).

Like other C sequestration options, soil C sequestration has limitation and drawbacks. The main limitations are i) the finite capacity of soils to sequester C (Six et al., 2002), ii) gains in SOC can be quickly reversed particularly if poor management practices are reinstated (Rasmussen et al, 1998); iii) addition of C can under particular conditions immobilize plant nutrients such as N thereby increasing need for N fertilizer, iv) changes in emissions of other GHGs particularly N₂O and CH₄ can offset part or all of the potential gains or even lead to a net increase in radiative forcing (Li et al., 2005); and v) soil can be slow to accumulate C (Powlson et al., 2011).

Many of the other win-win strategies examined herein are likely to lead to positive nutrient and C budgets thereby maximizing soil C sequestration and increasing global NPP. Agroforestry and perennial crops, for example, are extremely effective at moving C from the atmosphere into the soil via roots and
root exudates. Enhancement of crop yields via application of mineral fertilizer, composted excreta, and anaerobic digester effluent will increase the amount and quality of plant residues available for humification into recalcitrant C compounds.

2.2.2 Agroforestry and Perennial Cropping Systems

More than two thirds of global cropland is dedicated to the cultivation of annual crop species, mainly maize, wheat, soybeans and rice. Natural terrestrial ecosystems, on the other hand, are dominated by diverse and complex perennial plant communities (Chiras and Reganold, 2004). If natural ecosystems provide a blueprint for the design of human systems (Stockwell et al., 2009), then high-diversity, perennial-based farming systems can be an important strategy for increasing the resilience of global food production systems (Cox et al., 2006; Garrity, 2010; Snapp et al., 2010; Glover et al., 2012).

Agroforestry is defined as “a dynamic, ecologically based, natural resources management system that, through the integration of trees on farms and in the agricultural landscape, diversifies and sustains production for increased social, economic and environmental benefits for land users at all levels” (ICRAF, 2010). Agroforestry and perennial cropping systems can play a significant role in increasing food security and protecting ecosystem services including interception and use of water, flood prevention, prevention, nutrient retention and cycling, C sequestration, protection of biodiversity, and enhanced
precipitation (Postel et al., 1997; Sánchez et al., 1997; Cox, 2006; Garrity et al., 2010; Glover, 2010; Beedy et al., 2012; Glover, 2012).

Agroforestry systems can include a wide variety of tree utilization techniques including food forests, orcharding, alley cropping, riparian buffer strips, silvopasture, and windbreaks (Nair, 2009). They produce diverse outputs, including nutritious fruit and nut crops, fodder for livestock, medicines, edible fungi, saps and resins such as latex, timber and raw materials for craft and construction, biomass for cooking and heating, and other non-timber forest products vital to increasing purchasing power in many developing countries (Shackelton et al., 2011).

Agroforestry and perennial crops can play an important role in enhancing soil fertility (Sánchez and Swaminathan, 2005). In Malawi, for example, the leguminous N-fixing Acacia albida (*Faidherbia albida*) has been found to significantly increase maize yield from 1.3 to 4.1 Mg ha$^{-1}$ yr$^{-1}$ while also providing fuel wood, construction material and medicinal products (Garrity et al., 2010). Trees and perennial crops are more effective than annual crops in protecting soil against erosion, resisting pests, and managing water, nutrients and soil C (Cox et al., 2006).

The diverse, multi-story structure of agroforestry systems and the extensive rooting structure of perennial plants increase C cycling and storage in above- and below- ground C pools. On average, agroforestry systems produce 5 to 10 times the biomass of conventional annual cropping systems (Watson et al.,
increasing net above- and below-ground C storage. The rate of C cycling and storage depends on a variety of determinants including climate, tree species, planting density, soil type, and management strategies (Nair, 1993).

Agroforestry and perennials generally require far fewer inputs including pesticides, herbicides and tractor-passes thereby reducing embedded energy, and subsequent CO$_2$-eq emissions (Cox, 2010). Moreover, agroforestry and perennial cropping systems reduce the need for annual planting and tillage operation thereby reducing CO$_2$ emissions associated with soil disturbance and erosion.

In addition to mitigating climate change, agroforestry systems are useful in adapting human societies to future climate change (Matocha, 2012). Diverse perennialized systems are often more resilient to extreme weather events including droughts, floods, and fire (Kandji, 2006; Verchot et al., 2007). Because of their deeper root systems, trees and other perennials extract nutrients and water from lower layers of the soil making them more resilient to drought situations (Nair, 1993). Perennial and tree crops are not invulnerable to changes in climate, however. Yields from fruit and nut trees, for example, can be substantially reduced if there are wide variations in temperature at important developmental stages such as flowering (Tubiello, 2007) or if biological pollinator species undergo population declines or asynchronistic phenological changes due to climate warming (Tylianakis, 2010).
Challenges to adopting agroforestry and perennial cropping systems include the lag-time in productivity and revenue generation (Palm et al., 2004), higher initial labor requirements (although often followed by reduced labor demand) (Vosti et al., 2001), and resistance or hesitation to adopt new practices by risk-adverse farmers. Perennials (trees and grain crops) have been largely ignored due to the relative ease of breeding annual grain crops (Cox et al., 2006). Perennial grain crops tend to have smaller seed size and are more challenging to breed desirable, productive cultivars (Cox et al., 2006).

The total C sequestration potential of agroforestry and perenniation is poorly constrained in comparison with estimates for reforestation and afforestation which together have been estimated at a rate of 0.16-1.1 Pg C yr\(^{-1}\) through 2100 (Canadell and Raupach, 2008). The 2000 IPCC report (Watson et al., 2000) estimates that by 2040 agroforestry systems could sequester 0.59 Pg C yr\(^{-1}\).

2.2.3 Ecological Sanitation

Closing the nutrient loop between food production, consumption and human waste through “ecological sanitation” is critical to ensuring future food security (Esrey et al., 2001; Cordell, 2009; Cordell, 2011; Schröder et al., 2011; Haq and Cambridge, 2012). Without constant replenishment, the export of nutrients from farmland to urban areas will ultimately deplete soil fertility and, likely, lead to decreased crop yield thereby threatening food security. The reuse of N and P are of particular importance with the possible peaking of rock
phosphate extraction and increasing expense of N fertilizers. Adoption of low-cost appropriate technologies for sanitation could provide a means of increasing food security via improvements in soil quality, fertility, and crop yield. Additionally, pollution and pathogen loading of water bodies would be decreased and there would likely be a substantial decrease in mortalities and morbidity associated with lack of access to proper sanitation and clean drinking water.

Globally, 90% of urban human waste (>2000 million tons) goes untreated causing widespread damage to human health and aquatic ecosystems (UN-HABIT, 2009, Watson and Zakri, 2008). At present, 1.1 billion people lack access to clean drinking water and an additional 2.6 billion people (~1/3 of the world’s population) lack access to basic sanitation (WHO-UNICEF, 2010). An estimated 1.8 million deaths occur each year as a result of lack of clean drinking water and sanitation, 90% (1.6 million) of which are children under the age of five (UNICEF, 2003).

Large-scale, centralized sanitation systems that use water to convey excreta (i.e. “flush-based” sanitation systems) are common in developed countries. The significant amounts of energy, water and financial capital required to construct and maintain large-scale waste water treatment infrastructure are not practical in many developing countries (Esrey et al., 2001; Langergraber, and Muellegger, 2005; Fewtrell et al., 2005). Some regions face constraints such as highly rural populations, mountainous terrain, or near-surface
bedrock that make pipeline infrastructure for conventional sewage conveyance infeasible if not impossible.

An alternative to large-scale centralized systems is “ecological sanitation” whereby human excreta is treated to reduce pathogens and transformed into a valuable soil amendment. Ecological sanitation systems are simple, low-cost, appropriate technologies much more appropriate to developing countries compared with traditional centralized sewage treatment systems and reduce water demand. Only a relatively small proportion of nutrients are absorbed and assimilated into the human body; the vast majority of nutrients consumed are excreted as urine and feces (Jönsson et al., 2004). On average, an individual excretes ~12.5g, 1.5g and 3.5 g of N-P-K, respectively, on a daily basis (Esrey et al, 2001) which could, theoretically, be completely reused as a fertilizer. In actuality, some nutrients, particularly N, are lost during transport and use due to nitrification, mineralization, and leaching (Haq and Cambridge, 2012).

The impact of a global-scale implementation of ecological sanitation on food production, climate change mitigation, and human health have yet to be sufficiently quantified. An estimated 0.8-1.5 million preventable deaths occur each year as a result of lack of sanitation and clean drinking water (UNICEF-WHO, 2008) practically all of which are in developing countries. Many of these mortalities could theoretically be prevented by a global-scale implementation of low-cost composting toilets. The potential increase in global food production is also likely to be large. Not including possible losses via mineralization, etc., the
total technical potential of human excreta to offset 2010 mineral N-P-K fertilizer use (Heffer and Prud’homme, 2012) by 30%, 21%, and 37%, respectively.

2.2.4 Fertilizer Efficiency

Increased fertilizer use efficiency (FUE) is essential to ensuring future food security in a world of declining per capita energy availability and increasing fertilizer costs. Adoption of “precision agriculture,” the application of the right input at the right time and place (Gebbers and Adamchuk, 2010) is an important means of increasing agricultural intensification while reducing degradation to agricultural systems and the surrounding natural environment. Precision fertilization is likely to have significant co-benefits for climate change mitigation through reduced N₂O emissions as well as benefits for air and water quality, and human health.

Precision agriculture can refer to both “high-tech” systems as well as traditional knowledge and practices. Advanced methods have used proximate and remote sensing technologies to monitor water stress, nutrient availability, and other key soil and crop parameters using reflectance spectrograph, global navigation satellite systems (GNSSs), geographic information systems (GISs), microcomputers and other technologies (Gebbers and Adamchuk, 2010). Precise management of nutrients, water and other inputs need not rely upon technology, however. Adoption of traditional practices which make use of precise knowledge of landscapes, soils, and genetic resources is an important, but often
overlooked, means of increasing crop yield and the sustainability of agricultural systems (Perfecto et al., 2009; Raj, 2010).

A wide variety of BMPs can be used to increase FUE including: banding of fertilizer applications, subsurface application, and fertigation (Follet et al., 2005). Banding is a method of applying fertilizer directly to crop rows instead of applying uniformly across the entire field. Subsurface nutrient application refers to the practice of applying fertilizer in the root-proximate zone where N is more likely to be absorbed by the crop instead of volatilization into the atmosphere. Fertigation is a method of irrigating and fertilizing crops simultaneously, typically through high efficiency drip irrigation systems (Hillel and Vlek, 2005). The quantity of fertilizers can be adjusted according to crop nutrient demand. Fertigation lends itself well to vegetable production, but may not be as appropriate for large-scale grain production which accounts for >60% of global food production. Slow release fertilizers (e.g. polyolefin-coated ammonium nitrate) can be used in order to better time the availability of N with crop demand (Alexanders et al., 1997). Staggering fertilizer applications over the growing season by “side dressing” crops is an effective means of improving FUE use efficiency. Nitrification inhibitors such as nitrpyrin (Besler and Schmidt, 1981), dicyandiamide (Merino et al., 2002), encapsulated calcium carbide (Bronson and Mossier, 1991), and nano-enhanced materials can be used to decrease N₂O emissions.
Ultimately, ensuring food security in the long-term may require placing a greater emphasis on biological methods for increasing plant available nutrients. For example, N availability can be enhanced through the planting of N-fixing cover crops, green manures, and agroforestry systems, particularly in those systems with higher diversity and number of crop rotations. While P is often present in sufficient quantity but biologically unavailable for crop uptake at optimal levels in most soils (Khan et al., 2009). Available P can be increased through multiple biological strategies including phosphate solubilizing microorganisms (Khan et al., 2009), inoculation of crop lands with arbuscular mycorrhizal fungi (Plenchette et al., 2005), and planting of cover crops. Pigeon pea (*Cajanus cajan*) fixes N and increases iron-phosphate (Fe-PO$_4$) availability and uptake through exudation of piscidic acid from rooMg hairs (Ae et al., 1990; Vance, 2001).

A pragmatic, integrated approach to soil fertility management combining high-tech and traditional knowledge, synthesized mineral fertilizers and biological methods of increasing soil nutrients is required. Implementation of BMPs could potentially lower N$_2$O emissions by 15-20% (Cole et al., 1997; Mosier et al.; 1998). Although the published literature points to large potential benefits of increased FUE for global food production, human health, and ecosystem services, they have yet to be sufficiently quantified.

### 2.2.5 Water Use Efficiency
Leveraging the ability to efficiently capture, store, and utilize water is essential to ensuring food security. At present irrigation uses ~3,100 km$^3$ yr$^{-1}$. Without improvements to WUE, water demand for agriculture will have to increase an additional 5,160 km$^3$ yr$^{-1}$ to completely alleviate hunger by 2050 (Rockström et al., 2007). Even with optimistic assumptions about the development of irrigation, it is likely that the vast majority of crop production will still rely upon rainwater sources (Rockström et al., 2007). Increased WUE could decrease projected demand by 45% via adoption of BMPs (Rockström et al., 2007).

Many water engineers have started to distinguish between “blue water,” which are tangible liquid reserves in ponds, lakes, aquifers, and dams, and “green water,” which refers mainly to water bound to soil surfaces which is not a “body of water” per se but moisture or vapor flows moving into and out of soils (Falkenmark and Biswas, 1995; Rockström et al., 2007; Liu, 2009). Water projects have focused mainly on blue water resources and the deployment of large-scale downstream systems such as mega dams, extensive ditch irrigation systems, and pumping of water from groundwater aquifers. There are limitations and drawbacks to such an approach, however. First, the cost of large-scale, downstream systems is prohibitive in many regions of the world. Second, the energy is required to move water, a heavy medium with a mass of 1 kg L$^{-1}$, against the force of gravity is substantial. Large-scale downstream systems are in many cases unable to provide irrigation water to upstream croplands unless a large amount of energy is used. Similarly, pumping water from aquifers
consumes a considerable amount of energy globally and subsequently produces significant CO₂ emissions. The U.S., for example, expends 10% of annual energy use to pump water (Pimentel et al., 1997). Third, many of the large-scale blue water irrigation systems are susceptible to high levels of evaporative losses which substantially decrease the efficiency of dams and flood irrigation. Evaporative loss rates are likely to increase with climate warming (Beyene et al., 2010).

There is an increasing shift towards a greater consideration of green water resources held in soil which constitute >80% of the consumptive water used for crop production (Liu et al., 2009). Thus, the emphasis has turned from centralized, large-scale systems, to distributed, small-scale, upstream water catchment, storage and irrigation systems (Rockström 2000, Rockström et al., 2010). The benefits of tapping into green water resources and use of smaller-scale systems is that water can be caught and stored where it is needed—one farms and in soils using much less expensive infrastructure. Rockström et al. (2007) using “optimistic” assumptions, find that up to 725 km³ yr⁻¹ of “blue” irrigation water could be added by 2050 assuming system wide increases in efficiency. By contrast, green water assets will need to be increased to provide 2,125 km³ yr⁻¹ by 2050 in order to ensure food security (Rockström et al., 2007).

Reducing runoff, promoting infiltration and preventing evaporative vapor flows are the lowest costs means of increasing WUE (Rockström, 2000). In addition to sequestering C, agroforestry, reduced tillage, and mulch-based farming systems (discussed above) can also significantly reduce runoff,
evaporation, and leaching. Multi-purpose trees and shrubs, for example, can be planted can provide shade, prevent evaporative losses, and function as biotic pumps to bring water from subsoil to the surface for use by shallow-rooted annual crops (Castro et al., 2008). “Soft technologies” such as “swales” (infiltration ditches built on contour to the landscape), gabions (rock structures used to slow the flow of rivers), various pitting techniques (which encourage water infiltration and accumulation of surface residues) can be used to maximize water infiltration, prevent runoff, and recharge soil moisture and groundwater resources (Ouedraogo and Kaboré, 1996; Martin et al., 1996; Rockström, 2000). If properly constructed and sized, swale systems could potentially reduce surface flow completely thereby significantly reducing losses from runoff and promoting maximum infiltration (Kagabo et al., 2013).

Rainwater catchment and storage in a constructed tank or dam can provide farmers with a vital source of water during dry periods and droughts (Botha et al., 2012). Rainwater can be collected from impervious surfaces such as roofs, pavement, surface runoff (sheet, rill, gully and stream flow) and seasonal streams (Ngugi, 2003; Rockström et al., 2007). Water can be stored in open ponds, reservoirs and dams, aquaculture systems and above- and below-ground storage including plastic, ferro-cement, earthen dams, and sand dams (Lasage et al., 2008). Systems which prevent direct contact between water and the atmosphere can greatly reduce evaporative losses (Lassage et al., 2008). Storage of water at the highest possible elevation allows for the use of gravity to convey water over practically the landscape using minimal energy resources.
Distribution techniques include flooding, ditches or swales, high efficiency and subsurface drip irrigation and fertigation (Hillel and Vlek, 2005; Burney et al., 2009), and deep pipe irrigation (Bainbridge, 2007). Research, development and deployment of low energy desalinization (Elimelech, 2011), and multi-purpose halotrophic crops (Rosema and Flowers, 2008) may become important means of increasing water availability in the future. If implemented over enough area, small-scale distributed water catchment and storage systems could significantly increase plant water availability, global food production, NPP, and C sequestration.

2.2.6 Biochar

Biochar has been proposed as one means of increasing soil quality and crop productivity while simultaneously sequestering C and generating renewable energy (Glasser et al., 2002; Sombroek et al., 2004; Lehmann et al., 2006; Lehmann and Joseph, 2009). Biochar is a relatively stable and porous, C-rich, charcoal-like product that is derived from a biomass-to-energy process called “pyrolysis.” Pyrolysis can be accomplished at a range of scales and technological sophistication including low-cost improved cookstoves and on-farm units which are more appropriate for developing countries through large-scale “biorefineries.”

When incorporated into soils, biochar has been widely observed to increase crop yield, although impacts are contingent on a number of factors including the feedstock material, processing temperature, and the soil’s initial
quality, pH, cation exchange capacity (CEC) and moisture holding capacity (Lehmann, 2006). A limited number of results have documented detrimental impacts possibly due to N immobilization or introduction of toxins (e.g. Baronti et al., 2008; Rajkovitch et al., 2011). Improved nutrient and water retention, decreased soil acidity, and reduced soil strength and bulk density are among the explanations given for observed in (Chan and Xu, 2009). Increased yield is likely to be observed more in highly weathered and/or degraded soils, particularly acid soils in the tropics, and in those with low CEC or SOC contents (Lehmann, 2007).

Many studies demonstrate relatively small increases in crop yield when soils are amended with biochar alone. In general, biochar does not provide significant input of plant nutrients unless it is derived from a nutrient-rich source such as poultry litter (Chan et al., 2008). As such biochar is not a fertilizer per se, but a soil amendment which can potentially increase nutrient availability. When combined with additional sources of fertility (e.g. mineral fertilizer, manure, compost, human urine, etc.) observed impacts have been much larger. Steiner et al. (2007), for example, reported that the yield of sorghum and rice on a highly weathered Ferrasol near Manos, Brazil was only increased modestly with application of biochar alone, whereas the application of biochar plus mineral fertilizer or chicken manure increased yields significantly, more so than the application of mineral fertilizer or chicken manure alone (Steiner et al., 2007).
Energy can be generated during the production of biochar in the form of electricity, bio-oils, and/or heat depending on the pyrolysis process utilized. Slow pyrolysis may have a net energy ratio of 2-8 (Gaunt and Lehmann, 2007), meaning that more energy is generated than is invested in the process of producing biochar. (By comparison, corn ethanol has a net energy ratio of ~1.25 [Hill et al., 2006]). Heat from pyrolysis can be used for cooking, food dehydration and drying, thermal treatment of composted human waste, and/or to warm livestock barns, greenhouses, and other structures. Biochar may have synergies with other win-win strategies examined herein. Products from agroforestry systems including prunings, chipped and waste wood, for example, could provide low cost feedstock materials for biochar production (Blackwell et al., 2009). Biochar can be used as a sorbent in urine diverting ecological sanitation systems (Knowles et al., 2011). Effluent from anaerobic biogas digesters (which also generate energy) can be combined with biochar to create a low-cost, slow release fertilizer that can be made on farms in developing countries (Sekar et al., 2013).

Globally, biochar produced from sustainable sources has a maximum technical potential to sequester 1.0-1.8 Pg C-eq. yr\(^{-1}\) for a cumulative net reduction of 10-25 Pg C-eq by 2050, equivalent to ~5-12 ppmv CO\(_2\) (Woolf, 2010). Biochar application globally could significantly increase global food production, but the extent to which it could increase productivity, to our knowledge, has yet to be accurately assessed.
2.2.7 Targeting Non-CO₂ Forcers

Anthropogenic emissions of non-CO₂ climate forcers (e.g. CH₄, T-O₃ and BC) degrade air quality increasing the global burden of disease, reduce global food production, and contribute significantly to climate change (Hansen et al., 2000; Molina et al., 2009; Shindell et al., 2012; Wilkinson et al., 2012). Improving air quality provides a clear win-win strategy for dealing with food security, climate change, and public health. In total non-CO₂ forcers contribute to ~40% of observed warming and lead to >2.0 million premature mortalities annually (Anenberg et al., 2012; Shindell et al., 2012).

2.2.7.1 Methane Emissions and Ozone Concentration Reductions

Methane (CH₄) is a powerful GHG with 25 to 72 times more GWP than CO₂ over time periods of 100 and 20 years, respectively (IPCC, 2007). IMg has a relatively short mean residence time (MRT) in the atmosphere of 8.4 years (WMO, 2012). Methane is one of the primary precursor to the formation of tropospheric ozone (T-O₃). Tropospheric or “ground-level” ozone (T-O₃) is a potent GHG and a highly destructive oxidizing agent that negatively impacts human health (Bell et al., 2004), crop yield (Wilkinson et al., 2012), and natural ecosystems (Tubiello and Howden, 2007; Wittig et al., 2009). T-O₃ causes a wide variety of harmful effects to crops including damaging leaf tissue, reducing uptake and translocation of plant nutrients, causing early senescence, and oxidation of the critical enzyme RuBIsco (Ribulose-1.5 biphosphate carboxylase/oxygenase) (Wilkinson et al., 2012). T-O₃ can decrease the ability of some plants to withstand drought which may be a vital adaptation for crops in
a changing climate. Significant negative impacts of T-O$_3$ to crops have been reported. Wilkinson et al. (2012) estimate that T-O$_3$ has decreased the yield of maize, wheat and soybeans by 2.2-5.5%, 3.9-15% and 8.5-14%, respectively. Thus, higher T-O$_3$ concentrations reduce global NPP and C cycling and storage in SOC pools (Loya et al., 2003).

Effective measures of reducing CH$_4$ have been identified (Anenberg et al., 20012; Shindell et al., 2012) which include i) degasification of coal mines; ii) recovery and use of CH$_4$ from natural gas and oil production instead of direct venting; iii) reduced leakage from natural gas pipelines; iv) treatment of organic waste through aerobic composting or anaerobic digestion; v) CH$_4$ capture and use with from waste water treatment plants; vi) reduced CH$_4$ emissions from livestock, mainly with aerobic digestion of manure; and vii) aeration of continuously flooded rice paddies. Future sources of CH$_4$ emissions such as fugitive emissions from hydraulic fracturing may also need to be taken into account (Osborn et al., 2011; Howarth et al., 2011). Because CH$_4$ is also a fuel source, capturing and combusting CH$_4$ can often have negative cost (i.e. they are profitable).

Several measures to decrease anthropogenic CH$_4$ emissions, such as aerobic rice and anaerobic biodigestion, have synergies with the goal of increasing food production and food security. Rice production is essential to global food security with ~3 billion people eating rice at least once per day (Branca et al., 2011). More people depend on rice for a source of income and
calories than any other food source in the world. Rice production is also a major source of anthropogenic CH$_4$ emissions, contributing ~12% of global methane emissions. Globally, ~144 Mha are under rice production (Branca et al., 2011), requiring significant quantities of water. Infrequent or intermittent irrigation and improved drainage can allow for better management over water levels, thereby preventing unnecessary flooding and saturation of soils. Transitioning from flood irrigation rice production to “aerobic rice” cultivars can reduce water use and CH$_4$ emissions (Bouman et al., 2002). The practices promoted by the “System of Rice Intensification” (SRI) including early transplanting, wider plant spacing, infrequent irrigation, integrated nutrient and pest management, may be an important means of increasing production while reducing water use and CH$_4$ emissions (Stoop et al., 2002; Uphoff, 2013). CH$_4$ emissions have been found to be substantially decreased if organic residues are first composted (Cole et al., 1997; Madjumdar, 2003) or pyrolyzed to produce biochar (Zhang et al., 2010).

Animal manure from livestock production is another significant source of global CH$_4$ emissions. Manure left untreated or poorly managed can have adverse effects on air and water quality including emissions of CH$_4$ and N$_2$O. Managed properly manure and other organic waste streams could generate energy to replace fossil fuels and nutrient sources to increase soil fertility and food production (Holm-Nielsen et al., 2009). Anaerobic biodigesters or “biogas plants” produce CH$_4$ rich gas streams from decomposition of organic waste materials in an oxygen-free or oxygen-limited environment through microbially-mediated processes. Low-cost digester technologies are likely to be appropriate
in the context of developing countries to produce CH₄ for cooking and heating. Anaerobic digester effluent, the “waste” product from digesters, retains many of the nutrients contained within the feedstock material and can be used as a fertilizer to increase crop productivity.

Reducing CH₄ emissions and atmospheric T-O₃ concentrations could decrease crop loss by 27 million tons of grain annually, avoid 0.28°C of warming by 2050, and prevent 47,000 premature deaths annually (Anenberg et al., 2012; Shindell et al., 2012). The total economic valuation for reducing CH₄ emissions is US $483 billion by 2030 (Anenberg et al., 2012; Shindell et al., 2012).

2.2.7.2 Black Carbon Emission Reduction

Black carbon (BC) is an aerosol “soot” particle that results from incomplete combustion of fossil fuels or biomass. BC emissions decrease crop yields, contribute to climate warming, and negatively impact human health. BC has a large but uncertain impact on Earth’s climate systems with a GWP of 680 to 2200 over 100 and 20 year time periods, respectively (Bond and Sun, 2005). BC has a radiative forcing effect of +1.1 W m⁻², second only to CO₂ and more powerful than CH₄ as an anthropogenic forcing agent (Bond et al., 2013). BC has a disproportionate warming effect on ice and snow compared with other climate forcing agents. Emissions of BC and other aerosols could be responsible for a significant amount of warming in the Arctic (Shindell and Faluvegi, 2009) which is considered to be a critical tipping point in the Earth system that could
act as a positive feedback mechanism to anthropogenic warming (Lenton, 2008; Eisenmen et al., 2009). BC is also a large contributor to melting of the Greenland ice sheet which along with the Hindu-Kush-Himalaya-Tibetan glacier system which provides freshwater to >500 million people (Ramanathan and Carmichael, 2008). BC has an atmospheric MRT of days to weeks (Ramanathan and Xu, 2010.)

Like CH$_4$, BC emissions can be reduced at relatively low costs due to large ancillary benefits, particularly to human health and global crop production. Practical strategies for reducing BC emissions include diesel particle filters on vehicles, clean-burning biomass cook-stoves, liquid natural gas (LPG) or biogas technologies in developing countries as alternatives to traditional biomass burning, improved brick kilns, modern recovery coke ovens, and reduction or elimination of high-emissions transport (Anenberg et al., 2012; Shindell et al., 2012).

