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Samuel JW Peters Date

The Environmental and Health Effects of Emerging Agricultural Systems

By

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Doctor of Philosophy

Environmental Health Sciences

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The Environmental and Health Effects of Emerging Agricultural Systems

By

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B.A., St. Olaf College, 2014

Advisor: Eri Saikawa, Ph.D.

An abstract of
A dissertation submitted to the Faculty of the
James T. Laney School of Graduate Studies of Emory University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in
Environmental Health Sciences
2019

Abstract

The Environmental and Health Effects of Emerging Agricultural Systems
By Samuel James Windsor Peters

As we strive to discover new ways of producing food for a growing and urbanizing population, we need to assess the impacts of these emerging systems on the environment and health. The first study of this dissertation analyzed the soil greenhouse gas (GHG) and ammonia ($NH_3$) fluxes in a living mulch system compared to three other conventional systems to understand the differences and potential soil parameters driving them. Carbon dioxide ($CO_2$), nitrous oxide, and $NH_3$ fluxes were higher between rows of corn in living mulch plots compared to other systems, influenced partially by soil moisture, temperature and nitrogen compounds. Increased soil organic carbon in living mulch plots indicated an overall sink for carbon. The second study measured the same soil trace gases in corn with five nitrogen sources including cowpea intercropping and biochar amended systems and calculated a net carbon equivalent (CE) for each system accounting for other agricultural inputs. $CO_2$ fluxes and net CE were higher in intercropping and urea fertilizer plots when controlling for soil moisture and temperature. $CO_2$ and $NH_3$ fluxes were lower in plots with biochar compared to those without. Plots with biochar had lower net CE, until accounting for the production of biochar, indicating the importance of assessing agriculture wholistic to understand the overall impacts. The final study used community engaged research (CER) to assess heavy metal soil concentrations in Atlanta urban agricultural and residential sites under two different risk frameworks. Most samples were below Environmental Protection Agency regional screening levels, but several sites were above University of Georgia low risk levels, indicating potential changes in risk depending on the framework used. This study also indicated some best practices to reducing concentrations below low risk levels in both frameworks. Finally, through community and regulatory partnerships, this study led to the discovery and subsequent cleanup of a residential lot with illegally dumped slag, indicating the potential of CER to create direct impacts on environmental justice issues. Each of these studies highlights the tradeoffs that sometimes exist between the benefits of emerging agricultural systems and impacts on the environment and health.

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# Acknowledgements

There are countless people who have made this dissertation possible, and I will be forever grateful for their help. I would like to thank most of all, my advisor, Dr. Eri Saikawa. Dr. Saikawa has been my biggest supporter from the moment I applied to the PhD program. She has pushed me to become a better scientist, while encouraging me to carry out research that excited me and made an impact in the community. I can say without a doubt, I would not have finished this journey without her.

I would also like to thank Drs. Nicholas Hill, P. Barry Ryan, Dana Barr, Diana Signor, Paulo Ivan Fernandes, and Alexander Avramov for their mentorship throughout each project. I am also indebted to the numerous colleagues who have helped with lab analysis including but not limited to Dr. Lori Sutter, countless EMBRAPA employees, Priya D’Souza, MPH and Parinya Panuwet, PhD. Several other students have helped with field work for all of these projects, especially in the Saikawa lab, and I am very grateful to all of the hard days in the field.

I’d like to also express gratitude to my family and friends for supporting me from start to finish of this journey. To my parents, Dale and Tally Peters, for being there whenever I felt like I wasn’t PhD material. To my sister, Erin Peters, who was always willing to listen to me vent or study together down the final stretch. To my friends, especially Tyler Chavers, who reminded me that there was life outside of school when I needed it. To Grete Wilt, for believing in me when I didn’t always believe in myself and pushing me to be the best person I could be. Finally, to my two dogs, Sasha and Ranger, for reminding me that no matter how bad a day can be, there will always to two barking, smiling faces at home letting me know life is pretty good.