Many people in developing countries rely upon traditional biomass for cooking and heating and are, as a result, exposed to extremely high levels of indoor air pollutants including BC soot, carbon monoxide, nitrogen oxides, polycyclic aromatics, and dioxins while cooking and heating (Smith et al., 2011). These products of incomplete combustion have been linked to pulmonary-cardiovascular disease, myocardial infarctions, eye infections, and chronic obstructive pulmonary disease (Peters, 2001; Highwood, 2006; Naether, et al., 2007) resulting in an estimated 1.8 to 2.0 million deaths per year (Ezzati et al., 2011).
2006) more than HIV/AIDS (1.8 million per year), tuberculosis (1.3 million), diabetes (1.3 million), traffic accidents (1.2 million), and malaria (0.7 million) (WHO, 2011). Practically all the mortalities occur in the developing countries—approximately half are children under the age of five (Ballis, 2009). By 2050, the number of deaths per year is expected to rise to 3.6 million (UNEP-WMO, 2011). Wood-based cook-stoves, which contribute to ~18% of anthropogenic BC emissions (Bond et al., 2007), are widespread among households in South Asia and SSA where use is upwards of 80% to 90% of the population (IEA, 2006).

Open biomass burning from agricultural fires, residue combustion, and slash-and-burn agriculture contributes to ~42% of total BC emissions (Bond et al., 2007). Forest and agricultural fires, particularly in eastern Asia, Siberia and northern Europe, are a significant source of BC in the Arctic where if deposited on ice or snow contribute significantly to regional warming (Klonecki et al, 2003; Generoso et al, 2007; Stohl et al, 2006). Similarly, biomass burning in southern and eastern Asia disproportionately impact melting of the Himalayan-Hindu-Kush-Tibetan (HKHT) glacial complex (Ramanathan and Carmichael, 2008).

Alternatives to “slash-and-burn” agriculture and traditional charcoal production are needed (Palm et al., 2005). Globally, ~410 Mha or ~30% of total arable land is presently under slash-and-burn management practiced by ~ 300 to 500 million people, mostly in the tropics (Brady, 1996). With an increasing
population in the tropics and risk of megafires, slash-and-burn is no longer a sustainable management practice. Alternatives to open biomass burning and slash-and-burn agriculture include strategies such as composting, mulching, cover cropping, agroforestry, and biochar production which could (as discussed previously) simultaneously increase global food production and C sequestration.

Jacobson (2002) estimated that a theoretical elimination of all BC and organic matter would reduce total positive radiative forcing by 8-18% within 3-5 years. Ramanathan and Xu (2010) estimated MTFR for BC of 50% by 2050. Reducing from key sources of BC emissions could avoid an estimated 0.19°C of warming by 2050, avoid crop losses of 26 million tons of grain per year, and avoid 2.3 million deaths annually with a total economic value of 5.4 trillion dollars (Anenberg et al., 2012; Shindell et al., 2012).

2.3 Conclusion

Strategies at all levels are necessary to deal with the food-water-energy-soil-population-climate nexus surrounding food security. There exist a range of practical, low-cost strategies to deal with food security including: i) soil C sequestration, agroforestry; ii) ecological sanitation; iii) fertilizer use efficiency; iv) increased water use efficiency; v) biochar production; vi) sustainable protein; vii) CH₄ emissions and T-Ο₃ concentration reductions; and viii) BC emissions reductions. The emphasis of food security experts and organizations on increasing access to synthetic mineral fertilizers needs to shift toward a systems approach. Strategies to improve soil, air, and water quality has an untapped
potential for increasing global food security, mitigating climate change, improving human health, and protecting ecosystem services.
2.4 References


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2.5 Figures and Tables

<table>
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<td>Bongaarts, 2009</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Food</th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Global Food Production (million metric tons)</td>
<td>3900</td>
<td>6240</td>
<td>60%</td>
<td>FAOSTAT, 2013</td>
</tr>
<tr>
<td>Chronic hunger (millions of people)</td>
<td>850</td>
<td>&gt;1000</td>
<td>&gt;18%</td>
<td>Schmidhuber and Tubiello, 2011</td>
</tr>
<tr>
<td>Chronic malnutrition (millions of people)</td>
<td>3000</td>
<td>-</td>
<td>-</td>
<td>Welch and Graham, 2004</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Climate Change</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric carbon (ppmv CO2)</td>
<td>394</td>
<td>&gt;500</td>
<td>27%</td>
<td>IPCC, 2001</td>
</tr>
<tr>
<td>BAU warming scenario (°C warming since 1890-1910)</td>
<td>0.80</td>
<td>2.76</td>
<td>245%</td>
<td>IPCC, 2001</td>
</tr>
<tr>
<td>CO2 fertilization impact (%)</td>
<td>+0-3%</td>
<td>+0-13%</td>
<td>-</td>
<td>Long et al., 2006</td>
</tr>
<tr>
<td>Climate change impact on crop productivity (% ca. 1980)</td>
<td>-2.3%</td>
<td>-7.9%</td>
<td>-</td>
<td>Lobell and Gourdji, 2012</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water and Sanitation</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Global water use (km³)</td>
<td>4430</td>
<td>6910</td>
<td>56%</td>
<td>Ercin and Hoekstra, 2012</td>
</tr>
<tr>
<td>Water demand for agriculture (km³)</td>
<td>3100</td>
<td>5580</td>
<td>80%</td>
<td>Ercin and Hoekstra, 2012</td>
</tr>
<tr>
<td>Lack of access to clean drinking water (millions of people)</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>WHO, 2012</td>
</tr>
<tr>
<td>Lack of access to basic sanitation (millions people)</td>
<td>2600</td>
<td>-</td>
<td>-</td>
<td>WHO, 2012</td>
</tr>
</tbody>
</table>

Table 2. Projected changes from 2005 through 2030 for key demographic, agronomic, environmental and public health indicators.
Figure 2: Global land use in 2005 (data from Lambina and Meyfroidt, 2011)
Figure 3: Schematic of population, food, water, energy, soil, and climate nexus (a) at present and (b) in 2050 under business as usual (BAU) conditions.
Figure 4: Major inputs, outputs, and feedbacks surrounding global food production at present (A) and as projected in 2050 (B).
Figure 5: Schematic of various strategies for increasing global food production.
Figure 6: Impacts and strategies of conventional annual monoculture (A) and integrated sustainable intensification of food production (B) using novel methods.
### Table 3: Projected impacts of select measures on food security, climate change, and public health with economic valuation.

<table>
<thead>
<tr>
<th></th>
<th>Food Security</th>
<th>Climate Change</th>
<th>Public Health</th>
<th>Economic Valuation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(million metric tons)</td>
<td>(°C in 2050)</td>
<td>(thousands of people)</td>
<td>(billions of dollars)</td>
</tr>
<tr>
<td>Soil Carbon Sequestration</td>
<td>32</td>
<td>0.06</td>
<td>-</td>
<td>71</td>
</tr>
<tr>
<td>Agroforestry</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>Ecological Sanitation</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Biochar Production</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Fertilizer Use Efficiency</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>Water Use Efficiency</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Methane Measures</td>
<td>27</td>
<td>0.28</td>
<td>5142</td>
<td>483</td>
</tr>
<tr>
<td>Black Carbon Measures</td>
<td>26</td>
<td>0.19</td>
<td>2339</td>
<td>5371</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>85</strong></td>
<td><strong>0.63</strong></td>
<td><strong>7481</strong></td>
<td><strong>6037</strong></td>
</tr>
<tr>
<td>Country</td>
<td>Crop</td>
<td>Soil/region</td>
<td>Yield increase (Kg ha⁻¹ yr⁻¹ Mg⁻¹ of SOC)</td>
<td>Reference</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td>---------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Nigeria</td>
<td>Maize</td>
<td>Egbeda/Alfisol</td>
<td>254</td>
<td>Lal (1976)</td>
</tr>
<tr>
<td>Nigeria</td>
<td>Cowpea</td>
<td>Egbeda/Alfisol</td>
<td>20</td>
<td>Lal (1976)</td>
</tr>
<tr>
<td>Thailand</td>
<td>Maize</td>
<td>Northeastern</td>
<td>408</td>
<td>Petchawee and Chaitep (1999)</td>
</tr>
<tr>
<td>India</td>
<td>Mustard</td>
<td>Inceptisol/UP</td>
<td>360</td>
<td>Shankar et al. (2002)</td>
</tr>
<tr>
<td>India</td>
<td>Maize</td>
<td>Inceptisol/Haryana</td>
<td>210</td>
<td>Kanchikerimath and Singh (2001)</td>
</tr>
<tr>
<td>India</td>
<td>Wheat</td>
<td>Inceptisol/Haryana</td>
<td>38</td>
<td>Kanchikerimath and Singh (2001)</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>Rubber</td>
<td>Alfisol/Ultisol</td>
<td>66</td>
<td>Samarppuli et al. (1999)</td>
</tr>
</tbody>
</table>

Table 4: Impact of increased SOC on crop yield (from Lal 2006).
<table>
<thead>
<tr>
<th><strong>Conventional Methods</strong></th>
<th><strong>Carbon Farming Methods</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning and residue removal</td>
<td>Residue returned to surface</td>
</tr>
<tr>
<td>Conventional plowing</td>
<td>Conservation tillage, no till and mulching</td>
</tr>
<tr>
<td>Bare or idle fallow</td>
<td>Growing cover crops during off-season</td>
</tr>
<tr>
<td>Continuous monoculture</td>
<td>Crop rotations with high diversity</td>
</tr>
<tr>
<td>Soil fertility mining</td>
<td>Judicious use of off-farm input</td>
</tr>
<tr>
<td>Intensive use of chemical fertilizers</td>
<td>Integrated nutrient management</td>
</tr>
<tr>
<td>Intensive cropping</td>
<td>Integrating trees and livestock with crops</td>
</tr>
<tr>
<td>Monocropping and annual crops</td>
<td>Policultures and perennial crops</td>
</tr>
<tr>
<td>Slash-and-Burn Agriculture</td>
<td>Slash-and-Char agriculture</td>
</tr>
</tbody>
</table>

**Table 5:** List of conventional methods (left) that can lead to net soil C loss and best management practices (right) that can enhance soil C storage (adopted from Lal, 2004).
### Table 6: Nutrient content of human excreta (data derived from Esrey, 2000).

<table>
<thead>
<tr>
<th></th>
<th>Daily Human Excreta(^1) (g person(^{-1}) day(^{-1}))</th>
<th>Global Human Excreta (2010) (million metric tons yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Urine</td>
<td>Feces</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>11.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Organic Carbon (C)</td>
<td>6.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Wet Weight</td>
<td>1200.0</td>
<td>105.0</td>
</tr>
<tr>
<td>Dry Weight</td>
<td>60.0</td>
<td>35.0</td>
</tr>
</tbody>
</table>

### Table 7: Global fertilizer use, and total potential nutrient availability from human excreta and fertilizer offset potential (Esrey, 2000; Heffer and Prud’homme, 2012).

<table>
<thead>
<tr>
<th></th>
<th>Global Fertilizer Use (MM t yr(^{-1}))</th>
<th>Fertilizer Potential from Human Excreta (MM t yr(^{-1}))</th>
<th>Fertilizer Offset Potential (% of global demand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N)</td>
<td>108.2</td>
<td>31.9</td>
<td>30%</td>
</tr>
<tr>
<td>Phosphate (P(_2)O(_5))</td>
<td>41.0</td>
<td>8.7</td>
<td>21%</td>
</tr>
<tr>
<td>Potash (K(_2)O)</td>
<td>27.7</td>
<td>10.2</td>
<td>37%</td>
</tr>
</tbody>
</table>
Chapter 3:

Biochar to address climate change and food security: A review

3.1 Abstract

Anthropogenic interference with Earth’s carbon cycle is likely to necessitate mitigation efforts in order to prevent dangerous climate change. There exist a limited number of strategies for direct atmospheric carbon sequestration having varying degrees of technological readiness, cost effectiveness, and sink capacity. The production and application of “biochar” has been proposed as a means of directly sequestering atmospheric carbon with ancillary benefits of replacing fossil fuel energy, and, when incorporated into the soil, increasing crop productivity. Biochar is a highly porous, relatively stable and carbon-rich byproduct of “pyrolysis,” an energy generation process wherein biomass is thermally decomposed at 300-700°C. When applied to soils, biochar has been observed to increase nutrient retention, reduce soil acidity, improve water retention capacity, reduced bulk density, and increase microbial and fungal activity. Biochar carbon sequestration values have been estimated at 0.14 to 3.5 Pg C yr⁻¹ by 2050 (2 to 42% of present annual anthropogenic C emissions from
fossil fuels) with more recent estimates suggesting a maximum carbon sequestration potential of 1.0-1.8 Pg carbon annually. Despite potential benefits of biochar, there remain significant research questions that need to be addressed such as environmental impacts from appropriation of biomass, introduction of harmful substances into the soil, and increased mineralization of native carbon stocks. The feasibility and necessary scaling of biochar rests critically on whether and how these questions can be answered. This review examines the current literature on the ability and extent to which biochar can be used to mitigate climate change and increase food security.

3.1 Background

Atmospheric carbon dioxide (CO\textsubscript{2}) levels have increased from 278 parts per million by volume (ppmv) in the Pre-Industrial era to around 400 ppmv today as the result of fossil fuel burning, deforestation and industrial activities such as cement production (IPCC, 2007; Tans, 2013). Since 1900 the planeMg has warmed approximately 0.8°C as a result of increased CO2 and other climate forcing agents such as methane (CH\textsubscript{4}), black carbon (BC), and nitrous oxide (N\textsubscript{2}O). There is high probability that if humanity continues with business-as-usual emissions scenarios that planet is likely to surpass 2°C of warming, a level considered to be the safe threshold of warming. Beyond this point, the world could cross one or more “tipping points” which would drive the Earth system
into a state of positive feedback that would amplify warming beyond our
capacity to manage it (Lenton, 2008).

In addition to reducing CO$_2$ emissions from energy generation and industrial
processes, it may be necessary to remove CO$_2$ directly from the atmosphere, a
process referred to as “carbon sequestration.” One means for sequestering
carbon (C) is by increasing the size of the soil C sink. The global soil layer or
“pedosphere” constitutes an extremely large but labile source of carbon (C) with
~ 2500 Pg C at a depth of 3 m globally (Batjes, 1996). This is approximately 3
times greater than the entire atmospheric C pool of 760 Pg. 1550 Pg C is soil
organic matter (SOC) and 950 Pg C is soil inorganic matter (SIC).

Techniques employed to sequester C in soils include use of no-till and
conservation tillage, cover cropping and use of perennial crops, incorporation of
manure and other carbonaceous materials, intensive-grazing pasture
management, sustainable agroforestry practices, and restoration of marginal
farmland to natural conditions. The total global potential for soil C sequestration
using best management strategies has been estimated by Lal (2004) to be 0.6 to
1.2 Pg yr$^{-1}$. Soil C sequestration is widely considered an important strategy for
mitigating climate change and dealing with food security due to the large
potential C sink capacity and the immediacy with which it can be employed to
counteract climate change (Lal, 2004). Further, soil C sequestration has a wide
range of ancillary benefits beyond climate mitigation including increasing
agronomic productivity and food security. The ability to simultaneously remove
carbon from the atmosphere and buffer human populations from likely effects of climate change by has been widely understood as a “win-win,” “no-regrets” strategy (Lal, 2004).

There are, however, potential drawbacks and limitations with some soil C sequestration approaches. First, soil is slow to accumulate C and may be subject to a point of saturation due to finite holding capacity (Six et al., 2001). Second, accumulated C can rapidly lost if poor practices are reinstated (Rasmussen et al, 1998). Third, additional nutrient inputs, particularly nitrogen (N), may be necessary due to nutrient immobilization (Lal, 2009). Fourth, C “leakage” can occur as sequestered C is often offset by other GHG emissions from the production and use of mineral fertilizers or energy used for pumping of irrigation water (Schlesinger, 1999). Fifth, some soil C sequestration practices, particularly no-till and reduced tillage, may, under certain circumstances, lead to increased emissions of nitrous oxide (N$_2$O) which could offset significant amounts of radiative forcing potentially even leading to a net increase in radiative forcing (Li et al., 2008).

Recently, the use of “biochar,” a C-rich charcoal-like material, has been proposed for use as a soil amendmentMg having large C sequestration potential with benefits beyond those of conventional soil C management methods due to its recalcitrant physiochemical stability. (See, for instance, Sombroek et al, 2003; Lehmann et al, 2006; Glaser, 2007; Laird, 2008; and Hansen et al, 2008.) First, soil C can be quickly increased by the application of biochar. Second, the
physiochemical recalcitrance of biochar prevents it being rapidly decomposed even if subjected to tillage. Third, biochar may in some situations increase both nutrient and water holding capacity thereby reducing the need for additional inputs. Fourth, biochar has been found to reduce soil emissions of CH$_4$ and N$_2$O although the data are still extremely limited. Because of these properties, biochar may provide an important and unique role in both mitigating and adapting to climate change.

3.1.2 Biochar carbon sequestration

Biochar is a C-rich, fine-grained, highly-porous, charcoal-like product of a biomass-to-energy process called “pyrolysis.” When incorporated into soils, biochar has been observed to enhance soil quality and plant productivity while effectively sequestering atmospheric C for centennial to millennial time scales. These three benefits—for energy, soils, and climate—appear to offer a large lever for addressing multiple global challenges (Lehmann and Joseph, 2009).

Pyrolysis is the thermal decomposition of C-rich materials under oxygen limited conditions. The remaining uncombusted biochar is highly recalcitrant, poly-aromatic material comprised of 65% to 95% C with the remaining portion being various amounts of mineral ash and volatile matter (VM) (Antal and Gronli, 2003). The C contained within the biochar typically constitutes 10-50% of the originally biomass C depending upon pyrolytic processes. Strictly defining what constitutes biochar within quantifiable constraints is problematic because it is not a single entity, rather it is comprised a wide variety of pyrolytic
“black C” substances which change over a continuum of chemical and physical properties (Hammes et al, 2007). Further, given the wide variety of feedstocks and process conditions, there is high degree of heterogeneity and care must be taken to distinguish various types of biochars.

3.3 Agronomic impacts of biochar

Biochar is a unique soil amendment because it simultaneously alters soil physics, chemistry, and biological processes for an extended period of time with a single application. Observational evidence of historic biochar applications and modern experimental data suggest that, when added to soils, biochar has multiple, interacting positive impacts on soil health and plant productivity. These impacts, however, are not uniform nor are they fully understood.

Lehman and Joseph (2009) have suggested that biochar is fundamentally more effective than other soil amendments due to its high degree of stability in soils and its ability to improve nutrient availability, particularly in highly weathered or degraded soils. The ability to produce biochar locally from a wide variety of regionally available materials has strong economic, energetic and ecological benefits over most other commonly used agrochemical inputs, especially in developing countries where costs are prohibitive for subsistence farmers.

The main agronomic functions of biochar can be characterized into five general categories: i) direct nutrient supply from the biochar; ii) indirect increase in nutrient bio-availability with increased ability of the soil to retain
nutrients; iii) provision of habitat to beneficial soil microbial and fungal populations; and iv) increased water retention; and v) changes in physical properties such as increased aeration and decreased bulk density which allow for greater root penetration. The effects of biochar application are likely to vary significantly among soil types, climates, and agricultural systems.

The oldest and most well known use of biochar in agriculture dates back to the ancient Amazonians 7000 yr BP. Interest in biochar grew out of research on rich, dark soils in the Amazon known as Terra Preta or “Amazonia Dark Earth” (ADE). Many researchers have hypothesized that the these soils were created by Amerindians adding large quantities of biochar and other forms of organic matter 7000 to 500 yr BP (Neves et al, 2001). Whether intentional or simply the result of habitation, the result was a large-scale C sequestration and long-lasting improvement to otherwise poor and highly weathered tropical soils thereby permitting permanent agriculture and human settlement (Sombroek, 1966). As such terra preta soils are considered to be “anthrosol,” anthropogenically formed soils unique from native soils. Biochar has been used by other cultures as well; for instance, Japanese farmers were using a method called “haigoe” whereby human waste was mixed with rice husk biochar and was allowed to age prior to application to crops (Ogawa, 1994). Similarly, use of biochar in greenhouses and on farms to improve plant growth has been well documented for over a hundred years in several Western countries.

3.3.1 Impact on crop yield
Application of biochar has been observed to increase plant productivity and yields, although a small number of studies have also shown decreases. Generally, data indicate increases of 20-240% in plant productivity with greater responsiveness occurring in highly weathered or degraded soils with low SOC and CEC levels (Lehmann, 2007). Many studies demonstrate low-level increases in productivity when amended with biochar alone and highly significant increases when combined with use of additional fertility input (e.g. mineral fertilizer, manure, compost, etc.). Steiner et al (2007), for instance, reported an increase in sorghum (*Sorghum bicolor* L.) and rice (*Oryza sativa* L.) production of 100% with the application of mineral fertilizer (NPK and lime) and wood-derived biochar at a rate of 11 Mg ha\(^{-1}\) with respect to the plot with the mineral fertilizer alone. The increase of the biochar and mineral fertilizer with respect to the unamended control plot, however, had increases of greater than 800% on highly weathered Xanthic Ferrasol soils near Manos, Brazil.

Various explanations for increased productivity have been provided by authors studying biochar. These include improved direct fertilizer effect (“direct” effect), increased fertilizer efficiency (“indirect” effect), increased pH, decreased toxicity (particularly from Al), increased water retention, and reduced soil strength and bulk density (Chan and Xu, 2009). These effects are likely to have complex and concurrent interactions.

**3.3.2 Impact on the soil food web**
The “soil food web” includes diverse communities of micro and macro-organisms including archaea, arthropods, bacteria, fungi, invertebrates, nematodes, and protozoa which provide a wide range of ecosystem services vital for many soil functions. Observations indicate that biochar can significantly enhance the activity, population size and distribution of many microbial communities in soil. Explanations for increased microbial activity include i) provision of habitat and refugia (sites free from predacious “grazers”); ii) direct supply of nutrients particularly Ca and K which tend to be readily available in wood ash; iii) increased moisture retention; iv) increased pH; v) change in surface charge; vi) alteration of aerobic/anaerobic conditions; vii) amplification or reduction in soil signaling processes (Warnock et al, 2007; Theis and Rillig, 2009).

A metaphor used to describe biochar has been that of an “underground reef” owing to the highly porous cellular structure of biochar residues which are thought to provide beneficial habitat to microorganisms (Ogawa, 1994). Biochar surface areas can vary from 5 m² g⁻¹ (Alaya, 2000) to >2000 m² g⁻¹ (Stravropoulos, 2005). Similarly, pore sizes are also highly variable which are likely to influence which microorganisms are able to colonize the biochar. Thies and Rillig (2009) predict that presence of particular microbial communities will depend on type and amount of biochar added and that these communities are likely to change over time as the nutrient availability and cycling takes place. Pioneer colonizers are likely to be those organisms capable of metabolizing
condensed pyrolytic compounds and nutrients contained in mineral-ash complexes, followed by a complex evolution of microbial populations over time.

Evidence of biochar providing habitat for microbial populations stems from successful use of biochar as an inoculum for transporting rhizobia and mycorrhizal fungi in Japan (Takagi, 1990; Ogawa; 1994). Many studies have reported increased presence and root colonization by arbuscular mycorrhizal fungi (AMF) (Ishii and Kadoya, 1994; Matsubara et al, 2002; Yamato et al, 2006; Warnock et al, 2007); however, a few studies have reported negative responses (Gaur and Adholeya, 2000; Warnock et al, 2008). Matsubara et al (2002) suggested that addition of biochar may decrease the incidence of disease in plant colonized with AMF.

Rondon, et al (2007) found greater biological N₂ fixation (BNF) by mutualist rhizobia in common beans (Phaseolus vulgaris L.) when biochar (derived from Eucalyptus deglupta) was added to soil (clay-loam Oxisol, Typic Haplustox). The authors attributed this primarily to availability of boron (B) and molybdenum (Mo), and secondarily to availability of potassium (K), calcium (Ca) and phosphorous (P), higher pH, and aluminum (Al) saturation, but did find mycorrhizal fungi to account for greater net N fixation.

Large research gaps exist in understanding the likely effects of biochar applications on the soil food web in a given edaphic or under a specific agricultural regime. Quantifying the impacts is a vital area of research as
microbial communities—particularly AMS and N-fixing bacteria—are important for plant productivity.

### 3.3.3 Heterogeneity between biochars

Biochar products are highly heterogeneous. The ultimate quality and characteristics of a given biochar is highly dependent on multifarious conditions including feedstock material, particle size, pyrolyization process (e.g. slow pyrolysis vs. fast pyrolysis vs. hydrothermal conversion, etc.), reactor vessel type, highest treatment temperature (HHT), residence time, and pre- and post-processing (Downie et al, 2009).

Contingent on these conditions biochars can range from being highly basic to acidic; nutrient poor to nutrient rich; and hydrophobic to hydrophilic: Lehmann (2007) found biochar pH ranging from 4 to 12; Chan and Xu (2009) reported extremely large biochar nutrient variations for total N (1.8 g kg\(^{-1}\) to 56.4 g kg\(^{-1}\)), total P (2.7 g kg\(^{-1}\) to 480.0 g kg\(^{-1}\)), total K (1.0 g kg\(^{-1}\) to 58.0 g kg\(^{-1}\)) and C content (172 g kg\(^{-1}\) to 905 g kg\(^{-1}\)); Glaser et al (2002) found 18% greater water holding capacity in Terra Preta soils as compared to neighboring soils (Glaser et al, 2002) and Pietikainen et al (2000) found WHC to be high; whereas, McClellan, et al (2007) found strong hydrophobic properties of freshly produced macadamia nut biochar under fast pyrolysis conditions.

Further complicating simple analysis, biochars biophysiochemical properties have been observed to change once incorporated into soils (Cheng et al, 2006; Hockaday, 2006). CEC is a good example of this. CEC of Terra Preta
soils have been observed to be much higher than neighboring Oxisols (Glasser, 2002); however, it is often relatively low among freshly produced biochar (Cheng et al., 2006; Lehmann 2007). Oxidation and hydrolysis of biochar surfaces can create higher CEC levels fairly quickly once incorporated into soils (Liang et al., 2006; Cheng et al., 2008).

Direct nutrient supply is extremely variable depending significantly on the feedstock material utilized. Generally, biochars derived from high nutrient feedstocks such as sewage sludge, cow manure and chicken litter has higher nutrient content than biochars derived from green waste biomass (Chan et al., 2007a). “Charging” biochar with mineral fertilizers, compost, anaerobic digester effluent, human feces and urine, and other sources of fertility is likely to have promising results.

Process conditions are also of primary importance with highest treatment temperature (HTT) and residence time being the most critical. Generally, increased HTMg has been associated with a loss of N content, decreased S availability, increase in total P but a decrease in bioavailability, higher C concentrations, greater hydrophilic characteristics, lower porosity and surface area, higher CEC, and an increased presence of polyaromatic hydrocarbons (PAHs) (Chan and Xu, 2009). Research of the final biochar characteristics and quality from the given feedstocks under various pyrolyzer types and conditions is nascent but essential.
The lack of published material on biochar qualities and the large degree of heterogeneity creates challenges for characterizing and quantifying the likely impacts of biochar application in a given edaphic region or agronomic system. Recognition of differences between biochars has led to discussion about the need to optimize biochar characteristics through feedstock selection and pyrolysis conditions in order to create regionally appropriate “designer” biochars (Busscher, 2008) applied at rates determined by local needs (Glaser et al, 2002). Arid climates, for example, may optimize for biochars with the highest moisture retention field capacity, whereas biochars for highly weathered soils in the tropics may optimize for CEC.

3.3.4 Potential for negative impacts

An important concern is whether biochar could have unintended deleterious effects on soil quality or plant productivity. Several studies have reported negative results in crop yields from biochar applications. Kishimoto and Sugiura (1985) observed a 37% and 71% decrease in soybean yield with biochar applied to soils (volcanic ash loam) at rates of 5 Mg ha\(^{-1}\) and 15 Mg ha\(^{-1}\), respectively. Similarly, Baronti et al (2008) reported decreased ryegrass (Lolium perenne L.) production of 8% and 30% vis-à-vis the control at application rates of 100 Mg ha\(^{-1}\) and 120 Mg ha\(^{-1}\), respectively; despite, observing increases of 20% and 52% at application rates of 20 Mg ha\(^{-1}\) and 60 Mg ha\(^{-1}\), respectively.
Negative results have been hypothesized to result from a number of factors. N immobilization due to high C:N ratios (Gaur and Adholeya, 2000; Lehmann et al, 2003b; Rondon et al, 2007), liming of alkaline-intolerant species (Mikan and Abrams, 1995), and hydrophobic properties associated with some biochars (McClellan et al, 2007) have been provided as explanation.

The formation of PAH during pyrolysis has been well documented (Painter, 2001; Ledesma et al, 2002) although the concentration and availability of PAH with respect to biochars is still uncertain. Garcia and Perez (2008) reported lower presence in bio-oils derived under fast pyrolysis conditions (<10 ppm) and higher in slow pyrolysis conditions (>100 ppm). While PAH may be harmful to most plant and microbial communities, relatively rapid decomposition of these compounds by certain microbial populations has been observed (Ogawa, 1994; Zackrisson et al, 1996) and PAH compounds may be fully consumed within one to two growing seasons under many conditions (Thies and Rillig, 2009).

Additional concerns are whether biochars could introduce toxins such as volatile organic compounds (VOC), dioxins, cresols, xylenols, formaldehyde, and acrolein (Thies and Rillig, 2009; Garcia-Perez, 2008;McClellan, et al, 2007) High concentrations and availability of heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), and zinc (Zn) have been reported from pyrolyzed biosolids and sewage sludge (Brindle and Pritchard, 2004; Hospido et al, 2005).
The above concerns highlight the need for standardized protocols for characterization, classification, and safety insurance of biochar products (Joseph et al, 2009) through the third-party providers such as the American Society for Testing Materials (ASTM) or similar organizations. In many cases, it appears that introduction of harmful compounds can be mitigated or prevented entirely through careful selection of feedstock material, well designed pyrolysis units, and post-production testing. More research into possible negative impacts is warranted.

3.4 Energy generation from pyrolysis

The continued availability, environmental impacts and rising costs of fossil fuels has necessitated a transition to renewable and alternative energy sources. The most significant threats of continued fossil fuel dependence are i) emissions of CO$_2$ leading to dangerous perturbations to the climate system (IPCC, 2007), and ii) the possible near-term peaking of world oil supplies which could lead to social, political and economic difficulty (Hirsch, 2005).

Bioenergy production has been proposed as an alternative source of energy to offset fossil fuels along with development of wind, solar, hydro, and nuclear energy sources. Sims et al (2007) have estimated current global potential biomass supply of 46 EJ yr$^{-1}$, while a review by Berndes et al (2003) found total potential biomass supply by 2050 to range from 100 EJ yr$^{-1}$ to 400 EJ yr$^{-1}$ according to various estimates. By contrast, total global energy production in 2005 was 489 EJ (EIA, 2007). As such, it is unlikely that
bioenergy sources alone will be able to meet future global demand or offset current fossil fuel use, but is capable of providing a non-trivial portion of future demand. One estimate by Moreira (2006), however, found potential biomass energy generation potential of >1,000 EJ yr⁻¹, however, the sustainability of such large-scale biomass harvesting is problematic in terms of environmental sustainability (Lal, 2005).

Several platforms for transferring biomass into energy exist. These include i) direct combustion (e.g. co-firing biomass in coal plants), ii) pyrolysis/gasification, iii) bio-oil production (e.g. palm, algae, jatropha, and soy) and iv) microbial fermentation (e.g. corn, sugar cane, and cellulosic ethanol). Each of these platforms must be critically examined based on a full accounting of lifecycle costs and benefits.

Bioenergy systems have come under intense scrutiny as converting land and food crops to energy production has been heavily criticized. Among the concerns are conversion of “food-to-fuel” leading to increases in grain prices and food insecurity in developing countries; higher rates of deforestation from the conversion of primary forests into monoculture energy plantations; and the removal of crop residues from fields for cellulosic ethanol production which can be highly deleterious since these residues are essential for preserving soil quality through nutrient cycling and erosion control (Wilhelm et al, 2004).

Pyrolysis has three advantages which make it less problematic than other proposed bioenergy systems. First, unlike first generation biofuels such as corn
ethanol pyrolysis has a relatively high net energy ratio (energy returned on energy invested—EROEI) suggesting it is energetically efficient. Second, pyrolysis capable of utilizing a wide variety of feedstock materials including waste streams and perennial bioenergy crops grown on marginal lands thereby diminishing competition with land for food crops or need for monoculture plantations. Third, nutrients and C can be cycled back into the ecosystems through application of biochar.

3.4.1 The pyrolytic process

During pyrolysis, solid carbonaceous materials are heated under oxygen (O₂)-limited conditions to between 300 and 700°C (Brown, 2003). The various components of the organic feedstock material including hemicellulose, cellulose and lignin progressively undergo thermal decomposition breaking down into a stream of synthetic producer gases. The resultant “syngas” is comprised of various amounts of hydrogen (H), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and lesser quantities of ethane, propane, and other compounds. These gases can be directly combusted in order to produce electricity or cleaned and condensed into a liquid fuel such as H (Day et al, 2005). Another product of pyrolysis, bio-oil, can be gasified or refined for energy use.

3.4.2 Feedstock materials

A perceived advantage of pyrolysis is the wide variety of feedstock materials capable of being utilized (Yaman, 2004) including waste materials
(such as sawdust or forest waste materials); agriculture crop residues (such as corn stover, wheat straw, rice hulls, or nut shells); and dedicated “low-input high-diversity” (LIHD) bioenergy crops (such as miscanthus, switchgrass, hybrid poplar, karnal grass, or short-rotation willow coppice) which are capable of sequestering C through deposition of root biomass within the soil layer (Tilman et al, 2006).

Biochar can be produced at many scales including cookstoves, distributed combined heat and power (CHP) units, and large-scale biorefineries. Flexibility in feedstock and scale of operation are seen to provide for a wide degree of technological appropriateness and can be selected and optimized based on regional biomass availability and infrastructural development (Lehmann and Joseph, 2009).

3.4.3 Net energy balance

Gaunt and Lehmann (2008) have performed lifecycle analyses which suggest a net energy ratio for slow pyrolysis of 2-7 when optimized for biochar production and 3-9 when optimized for energy production. Slow pyrolysis is typically used to maximize for syngas or biochar production. Typical conversion rates for biomass-to-biochar using slow pyrolysis systems are 25-50%. Fast pyrolyzers are capable of creating a larger quantity of “bio-oil” which can be used to offset petroleum. This oil is typically of significantly lower energy density (~25-50%) than that of petroleum diesel (Brown, 2009). It usually contains relatively high water content which makes it highly corrosive,
thus bio-oil of significantly lesser quality than petroleum. Typically bio-oil is gasified, refined into higher quality fuel, or turned into chemical feedstock material. Conversion rates for biomass-to-biochar using fast pyrolysis systems are generally between 10-35% (Brown, 2009). Waste heat from biochar production can be utilized for cooking, space heating, industrial processes, or cooling with absorptive refrigeration technologies.

Biochar can be combusted rather than incorporated into soils in order to increase net energy output; however, this would greatly reduce net avoided C emissions (Gaunt and Lehmann, 2008). Other methods of biochar production beyond pyrolysis include gasification, hydrothermal conversion, torrefaction and carbonization. These methods typically have lower biomass-to-biochar conversion rates than pyrolysis.

Quantifying the net energy of the process through a life cycle analysis (LCA) is necessary to determine the energy efficiency of the process. The overall efficiency and economic feasibility are highly constrained by the transport of biomass. For instance, if one fleet of trucks are used for collection of biomass and another for distribution of biochar this would imply that for every one mile in distance from the pyrolysis plant, four miles of transportation costs must be traveled. The above consideration implies that distributed, on-farm, mobile and village-scale approaches to biochar production will have comparative advantages over large-scale biorefineries despite apparent gains by scales-of-economy. A network of distributed combined heat and power (CHP)
pyrolysis units may promising strategy for offsetting coal generation with carbon negative electricity from biomass (Laird, 2008).

**3.5 Climate change mitigation potential**

Biochar has been proposed as a large-scale means of removing atmospheric C by stabilizing photosynthetic biomass in soils. Many believe biochar may be capable of C sequestration on the Pg C yr\(^{-1}\) magnitude thereby constituting a significant “stabilization wedge” as described by Pacala and Socolow (2005). Beyond direct C sequestration, biochar may provide several additional mitigative pathways including:

i) reduced C emissions through replacement of fossil fuel energy with bioenergy;

ii) reduced emissions associated with production fertilizers through greater fertilization efficiency;

iii) decrease in methane (CH\(_4\)) and nitrous oxide (N\(_2\)O) emissions from soils;

iv) reduction emissions of black carbon (BC) particles and atmospheric brown clouds (ABCs) created from incomplete combustion of biomass and fossil fuels;

v) reduced deforestation as a result of providing alternatives to slash-and-burn agricultural practices;

vi) prevention of large-scale forest fires through pyrolization of accumulated fodder biomass in forests systems;

vii) increase of global net primary productivity (NPP).

The total global potential for biochar C sequestration is uncertain with large discrepancies among estimates ranging from 0.16 to 4.8 Pg C-eq yr\(^{-1}\) with
the mostly likely maximum sequestration potential of sustainable biochar production being 1.0 to 1.8 Pg C yr\(^{-1}\) (Woolf et al., 2010). Much of the variability in estimates is due to generalized estimates of emissions and energy balance, economic feasibility, scaling requirements, and availability of biomass. At this point these factors are difficult to quantify and will depend heavily on socioeconomic and political factors as well as international treaties on climate change. Complete lifecycle analysis and emissions balance with realistic estimates of scaling from each particular pyrolysis technology based on economic cost-benefit calculations with necessary sensitivity analysis and constraints of biomass harvesting for major regions is necessary to fully estimate biochar C sequestration and will inherently involve many “best guesses”.

### 3.5.1 Direct carbon sequestration

When incorporated into soils biochar can persist for centennial or millennial time scales, with mean residence times ranging from 1,000 to 10,000 years (Skjemstad et al, 1998; Krull et al, 2003). In contrast, 80-90\% of C added in the form of uncharred biomass can be mineralized in 5-10 years in tropical environments, whereas biochar has been found to persist 1-2 orders of magnitude longer(Lehmann et al, 2006; Cheng et al, 2008). Thus, the mechanism for C sequestration is to transform labile biomass through pyrolysis into highly recalcitrant biochar that can persist for hundreds or thousands of years. Yet, this must accomplished in an energy efficient and environmentally sustainable manner lest potential benefits are offset by increased C emissions and destruction of environmentally sensitive areas.
Lehmann et al (2007a) have argued that biochar constitutes a large and long term repository for C that may have benefits over other soil C sequestration methods. Possible benefits of biochar C sequestration over other forms of soil C sequestration include: i) biochar does not appear to be subject to a C saturation point (Sohi et al, 2009) and the maximum amount of biochar that can be applied to soils before negative effects on plant growth is estimated to be large (>50-150 Mg ha⁻¹) ii) application of labile forms of C to soils generally requires additional nutrients due to nutrient immobilization (particularly of N), however, there is evidence that biochar, in some cases, may not lead to immobilization because of its physiochemical stability (Chan and Xu, 2009); iii) the stability of biochar in soils prevents rapid mineralization (as can occur, for instance, when no-till is converted back to tillage) and iv) biochar allows for greater quantification and verification activities for purposes of C accounting.

Importantly, the advantages of biochar do not suggest that it is mutually exclusive to other soil C management strategies or sustainable agricultural practices. For instance, the use of crop residues in no-till (NT) allow for the creation of a protective top-layer that prevents wind and water erosion—an important function that biochar alone would not be able to achieve. In such a situation the most intelligent approach would be to combine the two strategies, taking only the percent of crop residue that can be harvested without detrimental effects and to use that as the feedstock with which to make biochar that would be incorporated back into the soil. Similar arguments can be made for the use of leguminous cover crops, manuring, and mulching. Thus, biochar, if eventually
adopted as an agricultural and climate mitigation strategy, should work in
synergy with current recommended management practices (RMPs) not in
exclusion of them.

A number of studies have found that a certain portion of freshly made
biochar is labile and therefore subject to decomposition and mineralization
(Shneour, 1966; Brodowski, 2004; Hamer et al, 2004). The total percentage of
biochar susceptible to mineralization, however, appears to be quite low—on the
order of <2% (Baldock and Smernik, 2002; Wardle et al, 2008; Cheng et al,
2008). The stability of biochar in soils is not infinite—mineralization is indeed
inevitable. Yet, the mean residence time of biochar provides a sufficient
sequestration period to be considered as a tool for climate mitigation (Lehmann,
2007).

Impact on net C stabilization in soils is an important area of concern
regarding biochar sequestration efficiency. Wardle et al (2008) reported a high
degree of stability of biochar, but a significant loss of native C stocks when
placing mesh bags containing biochar in boreal forests in northern Sweden. This
finding suggests that biochar applications could lead to a rapid loss of humus
and belowground biomass thereby counteracting biochar C sequestration.
Wardle et al hypothesized that the loss of native C likely resulted from a priming
effect on litter decomposition thereby leading to increased rates of
decomposition and mineralization.
The methodology and conclusions of the experiments have been challenged by Lehmann and Sohi (2008) who argued that the use of mesh bags in the forest leaf litter was not sufficiently realistic to assess application of biochar in agricultural contexts; the gaseous and dissolved C were not distinguished; and the labile portion of biochar was not accounted for. Further, Sohi et al (2006) suggested that biochar amended soils are capable of stabilizing greater amounts of C than soils without biochar as is evidenced by Terra Preta soils in the Amazon. Clearly, more research is needed to determine the extent to which biochar leads to a net accumulation or loss of non-biochar C stocks in the soil and this could likely vary significantly depending on soil type and percentage of TOC.

3.5.2 Soil greenhouse gas emissions

Initial experiments have demonstrated ability of biochar to reduce emissions of GHGs from soil. CH$_4$ and N$_2$O, which have global warming potentials (GWP) ~24 and ~300 times that of CO$_2$ on a molecular basis, respectively, have been found to be lower after application of biochar. However, the data supporting these findings are extremely limited and incongruous. Therefore, impacts of biochar application on soil GHG emissions remains highly uncertain and will likely depend significantly on soil condition, agricultural practices employed and biochar type.

In a greenhouse study, Rondon et al (2005) reported decreases in N$_2$O emissions by 50% in soybeans and 80% in grass (B. humidicola) when biochar
was applied to soils (Typic Haplustox) at rates of 20 g kg\(^{-1}\) and a nearly complete suppression of CH\(_4\) emissions with application of 15 g kg\(^{-1}\) in a grass stand and 30 g kg\(^{-1}\) in a soybean stand. In a field experiment, Rondon et al (2006) reported an increase of methane sinks by 200 mg CH\(_4\) m\(^{-2}\) and emissions reductions of nitrous oxide by 15 mg N2O m\(^{-2}\) when added at rates of 20 Mg ha\(^{-1}\).

In an incubation study, Yanai et al (2007) reported 85% to 90% reduction in N2O emissions when biochar derived from municipal waste was applied to rewetted (73% of water filled pore space) soil (Typic Hapludand) at rates of ~150-180Mg ha\(^{-1}\). However, in the same experiment, Yanai et al found 47%-51% increase in N\(_2\)O emissions when water filled pore space was increased to 83%.

In an incubation study, Sohi (2008) found a 15% decrease in N\(_2\)O emissions when biochar derived from willow was applied to soils (arable with low C-content) at a rate of 10 Mg ha\(^{-1}\). An incubation study by Zwieten et al (2009) found a nearly complete suppression of N\(_2\)O emissions when biochar derived from poultry litter was applied to soil (Ferrosol) at rates of 10 Mg ha\(^{-1}\). However, when biochar derived from green waste was applied to the same soil at the same rate emissions of N2O were found to be increased 100% over the control.

Zwieten et al suggest that multiple biotic and abiotic mechanisms lead to the suppression of CH\(_4\) and N\(_2\)O emissions as a result of biochar applications to
soils. Suppression of denitrifier communities, pH, moisture levels, changes in red-ox reactions and other variables are hypothesized to change rates of CH$_4$ and N$_2$O emissions. A more detailed understanding of the impact of biochar under a variety of conditions and corroborating data that supports the claim that biochar can reduce emissions is needed before this benefit can be included in GHG budgeting. A particularly important area of investigation may be the impacts of biochar application on CH$_4$ emissions from rice paddy productivity.

### 3.5.2 Increased fertilizer efficiency

GHG emissions associated with the production, transport, and use of mineral fertilizers is large. The manufacture of N fertilizers accounts for 1.2% of GHG emissions (Kongshaug, 1998) and 3-5% of global natural gas use (Smil, 2001). The vast majority of N fertilizer is derived from natural gas or other fossil fuels through the Haber-Bosch process whereby triple-bonded atmospheric N$_2$ is fixed into biologically available anhydrous ammonia, ammonium nitrate and urea (Smil, 2001). Wood and Cowie (2004) have reported that emissions from N fertilizer production range from 3 to 10 kg CO$_2$ kg$^{-1}$. Thus, reduction in use of N fertilizer can have strong mitigation benefits.

Biochar has been observed to increase nutrient uptake by directly supplying nutrients and indirectly through increased nutrient retention in soils, thereby decreasing fertilizer inputs while maintain baseline crop production. In a GHG budget calculation, Gaunt and Cowie (2009) examined 10%, 20%, and 30% fertilizer reduction from biochar application which they find to result in
avoided emissions of 0.03 to 0.39 t CO\textsubscript{2}-e ha\textsuperscript{−1} yr\textsuperscript{−1} depending on crop type and fertilizer regime (not including emission reductions of N\textsubscript{2}O which is considered above). Extending this assessment with a mean value N fertilizer reduction value of 0.2 CO\textsubscript{2}-e ha\textsuperscript{−1} yr\textsuperscript{−1} applied on 50% of the 1.54 billion ha of cropland in the world produces a net emissions reduction of ~42 Tg C yr\textsuperscript{−1}, or ~0.5% of global annual emissions. Thus, reduction of N\textsubscript{2}O emissions from soils are likely to be a more important factor than reductions in fertilizer use for GHG budgeting purposes; however, reduced N fertilizer costs is likely to provide a stronger economic incentive for adoption by farmers.

3.5.2 Reduced black carbon aerosol emissions

Black carbon (BC) is a soot particle that results from incomplete combustion of fossil fuel and biomass burning. BC is a short-lived but powerful anthropogenic aerosol that may the second or third leading contributor to climate change (Jacobson, 2000; Sato et al, 2003; Ramanathan, 2007). BC is sometimes referred to as atmospheric brown clouds (ABCs) when forming large smog formations as are common many parts of India and Asia. Unlike GHGs, large uncertainty exists in quantifying the role of BC as a climate forcing agent due to extreme heterogeneity over temporal and spatial scales (IPCC, 2007). Estimates of total climate forcing effect of BC range from: 0.2± 0.15 W m\textsuperscript{−2} (IPCC, 2007), ~0.8 W m\textsuperscript{−2} (Hansen et al, 2005), and 0.9 W m\textsuperscript{−2} (Ramanathan, 2007).

Globally, 35% of BC emissions are the result of fossil fuel burning and 65% from biomass burning, with the majority of biomass burning occurring in
the tropics (Bond et al, 2004; Bond et al, 2007). Forest and agricultural fires, particularly in eastern Asia, Siberia and northern Europe, are a significant source of BC and non-methane volatile organic compounds (NMVOCs) in the arctic (Klonecki et al, 2003; Generoso et al, 2007; Stohl et al, 2006). The total forcing of BC on increasing temperatures in the arctic has been estimated to be 45% or greater during the period from 1976-2007 (Shindell and Faluvegi, 2009) and is contributing to the melting of the Greenland Ice Sheet and the Hindu-Kush-Himalaya-Tibetan glaciers (HKHT) (Kehrwald et al, 2008). At the current melt rate the HKHT glacier complex, which supplies 500 million people or more, is predicted to experience 75% deglaciation by 2050 (Ramanathan, 2008).

Due to the short lifetime of the aerosol and the apparently large but uncertain forcing effect, targeting BC has been proposed as a fast-action strategy for mitigating climate change (Bond, 2005). Because BC also has adverse effects on human health and environmental sustainability, there is strong reason to reduce BC emissions for purposes other than that of climate. Clean and efficient pyrolyization of biomass in biochar cookstoves, improved charcoal production techniques, and distributed farm or community scale pyrolyzers offers a strategy for targeted BC emissions reductions (Joseph, 2009). Auxiliary benefits of this strategy include increasing agricultural productivity in developing countries where soil quality is often poor and benefits to human health and productivity.

3.5.3 Reduced deforestation
Reduced pressure on forest ecosystems is a proposed benefit of pyrolysis. More efficient “biochar cookstoves” may reduce pressure on forests in developing countries given that they are more efficient than traditional methods of biomass burning and that they can utilize a wide variety of feedstock materials such as perennial grasses and therefore do not require the use of hardwood biomass. Pyrolysis may offer important alternatives to slash-and-burn agricultural systems which would also reduce pressure on forest ecosystems in the tropics.

Presently, deforestation accounts for ~0.9-1.5 Pg C yr\(^{-1}\) or 10-15% of total anthropogenic global emissions with the bulk coming from tropical rainforests and peatlands (Brady, 1996). Slash-and-burn (otherwise known as assarting, swidden, or shifting cultivation) is practiced on more than 410 million ha, accounting for the majority of biomass burning in the tropics (Brady, 1996).

Despite obvious climatic and environmental drawbacks, slash-and-burn has multiple important agronomic functions. Beyond simply clearing land for cultivation, slash-and-burn provides a pulse of vital nutrients in otherwise nutrient void soils; creates a liming effect thereby reducing Al toxicity; improves CEC; and destroys pathogens, pests, and weed seeds (Sanchez et al, 1982). However, these effects are short-lived and abandonment of the site usually takes place within 2-7 years due to lack of soil fertility and weed pressure. While sustainable within certain constraints, growing population pressures coupled with increased land clearing for cattle and timber has created a situation under
which slash-and-burn can no longer be considered ecologically tenable (Sanchez et al, 1987) and sustainable alternatives are therefore needed.

“Slash-and-char” has been proposed as an alternative to slash-and-burn systems (Lehmann et al, 2002; Lehmann and Rondon, 2006; Steiner et al, 2007) whereby biomass is converted into biochar instead of being completely reduced to ash through combustion. Biochar can provide similar benefits to tropical soils as can slash-and-burn (such as higher CEC) without negative impacts to the environment and climate. If adapted on a massive scale, this could prevent a large portion of the 1.7 Pg C yr⁻¹ of emissions and a large portion of BC from entering the atmosphere.

Collecting, drying, and preparing biomass requires greater labor than does slash-and-burn, however. Thus, an economic incentive is required to drive inclusion of slash-and-char into existing agricultural practices. Since conversion to slash-and-char has many benefits including reduced deforestation and soil C sequestration that will benefit humanity as a whole in terms of climate change mitigation, it seems a logical and necessary policy priority to compensate slash-and-burn agriculturalists—particularly in tropical countries—in order to incentivize slash-and-char systems.

3.5.4 Prevention of “megafires”

Higher global temperatures, changes in precipitation patterns including increased drought frequency and severity in many areas, increased incidents of pest infestation and human pressures on forest systems will increase the
likelihood of large-scale, potentially catastrophic forest fires. The Western U.S., for example, is likely to experience large increase in fire extent with moderate warming (McKenzie et al, 2004) Similarly, some researchers are predicting a large-scale die-off of the Amazon as result of increased temperatures, drought events, and fire extent (Malhi et al, 2008, Cox et al, 2008).

Large-scale fires can lead to emissions of large amounts of terrestrial C (both from biomass and soil sinks) into the atmosphere and reduction in the capability of Earth’s biosphere to absorb atmospheric C. Together these impacts suggest a positive feedback mechanism that will exacerbate changes to the climate system.

Pyrolyzation of forest biomass fodder as a means of suppressing, reducing, or controlling fires may provide an important opportunity for reducing the risk of catastrophic forest fires while simultaneously reducing emissions from the decomposition of woody biomass. Increased NPP from forests may also lead to the increase of C density of the forest stand. Quantifying fire extent from increased warming is difficult to predict. Therefore, determining the extent to which pyrolyzing fodder in forests could reduce C loading of the atmosphere is difficult. Nonetheless, reducing the occurrence of large-scale catastrophic forest fires—whether natural or anthropogenic—should be considered an important mitigation strategy along with reduced deforestation considering the large forcing that is “already in-the-pipeline.”

3.5.5 Increased net primary productivity
The global potential NPP (NPP₀) is estimated to be 65.51 Pg C yr⁻¹ whereas the actual NPP (NPPₜₐₑₜ) 59.22 Pg C yr⁻¹ due to less biologically-efficient use of land by human agriculture and settlement (Haberl, 2007). As such, some have suggested that a certain portion of this net loss (6.29 Pg C) should, theoretically, be recoverable through more productive use of agriculture land. Gains in biomass productivity from application of biochar could potentially recover a portion of this net biomass loss and therefore increase the capacity of terrestrial systems to cycle C.

Of particular interest is the use of biochar in dryland ecosystems which occupy 47.2% of the world’s land area. The ability to retain both water and nutrients makes biochar appealing for sequestering C in these areas. Lal et al (2003) that of the 20-30 Pg C lost from drylands, approximately 12-20 Pg are recoverable over a 50 year time period. Strategies for deploying biochar technologies in a sustainable manner within dryland ecosystems may be challenging as there is little extra biomass to be harvested, but also promising for large-scale regeneration and soil C sequestration activities.