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# Chapter 1: Introduction

Growing food for a world that is becoming more populated and urbanized is one of the great challenges facing humanity. The Green Revolution has allowed us to increase our agricultural yields, but often times at a cost to the environment and health[1]. Investigating and implementing novel systems that can reduce these negative impacts while maintaining productivity is essential to cultivate food in a wholistic manner. The following dissertation presents the original data and findings from three studies on emerging agricultural systems to discern how those systems affect the environment and human health compared to conventional methods. The goals and context of each study were 1) Measure soil trace gas fluxes, determine potential soil mechanisms contributing to the fluxes, and calculate the overall climate impact of a white clover living mulch system compared to conventional systems in northern Georgia. 2) Measure soil trace gas fluxes of corn cropping systems with five different sources of nitrogen including cowpea intercropping as well as with and without biochar to compare their overall global warming impact in Northeast Brazil. 3) Use community engaged research (CER) to explore soil heavy metal concentrations in urban growing spaces in Atlanta to understand how different risk frameworks affect the data and what common practices can reduce exposure.

Each of these studies investigated one or more emerging agricultural system in order to understand how they affect the environment and human health. Working to understand the complexities surrounding agriculture, the environment, and health will be crucial under the challenges of climate change and limited access to fresh food in cities. When taking into account these multiple impacts, it becomes clear that no agricultural system is a perfect answer to these challenges.  However, by studying these systems and assessing them holistically, we can continue to feed a growing and diverse population while reducing negative impacts on the environment and health.

## Study 1: Background and Design

Agriculture is one of the largest sources of the three major anthropogenic GHG's, carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), and methane ($CH_4$)[2,3,4], partially through soil fluxes and fertilizer application[5,6,7]. Additionally, fertilizer application can increase $NH_3$ fluxes[8] and form secondary inorganic aerosols (SIA), a species of particulate matter ($PM_{2.5}$), which can cause respiratory and cardiovascular health problems[9]. As the world continues to feel the effects of climate change through decreased food security[10,11], it is important to investigate agricultural systems that can produce food without the contributions to climate change and air pollution of conventional systems.

Cover crops have been shown to lower climate impacts through increased soil organic carbon (SOC)[12] and reduce soil GHG emissions[13,14], although this effect hasn't been seen for $N_2O$ fluxes in studies with more than one year of measurements[15]. A living mulch system (LMS) is a modified cover crop systems comprised of a legume cover crop that is kept alive during the growing season to provide nitrogen to the cash crop[16]. In this study, white clover was the cover crop and corn was the cash crop. LMSs have numerous benefits such as reduced fertilizer, pesticide, and runoff[16,17,18,19,20] making it an ideal candidate to study as a potential sustainable technique. Only the $N_2O$ soil fluxes have ever been observed in an LMS[21], and there is a need to measure other gases and soil parameters to gain a better understanding of the entire environmental impact of LMSs.

In order to understand how LMSs compare to other cover crops, this study measured the soil trace gas fluxes in the white clover and corn LMS and three conventional corn production systems; a suppressed crimson clover cover crop, a suppressed cereal rye cover crop, and no cover crop. We hypothesized that increased SOC in the LMS plots would indicate a net sequestration of carbon, that $N_2O$ fluxes would be higher in LMS plots as seen in Turner et al. (2016), and that $NH_3$ fluxes would be lowest in LMS plots due to reduced fertilizer application.

Gas fluxes were measured in three plots of each system over two growing seasons, 2016 and 2017. Fluxes were measured weekly using static chambers and gas chromatography (GC) or an infrared gas analyzer (IRGA) for the GHG's and vacuum pump acid traps for $NH_3$. Samples were taken once a week over the growing season, and background samples were taken during the winter of 2016-2017. All fluxes were analyzed using an ANOVA and then Tukey's comparisons to see how LMS plots differed from the others. Additionally, a variety of soil parameters including labile carbon were measured to determine factors affecting flux differences. $N_2O$ and $CO_2$ fluxes were put into a linear regression with a variety of soil parameters that were measured weekly to understand the processes that could be causing differences in soil fluxes.

## Study 2: Background and Design

Brazil is an ideal location to continue investigating the adaptability to and mitigation of climate change in agricultural systems due to increased stressors from heat and drought and large GHG contributions from agriculture in the country[22]. No till cropping systems and increased biological nitrogen fixation (BNF) have been estimated to offset land-use change carbon losses in South America by 24.3 and 4.2 percent respectively[23]. The semi-arid Caatinga region in the northeast has depleted soil organic carbon (SOC) pools[24] and is predicted to have significant detrimental effects on their agricultural sector from climate change[25,26,27]. This second project explored the impact of a variety of nitrogen sources on the soil trace gas fluxes of corn growing systems in Northeast Brazil working with EMBRAPA (The Brazilian Agricultural Research Corporation) Semiarido. Additionally, a net carbon equivalence (CE), or overall loss/gain of kg C, for each system was calculated to determine their overall climatic impact.