3.6 Conclusion

This paper the large uncertainties and possible risks of widespread use of biochar. The impacts of different biochars in different soils, under different management practices, over time are not well known. Issues of soil contamination and over-appropriation of biomass material from natural ecosystems and from agricultural fields warrants caution. Clearly more research,
standardized testing protocols, and appropriate international policies are needed to guide the development of biochar. Nevertheless, this paper also suggests that biochar may provide a large opportunity for both mitigating and adapting to changes to the climate system. Given the short period of time with which we may have to act in order to reduce atmospheric C levels, and the strong initial data which suggests biochar is an economical, effective, and large C sequestration technique, uncertainties can be addressed while proceeding with research, development, demonstration and deployment (RDD&D) of biochar technologies and applications. While pyrolysis technology on a pilot scale has been proven, it remains to be seen to what degree it will become operational on global scale and whether viable cost incentives and international agreements will allow for market acceptance in time for it to have substantial impacts on the global GHG budget. Soil C sequestration, in general, and biochar production, in particular, offer a large levers to simultaneously address many of the challenges facing humanity. Biochar should be incorporated with current soil C recommended management practices (RMPs) and into holistic agroecology systems that promote local food security and resilience. Importantly, the ability for direct C sequestration should not provide argument for the perceived ability to continue present levels.

3.7 References


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### 3.8 Tables and Figures

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<td>83% WFPS</td>
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<td>Rondon (2006)</td>
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<td>20</td>
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<td>-200 mg M2</td>
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<td>Smith et al, (2010)</td>
<td>Shano silt loam</td>
<td>na Switchgrass (Panicum virgatum), Walla Walla silt loam</td>
<td>0 50-day incubation</td>
<td>11.2 22.4 500⁰C</td>
<td>Increased short term CO2</td>
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Table 8: GHG emissions from biochar amended soils from previous studies.
Figure 1.1: Estimates of biochar C sequestration rates (Pg C yr⁻¹)

Hansen et al., 2008  0.16  0.2  2.2  2.4  3.15  4.8  8.4  2008 Fossil-C Emissions

Figure 7: Various estimates of carbon sequestration rates (Pg C yr⁻¹) for biochar production compared with total fossil fuel emissions in 2008.
Figure 8: Schematic of biochar carbon sequestration strategy.
Chapter 4:

Impact of biochar on yield and nutrient uptake of maize-soybean rotation on an Alfisol in Central Ohio

4.1 Abstract

The production and application of biochar, a carbon-rich byproduct of pyrolysis, has been proposed as a means of increasing crop yield while sequestering biotic carbon in the pedosphere. Research on highly weathered, degraded and/or acidic soils mainly in the tropics have demonstrated large crop yield increases with the application of biochar. Relatively few studies have examined the impact of biochar in temperate agroecosystems, however. Here we report on a 4-year field experiment (2010-2013) the application of oak-derived biochar from a slow pyrolysis process at ~425°C at three rates (0 Mg ha\(^{-1}\), 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\)) with 100% and 50% of nitrogen fertilizer (146 kg ha\(^{-1}\) N and 72 kg ha\(^{-1}\) N, respectively) on a maize -soybean rotation on an Ohio alfisol soil. No significant differences were detected in 2010 or 2012 when soybeans were grown, although there was a significant increase in the total above-ground
biomass and grain yield from maize in 2011. In the first year, total above-ground biomass of soybeans increased 8.1% and 14.5% with application of 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar, respectively. Maize grain yield decreased by -13.0 and -11.6% for the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in the plots receiving 50% of recommended N fertilizer, but increased by 1.3% and 18.3% for the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in plots receiving 100% N fertilizer. The specific surface area of the soil increased significantly with the application of biochar, while cation exchange capacity and pH did not significantly change. Increased available water content and increased plant uptake and assimilation of K and S are hypothesized to be contributing factors to observed increases in production at the 100% fertilization level. N immobilization is attributed to decreased production in the treatments receiving 50% N fertilizer. The results indicate the importance of addition of adequate levels of N fertilizer with the application of biochar and reject the hypothesis that biochar may increase nitrogen fertilizer use efficiency at 50% of recommended N levels.

4.2 Background

Maize (Zea mays) and soybeans (Glycine max L.) are crops of great significance to global agriculture and, specifically, to agriculture in the United States (U.S.) Midwest. In 2010, maize and soy were planted on 88,192,000 and 77,404,000 acres, respectively, accounting for >40% of the total cultivated land area in the U.S. (NASS, 2011; EPA 2012). In that same year, 275.8 and 271.0 teragrams (Tg; \(10^{12}\) grams or million metric tons) of maize and soy, respectively,
were harvested for a total combined economic value of greater than 105 billion dollars (NASS, 2011). More than 80% of U.S. maize is grown in the in the Midwest “corn-belt” states of Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Wisconsin, and South Dakota (NASS, 2011). Thus, the maize-soybean rotation is one of significant regional economic importance and importance globally as one of the world’s major grain belt regions in which staple crops are grown.

Increasing the yield and sustainability of grain production has emerged as a significant global challenge (Tillman, 2002). Global population levels are expected to increase from approximately 7.2 billion today to 9 to 10 billion by 2050 (UNESA, 2012). Population growth coupled with shifting dietary preferences toward higher levels meat consumption and growing demand for biofuels will require an increase in at least 50-70% by 2050 (FAO, 2009). Concurrent predictions using climate-crop models suggest decreases in U.S. maize and soybean production with rising temperatures and changing precipitation regimes (Schleckner and Roberts, 2009). Models have projected significant decreases in U.S. maize, soybean and cotton crop yields with climate change. Without action to adapt agricultural practices yields could show non-linear declines with rising temperatures that could amount to 30-46% by 2100 under the low warming projections (Schleckner and Roberts, 2009).

Problematically, while agriculture is extremely sensitive to a change climate it is also a key culprit in such changes. At present, agriculture is
responsible ~25% of global anthropogenic CO₂ emissions, ~50% of global anthropogenic CH₄ emissions, and >75% of global anthropogenic N₂O emissions (Watson et al., 2000; Tubeillo et al., 2009). Many opportunities exist to transform agriculture from being “part of the problem” to being “part of the solution” to climate change and other environmental challenges. Biochar, specifically, and soil C sequestration (SCS), more generally, could provide substantial means of mitigating climate change (Lal, 2004; Lehmann, 2006; Woolf et al., 2010). Fundamentally, SCS is the process of transferring atmospheric carbon dioxide (CO₂) through photosynthesizing plants into cellulose and lignin-rich biomass resulting in the accumulation recalcitrant C compounds in the soil ecosystem. C-rich compounds such as humic acid, humins, various aromatic C structures, charcoal and mycorrizally-produced glomalin can have mean residence times of years to centuries, thereby providing a short- to medium-term C sink. In total, SOC in agricultural soils could sequester an estimated 0.4-1.2 Pg C yr⁻¹ (Lal, 2004).

Maintaining and improving soil quality is a critical strategy to ensure global food security (Sanchez, 2005). Soil quality is defined as "the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation" (Karlen et al., 1997). Soil organic carbon (SOC) is a particularly useful indicator of soil quality (Mulumba and Lal, 2008) as crop yield tends to be strongly correlated with increased crop yields (Lal, 2006) and key indicators of soil quality. Increasing
SOC levels has been suggested as a means of increasing global food production while also removing atmospheric CO$_2$ through photosynthesis and soil C storage (Lal, 2010). Biochar provides one means of recarbonizing soils which have lost 78±12 petagrams (Pg; $10^{15}$ g or billion metric tons) C since 1850 (Lal, 2004). Biochar is chemiophysically much more recalcitrant than other forms of plant derived organic C, and therefore is likely to provide different functions from other means of recarbonizing soils.

Biochar production and application to soil ecosystems has been proposed as one mechanism through which SCS could be accomplished (Lehmann, 2007) with the technical potential to sequester 1.0 to 1.8 Pg of C yr$^{-1}$, equivalent to 10-18% of total annual global C emissions (Woolf et al., 2010). The aromatic structure of biochar is highly recalcitrant and can persist for centennial to millennial time scales (Preston and Schmidt, 2006; Hammes et al., 2008; Lehmann et al., 2008), generally, an order of magnitude or greater time period than un-charred precursor biomass feedstock material persists (Lehmann et al., 2006). Production of biochar can result in positive net energy generation used to offset fossil fuel use (Gaunt and Lehmann, 2008). When incorporated into soils, biochar has been observed to enhance soil quality and crop productivity (Sohi, et al., 2009). The climate mitigation, energy generation, and improved crop productivity of the biochar strategy appear to offer a large lever for addressing multiple global challenges (Laird, 2008; Lehmann and Joseph, 2009).
Biochar is produced through the thermal decomposition of C-rich feedstock materials under O$_2$ limited conditions, a process called “pyrolysis.” The remaining uncombusted biochar is highly recalcitrant, poly-aromatic material comprised of 65% to 95% C with the remaining portion being various amounts of mineral ash and volatile matter (Antal and Gronli, 2003). Generally, biochar tends to high levels of surface area, surface charge and porosity which may be associated with increased nutrient and moisture retention (Downie et al., 2009).

The main agronomic functions of biochar can be characterized into five general categories: i) direct nutrient supply from the biochar; ii) indirect increase in nutrient bio-availability with increased ability of the soil to retain nutrients; iii) provision of refugia to beneficial soil microbial communities; iv) increased available water content; and v) changes in physical properties including bulk density, penetration resistance, soil strength, aggregate stability, and water infiltration (Chan and Xu, 2009; Deluca et al., 2009). Application of biochar has been observed to increase plant productivity and yield, although a small number of studies have also shown decreases (Lehmann et al., 2006). Generally, data indicate increases of >20% in plant productivity with application varying from ~2 to 30 Mg ha$^{-1}$ on average among experiments. Greater yield responses have tended to occur on highly weathered or degraded soils with low SOC and CEC levels and on acidic soils in which case biochar could have provided a “liming effect” (Lehmann, 2007). Many studies have demonstrated significantly lower increases in plant productivity when amended with biochar.
alone. Crop yields tend to increase more significantly when biochar is used in combination with other fertilizing amendments, particularly those which contain N (Steiner et al. 2007).

A large number of studies have been conducted on the impact of biochar on maize and/or soybean yield (e.g. Major et al., 2010; Sukartono et al., 2011; Uzoma et al., 2011; Free et al., 2010). Most of these studies, however, have focused on tropical and sub-tropical climates on highly weathered and/or degraded soils. Few long-term field studies have been conducted on agroecosystems in temperate climates (Atkinson, 2010). Novak et al. (2010) quantified soil fertility improvements to a sandy soil in U.S. coastal plain region using a soil column leaching study. Laird et al. (2010) investigated changes in soil quality from a Clarion soil (Mesic Typic Hapludolls) from Boone County, Iowa by packing soil columns which were incubated for 500 days at 25⁰C. Significant differences were observed for moisture retention, pH, total N and C, and Mehlich III extractable P, K, Mg and Ca. Laird et al. concluded that, “The results indicate that biochar amendments have the potential to substantially improve the quality and fertility status of Midwestern agricultural soils.” This study would be the first long-term study we are aware of which actually reports on the impact of biochar in field conditions in the U.S. Midwest.

4.1.1 Nitrogen Use Efficiency

Nitrogen (N) is the principle limit for crop growth in agricultural and natural ecosystems (LeBauer and Treseder, 2008) and one of the most costly
inputs for farmers in the U.S. Midwest. Practically all synthesized N used in the U.S. is derived from natural gas and other fossil fuels via the Haber-Bosch process. Triple-bonded atmospheric N\textsubscript{2} is fixed into biologically available forms including anhydrous ammonia, ammonium nitrate and urea (Smil, 2004). Approximately 1-2\% of world energy supply and 3-5\% of natural gas supply is used to produce N fertilizers (Smil, 2004). Because fossil fuels are produced using fossil fuels, the cost of fertilizers are often strongly tied to global energy prices (Naylor et al., 2007).

Nitrogen fertilizer use efficiency (NFUE) surprisingly low, however, with only 18 to 49\% of applied N fertilizer actually utilized by crops (Raun and Johnson, 1999; Cassman et al., 2002; Ladha et al., 2005). N that is not used by the crops is susceptible to volatilization, leaching and runoff which has significant detrimental effects on the global environment including the contamination of drinking water (Camargo and Alonso, 2006; Powlson et al., 2006) eutrophication of coastal habitat (Diaz, 2001; Donner and Kucharik, 2008) and stratospheric ozone depletion (Hahn and Crutzen, 1982; Ravishankara, 2009). Additionally, 3\% to 5\% of applied synthetic N fertilizer is volatilized in the form of N\textsubscript{2}O (Cassman et al., 2002; Crutzen et al., 2008) which partially contributes to anthropogenic climate change (IPCC, 2007). Applying the proper rate at the proper time with the proper type of N fertilizer is the key to increasing nitrogen use efficiency NFUE (Roberts, 2007). Proven methods for increasing NFUE include root-zone proximate and subsurface N application; use of cover crops that scavenge residual N can be incorporated into crop rotations in order to
reduce leftover N bank at the end of growing seasons (Follet, 2005). The application of biochar has been suggested as one means of increasing NFUE (e.g. Singh et al., 2010).

A concern with any addition of large amounts of C (including biochar) to agricultural soils including biochar is the possibility of causing N immobilization which has documented in a number of studies (Novak et al., 2010; Clough and Condron, 2011). N immobilization is caused when large amounts of labile C are added to soils which increases uptake and assimilation of N by soil microorganisms. The N becomes unavailable, at least temporarily, for plant uptake. IMg has been hypothesized, however, that the physiochemical recalcitrance of biochar likely inhibits the microbial uptake of C thereby reducing the phenomenon of N immobilization (Lehmann, 2006). The labile fraction of biochar is estimated to be relatively low, between 3 and 10% (Lehmann et al., 2006), with the remainder being highly resistant to decompositional processes.

4.1.2 Hypothesis

Our hypothesis is that biochar is likely to increase above ground biomass and plant nutrient uptake by increasing water and nutrient availability. However, we also hypothesize that such benefits may take 3 yr or more to accrue, and that there may even be negative impacts on crop productivity for the first year due to N-immobilization or the presence of potentially harmful compounds contained within the biochar. We also hypothesize that any increase in yield as a result of
biochar application is likely to be significantly less than the results from biochar applications to highly degraded, water limited, nutrient poor, and/or acidic field conditions. We predict that the principle mechanism(s) that lead to observed changes in crop yield could be caused by a wide range of changes physical, chemical and/or biological properties and/or processes including nutrient retention and cation exchange capacity (CEC), changes in nutrient uptake via pH, bulk density and soil strength, available water capacity (AWC), and increased N use efficiency (NFUE). We did not predict the relative importance of these mechanisms from biochar due to the paucity of observational data for biochar experiments in temperate climates and, more importantly, due to the complexity of the soil ecosystem. Through this experiment we hope to provide a greater understanding of the relative importance of plant-biochar mechanisms. A caveat is that the results of this experiment are limited to the study of a single biochar type on a specific soil with a soybeans and maize crop rotation. The results could have differed with use of different biochar type (e.g. different feedstock material or high treatment temperature) or cropping system.

4.2 Materials and Methods

4.2.1 Field Trial

The field experiment is located at Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W, with elevation of 242 meters in the Olentangy River watershed and a soil type is Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the
“Crosby” soil series. Baseline soil bulk density and particle density were determined to be 1.43 g cm\(^{-3}\), 2.47 g cm\(^{-3}\). Long-term (27 yr) average annual precipitation was 1,021 mm yr\(^{-1}\) and mean annual temperature of 11.2 \(^{0}\)C. The climate is strongly season with average May-August temperatures of 22.78\(^{0}\)C and Dec. –2.78\(^{0}\)C Feb. (OARDC, 2012).

On April 17\(^{th}\), 2010, fields were treated with pre-emergent combination herbicide Metribuzin (4-Amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-1 Chlorimuron Ethyl (and Ethyl 2-[[[4-chloro-6-methoxypyrimidin-2-yl]amino]carbonyl]amino] sulfonylethyl)]benzoate) (“Canopy” manufactured by DuPont) and contact herbicide glyphosate (N-(phosphonomethyl)glycine; C\(_3\)H\(_8\)NO\(_5\)P) at 439 mL ha\(^{-1}\). Weeds were kept to minimum throughout the duration of the experiment through selective application of glyphosate using a backpack sprayer at a concentration of 0.384 mL L\(^{-1}\) water.

On May 5\(^{th}\), 2010 biochar was applied by hand to plots in a full-factorial randomized complete block design with 12 replicates. Application rates were 0, 5 and 25 Mg ha\(^{-1}\) on a total of 36 plots each 4 m by 6 m separated by a 2 m buffer. Biochar was produced by “Acticarbon” in Dunnellon, Florida from oak (Quercus) using a “Missouri Kiln” type-pyrolzer at \(~425\)\(^{0}\)C. On May 6\(^{th}\), biochar was incorporated into soil using “Rotovator” tractor to a depth of \(~12-18\) cm. Buffers were not tilled and were kept fallow through said herbicide application. On May 12\(^{th}\), 2010 “round-up ready” soybeans (company: Stine
Seed Company, 22444 Laredo Trail, Adel, IA 50003; brand: 2062-4; variety: 6636454; lot no.: UNOBK903) were seeded at a rate of ~ 67 kg ha⁻¹ (60lbs. a⁻¹). Leaf tissue was collected for nutrient analysis. Tissue and grain were kept frozen until analysis was performed. Two 1m x 1m subplots were randomly selected and harvested in order to determine above ground biomass and grain yield for soybeans. Two 3-m rows were harvested for maize analysis. Moisture content of the grain was determined for each plot and total bean yield was converted into total dry weight.

On April 14, 2011, maize was planted using no-till seed drill (GT 805 No-Till Drill). With glyphosate resistant (a.k.a. “round-up ready”) fungicide treated (“trifloxystrobin” with said trade name Trilex manufactured by Bayer) tested January 15, 2011, 99.6% pure seed, treated with Maxim, Apron, and Actellic) manufactured by The Clever Farms, Croton, Ohio. On May 4th, 2011, fields were sprayed with glyphosate via a backpack sprayer uniformly across the field at a rate of 439 mL ha⁻¹. On April 19th, 2011, plots received urea (CO(NH₂)₂- N fertilizer (46-0-0) at a rate of 156.9 kg ha⁻¹ and 79.5 kg ha⁻¹ for the high and low fertilizer treatments based upon recommendations by The Ohio State University (Vitosh et al., 1995). Seedling emergence and stand development was highly heterogeneous across the field and not correlated with plot treatments, likely due to record rainfalls in Columbus, Ohio for the month of April. As such replanting was deemed necessary. On June 1, 2011 corn was again planted using no-till seed drill with the aforementioned seed type. On June 3rd, 2011 the original maize stand was treated with post-emergent Fusilade II
On June 17\textsuperscript{th} and June 30\textsuperscript{th}, July 15\textsuperscript{th}, 2011 fields were again sprayed with glyphosate via a backpack sprayer uniformly across the field at a rate of \(\sim 440\) mL ha\(^{-1}\). Weeds were kept to minimum throughout the duration of the experiment through selective application of glyphosate using a backpack sprayer at a concentration of 0.384 mL L\(^{-1}\) water.

On April 22\textsuperscript{nd}, plots were treated with pre- and post-emergent herbicide combination containing canopy and glyphosate at said rates. On May 21\textsuperscript{st}, 2012, plots were planted with “round-up ready” soybeans (company: Stine Seed Company, 22444 Laredo Trail, Adel, IA 50003; brand: 2062-4; variety: 6636454) were seeded at a rate of \(\sim 67\) kg ha\(^{-1}\) (60lbs. a\(^{-1}\)). Stand emergence and plant development was again very poor and heterogeneous across the landscape, this time due to extreme drought conditions. Soybeans were not replanted in 2012.

\textit{4.2.2 Biochar Characterization}

Characterizing the biochar utilized is critical as there can be rather extreme differences among biochars produced from different feedstock materials using different production techniques (Lehmann and Joseph, 2009). Various techniques were used to analyze the oak-derived biochar used in this experiment. Bulk density was determined using water displacement (i.e. Archimedes principle) by submerging biochar in graduated cylinder. Apparent density was tested using electronic pycnometer (AccuPyn 1340 Pycnometer, Micrometrics,
Biochar pH was determined by standard soil analysis techniques 1:2.5 soil:water solution and 1 N KCl solution for H$_2$O pH and KCl pH, respectively (Thomas, 1996). Nutrients were extracted directly from samples using Mehlich III method (Mehlich, 1984), and Bray P1 ammonium (NH$_4$) acetate extraction (Kuo, 1996). Total C and N was determined by dry combustion on an elemental analyzer (vario MAX CN, Macro Elemental Analyzer, Hanau, Germany) using a thermal conductivity detector. A complete elemental analysis was done through digestion with HClO$_4$/HNO$_3$ followed by inductively coupled plasma (ICP) spectrometry (Teledyne Leeman Labs Prodigy Dual view ICP). External surface area was determined by the N-adsorption technique by Brunauer, Emmett and Teller (BET) (1938) on a continuous flow surface area analyzer (FlowSorb II 2300, Micromeritics Co.) which provide a single-point total BET surface area (m$^2$ g$^{-1}$). Tensile strength was determined using an aggregate crushing apparatus (Blanco-Canqui et al., 2006). Biochar characterization was determined from 5 analytical replicates except in the case of density (20 replicates), surface area as measured by N-adsorption techniques (>40 replicates) and tensile strength (100 replicates).

### 4.2.3 Soil Analysis

Baseline samples and subsequent samples were taken in all 36 plots in three locations and three depths (0-10, 10-20, 20-30 cm) (n=324). Soil particle density was determined to be 2.47 g cm$^{-3}$ using boiling pycnometer method and 2.49 g cm$^{-3}$ using an electronic pycnometer (Multivolume 1305 Electronic Pycnometer, Micromeritics, Norcross, Georgia, USA). Bulk density was
determined by taking cores (7.62 cm diameter 7.62 cm height copper cores) on triplicate randomly selected location on each plot at 0-10, 10-20 and 20-30 cm depths with a hand-held core sampler (AMS core sampler, American Falls, Idaho). Bulk density was calculated as ratio of oven dried soil (105°C for 72 h) over known volume of core (Grossman and Reinsch, 2002).

Soils were sampled after crop harvest after harvest in 2010, 2011, 2012 and 2013. Samples were gathered using a hand-held soil augur (AMS soil augur, American Falls, Idaho) in between planted rows. Five sampling locations were selected randomly on each plot using a random number generator. Each of the five bulk samples were aggregated into a single composite sample that was then used for physical and chemical analysis. The composited soil was kept on ice insulated container and later transferred to a temperature controlled room at 3.6 °C. Field moist subsamples were taken from bulk samples for gravimetric moisture determination. Available nutrients were determined using Mehlich III (1984). Soil pH was determined by using with H₂O and KCl using a 1:2.5 soil:water solution and 1 N KCl solution, respectively. Cation exchange capacity (CEC) was determined by extraction 1 N ammonium acetate was added to sample at pH 7. Flushing was performed three times with isopropyl alcohol followed by extraction with 2 N KCl. Total C and N was determined by dry combustion on an elemental analyzer (vario MAX CN, Macro Elemental Analyzer, Hanau, Germany).

4.2.4 Plant Tissue Sampling and Analysis
Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 and 2013 from flag leaf of 25 randomly selected plants at tasseling stage. The third year (2012) was a significant drought and no differences were found among treatments. Plant tissue and grain were not analyzed this year (2012 soybean) due to poor, non-uniform stand development from significant drought conditions. Plant tissue was kept in cooler on ice until oven drying at 65°C for 72 h. Soybeans were harvested from two randomly selected 1m by 1m subplots within each plot. Maize was selected from three randomly selected 1 linear 3 m rows. Soybeans were left to dry on the stem at 22°C for ~1 month until dehusking. Dehusking was performed with motorized sheller.

Maize husks were left on the plant at the time of harvest stored at 22.2°C for ~2 months. Shucking was performed manually. A motorized sheller was used to remove maize seed from the cob. Moisture content for both maize and soybeans was determined with grain moisture meter (Dickey-John GAC 2500UGMA) and gravimetrically before and after heating at 65°C for 72 h. On July 22, 2011, 10 randomly selected maize plants were harvested to measure total plant height, leaf length and width, and moist and dry weights. Dried leaf was ground using mortar and pestle. Maize grain and soybeans were ground using a laboratory mill and passed through 2 mm sieve. Total concentrations of elements in plant tissues were analyzed using HClO₄-HNO₃ digestion followed by inductively coupled plasma (ICP) emissions spectrometry (Allen, 1971; AOAC, 1998; Isaac and Johnson, 1985).
4.2.5 Statistical Analysis

Data was analyzed using the JMP® software package (JMP 10.0, 2013.)

Data was analyzed using PROC GLM procedure of least squares to fit general linear models.

4.3 Results

In the first and third year after application of biochar, no significant effects on crop yield were observed (p>0.05). In the third year, however, a significant increase in maize total above-ground biomass and grain yield was observed at the 100% rate of N fertilization. In the same year, at the 50% rate of N fertilizer, however, the observed grain yield of plots amended with biochar significantly decreased. The grain index of did not vary significantly among treatments or levels except in the third year in which there was a significant decrease in the grain index at both 5 Mg ha⁻¹ and 25 Mg ha⁻¹. Mean grain index was 0.38 in the first year of production (soybeans) with no variation among treatments. In 2011 (maize) grain index was 0.37%, 0.30% and 0.28% for control, 5 t biochar ha⁻¹, and 25 t biochar ha⁻¹, respectively for plots receiving 50% of recommended N. In 100% of recommended N, the grain index was 0.40%, 0.37%, and 0.37% for control, 5 Mg ha⁻¹ biochar, 25 Mg ha⁻¹ biochar respectively.

4.3.1 Biochar Analysis

Bulk density and apparent density of the unapplied biochar were found to be 0.44 g cm⁻³ and 0.57 g cm⁻³, respectively (see Table 8). Mean specific surface
area measured via N$_2$ adsorption, of the un-applied biochar was found to be 58 m$^2$ g$^{-1}$ which decreased over a 2 year period to 31 m$^2$ g$^{-1}$. The CEC of the biochar was measured to be 16.1 cmol+ kg$^{-1}$ compared with the native soil CEC of 12.4 cmol+ kg$^{-1}$ for baseline conditions. The applied biochar was found to be composed of potential plant nutrients particularly potassium and sulfur which were >10 times greater than baseline soil extractable rates. Significant differences were found using the perchloric acid extraction method versus the Mehlich III extraction method. The unapplied biochar was found to be comprised of 78.6% C, 0.54% N, and 26.9 μg g$^{-1}$ P, 1202.4 26.9 μg g$^{-1}$ K, 280.5 26.9 μg g$^{-1}$ P Ca, 76.8 26.9 μg g$^{-1}$ Mg, and 531.6 μg g$^{-1}$ S.

4.3.2 Crop yield and nutrient uptake

4.3.2.1 2010 Soybean Yields

In the first year (2010) after application of biochar and with no additional fertilizer added, average yield for total above biomass of soybean was +8.1% and +14.5% at 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$, respectively, compared with the control, however, none of the results were significant at a higher confidence level (p>0.05) (see Table 9). The total biomass yield for the highest rate of biochar was significantly greater at a lower confidence level (p>0.10). Grain yield followed a similar trend with mean increase of 12.8% and 12.5% at 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ but were also insignificant (Table 9). The grain index (the ration of grain to total above ground biomass) did not significantly change. No
trends were found in the nutrient analysis for either plant tissue or grain for soybeans in the first year.

4.3.2.2 2011 Maize

In the second year, the application of urea-N had a significant impact on yield of maize. Total above biomass and grain yield in all plots increased an average of 20 and 45%, respectively, with the application of 100% recommended N fertilizer (Table 9). Both the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) plots had higher productivity and grain yield than control plots. Total above-ground biomass increased by +7% and +14% in the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in the 50%-N plots, respectively, and by +8.2% and +28.3% in the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in the 100%-N plots. While total biomass was higher in the 50%-N plots, grain yield followed an opposite trend. On average, grain yield decreased by -13.0% and -11.6% in the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in the 50%-N plots. In the 100%-N fertilizer plots, grain yield increased by +1.5% and +18%, respectively, compared with control. Grain index decreased in biochar containing plots with both 50% N and 100% N. Grain index decreased by -18.9% and -22.0% in the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with control in the 50%-N plots. In the 100%-N fertilizer plots, grain yield decreased by -6.4% and -7.8%, respectively, compared with control.
The maize tissue analysis revealed significant differences in N, Ca and K uptake. N uptake decreased significantly (p<0.05) in plots receiving 50% of recommended fertilizer with the application of biochar (See Figures 13-17). Leaf tissue N was found to be 2.54, 2.37 and 2.03 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 50% N fertilizer. Among the plots receiving 100% N fertilizer, no significant differences in N fertilizer uptake was observed. Leaf tissue N was 2.85, 2.88 and 2.76 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 100% N fertilizer.

The concentration of Ca significantly decreased in plots receiving 25 Mg ha⁻¹ biochar. Leaf tissue Ca was found to be 5877.8, 5788.7 and 5008.2 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 50% N fertilizer. Leaf tissue Ca was found to be 6219.7, 6296.8 and 5886.6 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 100% N fertilizer. The concentration of K significantly increased in plots receiving biochar. Leaf tissue K was found to be 13,048.4, 12,956.0 and 14,592.6 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 50% N fertilizer. Leaf tissue K was found to be 11,679.7, 12,499.6 and 13,275.3 μg g⁻¹ in the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ biochar application within plots receiving 100% N fertilizer.

4.3.2.3 2012 Soybeans
In the third year, there was a major deficit of rainfall which resulted in a significant decrease in both total biomass and grain yield of the soybean crop that year. No significant differences were found among treatments. Soybean above-ground biomass were 3.37 Mg ha\(^{-1}\), 2.77 Mg ha\(^{-1}\), and 3.90 Mg ha\(^{-1}\) for the control, 5 Mg ha\(^{-1}\), and 25 Mg ha\(^{-1}\) plots, respectively, in the 50% N fertilizer plots and 4.24 Mg ha\(^{-1}\), 3.76 Mg ha\(^{-1}\) and 4.40 Mg ha\(^{-1}\), respectively in the 100% N fertilizer plots (see Table 9). Soybean grain yields were 1.36 Mg ha\(^{-1}\), 0.96 Mg ha\(^{-1}\), and 1.39 Mg ha\(^{-1}\) for the control, 5 Mg ha\(^{-1}\), and 25 Mg ha\(^{-1}\) plots, respectively, in the 50% N fertilizer plots and 1.55 Mg ha\(^{-1}\), 1.33 Mg ha\(^{-1}\) and 1.68 Mg ha\(^{-1}\), respectively in the 100% N fertilizer plots. Soybean grain index was 40%, 35%, and 36% for the control, 5 Mg ha\(^{-1}\), and 25 Mg ha\(^{-1}\) plots, respectively, in the 50% N fertilizer plots and 37%, 35% and 38%, respectively in the 100% N fertilizer plots. Leaf tissue nutrient data was not taken in this year due to highly heterogeneous senescence.

4.3.4 Soil Chemistry

No statistically significant (\(p<0.05\)) differences were found in N, P, K, Ca, or Mg in control versus plots receiving biochar in baseline samples (i.e. prior to receiving biochar). Over the duration of the experiment, biochar application resulted in significantly higher quantities of extractable K. The availability of other soil nutrients did not significantly increase or decrease (Table 10). The amount of extractable K was altered by -1% (NSD) and +13% (\(p<0.05\)) with the addition of 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with the control in the 50% recommended N plots. In the 100% recommended N plots, extractable
K was increased by 24% and 41% with the addition of 5 Mg ha\textsuperscript{-1} and 25 Mg ha\textsuperscript{-1}, compared with the control.

Biochar, which had a measured pH of 9.44, did not significantly affect soil pH which had a baseline pH of 7.30 (see Table 8). Soil pH, measured one and three years, after application of biochar were found to have a mean pH of 7.46, 7.57, and 7.58 for the 0 Mg ha\textsuperscript{-1}, 5 Mg ha\textsuperscript{-1}, and 25 Mg ha\textsuperscript{-1} biochar amended plots, respectively, at the 50% recommended fertilizer level. Plots at the 100% fertilized level were found to have a pH of 7.48, 7.52, and 7.51 for the 0 Mg ha\textsuperscript{-1}, 5 Mg ha\textsuperscript{-1}, and 25 Mg ha\textsuperscript{-1} biochar amended plots, respectively (see Table 10). CEC did not significantly change although there was a trend toward lower CEC with biochar application. One year after biochar application, CEC was 13.42, 13.06, and 12.93 cmol kg\textsuperscript{-1} the control, 5 Mg ha\textsuperscript{-1} and 25 Mg ha\textsuperscript{-1} biochar plots, respectively, receiving 50% recommended N. In plots receiving 100% N, the CEC was 13.29, 13.17, and 13.11 cmol kg\textsuperscript{-1}, respectively. SSA increased with the application of biochar. Post-biochar application SSA was measured to be 5.9, 6.6, and 7.9 m\textsuperscript{2} g\textsuperscript{-1} for the control, 5 Mg ha\textsuperscript{-1}, and 25 Mg ha\textsuperscript{-1} biochar plots, respectively.

4.4 Discussion

The application of biochar has been found to increase crop yields in a number of studies (reviewed by, for example, Lehmann et al., 2006; Sohi et al., 2010) and specifically in both soybean (Major et al. 2010) and maize (Major et al. 2010). A very limited number of experiments have operated in temperate
agroecosystems, however, particularly with long term field trials. Laird et al (2010) conducted a column study in which biochar was packed with swine manure. Biochar was found to significantly decrease bulk density, while increasing AWC, CEC, specific surface area, total N and C, and extractable P, K, Mg, and Ca (no effect on S, Cu, or Zn).

Understanding the potential impact of biochar on a convention, no-till maize-soybean cropping system was deemed a potentially valuable contribution to the scientific literature. Here we choose to specifically examine NFUE relative to two rates of biochar application. The environmental and human health impacts of inorganic N use are thought to be high, and increasing NFUE could potentially lower input cost for farmers. Oak-derived biochar pyrolyzed at relatively low temperatures was selected for the study based on previous research which found hardwood biochar created under slow pyrolysis to have general properties which make it well suited to our needs including high porosity and recalcitrance. We replicated on-farm conditions to the furthest extent possible using farm machinery both for tillage and sowing.

Total grain yield for soybeans in 2010 increased by 13% in both the 0 and 25 Mg ha⁻¹ amended plots, respectively. Maize grain yield decreased by -13 and -12% for the 5 Mg ha⁻¹ and 25 Mg ha⁻¹, respectively, compared with control in the plots receiving 50% of recommended N fertilizer, but increased by 1% and 18% for the 5 Mg ha⁻¹ and 25 Mg ha⁻¹, respectively, compared with control in plots receiving 100% N fertilizer. Our finding rejected the null hypothesis that
biochar would not impact crop growth. Biochar positively impacted crop growth of maize at the 100% recommended N fertilizer levels, but led to significant decrease (p>0.05) in grain production at the 50% recommended N fertilizer levels. Thus, the results rejected our hypothesis that biochar would increase NFUE. Instead a negative impact at lower N fertilization levels was found among grain yield data with 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar application for maize in 2011. Thus, despite an upward trend in total above ground biomass, there was a decrease in grain production in the 50% recommended N maize, but in the 100% recommended N maize significantly increased total above ground biomass and led to an observable but not significant increase in grain yield. In the same 2011 maize crop, the 100% N plots increased trends in both aboveground biomass and grain yield were observed. Collectively, the above data suggest that biochar, while having an overall positive impact to maize growth at the 100% of recommended N fertilizer application, is also significantly correlated in this experiment with decreased grain yields at 50% of recommended N fertilizer rates. Thus, biochar did not increase NFUE in the 5 Mg ha$^{-1}$ plots but instead may have inhibited N uptake. One explanation is that the biochar caused N immobilization among plants thereby reducing N uptake as was reflected in the plant tissue N measured at tasseling stage in the leaf tissue.

Soil N dynamics may have also altered by changes to the soil moisture conditions (discussed below). The presence of biochar may be able to alter the redox-environment and oxygen diffusion coefficients (Clough and Condron, 2010). Such changes could change either enhance either nitrification (aerobic)
or denitrification (anaerobic conditions) in multiple scales including in the pore spaces within the biochar architecture. Biochar could also change the presence of microbial communities including Nitrosomonas, Nitrobacter, and other genera responsible for transforming organic N into nitrite ($\text{NO}_2$) and nitrate ($\text{NO}_3$) and *Pseudomonas* and other denitrifying bacteria which reduce nitrate ($\text{NO}_3$)-N to gaseous $\text{N}_2$-N. Depending on how biochar alters the soil ecosystem the form of N compounds, there may be subsequent changes in the availability to the maize crop.

The unapplied biochar was found to contain quantities of plant nutrients including 0.54% N, and 26.9, 1202.4, 280.5, 76.8, 531.6 $\mu$g g$^{-1}$ P, K, Ca, Mg, and S, respectively. The actual availability of these plant nutrients is difficult to ascertain from laboratory extractions, however, as biochar is physiochemically extremely recalcitrant due to the high degree of aromacticity of the biochar material. Even if biochar contained relatively high quantities of critical plant nutrients, the total amount of plant available nutrients directly supplied by biochar could be significantly lower (Lehmann et al., 2006). The recommended amount of soil extractable P, K, Ca, and Mg is 15 to 30 $\mu$g mg$^{-1}$, 100 to 130 $\mu$g mg$^{-1}$, 400-8,000 $\mu$g mg$^{-1}$, and 75-1,000 $\mu$g mg$^{-1}$ (LaBarge and Lindsey, 2012). The baseline soil conditions were found to have sufficient quantities of P, Ca, and Mg (15-30 $\mu$g mg$^{-1}$, 400-1600 $\mu$g mg$^{-1}$, and 75-1000 $\mu$g mg$^{-1}$, respectively), but not K (100-155 $\mu$g mg$^{-1}$).
In addition to N availability, K was likely to be another influential factor in the experiment. Significant differences (p<0.05) in plant tissue K and soil extractable K at the 0-10 and 10-20 cm depths at the 25 Mg ha\(^{-1}\) rates. Biochar was also found to have high levels of extractable K compared with the native soil extractable K. The amount of extractable K from biochar was 1202.4 μg g\(^{-1}\) compared with the soil extractable K of 64.2 μg g\(^{-1}\) for the Mehlich III extraction, and 3968.3 μg g\(^{-1}\) extractable K for the biochar compared with 53.8 μg g\(^{-1}\) for soil using Bray NH\(_4\) acetate extraction. K was also the only major plant nutrient which was below the recommended level as provided the Ohio State University extension office which recommends a 100 to 155 μg g\(^{-1}\) Mehlich III extractable rate with soils within a CEC of 10-20 cmol+ kg\(^{-1}\) (LaBarge and Lindsey, 2012).

The biochar may have provided either a direct fertilization effect (i.e. the plant nutrients contained within the biochar were utilized by the crops) or indirect fertilization effect (i.e. biochar increased retention of K\(^+\) cations by increasing the CEC).

Surface area is a key characteristic of biochar as iMg has been strongly correlated with total porosity, nutrient retention, particularly CEC, and moisture retention (Downey et al., 2009). SSA of biochar has also been hypothesized to impact microbial populations (Lehmann, 2011). The mean SSA for the biochar used in this experiment was found to be 58 m\(^{2}\) g\(^{-1}\). While this value is significantly higher than the native soil (SSA=6), it was relatively low compared with the reported values of other charcoals (Downie et al, 2009). The original surface area was similar but not identical to oak-derived biochar analyzed by
Mukherjee et al. (2010) which found SSA from N$_2$-adsorption of 2±1 and 225±9 for oak-derived biochar produced at 400 and 650 °C, respectively, in laboratory settings. In the same experiment, the authors found CO$_2$ surface area (not determined in this experiment) to be 252±90 and 528±57 m$^2$ g$^{-1}$, thus highlighting the importance of the specific probe gas being used to establish the monomolecular layer. IMg has been argued that N$_2$ represent macro and mesopore surface area well, but may not represent micropore spaces sufficiently due to its relatively large size of 109.8 picometers (pm). Use of CO$_2$, MEGE, and other SSA determination techniques may be better suited to understanding the microporosity of biochar (Mukherjee et al., 2010).

The application of biochar with a relatively high SSA compared with the soil resulted in a statistically significant (p<0.05) increase in the SSA of soil at the 25 Mg ha$^{-1}$ level from 6 m$^2$ g$^{-1}$ to 8 m$^2$ g$^{-1}$ at the 0-10 cm depth. The observed increase in SSA suggested possible increases in nutrient retention (e.g. CEC) and moisture retention. Liang et al. (2006) hypothesized that one of the critical impacts of biochar on nutrient dynamics was increased retention of cationic plant nutrients (Ca, Mg, K, NH$_4$, etc.). Cheng et al. (2008) hypothesized that surface oxidation and CEC can increase over time. An associated increase in CEC was not found, however. The standard method (i.e. ammonium acetate extraction) for determining soil CEC was used in this experiment to determine biochar CEC. A “double extraction” method has been proposed as a more accurate method for determining CEC of biochar and biochar containing soils (Cheng et al., 2006). Although no increase in CEC was observed, the nutrient
uptake of K was significantly improved (p<0.05) suggesting biochar potentially directly provided K, increased K retention, or increased K availability in the soil.

We hypothesized an increase in pH based on the highly alkaline nature of the biochar. This hypothesis was rejected. Observed soil pH was not significantly impacted by the biochar. This may be due to a soil system with a large amount of “reserve” or “potential” acidity from H+ acids on the CEC complex. In this case, permanently changing pH would be difficult due to a high degree of buffering. Changes in pH alters the availability of essential, macro-, and micro-plant nutrients. Research in acid soils of the tropics in which an increase in pH has been hypothesized as one of the main mechanisms for increased crop growth (Yamato et al. 2006; Rondon et al. 2007; Major et al. 2010). It is unlikely that an increase in pH would significantly benefit crop growth in an alkaline soils in the U.S. Midwest, however. A pH range between the 6.2 and 7.0 pH are generally considered to be optimal for maize and soybean production (LaBarge and Lindsey, 2012). The baseline soil pH was measured to be 7.30, thus already above the optimal pH range. Any increase above the baseline pH would therefore, theoretically, not be expected to increase crop productivity unless specific plant nutrients which were limiting growth became more available.

Soil pH was measured determined to be 7.46, 7.57, and 7.58 for the 0, 5, and 25 Mg ha\(^{-1}\) biochar amended plots, respectively, at the 50% recommended fertilizer level. Plots at the 100% fertilized level were found to have a pH of
7.48, 7.52, and 7.51 for the 0, 5, and 25 Mg ha\(^{-1}\) biochar amended plots, respectively. One explanation is that very little of the biochar broke down due to its physiochemical stability via physical weathering, chemical reactions, or biological processes. The quantity of cationic nutrients (Ca, Mg, K, etc.) may have been insufficient to replace the H+ acid on the CEC-complex.

Soil moisture characteristics play a primary role in determining the yield of crops and as an indicator of soil physical properties including both overall soil porosity and pore size distribution. In addition to changing plant available nutrients, biochar can impact soil physical properties which may explain changes in plant growth. The biochar was observed to impact multiple soil physical properties including bulk density, and moisture retention (see Chapter 6). No changes were found to soil aggregation, saturated hydraulic conductivity, or infiltration rates. The application of biochar, which was determined to have a particle density of 0.44 g cm\(^{-3}\), significantly decreased soil \(\rho_b\) (p<0.05). A decrease in \(\rho_b\) is generally associated with greater porosity, decreased soil strength and increased root penetration. Moisture retention also improved available water capacity (AWC) at significant levels in the biochar plots compared with the control at the 0-10 cm depth (see Chapter 6).

In the third year there was a major deficit of rainfall which resulted in a significant decrease in both total biomass and grain yield of the soybean crop that year. Unlike, previous studies which have documented a preferentially beneficial effect in low-yielding growing seasons (Steiner et al. 2007; Major et
al. 2010), the impact of biochar on crops during that year were statistically indistinguishable from the control. Additionally, the progressive beneficial impact of biochar noted in previous studies (e.g. Steiner et al., 2007; Major et al., 2010) was not documented in this study. The most beneficial impacts of biochar were observed during the first two seasons after application. This could suggest that there was a direct fertilization effect from the biochar addition that diminished over time.

4.5 Conclusion

Application of oak-derived biochar to a relatively fertile Alfisol in the U.S. Midwest increased crop yields but did so inconsistently over the 4 year period of observation. It is uncertain which mechanism(s) were most responsible for observed increases in productivity in years where biochar applied plots had greater yields. There was likely to be a direct or indirect fertilization effect from K which was below recommended soil levels. A decrease in plant tissue N in the maize crops at the 50% of recommended N fertilizer suggests that N immobilization may have occurred. Overall, the above findings suggest that biochar may increase grain yield on maize-soybean rotations in the U.S. Midwest, but that the impact is likely to be significantly less than increased yields observed in tropical or degraded soils. Biochar may be a valuable tool for sustainable intensification of crops, but may also have negative impacts if not accompanied by judicious use of N fertilizer.
4.6 References


4.7 Tables and Figures

Figure 9: Experimental location. The field experiment is located at Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W, with elevation of 242 meters in the Olentangy River watershed and a soil type is Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the “Crosby” soil series.
<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Soil Baseline</th>
<th>Biochar</th>
</tr>
</thead>
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<tr>
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<td>(H$_2$O)</td>
<td>7.30</td>
<td>9.55</td>
</tr>
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<td>pH</td>
<td>(KCl)</td>
<td>na</td>
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<tr>
<td>CEC</td>
<td>(meq/100g)</td>
<td>12.4</td>
<td>16.1</td>
</tr>
<tr>
<td>Total C</td>
<td>(%)</td>
<td>2.66</td>
<td>78.6</td>
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<tr>
<td>Total N</td>
<td>(%)</td>
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<td>0.64</td>
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<td>B</td>
<td>(μg g$^{-1}$)</td>
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<td>(μg g$^{-1}$)</td>
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<tr>
<td>Fe</td>
<td>(μg g$^{-1}$)</td>
<td>85.7</td>
<td>153.13</td>
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† As determined by N2 adsorption.
*Perchloric acid digestions with ICP
<DL = below detection level.

Table 9: Chemical and physical properties of biochar and soil. Biochar was derived from oak (Quercus) feedstock produced in a “Missouri kiln” at ~425 °C. Biochar was incorporated into a Miamian soil (fine, mixed, active, mesic, Oxyaquic Hapludalfs). Unless otherwise noted, values were derived from 5 analytical replicates.
<table>
<thead>
<tr>
<th>Year</th>
<th>Crop</th>
<th>Measurement</th>
<th>Yield (Mg ha⁻¹)</th>
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<td></td>
<td></td>
<td>50% N</td>
<td>100% N</td>
</tr>
<tr>
<td></td>
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<td>0</td>
<td>5</td>
<td>25</td>
<td>0</td>
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<tr>
<td>2010</td>
<td>Soybean</td>
<td>Above-ground</td>
<td>6.53 (0.73)</td>
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<td>Maize</td>
<td>Above-ground</td>
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<td>Grain yield</td>
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Table 10: Above-ground biomass (Mg ha⁻¹), grain yield (Mg ha⁻¹), and grain index (Mg ha⁻¹ grain: Mg ha⁻¹ above ground biomass).
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<th>Year</th>
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<th>CEC (meq kg(^{-1}))</th>
<th>SSA (m(^2) g(^{-1}))</th>
<th>Available P (ug g(^{-1}))</th>
<th>K (ug g(^{-1}))</th>
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<td></td>
<td>12.07</td>
<td>4.9</td>
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<td>1821.8</td>
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Table 12: Nutrient content (ug g⁻¹) and soil properties of Ohio Alfisol 1, 2, and 3 years after application of biochar in 2010.
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Table 12 (cont’d): Nutrient content (ug g\(^{-1}\)) and soil properties of Ohio Alfisol 1, 2, and 3 years after application of biochar in 2010.
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**Table 13**: Soil carbon (g kg⁻¹) in 2010, 2011, and 2012 at three depths (SE = standard error; Med = median).
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Table 14: Soil carbon (g kg⁻¹) 2010, 2011, and 2012 at three depths (SE= standard error; Med = median).
Figure 10: Total above-ground biomass for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years.
Figure 11: Total grain yield for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years.
Figure 12: Grain index (grain yield/total AGB) for soybeans (2010 and 2012) and maize (2012). Letters indicate significant treatments between treatments and years.
Figure 13: Plant tissue nitrogen for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 14: Plant tissue phosphorus for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 15: Plant tissue potassium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 16: Plant tissue calcium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 17: Plant tissue magnesium for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 18: Plant tissue sulfur for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 19: Plant tissue boron for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 20: Plant tissue molybdenum for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 21: Plant tissue zinc for soybeans (2010) and maize (2012). Soybean tissue was taken in 2010 and from 25 randomly selected plants from newest mature, trifoliate leaf at early bloom. Maize tissue was taken in 2011 from flag leaf of 25 randomly selected plants at tasseling stage. Letters indicate significant treatments between treatments and years.
Figure 22: Results of the present experiment compared with results from other experiments (from Lehmann et al., 2006).
Figure 23: Cation exchange capacity at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 24: Cation exchange capacity at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 25: pH at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 26: pH at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 27: Extractable phosphorus at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 28: Extractable phosphorus at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 29: Extractable potassium at 50% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 30: Extractable potassium at 100% recommended nitrogen fertilizer at three depths (0-10, 10-20, and 20-30 cm) measured in 2011.
Figure 31: Plots planted in soybeans in 2010.
Figure 32: Plots planted in maize in 2011.
Chapter 5:

Impact of biochar on greenhouse gas emissions on maize-soy rotation on an Alfisol soil Central Ohio

5.1 Abstract

Increasing atmospheric concentration of GHGs from anthropogenic activities are very likely driving observed changes to the global climate system which has caused the planet to warm 0.8 °C over the past century. Agriculture contributes roughly 25% of anthropogenic emissions. Soils, specifically, play an important role in climate constituting both a large sink and source of multiple important greenhouse gases including CO$_2$, CH$_4$, and N$_2$O. Recently biochar production and application has been proposed as a method for sequestering C in the pedosphere while increasing agricultural productivity. Biochar is likely to multifarious effects on soil systems including alterations to basic physical, chemical, and biological properties than have been observed in a limited number of studies to impact soil GHG emissions. An experiment using closed chambers was designed to quantify the effect of biochar application on CO$_2$, CH$_4$, and N$_2$O
emissions from agricultural soils in Ohio. Here we report on GHG soil emissions from a field investigation using oak (Quercus) derived biochar from a slow pyrolysis process at ~475°C at two rates (5 Mg ha\(^{-1}\) and 25Mg ha\(^{-1}\)) plus a control with 100% and 50% of recommended N fertilizer on a maize-soybean rotation in Ohio on an alfisol. The flux of CO\(_2\) and CH\(_4\) did not significantly differ with application of biochar although consistent trends were found for both gases. Cumulative CO\(_2\) emissions tended to increase with the application of biochar. Within the 50% recommended N fertilizer plots, the cumulative CO\(_2\) flux over the observation period increased 3.5% and 11.1% with the application of biochar at the 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) treatments, respectively, and 8.8% and 9.3%, respectively, within the 100% N fertilizer plots. CH\(_4\) showed an opposite pattern—consumption (i.e. negative emissions) were correlated with application of biochar although the results were not significant. CH\(_4\) consumption increased by 572.5% and 951.7% from the control within the 100% N fertilizer plots. N\(_2\)O emissions decreased significantly with the application of biochar (p>0.05). N\(_2\)O emissions decreased by 28.2% and 35.7% with 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar added, respectively, compared with the control within plots receiving 100% N fertilizer. Cumulative GWP was dominated by emissions of CO\(_2\) followed by N\(_2\)O and, much less significantly, CH\(_4\). The GWP was highest for plots receiving greater quantities of biochar. In the 100% N fertilizer plots GWP was 38,203, 39,778 and 39,560 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\), respectively, for the plots receiving 0, 5, and 25 Mg ha\(^{-1}\) biochar application. Increased CO\(_2\) emissions were hypothesized to be the result of an increase in
labile C from biochar or an increase in microbial decomposition of native C. Decreased N₂O emissions were hypothesized to be the result of increased NH₄ and NO₃ adsorption on biochar surfaces.

### 5.2 Background

Climate change is unequivocal (IPCC, 2007), and humans are very likely to be the main cause of observed changes including an increase in mean global surface temperature of 0.8°C since 1900. Increasing atmospheric concentrations of greenhouse gases (GHGs) and aerosols, deforestation, and land use change from anthropogenic activities are driving climate change (IPCC, 2007). Soils act as both a source and sink for atmospheric GHGs including carbon dioxide (CO₂) and methane (CH₄), and mediate the release of nitrous oxide (N₂O) which are collectively responsible for ~68% of increased radiative forcing on the Earth’s energy budget (IPCC, 2007). Decreasing anthropogenic emissions of GHG is essential for mitigating climate change and preventing dangerous anthropogenic interference (DAI) with Earth’s climate system. Article II of the United Nations Framework Convention for Climate Change (UNFCCC) calls for the “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system,” and that this level, “should be achieved within a time-frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development proceed in a sustainable manner.”
Atmospheric CO₂ concentrations have increased from pre-Industrial levels of 280 parts per million (ppm) to present levels of ~390 ppmv, representing an increase of ~39% (Tans, 2010). This increase in CO₂ is partly responsible for observed warming of ~0.74 °C since 1900 (IPCC, 2007) and may have committed the Earth to a further warming of 1.4 – 4.3 °C over the 21st century (Ramanathan and Feng, 2008). Current anthropogenic C emissions are estimated to be ~10 Pg C yr⁻¹ of which ~8.5 Pg is from fossil fuel combustion and cement production with the remainder ~1.5 from land use change—mainly deforestation and degradation of ecosystems.

Agriculture and soil ecosystems are an important sector for emissions reductions. Globally agriculture is responsible for approximately 20% of annual emissions (Cole, 1997), but 52 and 84% of CH₄ and N₂O emissions, respectively (Smith, 2007). Targeted emissions reductions of CH₄ and N₂O can provide significant mitigation opportunities as the radiative forcing of these gases on a molecular basis is much greater than that of CO₂. This “multi-gas” approach has long been advocated over the past decade (Hayhoe et al., 1999; Hansen et al., 2000; Jensen and Thelle, 2001; Smith et al., 2000; Molina et al., 2009). The global warming potential (GWP) of CH₄ is 25 and 72 for time horizons of 20-yr and 100-yr, respectively. For N₂O, GWP is 300 and 310 for time horizons of 20-yr and 100-yr, respectively (Forester et al., 2010). In addition to its impact on the climate system, N₂O also contributes significantly to deterioration of the stratospheric ozone layer (Ravishankara, 2009).
Deliberate strategies for managing and sequestering C in soils has been proposed as a strategy for mitigating climate change (Lal, 2004) which offers multiple ancillary benefits including increased food security and protection of ecosystem services (Lal, 2004). One significant possible drawback of soil C sequestration strategies, particularly no-till, is the possibility of increased emissions of N\textsubscript{2}O emissions which have been both observed (Wagner-Riddle, 2007) and hypothesized using soil-crop models (Li et al, 2005). A tight coupling between C and N geochemical cycles exists in soil systems. As such, soil GHG emissions are heavily influenced by additions of organic matter and fertilizers. The addition of C to soils has been hypothesized to increase the microbial turnover rate of N and therefore lead to greater emissions of N\textsubscript{2}O which could potentially offset 75 to 310% of C sequestered. In the best case scenario, (i.e. 75% offset) such an increase in N\textsubscript{2}O emissions would greatly diminishing the efficacy of soil C sequestration; in the worst case scenario, (i.e. 310% offset) there would be a net increase in radiative forcing thereby exacerbating climate change instead of mitigating it. There remains debate over whether N\textsubscript{2}O emissions are actually increased with higher levels of SOC (Six et al, 2004), nevertheless, strategies for both increasing SOC without increasing N\textsubscript{2}O emissions and directly reducing N\textsubscript{2}O emissions from soils would provide significant climate benefits.

Recently, the use of “biochar,” a biomass-derived charcoal from oxygen-limited combustion process, has been proposed as a means of sequestering C in soils (Sombroek et al., 2003; Lehmann et al., 2006; Glaser, 2007; Laird, 2008;
and Lehmann and Joseph, 2009.) The maximum technical C sequestration potential of sustainable biochar has been estimated to be between 1.0 and 1.8 Pg C yr\(^{-1}\), thus potentially offering a significant means of reducing anthropogenic forcing on the global climate system (Woolf et al., 2010). Biochar may have merits over more widely recognized soil C sequestration strategies due to its physiochemical stability which makes it recalcitrant in soil ecosystems (Lehmann and Joseph, 2009). Among the potential benefits, biochar has been found in some situations to reduce emissions of CH\(_4\) and N\(_2\)O from soils (Van Zwieten et al., 2009).

### 5.2.1 Carbon dioxide emissions

Atmospheric CO\(_2\) concentration has increased from pre-Industrial levels of \(~280\) parts per million by volume (ppmv) to present levels of \(~396\) ppmv, representing an increase of \(>40\%\) (Tans, 2010). CO\(_2\) levels rose an estimated 2 ppmv from 1995 to 2005, compared to 1.25 ppmv from 1960 to 1995 (IPCC, 2007). This increase in CO\(_2\) has led to a warming of \(~0.80\) °C since 1900, and may have committed the Earth to a further warming of 1.4 – 4.3 °C over the 21\(^{st}\) century (Ramanathan and Feng, 2008).

Degradation and erosion of soils has been a large source of atmospheric C contributing an estimated 78±12 Pg C to the atmosphere since 1850. CO\(_2\) emissions from soils are regulated by a manifold of physical, chemical, and biological processes which oxidize C held within the pedosphere intoCO\(_2\) mainly through heterotrophic respiration. Application of biochar provides a means of
increasing net soil C storage due to its physiochemical stability compared with the biomass precursor used as feedstock material during the pyrolytic process. The high degree of aromacticity provided in the biochar structure resists microbially mediated decomposition and, in many cases, appears resistant to physical and chemical degradation (Schmidt and Noack, 2000; Harris, 2005; Bourke et al., 2007). The biochar can also influence net CO$_2$ emissions (and other GHGs) from soils by changing basic parameters known to regulate CO$_2$ emissions such as moisture holding capacity, pH, and changes to microbial communities and functioning (Van Zweiten et al., 2009).

Charcoal produced from forest fires in natural ecosystems are found to be on the order 10,000 years old (Preston and Schmidt, 2006). Globally, natural charcoal production in natural ecosystems is on the order of 0.05 to 0.3 Pg C yr$^{-1}$ (Sabine et al., 2004). Nevertheless, charcoal often constitute >10% of soil organic carbon (SOC). This provides strong evidence for the long term stability of naturally produced biochar analogs and that biochar is likely to have similar mean residence times (MRTs). The MRT of biochar has been variously estimated for (1) biochar found in Amazonian Dark Earths (ADE) using radiocarbon dating from 500 to 7000 years BP; (2) aged biochar has been estimated at 1335 years when held at a constant temperature of 10°C (Cheng et al., 2008); (3) charcoal produced from natural savannah fires 718 to 9259 years old (Lehman et al., 2008); and 293 years for charcoal produces from fires in Russian steppe ecosystems (Hammes et al., 2008). Collectively, the calculations
of the age of biochar suggest a relatively high MRT particularly compared with other forms of SOC.

Biochar has been found to change both the composition and population of microbial communities (Lehmann, 2011). Such changes could potentially increase the decomposition rate of the native soil C pool (Wardle, 2008). The presence of biochar could also alter the proportion of C from plant residues which is stabilized in the semi-stable and stable C fractions. The efficiency of biochar to stabilize soil C, therefore, must take into account the effects of biochar post-application in order to come to a more complete understanding of the full lifecycle analysis of biochar application.

5.2.2 Methane emissions

\( \text{CH}_4 \) is a powerful GHG that has a 20-yr GWP of 72, a 100-yr GWP of 25, a total radiative forcing of \( \sim 0.48 \text{ W/m}^2 \) and a mean residence time (MRT) of \( \sim 8.4 \text{ yr} \) (IPCC, 2007). Next to \( \text{CO}_2 \), \( \text{CH}_4 \) is the second or third most important anthropogenic forcing agent, 18.3\% of the total \( +2.63 \text{ W/m}^2 \) of the total positive anthropogenic forcing. Since the Industrial Revolution, global \( \text{CH}_4 \) concentration has risen from \( \sim 700 \text{ parts per billion by volume (ppbv) to} \sim 1775 \text{ ppbv} \) (IPCC, 2007), an increase of \( \sim 153\% \). \( \text{CH}_4 \) is also a precursor gas in the formation of tropospheric ozone and stratospheric water vapor —two other powerful forcing agents. This “indirect effect” of \( \text{CH}_4 \) may be understated in prior assessments (IPCC, 2007) and therefore \( \text{CH}_4 \) may have a radiative impact 10\% -40\% higher than the above stated 100-yr GWP of 25 (Shindell, 2009).
On a global scale, soils consume ~30 Tg CH\(_4\) yr\(^{-1}\) or 5\% of total annual CH\(_4\) emissions (Denman et al., 2007; Van Zwieten et al., 2009). Highly aerobic soils tend to be sinks for CH\(_4\) where it is oxidized by methanotropic bacteria, whereas anaerobic soils tend to be dominated by methanogenic bacteria and to be sources of atmospheric CH\(_4\) (Dalal et al., 2008). Methane emissions and uptake, therefore, the difference between methane generation by methanogenic bacteria and consumption by methanotrophic bacteria (Knowles, 1993). Redox potentials bellow -150 mV (i.e. highly anaerobic environments with >50-70\% of pore space filled with water and generally environments) and presence of degradable C substrates are necessary preconditions for the production of CH\(_4\).

It is hypothesized that the application of biochar creates a soil environment more conducive to methanotrophic bacteria and less conducive to methanogenic bacteria, thereby reducing CH\(_4\) emissions (Rondon et al, 2006). Due to the low density, high porosity, and soil aggregation potential of biochar it is hypothesized that application will, under certain circumstances, lead to the net reduction of CH\(_4\) emissions or, in highly aerobic environments, potentially lead to increased CH\(_4\) consumption i.e. oxidation (Rondon et al., 2006; Yanai et al., 2007; Van Zweiten, et al., 2009). The experimental data for this phenomenon, however, are both limited and inconclusive.

The structure of the biochar material may indicate one mechanism by which CH\(_4\) is oxidized. Electron spin resonance (ESR) has indicated a large number of free radicals and dangling bonds within the biochar structure (Bourke, 2007).
Such properties could lead to a large quantity of single O sites on which CH\textsubscript{4} could be chemiphysically absorbed and subsequently oxidized to CO\textsubscript{2} before being released from the soil (Bourke, 2007; Van Zweiten et al., 2009).

Multiple mechanisms could be used to explain either increased CH\textsubscript{4} emissions or consumption with the application of biochar:

1. Increased CH\textsubscript{4} oxidation via chemiophysical adsorption and subsequent oxidation (Bourke, 2007);

2. Change in the microbial communities and populations specifically methantrophs and methanogens (Van Zweiten et al., 2009).

3. Increased macroporosity resulting in decreased bulk density and increased aeration of soils thereby favoring anaerobic conditions which support higher levels of CH\textsubscript{4} consumption by methantrophs (Yanai et al., 2007);

### 5.2.3 Nitrous oxide emissions

Nitrous oxide (N\textsubscript{2}O) is a GHG with a 20 yr-GWP of 289 and a 100yr-GWP of 298. N\textsubscript{2}O has a net radiate forcing of +0.16 (~8% of total anthropogenic radiative forcing) and a MRT of 114 years (IPCC 2007). The concentration of N\textsubscript{2}O in the atmosphere has increased from ~270 ppbv to ~320 ppbv since the Industrial Revolution (IPCC, 2007), an increase of ~19%. N\textsubscript{2}O is among the mosMg harmful substances, contributing to the deterioration of the stratospheric ozone layer (Ravishankara, 2009).
Approximately 70-80% of anthropogenic \( \text{N}_2\text{O} \) emissions are from agriculture (primarily due to application of synthetic N fertilizers and, to a lesser extent, livestock), ~20% from industrial processes (Galloway, 2008), and ~10% from deforestation (Bouwman et al. 1995). Biomass burning, sewage treatment, waste incineration, disturbance of natural ecosystems, and fossil fuel combustion are all contributors, though the magnitude of these sources and sinks remains poorly understood (Bouwman et al., 1995).

\( \text{N} \) fertilizer application is the primary anthropogenic source of \( \text{N}_2\text{O} \) being released into the atmosphere and is also responsible for the emissions of \( \text{NO}_x \) which is a precursor gas to the formation of tropospheric ozone (Smith et al., 2007). Lack of plant available N is often the most limiting factor for crop production (LeBauer and Treseder, 2008; Robertson and Vitousek, 2009) and synthetic inorganic \( \text{N} \) fertilizer is the most widely used farm input. The vast majority of \( \text{N} \) fertilizer is derived from \( \text{H}_2 \) via oxidation of natural gas through the Haber-Bosch process. Through a series of chemical reactions, highly stable triple-bonded atmospheric \( \text{N}_2 \) (which comprises 78% of the atmosphere by volume) is fixed into reactive/biologically-available ammoniacal compounds including ammonium nitrate (\( \text{NH}_4\text{NO}_3 \)), ammonium sulfate (\( (\text{NH}_4)_2\text{SO}_4 \)), anhydrous ammonia (\( \text{NH}_3 \)), and urea (\( (\text{NH}_2)_2\text{CO} \)) (Smil, 2001).

\( \text{N}_2\text{O} \) emissions from agricultural soils is function of crop type, soil pH and moisture levels, and the rate and type of \( \text{N} \) being applied (Mosier, 1998). Due to the surface area and cation exchange capacity (CEC), biochar is
hypothesized to retain ammonium (NH$_4^+$) on the cation exchange complex (Liang et al., 2006). Fresh biochar may also have sites of anion exchange which could retain anions including nitrate (NO$_3^-$) (Cheng et al., 2008). The ability of biochar to retain N ions on the solid phase would reduce availability of N for microbial processes including denitrification which could reduce emissions of N$_2$O (Karhu et al., 2011).

Soil N$_2$O emissions is controlled almost entirely through three processes all of which are biological (Reay et al., 2012): nitrification, denitrification and nitrifier denitrification. Nitrification involves the oxidation of ammonia (NH$_3$) into, first, nitrite (NO$_2^-$) mainly through metabolic activity of a genera of soil bacteria called *nitrosomonas* and, second, into nitrate (NO$_3^-$) mainly through the metabolic activity of a genera of soil bacteria called *nitrobacter*:

\[
2\text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{NO}_2^- + 2 \text{H}_2\text{O} + 2 \text{H}^+ \quad \text{(nitrosomonas)} \quad \text{Eq. [1]}
\]
\[
2\text{NO}_2^- + 1 \text{O}_2 \rightarrow 2 \text{NO}_3^- \quad \text{(nitrobacter)} \quad \text{Eq. [2]}
\]

Denitrification involves the reduction of NO$_3^-$ to produce N$_2$ gas through a series of microbially mediated reduction processes:

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} + \text{N}_2\text{O} \rightarrow \text{N}_2 \quad \text{(pseudomonads)} \quad \text{Eq. [3]}
\]

During both nitrification and denitrification significant quantities of N$_2$O are emitted which is thought to be the primary source of N$_2$O emissions from soils. Microorganisms involved in denitrification are primarily heterotrophic bacteria (e.g. *Paracoccus denitrificans* and *pseudomonads*). Biochar is likely to change the structure, population level and functioning of microbial communities (Theis
and Rillig, 2009; Lehmann et al., 2011), thereby leading to changes in the emissions.

In summary, multiple mechanisms—many of which may be interactive—could be used to explain potential mechanisms for reduce N$_2$O emissions with the application of biochar:

1. N-immobilization caused by high C:N ratio of biochar which, in the short term, may reduce nitrification (Lehmann et al., 2006; Warnock et al., 2007);
2. Changes in pH from highly alkaline biochar or ash (e.g. Ca, Mg, and K oxides and hydroxides) which decreases the N$_2$O:N$_2$ ratio (Van Zweiten et al., 2009);
3. Adsorption of NH$_4^+$ and NO$_3^-$ onto the negatively and positively charged sites, respectively (Cheng et al., 2008; Karhu et al., 2010)
4. Suppression of nitrification, denitrification, or nitrifier denitrification through changes to microbial populations and dynamics (Yanai et al., 2007)
5. Adsorption and deactivation of N-oxidizing or reducing enzymes (e.g. nitric oxide oxide reductase, nitrous oxide reductase, etc.) (Van Zweiten et al., 2009).

5.2.4 Previous research

Research on biochar, otherwise referred to as black carbon and charcoal in previous research, has only been seriously conducted for the past 10-15 years, mainly examining changes to soil chemistry and crop productivity. There exists only a small amount of research on the impacts of biochar on soil GHG emissions.
emissions, many of which have found significant changes in critical fluxes, but
two of which have also been inconclusive or contradictory. Uncertainty is
likely to stem from the highly variable and complex factors which regulate
emissions.

In an incubation study, Yanai et al (2007) reported 85% to 90% reduction
in N₂O emissions when biochar derived from municipal waste was applied to
rewetted (73% of water filled pore space) soil (Typic Hapludand) at rates of
~150-180 Mg ha⁻¹. However, in the same experiment, Yanai et al found 47%-51% increase in N₂O emissions when water filled pore space was increased to
83%.

In an incubation study, Sohi (2008) found a 15% decrease in N₂O
emissions when biochar derived from willow was applied to soils (arable with
low C-content) at a rate of 10 Mg ha⁻¹. An incubation study by Van Zwieten et
al (2009) found a nearly complete suppression of N₂O emissions when biochar
derived from poultry litter was applied to soil (Ferrosol) at rates of 10 Mg ha⁻¹.
However, when biochar derived from green waste was applied to the same soil at
the same rate N₂O emissions were 100% greater than the control.

In a greenhouse study, Rondon et al (2005) reported decreases in N₂O
emissions by 50% in soybeans and 80% in grass (B. humidicola) when biochar
was applied to soils (Typic Haplustox) at rates of 20 g kg⁻¹ and a nearly
complete suppression of CH₄ emissions with application of 15 g kg⁻¹ in a grass
stand and 30 g kg⁻¹ in a soybean stand. In a field experiment, Rondon et al
(2006) reported an increase of methane sinks by 200 mg CH₄ m⁻² and emissions reductions of nitrous oxide by 15 mg N₂O m⁻² when added at rates of 20 Mg ha⁻¹. In an incubation study, Yanai et al (2007) reported 85% to 90% reduction in N₂O emissions when biochar derived from municipal waste was applied to rewetted (73% of water filled pore space) soil (Typic Hapludand) at rates of ~150-180 Mg ha⁻¹. However, in the same experiment, Yanai et al found 47%-51% increase in N₂O emissions when water filled pore space was increased to 83%.

5.2.5 Hypothesis

Our hypothesis is that there is very likely to be changes in CO₂, CH₄, and N₂O emissions as biochar influences critical parameters such as microbial activity, water holding capacity, bulk density, aeration and other critical parameters which will influence soil gaseous emissions. Specifically, we hypothesized that there was likely to be an increase in CO₂ emissions, in the first year or two, due to decomposition of the labile portion of the biochar. There is likely to be various carbonaceous compounds present such as condensates deposited within the pore structure which can be accessed and metabolized by soil microbes. Increased surface temperature, particularly in spring and fall, may also contribute to greater microbial activity and resulting CO₂ emissions as the darker surface of the biochar facilitates greater radiative capture. Whether and to what extent CO₂ emissions are likely to remain elevated we did not hypothesize about. We find it likely that whatever treatments lead to greater aboveground biomass are likely to increase CO₂ emissions as a result of greater quantities of
potentially mineralizable inputs. We hypothesized a highly uncertain effect on CH$_4$ emissions due to the two competing influences of i) increased aeration and ii) greater moisture retention which may have opposite impacts on CH$_4$ emissions. We predicted a decrease in N$_2$O emissions due to previous studies which show NH$_4^+$ and NH$_3$ adsorption on reactive biochar surfaces.

5.3 Materials and Methods

5.3.1 Site Location

The field experiment is located at Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W, with elevation of 242 meters in the Olentangy River watershed and a soil type is Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the “Crosby” soil series. Baseline soil bulk density and particle density were determined to be 1.43 g cm$^{-3}$, 2.47 g cm$^{-3}$. Long-term (27 yr) average annual precipitation was 1,021 mm yr$^{-1}$ and mean annual temperature of 11.2 °C. The climate is strongly season with average May-August temperatures of 22.78°C and Dec. −2.78°C Feb. (OARDC, 2012).

On April 17$^{th}$, 2010, fields were treated with pre-emergent combination herbicide Metribuzin (4-Amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-1) Chlorimuron Ethyl (and Ethyl 2-[[[(4-chloro-6-methoxypyrimidin-2-yl)amino]carbonyl]amino] sulfonyl]benzoate) (“Canopy” manufactured by DuPont) and contact herbicide glyphosate (N-
(phosphonomethyl)glycine; C₃H₈NO₅P) at 439 mL ha⁻¹. Weeds were kept to minimum throughout the duration of the experiment through selective application of glyphosate using a backpack sprayer at a concentration of 0.384 mL L⁻¹ water.

On May 5th, 2010 biochar was applied by hand to plots in a full-factorial randomized complete block design with 12 replicates. Application rates were 0, 5 and 25 Mg ha⁻¹ on a total of 36 plots each 4 m by 6 m separated by a 2 m buffer. Biochar was produced by “Acticarbon” in Dunnellon, Florida from oak (Quercus) using a “Missouri Kiln” type-pyrolzer at ~425 ºC. On May 6th, biochar was incorporated into soil using “Rotovator” tractor to a depth of ~12-18 cm. Buffers were not tilled and were kept fallow through said herbicide application. On May 12th, 2010 “round-up ready” soybeans (company: Stine Seed Company, 22444 Laredo Trail, Adel, IA 50003; brand: 2062-4; variety: 6636454; lot no.: UNOBK903) were seeded at a rate of ~ 67 kg ha⁻¹ (60lbs. a⁻¹). Leaf tissue was collected for nutrient analysis. Tissue and grain were kept frozen until analysis was performed. Two 1m x 1m subplots were randomly selected and harvested in order to determine above ground biomass and grain yield for soybeans. Two 3-m rows were harvested for maize analysis. Moisture content of the grain was determined for each plot and total bean yield was converted into total dry weight.

On April 14, 2011, maize was planted using no-till seed drill (GT 805 No-Till Drill). With glyphosate resistant (a.k.a. “round-up ready”) fungicide
treated ("trifloxystrobin" with said trade name Trilex manufactured by Bayer) tested January 15, 2011, 99.6% pure seed, treated with Maxim, Apron, and Actellic) manufactured by The Clever Farms, Croton, Ohio. On May 4th, 2011, fields were sprayed with glyphosate via a backpack sprayer uniformly across the field at a rate of 439 mL ha\(^{-1}\). On April 19th, 2011, plots received urea (CO(NH\(_2\))\(_2\)- N fertilizer (46-0-0) at a rate of 156.9 kg ha\(^{-1}\) and 79.5 kg ha\(^{-1}\) for the high and low fertilizer treatments based upon recommendations by The Ohio State University (Vitosh et al., 1995). Seedling emergence and stand development was highly heterogeneous across the field and not correlated with plot treatments, likely due to record rainfalls in Columbus, Ohio for the month of April. As such replanting was deemed necessary. On June 1, 2011 corn was again planted using no-till seed drill with the aforementioned seed type. On June 3rd, 2011 the original maize stand was treated with post-emergent Fusilade II (Butyl(RS)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoate). On June 17th and June 30th, July 15th, 2011 fields were again sprayed with glyphosate via a backpack sprayer uniformly across the field at a rate of ~440 mL ha\(^{-1}\). Weeds were kept to minimum throughout the duration of the experiment through selective application of glyphosate using a backpack sprayer at a concentration of 0.384 mL L\(^{-1}\) water.

On April 22nd, plots were treated with pre- and post-emergent herbicide combination containing canopy and glyphosate at said rates. On May 21st, 2012, plots were planted with “round-up ready” soybeans (company: Stine Seed Company, 22444 Laredo Trail, Adel, IA 50003; brand: 2062-4; variety:
were seeded at a rate of ~ 67 kg ha\(^{-1}\) (60 lbs. a\(^{-1}\)). Stand emergence and plant development was again very poor and heterogeneous across the landscape, this time due to extreme drought conditions. Soybeans were not replanted in 2012.

### 5.3.2 Experimental Design

Biochar was applied by hand to plots in a full-factorial randomized complete block design with 6 replicates and subsequently tilled into the soil at a depth of ~15 cm. Application rates were 0 Mg ha\(^{-1}\), 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) on a total of 36 plots each 4 m by 6 m separated by a 2 m buffer. Control plots not receiving biochar were also tilled in order to maintain treatments. Plots were maintained as no-tillage after in years following application. Plots received urea (CO(NH\(_2\))\(_2\)-N fertilizer (46-0-0) at a rate of 156.9 kg ha\(^{-1}\) and 79.5 kg ha\(^{-1}\) for the 100% N and 50% N plots.

### 5.3.3 In-situ gas measurements

Gas flux was measured from May 2010 through August 2011 on an approximately bi-weekly basis during the growing seasons on an approximately monthly basis during the non-growing seasons using a non-ventilated static chamber method (Hutchinson and Livingston, 2003; Livingston and Hutchinson, 1995; Jacinthe and Dick, 1997). One chamber was placed on each of the 36 subplots. Chambers were constructed of polyvinyl chloride (PVC) pipe 20.7 cm in diameter and 25 cm in height. A gas sampling port was attached to the top of the chamber caps fitted with a ¼ inch Swagelock fitting
with non-reactive UV resistant butyl rubber septa. The bottom of the chambers were machine beveled in order to facilitate insertion into the soil. Chambers were inserted approximately 5-7 cm into the soil. A cap, also constructed of PVC, tightly coupled onto the top of the chamber fitting into the trough. One chamber was installed into each plot 2 weeks prior to the first measurements for a total of 36 chambers, or 6 replicates per treatment.

After installing measurements of chamber heights were taken in order to determine volume of each chamber. Once installed, chambers remained in place until field operations involving use of tractor (tilling, seeding, and harvesting) were conducted, and were immediately reinstalled thereafter. On several occasions chambers had to be removed from soil in order to remove cap. After reinstalling chambers, heights were again taken and volumes recalculated. Prior to gas sampling, troughs were carefully filled with water in order to create an air tight barrier that prevented diffusion.

Gas sampling was conducted at 0, 30, 60 and 120 minute intervals. Gas sampling was conducted on a bi-monthly basis through the growing season (April through October) and on a monthly basis during the non-growing season (November through March). Soil temperature at 5 and 15 cm depths were take using a soil thermocouple probe. Soil moisture samples for the 0-10 cm depth were collected for determination of gravimetric water content.

5.3.4 Soil Sampling
Baseline samples and subsequent samples were taken in all 36 plots in three locations and three depths (0-10, 10-20, 20-30 cm) (n=324). Soil particle density was determined to be 2.47 g cm$^{-3}$ using boiling pycnometer method and 2.49 g cm$^{-3}$ using an electronic pycnometer (Multivolume 1305 Electronic Pycnometer, Micromeritics, Norcross, Georgia, USA). Bulk density was determined by taking cores (7.62 cm diameter 7.62 cm height copper cores) on triplicate randomly selected location on each plot at 0-10, 10-20 and 20-30 cm depths with a hand-held core sampler (AMS core sampler, American Falls, Idaho). Bulk density was calculated as ratio of oven dried soil (105$^\circ$C for 72 h) over known volume of core (Grossman and Reinsch, 2002).

Soils were sampled after crop harvest after harvest in 2010, 2011, 2012 and 2013. Samples were gathered using a hand-held soil augur (AMS soil augur, American Falls, Idaho) in between planted rows. Five sampling locations were selected randomly on each plot using a random number generator. Each of the five bulk samples were aggregated into a single composite sample that was then used for physical and chemical analysis. The compositcd soil was kept on ice insulated container and later transferred to a temperature controlled room at 3.6 $^\circ$C. Field moist subsamples were taken from bulk samples for gravimetric moisture determination. Available nutrients were determined using Mehlich III (1984). Soil pH was determined by using with H$_2$O and KCl using a 1:2.5 soil:water solution and 1 N KCl solution, respectively. Cation exchange capacity (CEC) was determined by extraction 1 N ammonium acetate was added to sample at pH 7. Flushing was performed three times with isopropyl alcohol
followed by extraction with 2 N KCl. Total C and N was determined by dry combustion on an elemental analyzer (vario MAX CN, Macro Elemental Analyzer, Hanau, Germany).

5.3.5 Gas analysis

Gaseous emissions from the soil were collected in a 20 mL syringe through the chamber septum and injected into evacuated 10 mL glass vials with a butyl rubber septa. Air samples were analyzed with a gas chromatograph (Shimadzu GC 14A, Kyoto, Japan) using a thermal conductivity sensor and a Hayesep D column (Alltech, Deerfield, IL). Helium gas was used as the carrier at a flow rate of 25 cm$^3$ min$^{-1}$. Standards of 0.1, 10, 100 and 1,000 ppmv CO$_2$ were used for calibration. Daily gaseous fluxes were calculated by:

$$F = \left( \frac{\Delta g}{\Delta t} \right) \left( \frac{V}{A} \right) k \hspace{1cm} \text{Eq. [1]}$$

Where $\Delta g/\Delta t$ is the linear change of gas concentrations within the chamber over time (i.e. g CO$_2$-C m$^2$ min$^{-1}$; mg CH$_4$-C m$^2$ min$^{-1}$; mg N$_2$O-N m$^2$ min$^{-1}$); $V$ is the chamber volume (m$^3$); $A$ is the surface area of the bottom of the chamber (m$^2$); and $k$ is the conversion factor of minutes to days (1440 min day$^{-1}$). All gas calculations assumed ideal gas law (i.e. PV = nRT). A positive F-value indicated net GHG emissions whereas a negative F-value, as was the case for some observed CH$_4$ values, indicated net consumption or oxidation. The chamber gas ratio was converted from a molar mixing ratio to parts per million by volume (ppmv). Hourly gas fluxes were calculated from the time-concentration data.
using linear regression or, when data was curvilinear, using the an algorithm
(Hutchinson and Mosier, 1981). Cumulative emissions were calculated by linear
interpolation and numerical integration (Whitaker and Robinson, 1967). 100-
year and 20-year global warming potentials were used for transformation of CH₄
and N₂O into CO₂-equivalents (CO₂-eq). Namely, 25 and 72 for CH₄,
respectively, and 289 and 298 for N₂O, respectively, for 100 and 20 year-GWPs)

5.3.5 Data analysis

Data was analyzed using the ANOVA GLM procedure of SAS (SAS, 2010).
Tests of significance were analyzed using a p-value of 0.05.

5.4 Results

5.4.1 Carbon dioxide emissions

The cumulative CO₂ flux from plots was insignificant among treatments.
Within the 50% recommended N fertilizer plots, the cumulative CO₂ flux over
the observation period was 71.59, 73.55, and 77.72 g CO₂-C m² for the control, 5
Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively. The cumulative flux from
the 100% of recommended N fertilizer plots was 76.41 g CO₂ m², 81.34 g CO₂
m², and 82.41 g CO₂ m² for the control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates,
respectively.

The mean daily flux of CO₂ (g CO₂-C m⁻² d⁻¹) was lowest in winter
months and highest in summer months corresponding with mean daily
temperature with the lowest emissions of 0.13 g CO₂-C m⁻² d⁻¹ and the highest
emissions 8.82 g CO₂-C m⁻² d⁻¹. Daily CO₂ flux measurements were similar to previous studies (e.g. Fortin et al., 1996; Jacinthe et al., 2002; Jarecki and Lal, 2006; Drury et al., 2006; Ussiri and Lal, 2009). Ussiri and Lal, for example, found daily CO₂ fluxes ranging from 0.15 to 6.74 g CO₂-C m⁻² d⁻¹.

The highest CO₂ peak occurred within several weeks after the application of N fertilizer. The highest CO₂ peaks observed also corresponded with higher soil temperature. The CO₂ fluxes were highly variable on a temporal basis corresponding with season temperature changes. The observation period was divided into four sampling periods corresponding with the four basic seasons: spring (March 22 through June 21), summer (June 22 through September 21), fall (September 22 through December 21) and winter (December 22 through March 21). Within each season there were 3-6 sampling points. Regardless of treatment, CO₂ flux strongly followed the seasonal patterns with summer>autumn>spring>winter.

During summer the mean rate of CO₂ flux from soils receiving 50% N was 4.23, 4.71 and 4.89 g CO₂-C m⁻² d⁻¹ for the control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively. For the plots receiving 100% N, the mean rate of CO₂ flux was 4.85, 4.96, and 5.06 g CO₂-C m⁻² d⁻¹ for control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively.

5.4.3 Methane emissions

The cumulative CH₄ flux from plots was insignificant among treatments. Within the 50% recommended N fertilizer plots, the cumulative CH₄ flux over
the observation period was -2.29 mg CH\(_4\) m\(^2\), -6.98 mg CH\(_4\) m\(^2\), and -11.72 mg CH\(_4\) m\(^2\) for the control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively. The cumulative flux from the 100% of recommended N fertilizer plots was -0.67 mg CH\(_4\) m\(^2\), -5.15 mg CH\(_4\) m\(^2\), and -5.61 mg CH\(_4\) m\(^2\) for the control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively. Daily CH\(_4\) flux measurements were similar to previous studies (e.g. Jarecki and Lal, 2006; Omonde et al., 2007; Ussiri and Lal, 2010).

During summer the mean rate of CH\(_4\) flux from soils receiving 50% N was -0.34, -0.22 and -0.49 mg CH\(_4\)-C m\(^{-2}\) d\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively. For the plots receiving 100% N, the mean rate of CH\(_4\) flux was -0.05, -0.43, and -0.11 mg CH\(_4\)-C m\(^{-2}\) d\(^{-1}\) for control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively. During winter the mean rate of CH\(_4\) flux from soils receiving 50% N was 0.18, -0.37 and -0.48 mg CH\(_4\)-C m\(^{-2}\) d\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively. For the plots receiving 100% N, the mean rate of CH\(_4\) flux was -0.22, -0.12, and -0.48 mg CH\(_4\)-C m\(^{-2}\) d\(^{-1}\) for control, 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) biochar rates, respectively.

5.4.4 N\(_2\)O Emissions

N\(_2\)O emissions was not significant. Treatments receiving 50% of recommended N fertilizer with higher levels of biochar having the lowest level of instantaneous and cumulative N\(_2\)O flux. Cumulative N\(_2\)O emissions from plots receiving 50% recommended N fertilizer were 28.84, 33.70, and 30.19 mg
N₂O-N m⁻² d⁻¹ for control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively. From plots receiving 100% recommended N fertilizer N₂O emissions were 59.48, 40.66, and 35.85 mg N₂O-N m⁻² d⁻¹ for control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively.

The highest N₂O peak in the Spring 2012 after the application of N fertilizer. N₂O flux by season were spring>summer>autumn>winter. During spring the mean rate of N₂O flux from soils receiving 50% N was 1.72, 1.71 and 1.61 mg N₂O-N m⁻² d⁻¹ for the control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively. For the plots receiving 100% N, the mean rate of N₂O flux was 3.72, 2.44, and 2.04 mg N₂O-N m⁻² d⁻¹ for control, 5 Mg ha⁻¹ and 25 Mg ha⁻¹ biochar rates, respectively. The observed daily N₂O flux was similar to other studies (e.g. Jacinthe and Dick, 1997; Ball et al., 1999; Ussiri and Lal, 2010).

5.4.5 Global warming potential

The overall impact of biochar treatments on GWP were dominated by soil CO₂ emissions followed by N₂O, with emissions/consumption of CH₄ playing a relatively minor role. The 100-yr GWP of CO₂, CH₄ and N₂O emissions were 31,351 to 36,660, -55.04 to 4.11, and 4,524 to 2,305 kg CO₂-equivalent ha⁻¹ yr⁻¹, respectively for all treatments.

CO₂ emissions, although not significantly different, were positively correlated with application of biochar and with application of N fertilizer. The 100-yr GWP of CO₂-C emissions were 31,351, 32,451 and 34,818 kg CO₂-equivalent ha⁻¹ yr⁻¹ for the control, 5 Mg ha⁻¹ biochar, and 25 Mg ha⁻¹ biochar treatments,
respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the GWP of CO$_2$-C emissions were 33,527, 36,484, and 36,660 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar, and 25 Mg ha$^{-1}$ biochar treatments, respectively. CH$_4$ consumption was positively correlated with application of fertilizer and negatively correlated with application of N fertilizer. The 100-yr GWP of CH$_4$-C emissions were -2.20, -37.47 and -55.04 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar, and 25 Mg ha$^{-1}$ biochar treatments, respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the 100-yr GWP of CH$_4$-C emissions were 4.11, -19.41, and -34.99 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar, and 25 Mg ha$^{-1}$ biochar treatments, respectively. N$_2$O emissions were strongly correlated with N fertilizer application and significantly decreased with the application of biochar. The 100-yr GWP of N$_2$O-N emissions were 2,305, 2790, and 2567 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar, and 25 Mg ha$^{-1}$ biochar treatments, respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the 100-yr GWP of N$_2$O-N emissions were 4,524, 3,248 and 2,910 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar, and 25 Mg ha$^{-1}$ biochar treatments, respectively. In sum, the 100-yr GWP for was lowest for the control plot (0 Mg ha$^{-1}$ biochar) receiving 50% N fertilizer which was calculated to have a 100-yr GWP of 33,645. The highest GWP was recorded for the 25 Mg ha$^{-1}$ with 100% N fertilizer with a 100-yr GWP of 39,535 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$.

The 20-yr GWP of CO$_2$-C emissions were identical to the 100-yr GWP: 31351, 32,451 and 34,818 kg CO$_2$-eq ha$^{-1}$ yr$^{-1}$ for the control, 5 Mg ha$^{-1}$ biochar,
and 25 Mg ha\(^{-1}\) biochar treatments, respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the 20-yr GWP of CO\(_2\)-C emissions were 33,527, 36484, and 36,660 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) biochar, and 25 Mg ha\(^{-1}\) biochar treatments, respectively. The 20-yr GWP of CH\(_4\)-C emissions were -6.34, -107.92, and -158.53 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) biochar, and 25 Mg ha\(^{-1}\) biochar treatments, respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the 20-yr GWP of CH\(_4\)-C emissions were 11.83, -55.90, and -100.77 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) biochar, and 25 Mg ha\(^{-1}\) biochar treatments, respectively. The 20-yr GWP of N\(_2\)O-N emissions were 2,377, 2,877, and 2,647 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) biochar, and 25 Mg ha\(^{-1}\) biochar treatments, respectively, with addition of 50% N fertilizer. At 100% N fertilizer, the 20-yr GWP of N\(_2\)O-N emissions were 4,665, 3,349, and 3,000 kg CO\(_2\)-eq ha\(^{-1}\) yr\(^{-1}\) for the control, 5 Mg ha\(^{-1}\) biochar, and 25 Mg ha\(^{-1}\) biochar treatments, respectively. Overall, the general trend for the 20-yr GWP was the same as the trend of the 100-yr GWP which had a positive correlation with the application of biochar. The 20-yr GWP for was lowest for the control plot (0 Mg ha\(^{-1}\) biochar) receiving 50% N fertilizer which was calculated to have a 20-yr GWP of 33,722. The highest GWP was recorded for the 25 Mg ha\(^{-1}\) with 100% N fertilizer with a 100-yr GWP of 39,535.

5.5 Discussion

Generally, the application of biochar was found to increase net radiative forcing from soil GHG emissions, although none of the individual fluxes were
statistically significant. $N_2O$ emissions, and associated radiative forcing, decreased with the application of biochar but not significantly. While neither $CO_2$ nor $CH_4$ emissions were statistically significant, both followed a discernable trend. The flux of $CO_2$ and $CH_4$ did not significantly differ with application of biochar although consistent trends were found for both gases. Cumulative $CO_2$ emissions tended to increase with the application of biochar. Within the 50% recommended $N$ fertilizer plots, the cumulative $CO_2$ flux over the observation period increased 3.5% and 11.1% with the application of biochar at the 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ treatments, respectively, and 8.8% and 9.3%, respectively, within the 100% $N$ fertilizer plots. $CH_4$ showed an opposite pattern—consumption (i.e. negative emissions) were correlated with application of biochar although the results were not significant. $CH_4$ consumption increased by 572.5% and 951.7% from the control within the 100% $N$ fertilizer plots. $N_2O$ emissions decreased by 28.2% and 35.7% with 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar added, respectively, compared with the control within plots receiving 100% $N$ fertilizer. Cumulative GWP was dominated by emissions of $CO_2$ followed by $N_2O$ and, much less significantly, $CH_4$. The GWP was highest for plots receiving greater quantities of biochar. In the 100% $N$ fertilizer plots GWP was 38,203, 39,778 and 39,560 kg $CO_2$-eq ha$^{-1}$ yr$^{-1}$, respectively, for the plots receiving 0, 5, and 25 Mg ha$^{-1}$ biochar application.

$CO_2$ emissions from soils was the largest source of GHG emissions overall which had a positive correlation with the application of biochar. $CO_2$ emissions did not, however, differ among treatments. There could be multiple
causes for no observed significant differences. First, the biochar may noMg have altered the physical, chemical or biological properties which mediate soil CO₂ emissions. This would imply that the biochar did not significantly impact the rate of decomposition. The oak-derived biochar may have provided little labile feedstock material which was rapidly decomposable, and had little effect on soil microbiology which is largely responsible for decomposition of organic substrates. The second possible explanation for no observed impacts of biochar on soil CO₂ emissions is that the biochar could have had multiple impacts which effectively negated one another. For example, the biochar may have introduced greater quantities of labile C thereby increasing emissions, but concurrently had negative impact on soil microbial activity thereby lowering the rate of decomposition. If the two impacts were of similar order of magnitude, no direct impacts from CO₂ evolution would be observed. Third, the biochar may have impacted soil CO₂ emissions but did so below the detection level of the either the method being used or requiring greater replication.

The positive trend of increased CO₂ emissions with biochar application is suggestive that the biochar may have either increased the rate of decomposition of the native soil C pools, or that the biochar directly provided labile C material which was readily used by soil microorganisms. Over a longer time period it is conceivable that CO₂ emissions associated with biochar application could change. First, if labile material from biochar did contribute to observed elevated CO₂ flux it is likely that labile C sources would readily decompose within a relatively short period of time, less than 2 years (Lehmann et al., 2009) with CO₂
emissions from plot receiving biochar returning to background levels. Ultimately increases or decrease in above and below-ground biomass and thus carbon inputs is likely to be the most important variable altering CO₂ emissions by changing the availability of residues available to microbes for decomposition.

CH₄ emissions did not significantly differ among treatments although there was a trend negative correlation between the rate of biochar application and CH₄ emissions. The net cumulative emissions from the control was higher than both biochar treatments within each fertilization level, and the 5 Mg ha⁻¹ biochar rate had higher emissions in both levels of fertilization than the 25 Mg ha⁻¹. As such, there is suggestive but inconclusive data that suggests that biochar may be effective at suppressing CH₄ emissions from agricultural soils.

N₂O emissions decreased significantly with the application of biochar. The mechanism(s) responsible for reducing N₂O emissions are difficult to identify. Nevertheless, within the study potential N-immobilization was identified (Hottle and Lal, 2013), as was an increase in total N likely in the form of NO₃ or NH₄ which can be readily adsorbed onto biochar surfaces (Hottle and Lal, 2013).

5.6 Conclusion

Average annual CO₂-eq emissions were highest for plot receiving biochar regardless of N fertilizer application. The application of N fertilizer increased both CO₂ emissions as well as N₂O emissions but was negatively correlated with CH₄ emissions. Although the results presented here support the conclusion that:
(i) biochar may reduced emissions of N$_2$O from soils, particularly when higher
rates of N fertilizer were added; (ii) biochar may increase CO$_2$ emission either by
supplying directly available labile C substrates or by increasing the rate of
decomposition of native C compounds; (iii) biochar may be able to increase the
consumption of CH$_4$ as there was an observable trend of higher consumption
with greater levels of biochar application although the results were not
significant. The results presented here demonstrate both the potential and
pitfalls of biochar application to soils. Future research of long-term field-scale
trials in a wide variety of agroecosystems and soil conditions are necessary to
evaluate the impact of biochar on GHG emissions.
5.7 References


Kennedy, T., Suddick, E., & Six, J. (2011). Reduced nitrous oxide emissions in tomato cropping systems under drip irrigation and fertigation. AGU Fall Meeting Abstracts, 1, 0402.


312


5.8 Tables and Figures
Figure 33: Meteorological data at the experimental location (Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02' 29.16” W) over the observation period (May 2010 through September 2011).
<table>
<thead>
<tr>
<th>Season</th>
<th>Daily mean CO₂ flux (g CO₂-C m⁻² day⁻¹)</th>
<th>50% N</th>
<th>100% N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 Mg ha⁻¹</td>
<td>5 Mg ha⁻¹</td>
</tr>
<tr>
<td>Winter</td>
<td></td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>Spring</td>
<td></td>
<td>2.47</td>
<td>2.42</td>
</tr>
<tr>
<td>Summer</td>
<td></td>
<td>4.27</td>
<td>4.71</td>
</tr>
<tr>
<td>Autumn</td>
<td></td>
<td>1.45</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Table 15: Rate of CO₂ flux (mg CO₂-C m⁻² d⁻¹) by season as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th>Season</th>
<th>Annual mean CO₂ flux (g CO₂-C m⁻² year⁻¹)</th>
<th>50% N</th>
<th>100% N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 Mg ha⁻¹</td>
<td>5 Mg ha⁻¹</td>
</tr>
<tr>
<td>Winter</td>
<td></td>
<td>96.1</td>
<td>95.0</td>
</tr>
<tr>
<td>Spring</td>
<td></td>
<td>225.3</td>
<td>220.7</td>
</tr>
<tr>
<td>Summer</td>
<td></td>
<td>389.5</td>
<td>430.1</td>
</tr>
<tr>
<td>Autumn</td>
<td></td>
<td>132.7</td>
<td>139.2</td>
</tr>
<tr>
<td>Annual</td>
<td></td>
<td>843.5</td>
<td>885.0</td>
</tr>
</tbody>
</table>

Table 16: Rate of CO₂ flux (mg CO₂-C m⁻²) by season as impacted by biochar and fertilizer treatments.
Table 17: Rate of CH$_4$ flux (mg CH$_4$-C m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th>Season</th>
<th>Daily mean CH$_4$ flux (mg CH$_4$-C m$^{-2}$ day$^{-1}$)</th>
<th>50% N</th>
<th>100% N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 Mg ha$^{-1}$</td>
<td>5 Mg ha$^{-1}$</td>
</tr>
<tr>
<td>Winter</td>
<td>0.18 -0.37 -0.48</td>
<td>-0.22 -0.12 -0.48</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>-0.02 -0.16 0.00</td>
<td>-0.25 -0.21 -0.25</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>-0.34 -0.22 -0.49</td>
<td>-0.05 -0.43 -0.11</td>
<td></td>
</tr>
<tr>
<td>Autumn</td>
<td>0.10 -0.51 -0.48</td>
<td>-0.27 0.11 -0.36</td>
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</tr>
</tbody>
</table>

Table 18: Rate of CH$_4$ flux (mg CH$_4$-C m$^{-2}$ d$^{-1}$) by season as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th>Season</th>
<th>Annual mean CH$_4$ flux (mg CH$_4$-C m$^{-2}$ yr$^{-1}$)</th>
<th>50% N</th>
<th>100% N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 Mg ha$^{-1}$</td>
<td>5 Mg ha$^{-1}$</td>
</tr>
<tr>
<td>Winter</td>
<td>16.8 -33.4 -43.6</td>
<td>-20.1 -11.2 -43.6</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>-2.2 -14.4 -0.2</td>
<td>-23.0 -18.8 -22.5</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>-31.0 -20.5 -44.6</td>
<td>-4.3 -39.5 -9.9</td>
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<tr>
<td>Autumn</td>
<td>9.4 -46.9 -44.0</td>
<td>-24.3 9.9 -32.4</td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>-7.0 -115.3 -132.4</td>
<td>-71.7 -59.7 -108.5</td>
<td></td>
</tr>
<tr>
<td>Season</td>
<td>Daily mean N₂O flux (mg N₂O-N m² day⁻¹)</td>
<td>50% N</td>
<td>100% N</td>
</tr>
<tr>
<td>----------</td>
<td>----------------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 Mg ha⁻¹</td>
<td>5 Mg ha⁻¹</td>
</tr>
<tr>
<td>Winter</td>
<td></td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Spring</td>
<td></td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Summer</td>
<td></td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Autumn</td>
<td></td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Annual</td>
<td></td>
<td>3.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 19: Rate of N₂O flux (mg N₂O -N m² d⁻¹) by season as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th>Season</th>
<th>Annual mean N₂O flux (mg N₂O-N m² year⁻¹)</th>
<th>50% N</th>
<th>100% N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 Mg ha⁻¹</td>
<td>5 Mg ha⁻¹</td>
</tr>
<tr>
<td>Winter</td>
<td></td>
<td>18.8</td>
<td>24.1</td>
</tr>
<tr>
<td>Spring</td>
<td></td>
<td>140.5</td>
<td>155.6</td>
</tr>
<tr>
<td>Summer</td>
<td></td>
<td>94.6</td>
<td>146.0</td>
</tr>
<tr>
<td>Autumn</td>
<td></td>
<td>20.0</td>
<td>25.3</td>
</tr>
<tr>
<td>Annual</td>
<td></td>
<td>273.9</td>
<td>351.0</td>
</tr>
</tbody>
</table>

Table 20: Rate of N₂O flux (mg N₂O -N m²) by season as impacted by biochar and fertilizer treatments.
### Table 21: Greenhouse gas flux from soils as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th>Season</th>
<th>50% N 0 Mg ha(^{-1})</th>
<th>50% N 5 Mg ha(^{-1})</th>
<th>50% N 25 Mg ha(^{-1})</th>
<th>100% N 0 Mg ha(^{-1})</th>
<th>100% N 5 Mg ha(^{-1})</th>
<th>100% N 25 Mg ha(^{-1})</th>
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<tbody>
<tr>
<td>Winter</td>
<td>18.8</td>
<td>24.1</td>
<td>30.9</td>
<td>19.2</td>
<td>24.4</td>
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<tr>
<td>Spring</td>
<td>140.5</td>
<td>155.6</td>
<td>146.6</td>
<td>212.1</td>
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<tr>
<td>Summer</td>
<td>94.6</td>
<td>146.0</td>
<td>118.0</td>
<td>193.8</td>
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<td>122.1</td>
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<tr>
<td>Autumn</td>
<td>20.0</td>
<td>25.3</td>
<td>27.4</td>
<td>17.2</td>
<td>35.5</td>
<td>26.9</td>
</tr>
<tr>
<td>Annual</td>
<td>273.9</td>
<td>351.0</td>
<td>323.1</td>
<td>442.3</td>
<td>408.7</td>
<td>348.6</td>
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</tbody>
</table>

### Table 22: Greenhouse gas flux from soils as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th></th>
<th>100-yr GWP of GHG emissions (kg CO(_2)-eq ha(^{-1}) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50% N 0 Mg ha(^{-1})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>30.93</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.00</td>
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<td>N(_2)O</td>
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<tr>
<td>Total</td>
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</table>

### Table 23: 20-yr global warming potential as impacted by biochar and fertilizer treatments.

<table>
<thead>
<tr>
<th></th>
<th>20-yr GWP of GHG emissions (kg CO(_2)-eq ha(^{-1}) yr(^{-1}))</th>
</tr>
</thead>
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<tr>
<td></td>
<td>50% N 0 Mg ha(^{-1})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>30.93</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>-0.01</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>2.24</td>
</tr>
<tr>
<td>Total</td>
<td>33.17</td>
</tr>
</tbody>
</table>
Figure 34: CO₂ emissions rate (CO₂-C g m⁻² day⁻¹) from plots receiving 50% recommended N fertilizer.
Figure 35: CO₂ emissions rate (CO₂-C g m⁻² day⁻¹) from plots receiving 100% recommended N fertilizer.
Figure 36: Cumulative CO₂ emissions over the observational period (CO₂-C g m⁻²) from plots receiving 50% recommended N fertilizer.
Figure 37: Cumulative CO$_2$ emissions over the observational period (CO$_2$-C g m$^{-2}$) from plots receiving 100% recommended N fertilizer.
Figure 38: CH$_4$ emissions rate (CH$_4$-C mg m$^{-2}$ day$^{-1}$) from plots receiving 50% recommended N fertilizer.
Figure 39: \( \text{CH}_4 \) emissions rate (\( \text{CH}_4\text{-C mg m}^{-2} \text{ day}^{-1} \)) from plots receiving 100% recommended N fertilizer.
Figure 40: Cumulative CH$_4$ emissions over the observational period (CH$_4$-C mg m$^{-2}$) from plots receiving 50% recommended N fertilizer.
Figure 41: Cumulative CH₄ emissions over the observational period (CH₄-C mg m⁻²) from plots receiving 100% recommended N fertilizer.
Figure 42: N$_2$O emissions rate (N$_2$O-N mg m$^2$ day$^{-1}$) from plots receiving 50% recommended N fertilizer.
Figure 43: N₂O emissions rate (N₂O-N mg m⁻² day⁻¹) from plots receiving 100% recommended N fertilizer.
Figure 44: Cumulative N₂O emissions over the observational period (N₂O-N mg m⁻²) from plots receiving 50% recommended N fertilizer.
Figure 45: Cumulative N$_2$O emissions over the observational period (N$_2$O-N mg m$^{-2}$) from plots receiving 100% recommended N fertilizer.
Figure 46: Net annual CO₂ emissions (g CO₂-C m⁻² yr⁻¹) by season.

Figure 47: Net annual CH₄ emissions/consumption (g CH₄-C m⁻² yr⁻¹) by season.
Figure 48: Net annual N₂O emissions (g N₂O-N m⁻² yr⁻¹) by season.
Figure 49: Annual GHG emissions (Mg CO$_2$-eq ha$^{-1}$ yr$^{-1}$) expressed in terms of 20-year global warming potential by gas as impacted by biochar and fertilizer treatment.
Figure 50: Annual GHG emissions (Mg CO$_2$-eq ha$^{-1}$ yr$^{-1}$) expressed in terms of 100-year global warming potential by gas as impacted by biochar and fertilizer treatment.
Figure 51: Gas chambers in field (2011).
Chapter 6:

Impact of oak-biochar on soil physical properties to an Alifosl in Central Ohio

6.1 Abstract

Biochar, a carbon-rich byproduct of pyrolysis, has been found to significantly enhance crop productivity over a wide range of field conditions and cropping systems. There are likely to be many impacts associated with application of biochar including those to physical, chemical, and biological systems. Here we report on the impacts on soil physical properties with the addition of oak (Quercus ssp.) derived biochar from a slow pyrolysis process at ~425 °C at three rates (0, 5 and 25 Mg ha$^{-1}$) with 100% and 50% of N fertilizer (146 kg ha$^{-1}$ and 72 kg ha$^{-1}$, respectively) on a maize (Zea mays)-soybean (Glycine max L.) rotation in Ohio on an Miamian soil (fine, mixed, active, mesic, Oxyaquic Hapludalfs). Bulk density decreased significantly by 15% with the application of 25 Mg ha$^{-1}$ biochar. Available water capacity increased by 8%. No significant differences were found in soil texture, hydraulic saturated conductivity, penetration resistance or infiltration rate. The specific surface area
of the biochar was measured to be 58 m$^2$ g$^{-1}$. When added to soil, biochar was found to increase overall specific surface area by +12% and +34% with the addition of 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar, respectively. Measures of water stable aggregates were significantly different, however, such changes were likely to be the result of highly stable biochar fragments rather than actual soil aggregates although some characteristics of the biochar quasi-aggregates were likely to function much in the same way as naturally occurring soil aggregates. The resulting changes indicate that biochar amendments to agricultural soils in the Midwest are likely to generally improve soil physical properties of most soils in these areas.

6.2 Background

Biochar is a carbon (C)-rich by-product of the thermal degradation of biomass in an oxygen-free or oxygen-limited environment. Chemically many characteristics of the biomass are fundamentally altered during the thermal degradation process. Cellulosic-lignin C structures, for example, are transformed into aromatic C compounds. Depending on the degree of alteration, many of the original physical properties of the biomass material are retained (Downie et al., 2009). The macro-pore architecture of biomass material including pore space for the conveyance of water and nutrients (e.g. xylem and phloem) are significantly preserved during biochar production as can been visualized in scanning electron microscopy of biochar surfaces (Wildman and Derbyshire, 1991).
When added to soil biochar can have multiple interacting effects on soil physical qualities including fundamental changes to texture and structure which can change the ratio and distribution of air, water, and minerals. Changes have been documented to bulk density ($\rho_b$), soil tensile strength ($T_s$), aggregate stability, hydraulic conductivity ($K_s$), moisture retention and available water content (AWC), shrink-swell dynamics, and thermal adsorption and conductance of heat. Secondary effects from changes to pH, microbial and macoinvertebrate communities and other processes are also likely impact soil physical properties.

The impacts are a function both of the characteristics of the biochar being applied and the soil to which it is applied to. High heating temperature (HHT) is likely to be the most important determinant of the final characteristics of biochar produced from a single feedstock material as many processes and properties are temperature dependent (Downey et al., 2009). According to Sjosttrom (1993), significant quantities of hemicellulose are degraded at 200°C to 260°C. Cellulose and lignin are degraded at 240°C to 350°C and 280°C to 500°C, respectively. At higher temperatures, a greater proportion of ash (inorganic minerals) are created, which strongly influences physical properties and increases the availability of non-volatilizable nutrients (e.g. K, Mg, Ca, Fe, Mn, etc.).

Research on biochar application to agricultural soils has monitored soil chemistry, biology and greenhouse gas emissions. Relatively little work has been done to characterize changes to soil physical parameters. Asai et al. (2009)
found that wood-derived-biochar increased $K_S$. Laird et al. (2010) used repacked soil columns to study the impact of biochar on Midwestern soils. The authors reported significantly lower bulk density ($\rho_b$), increased available water capacity (AWC), greater specific surface area (SSA), but no impact on saturated hydraulic conductivity ($K_{sat}$).

In the following experiment, we used oak (Quercus ssp.) pyrolyzed with a HHT of ~425°C was applied to a Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the “Crosby” soil series. Our hypothesis is that biochar would result i) decreased bulk density and soil strength, ii) increased porosity and root penetration, iii) increased aggregate stability; iv) increased AWC, and v) little or no observed change to water infiltration. We predict, however, that not all of these changes may be concurrent. It is likely that certain changes may take a significant amount of time (e.g. aggregate stability), while others may be instantaneous (e.g. $\rho_b$), and others still (e.g. SSA and AWC) may change throughout the ageing process of the biochar.

6.3 Materials and Methods

6.3.1 Field Trial

The field experiment is located at Waterman Research Farm on The Ohio State University campus in Columbus, Ohio (40° 00’ 33.09” N, 83° 02’ 29.16” W, with elevation of 242 meters in the Olentangy River watershed and a soil type is Miamian (fine, mixed, active, mesic, Oxyaquic Hapludalfs) in the
“Crosby” soil series. Long-term (27 yr) average annual precipitation was 1,021 mm yr\(^{-1}\) and mean annual temperature of 11.2 °C.

On May 5\(^{th}\), 2010 biochar was applied by hand to plots in a full-factorial randomized complete block design with 12 replicates. Application rates were 0, 5 and 25 Mg ha\(^{-1}\) on a total of 36 plots each 4 m by 6 m separated by a 2 m buffer. Biochar was derived from oak (\textit{Quercus}) having been produced by “Acticarbon” in Dunnellon, Florida using a “Missouri Kiln” type-pyrolyzer at ~425 °C. Prior to application biochar was passed through 5 mm sieve and thoroughly mixed in order to homogenize. One day later biochar was incorporated into soil using “Rotovator” tractor to a depth of ~10-12 cm. Buffers were not tilled and were kept fallow through said selective herbicide application. A complete description of the “Field Trail” materials and methods is provided in Chapter 4.

\subsection*{6.3.2 Biochar Characterization}

The bulk density of biochar was determined using water displacement (i.e. Archimedes principle) by submerging biochar in graduated cylinder. Apparent density was tested using electronic pycnometer (AccuPyn 1340 Pycnometer, Micrometrics, Norcross, Georgia). Tensile strength was determined using a crushing apparatus described below for soils.

\subsection*{6.3.3 Soil Analysis}

Soil samples were collected in the spring 2010 and spring of 2012 from all 36 plots in three randomized locations at three depths (0-10, 10-20, 20-30 cm)
Samples were gathered using a hand-held soil augur (AMS soil augur, American Falls, Idaho) in between planted rows. Five sampling locations were selected randomly on each plot using a random number generator. Each of the five bulk samples were aggregated into a single composite sample that was then used for physical and chemical analysis. The compositing soil was kept on ice insulated container and later transferred to a temperature controlled room at 3.6 °C. Field moist subsamples were taken from bulk samples for gravimetric moisture determination. Bulk density was determined by taking cores (7.62 cm diameter 7.62 cm height copper sleeves) on triplicate randomly selected location on each plot at 0-10, 10-20 and 20-30 cm depths with a hand-held core sampler (AMS core sampler, American Falls, Idaho) by the methods described by Blake and Hartage (1986). Bulk density was calculated as ratio of oven dried soil (105°C for 72 h) over known volume of the core (Grossman and Reinsch, 2002) corrected for gravel (>2mm) content. Soil particle density was determined to be 2.47 g cm⁻³ using boiling pycnometer method and 2.59 using an electronic pycnometer (Multivolume 1305 Electronic Pycnometer, Micromeritics, Norcross, Georgia, USA).

Aggregate stability was determined using the water-stable wet sieve method (Yodder, 1936). Aggregates between 8 mm and 5 mm were placed on a series of five nested sieves having mean diameters of 5, 2, 1, 0.5 and 0.25 mm. Aggregates were agitated for 30 min at a rate of 30 strokes min⁻¹ over a distance of 32 mm. The soil retained on each sieve was quantitatively removed and oven dried at 105°C for 48 hr. Only one replicate of soil cores (36 sampling locations
at three depths [0-10, 10-20, 20-30 cm]) were used to determine moisture retention (n=108). Soil moisture characteristics were determined by placing core samples on a tension table (pressures of -0 to -6 kPa) and pressure plates (pressure of -10 to -1,500 kPa).

The proportion of water stable aggregates (WSA) >0.25 mm, geometric mean diameter (GMD), and mean weight diameter (MWD) were calculated using standard methods (Kemper and Rosenau, 1986). MWD was calculated by the following equation:

\[ MWD = \sum m_i \times x_i \]  
\[ \text{GMD} = e^{\left( \frac{\sum m_i \log x_i}{\sum m_i} \right)} \]  
\[ MWD = \sum x_i \times m_i \]  
\[ MWD_c = 0.876 \times (MWD) - 0.079 \]

where \( m_i \) is the mass of the aggregates within each size range, and \( x_i \) is the corresponding mean diameter of each aggregate size range. Wet-sieved aggregates were than left to dry at 45°C. Dried aggregates were measured using calipers in three planes.

Pore size distribution was calculated by:

\[ R = \frac{0.1478}{h} \]  
\[ \text{Eq. [5]} \]
where R is the pore size (µm) and h is the negative pressure being applied (cm H$_2$O). Tensile strength (TS) was then measured using a crushing apparatus (Dexter and Watts, 2001). TS was calculated by:

$$TS = 0.576 \left( \frac{F}{d_{agg}} \right)^2$$  \hspace{1cm} \text{Eq. [6]}

where $F$ is the vertical force required to cause permanent deformation, and $d_{agg}$ is the mean diameter of the three measured planes of the aggregate.

One sub-replicate of soil cores (36 sampling locations at three depths [0-10, 10-20, 20-30 cm]) were used to determine moisture retention (n=108). Soil moisture characteristics were determined by placing core samples on a tension table (negative pressures of 0-6 kPa) and pressure plates (negative pressure of 10 to 1,500 kPa). 20g of <2 mm aggregates were used to determine moisture content (permanent wilting point). Total porosity ($f_T$) was calculated by the following equation:

$$f_T = \frac{\omega_s \cdot \rho_s}{\omega_s \cdot \rho_s + \rho_w}$$ \hspace{1cm} \text{Eq. [7]}

where $\omega_s$ is gravimetric water content at saturation; $\rho_s$ is a particle density; and $\rho_w$ is the density of water. $\omega_s$ was converted to volumetric water content ($\theta$) through the following equations:

$$\rho_b = (1 - f_i) \rho_s$$ \hspace{1cm} \text{Eq. [8]}

$$\theta_i = \frac{\omega_i \cdot \rho_b}{\rho_w}$$ \hspace{1cm} \text{Eq. [9]}
where $\theta_i$ is the volumetric water content; $i$ is negative pressure; and $\omega_i$ is the gravimetric water content at suction $i$. AWC was calculated by:

$$\text{AWC} = \text{FC} - \text{PWP}$$  
Eq. [10]

where FC is field capacity (gravimetric water content at -33 kPa of negative pressure) and PWP is permanent wilting point (gravimetric water content at -1500 kPa of pressure).

Pore size distribution was calculated according to the classification system by Greenland (1977) whereby gravitational or transmission pores are $>50\ \mu\text{m}$, storage pores are 0.5-50 $\mu\text{m}$, and residual or bonding pores are ($<0.5\ \mu\text{m}$). The total volume of the pore space in each of these was calculate by differences in volumetric water content at specific matric potentials.

$$f_{T(\text{transmission})} = f_T - \theta_{6\text{kPa}}$$  
Eq. [11]

$$f_{T(\text{storage})} = \theta_{6\text{kPa}} - \theta_{600\text{kPa}}$$  
Eq. [12]

$$f_{T(\text{storage})} = \theta_{600\text{kPa}}$$  
Eq. [13]

### 6.3.4 Earthworm population

Earthworm (Oligochaeta) population density was determined via chemical extractant using formalin (37% mL mL$^{-1}$ formaldehyde solution) at ~0.02% strength. 50 mL formalin solution was mixed with 8 L H$_2$O and applied over two 50 cm by 50 cm subplots within each plot. Earthworms were hand collected, placed in refrigerated cooler and weighed and then returned to the
field. Both the number (population) and mass were recorded. Sampling was conducted twice annually during the April-May and November-December in 2010-2012.

6.3.5 Statistical Analysis

Statistical analysis was carried using analysis of variance (ANOVA) and least statistical difference (LSD) using the PROC GLM procedure in SAS© (SAS 9.2).

6.4 Results

6.4.1 Biochar physical properties

Bulk density ($\rho_b$) and apparent density were found to be 0.44 g cm$^{-3}$ and 0.47 g cm$^{-3}$, respectively, considerably less dense than H$_2$O which has a density of 1.0 g cm$^{-1}$ at 4°C making the biochar prone to both wind and water erosion. Specific surface area (SSA) of the biochar was found to be 58 m$^2$ g$^{-1}$. After one year SSA of biochar decreased 31 m$^2$ g$^{-1}$ and after two years to 32 m$^2$ g$^{-1}$. Complete chemical analysis of biochar can be found in Chapter 4.

6.4.2 Bulk density and total porosity

Bulk density decreased significantly at both rates of biochar application in the 0-10 and 10-20 cm depths compared with control, while N application had no apparent impact on bulk density. No significance differences were found at the 20-30 cm depth. Soil amended with 5 Mg ha$^{-1}$ and 25 Mg ha$^{-1}$ biochar application bulk density significantly decreased (p<0.05) by 3.6% and 12% with
the application of 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with the control averaged over both rates of N application. At 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), bulk density decreased by 5.9% and 13.8% at the application of 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\), respectively, compared with the control averaged over both rates of N application.

6.4.3 Soil moisture

Field measurements showed no statistical difference between biochar or fertilizer treatments. Laboratory measurements of soil moisture content indicated a statically significant greater (p<0.05) ability of biochar to retain and provide moisture at the 25 Mg ha\(^{-1}\) rate of biochar application level, but not at the 5 Mg ha\(^{-1}\) rate. Moisture did not vary significantly between fertilizer treatment levels in any of the analyses.

Laboratory measurement of moisture retention (i.e. tension table and pressure plate analysis) was not statistically significant at any of the tested matric potentials (0.1-1500 kPa). However, AWC was significantly greater at the 25 Mg ha\(^{-1}\) application on both 50% and 100% N fertilizer plots at 0-10 cm and 10-20 cm depths. The mean AWC, calculated by the difference between FC (-33 kPa) and PWP (-1500 kPa), from both N fertilizer treatments was calculated to be 0.21, 0.21, and 0.26 cm\(^3\) cm\(^{-3}\) for the control, 5 Mg ha\(^{-1}\), and 25 Mg ha\(^{-1}\) soils, respectively.

6.4.4 Specific surface area
SSA of the soil increased in all years following application of biochar although the results were not significant at the p<0.05 confidence level. In the first, second and third years after application SSA was calculated to be 4.88, 5.50 and 9.55 m² g⁻¹ for the control, 5 Mg ha⁻¹, and 25 Mg ha⁻¹ soils, respectively. No differences were found between fertilizer treatments.

6.4.5 Aggregation

Determination of WSA, GMD, and MWD were severely confounded by the presence of biochar. Although there were statistically significant differences in WSA, for example, these included many “quasi-biochar aggregates” in which both large and small quantities of biochar were attached. Simply removing these quasi-biochar aggregates was not possible due to the high percentage of aggregates which had some amount of biochar present within. Both GMD and MWD, which are derived from the same methodological approach, were not able to be adequately quantified.

6.4.6 Earthworm population

Extraction of earthworms using formalin showed no statistically different treatments by plot. There was significant heterogeneity among plots. The number of earthworms varied by 8 to 124 m⁻² subplots. The total wet mass varied by 3.88 g m⁻² to 124.48 g m⁻². No significant differences were found in the mean weight of earthworm individuals.

6.5 Discussion
Biochar significantly impacted bulk density ($\rho_b$), total porosity ($f_t$), and available water capacity (AWC) at the p<0.05 confidence interval. Specific surface area (SSA) increased with biochar application but not significantly. The results of aggregation study (water stable aggregates [WSA], geometric mean diameter [GMD], and mean weight diameter [MWD]) were cofounding by the presence of biochar. No significant differences were found in in-situ gravimetric moisture, penetration resistance, or earthworm populations.

The decrease in soil $\rho_b$ was not surprising given the significantly lower density of the biochar (0.45 g cm$^{-3}$) compared with the bulk density of the native soil at the 0-10 cm depth (1.54 g cm$^{-3}$). The resulting increase in $f_t$ with biochar was therefore also expected. The increase of storage porosity corroborated the significant increase in AWC. The ability of biochar amended soils to retain moisture is

The measured SSA of oak-derived biochar was somewhat similar to results obtained by Mukherjee et al. (2011) which found SSA from N$_2$-adsorption of 2±1 and 225±9 for oak-derived biochar produced at 400 and 650 °C, respectively, in a laboratory setting. In the same experiment, the authors found CO$_2$ surface area (not determined in this experiment) to be 252±90 and 528±57 m$^2$ g$^{-1}$, thus highlighting the importance of the specific probe gas being used to establish the monomolecular layer. Use of CO$_2$ or ethylene glycol monoethyl ether (EGME) may provide a more accurate means of determining...
actual surface area of microporous materials (Heilman et al., 1965; Laird et al., 2010).

Freeze-thaw dynamics are likely to be the dominant physical breakdown process of biochar in temperate soils (Lehmann et al., 2009). Breakdown of biochar through freeze-thaw cycles can increase the accessibility to internal micropore space and, in turn increase the retention of water and nutrients as well as increasing refugia for microorganisms. It can also lead to increased mineralization and transport of biochar particles (Lehmann et al., 2009). Eastman (2011) found that freeze thaw cycles resulted in a decrease in the tensile strength of the oak-derived biochar used in the same experiment and increased the proportion of small biochar fractions. The biochar was found to decrease in tensile strength by 59% after nine cycles of freeze thaw in a laboratory setting.

Geophagous earthworms may play an important role in reducing the size, chemical modifying and transporting biochar materials through the soil profile (Lehmann, 2011). Biochar ingestion and excretion of biochar particles is well documented (Topoliantz and Ponge, 2003; Van Zweiten et al., 2010; Gomez-Eyles et al., 2010). Topoliant and Ponge (2003) documented the ability of earthworms to decrease the size of biochar particles after ingestion and extraction. Reduction of biochar size within the gizzard of the earthworms could increase the quantity of reactive surfaces available for increasing nutrient retention and increased nutrients for plant uptake or microbial decomposition. Both positive and negative impacts have been found with the use of biochar. Van
Zweiten et al. (2010) found a preference of some earthworms toward soils amended with biochar in an Australian Ferrosol. Decrease in the mass of earthworms following hardwood biochar application has also been noted potentially due to the presence of polyaromatic hydrocarbons (PAHs) (Gomez-Eyles et al., 2011). Ultimately, earthworm populations are likely to be most impacted by the availability of above- and below-ground biomass which is the main food source for metabolic activity and, thus, survival and reproduction. That there was no directly observable impact on earthworm population in this study suggests that the biochar did not have a significant negative impact on earthworm populations. It could be deduced that either biochar did not lead to lasting increased mortality or deterrence of earthworms from plots containing biochar. Topoliantz et al. (2006) have hypothesized that excretion of biochar by earthworms may play an important process in mixing, and stabilization biochar residues within aggregates.

Although the impact of biochar on WSA, MWD, and GMD were not able to be quantified due to the confounding nature of the biochar material on the methodology used to quantify soil aggregates, it is likely the biochar has a significant and important impact on the actual processes and impacts of soil aggregation. The quasi-aggregates formed from biochar, soil, root biomass, and fungal hyphae may have an analogous function in terms of providing soil structure and preventing erosion and compaction. The observations of biochar inclusion within aggregate formation confirms other research finding that biochar preferentially tends to reside within aggregates as opposed to free, non-
associated particles (Brodowski et al., 2006; Liang et al., 2008). Aggregates may form around biochar due to the highly reactive oxidized surfaces which promote nutrient retention and biological activity and, thus, the accumulation of organic matter and organic matter coatings on biochar surfaces (Lehmann, et al., 2009). Root biomass and mycorrhizal fungal hyphae increase the formation and stabilization of biochar-quasi aggregates (Warnock et al., 2007, Lehmann et al., 2009).

Peng et al (2011) reported a decrease in aggregate stability of 1-17% when amended with rice-derived biochars at varying high treatment temperatures with the exception of one biochar type. Peng et al. used a simple method (Le Bissonnais’, 1996) whereby soil are immersed in water and ethanol and subsequently agitated and sieved by hand. Differences between the observations found here and those of Peng et al. are likely to be due to both the biochar type being utilized and to the methodology for determining WSA.

6.6 Conclusion

The application of biochar at both 5 Mg ha\(^{-1}\) and 25 Mg ha\(^{-1}\) significantly impacted several significant soil physical properties including decreased \(\rho_b\), and increased AWC, \(f_T\), SSA. No impacts were found among in-situ gravimetric moisture content and earthworm populations. Although WSA was significantly increased as was MWD and GMD, the results were also confounded by the biochar particles themselves which tended to form quasi biochar-soil aggregates. The formation of these quasi-aggregates may play an important role in providing
soil structure and preventing erosion. Overall, the results of this study point to an improvement in soil physical properties and to, more broadly, an increase in soil quality measurements in maize-soybean rotations in the U.S. Midwest. More research is likely necessary in other cropping systems and soil types to determine whether such impacts are likely in other agroecosystems.
6.7 References


Lehmann et al., 2009


**6.8 Tables and figures**
<table>
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<th>$f_T$</th>
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<td>0.21</td>
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</tr>
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</tr>
<tr>
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<tr>
<td><strong>100% N</strong></td>
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<td>0.13</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
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<td>-0.01</td>
<td>0.22</td>
<td>-0.01</td>
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<td><strong>25 Mg ha$^{-1}$</strong></td>
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<td>0.26</td>
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</tr>
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</table>

Table 24: Total porosity ($f_T$), transmission porosity ($f_{trans}$), storage porosity ($f_{storage}$), and residual porosity ($f_{residual}$) in cm$^3$ cm$^{-3}$. SE = standard error, med. = median.
Matric potential (kPa)

<table>
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<tr>
<th>Matric Potential (kPa)</th>
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<th>0.6</th>
<th>10</th>
<th>33</th>
<th>100</th>
<th>300</th>
<th>1500</th>
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<td>Volumetric Water Content (cm³ cm⁻³)</td>
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<td>SE</td>
<td>Med</td>
<td>Mean</td>
<td>SE</td>
<td>Med</td>
<td>Mean</td>
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<tr>
<td>0 Mg ha⁻¹ 50% N</td>
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<td>0.02</td>
<td>0.48</td>
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<td>0.01</td>
<td>0.43</td>
<td>0.39</td>
</tr>
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<td>0 Mg ha⁻¹ 10% N</td>
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<td>0.50</td>
<td>0.47</td>
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</tr>
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<td>0 Mg ha⁻¹ 5% N</td>
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<td>0.01</td>
<td>0.50</td>
<td>0.47</td>
<td>0.01</td>
<td>0.46</td>
<td>0.41</td>
</tr>
<tr>
<td>0 Mg ha⁻¹ 1% N</td>
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<td>0.01</td>
<td>0.47</td>
<td>0.44</td>
<td>0.01</td>
<td>0.44</td>
<td>0.39</td>
</tr>
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<td>0 Mg ha⁻¹ 0.5% N</td>
<td>0.48</td>
<td>0.02</td>
<td>0.49</td>
<td>0.44</td>
<td>0.02</td>
<td>0.45</td>
<td>0.38</td>
</tr>
<tr>
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<td>0.02</td>
<td>0.46</td>
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<td>0.02</td>
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Table 25: Moisture retention at various pressures (kPa) expressed in terms of volumetric water content (cm³ cm⁻³).
Table 26: Pearson correlation matrix for biochar applied at 25 Mg ha⁻¹ rate (Biochar) for bulk density (ρₚ), available water capacity (AWC), total porosity (fₜ), transmission porosity (fₜrans), storage porosity (fₜstorage), residual porosity (fₜresid), field capacity (FC), specific surface area (SSA), mean soybean biomass (S. Biomass), mean soybean grain yield (S. Grain), mean maize biomass (M. Biomass), and mean maize grain yield (M. Grain).
### Table 27: Bulk density (g cm\(^{-3}\)) of plots with 0, 5 and 25 Mg ha\(^{-1}\) biochar and two rates of N fertilizer at three depths (0-10 cm, 10-20 cm, and 20-30 cm). SE = standard error, med.= median.
Figure 52: Bulk density (g cm$^{-3}$) at three depths measured in 2011 using core technique (bars indicate standard error).
Figure 53: Sieving of soil with 25 Mg ha\(^{-1}\) biochar addition.
Figure 54: Soil-biochar complexed “quasi-aggregate.”
Figure 55: Two methods of bulk density determination showing biochar with 25 Mg ha\textsuperscript{-1} treatment.
Figure 56: Moisture characteristic curve at 0-10 cm depth expressed in terms of volumetric moisture content (cm$^3$ H$_2$O cm$^{-3}$ soil) (bars indicate standard error).
Figure 57: Field measurement of gravimetric moisture content (g H₂O g⁻¹ soil) bars indicate standard error of the mean.
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<th>(PWP)</th>
<th>(FC-PWP)</th>
<th>AWC</th>
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<td>0.38</td>
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<td>0.26</td>
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Table 28: Soil moisture retention expressed in terms of volumetric water content (cm$^3$ H$_2$O cm$^{-3}$ soil) for each plot at the 0-10 cm depth level.
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<th>Plot</th>
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Table 29: Soil bulk density ($\rho_b$; g cm$^{-1}$) for each plot at the 0-10, 10-20, and 20-30 cm depth levels in 2011 and 2012.
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<th>2012</th>
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Table 30: Specific surface area (SSA; m$^2$ g$^{-1}$) for each plot at the 0-10 depth level in 2010, 2011, and 2012.
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Table 31: Pore size distribution for each plot at the 0-10 depth level where gravitational or transmission pores are >50 µm, storage pores are 0.5-50 µm, and residual or boding pores are (<0.5 µm). The total volume of the pore space in each of these was calculate by differences in volumetric water content at specific matric potentials.
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Table 32: Earthworm count (#) and mass (g) per plot.
Figure 58: Earthworm (Oligochaeta) collection in May 2011.
Chapter 7:

Conclusion and synthesis

Strategies at all levels are necessary to deal with the food-water-energy-soil-population-climate nexus. There exist a large array of “fast-action and win-win strategies” which are practical, low-cost measures to deal with climate change and food security. There are potentially large ancillary benefits to public health and protection of ecosystem services. The research focus of this dissertation was on one potential win-win strategy, biochar application to agricultural soils and the resulting impacts to crop productivity, soil quality and GHG emissions. Overall, we found generally positive results in terms of improvements to soil quality and agronomic yield. Yet, the data also suggest a possible increase in CO$_2$ emissions and lowered productivity with reduction of N fertilizer.

The biochar did have a positive impact on a number of chemical properties and, particularly with the maize crop, lead to a significant increase in crop productivity (Chapter 4). However, the biochar did not significantly increase nitrogen fertilizer use efficiency (NFUE) as had been hypothesized.
Instead, the data indicate that the biochar decreased NFUE at the lower rate of application potential via N immobilization by microbial organisms. Whether this effect is lasting requires more in-depth and longer-term research. It is possible that once the labile C from the biochar was initially mineralized that the N that has been previously been immobilized by soil biota would again become plant available. Moreover, the oxidation of biochar surfaces over time could lead to increased net negative charge (e.g. greater CEC) of the biochar which would lead to enhanced NH$_4^+$ adsorption.

The soil GHG emissions resulting from biochar application also indicated mixed results (Chapter 5). N$_2$O emissions were significantly lower with plots receiving N-fertilizer application. CH$_4$ consumption was also greater on plots receiving biochar suggesting that either biochar lead to a greater predominance aerobic environments in which methanotrophs were likely to outnumber methanogens, that CH$_4$ was potentially captured on biochar surfaces and subsequently oxidized, or a combination of these and other factors. While soil emissions of N$_2$O and CH$_4$ decreased with biochar application, there was an increase in CO$_2$ flux from soil with biochar potentially due to an increase of labile C from the biochar itself or from stimulated decomposition of native SOC pools. The resulting increase in CO$_2$ emissions caused an overall increase in radiative forcing with the application of biochar, as the CO$_2$ emissions far outweighed the radiative forcing of either N$_2$O or CH$_4$. This suggests a more
limited role for biochar to actually reduce soil GHG emissions than has been suggested by other research. It is possible that observed increases in CO₂ emissions were only temporary. The study period was only two years. If biochar introduced labile C material that was the source of increased net emissions, it is likely that CO₂ emissions would decrease as the metabolically available C is decomposed and respired. More and longer-term research is clearly needed to better understand the impact of biochar on GHG emissions from soil which are likely to vary considerably among soil types, cropping systems, and climate.

The impact of biochar on soil physical properties (Chapter 6) showed overall positive overall effects. The application of biochar at both 5 Mg ha⁻¹ and 25 Mg ha⁻¹ significantly impacted several significant soil physical properties including decreased ρₚ, and increased AWC, fᵣ, and SSA. No impacts were found among in-situ gravimetric moisture content and earthworm populations. Although WSA was significantly increased as was MWD and GMD, the results were also confounded by the biochar particles themselves which tended to form quasi biochar-soil aggregates. The formation of these quasi-aggregates may play an important role in providing soil structure and preventing erosion. Overall, the results of the biochar research point to an improvement in soil physical and chemical properties and to, more broadly, an increase in soil quality measurements in maize-soybean rotations in the U.S. Midwest. More research is
required, however, corroborate and expand the knowledge of biochar impacts in temperate agroecosystems. Moreover, some of the results—namely, increased CO₂ emissions and decreased NFUE at lower levels of application—suggest the need for caution in ascribing potential benefits of biochar to GHG management.
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409


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437