Intercropping, or cultivating multiple crops at the same time, is becoming commonly used in Brazil and has the potential to increase or maintain productivity while lowering environmental impact[28,29]. Similar to LMS, the horticultural benefits of intercropping are well known, but the soil trace gases are relatively understudied and unexplained[30,31,32,33]. Bacterial inoculation of seeds is another potential method for reducing soil trace gas fluxes while improving soil health[34,35]. Biochar, or biomass burned in the absence of oxygen, has been debated as a soil amendment that can improve soil health as well as mitigate GHG's through a variety of mechanisms depending on the source of the biochar and the soil type[36,37,38]. However, several studies dispute the agricultural benefits of biochar, and its effect on seasonal gas fluxes is debated with the underlying mechanisms still relatively unknown[36,39]. Additionally, calculating a net CE could be particularly relevant to biochar amendments, as the production of the biochar itself leads to a large loss of carbon through $CO_2$ and black carbon emissions during the burning process[40,41]. To our current knowledge, this loss of carbon has not been accounted for in any studies assessing the climate impacts of biochar amendments.

To assess the impacts of these nitrogen sources and biochar, $CO_2$, $N_2O$, $CH_4$, and $NH_3$ fluxes were measured in corn growing systems with nitrogen supplied from five different sources; a cowpea intercropping system, urea-based fertilizer, a government-recommended bacterial inoculant, a bacterial inoculant created by the Fernandes lab at EMBRAPA Semiarido, and a control. Plots were then amended or not with biochar made from mango branches. The overall goals were to assess the potential of cowpea intercropping to match previous findings of other similar systems lowering net CE, determine if biochar was effective at reducing soil emissions and net CE, and explore how agricultural inputs affected net CE.

Eight plots of each nitrogen source were measured at two different agricultural research sites. Four plots of each nitrogen source at each site were amended with biochar made from mango branches. GHGs were sampled using static chambers and GC similarly to Study 1 and explained in detail in Chapter 3. $NH_3$ was sampled using a vacuum pump acid trap and static bottles. All plots were sampled over one growing season from January through June 2018. Samples were taken every two weeks throughout the growing season, with an two weekly measurements following fertilizer application. Differences in mean fluxes as well as seasonal sums were calculated. A linear regression for all gases was performed controlling for soil temperature and moisture described in detail in Chapter 3. Finally, the net CE for all N-sources and with/without biochar was calculated taking into account farming inputs such as fertilizer, irrigation, and tillage, as well as the production of biochar to obtain a more complete estimation of impact on climate change.

## Study 3: Background and Design

Novel agricultural systems are also being implemented in cities, as impeded access to fresh food is a serious public health problem in many urban spaces in the US[42]. Urban agriculture is being promoted as a solution to increase access to fresh food, due to the social, nutritional, and overall health benefits it can provide[43,44,45]. However, urban soils may be contaminated with heavy metals[46,47,48] and the contamination is often in sites where lower income or minority populations reside[49], areas where access to fresh food is especially limited. There is a risk of exposure to these metals, especially in children, through ingestion of the soil[50]. Previous research on lead (Pb) in urban growing spaces suggests that the benefits of urban agriculture outweigh the risks of exposure to Pb due to reduced soil contamination from soil amendments often used in urban agriculture and low uptake of Pb in plants[51]. However, further sampling of other metals is needed, and studies do not engage with the potentially exposed communities growing the food in the research process.

The third study of this dissertation used community engaged research (CER) to measure heavy metal concentrations in residential and urban growing soils in West Atlanta. Previous research on urban agriculture has been criticized for not working through an inclusive lens[43,52,53]. Factors such as social inclusion, access in underprivileged neighborhoods, and informational accessibility should be included in urban agriculture projects and research[54]. CER, or having community members involved through the research process, is one method that can better address these issues[55] and has been successfully employed in other studies regarding urban agriculture[56]. Using CER effectively can increase knowledge of the scientific process and trust between the public and scientists[57]. No studies to our knowledge have analyzed heavy metals at urban agriculture sites using CER, so there is an opportunity to assess the impacts on soil contamination and risk with community input and guidance.

This study employed CER in all facets including project development, sites election, sampling collection, and data presentation. Samples were taken from 3 rural background and 19 urban sites in West Atlanta in partnership with Historic Westside Gardens (HWG), an organization focused on creating home gardens to cultivate community relationships and development. Each site was divided into decision units (DU) according to potential differences in metal concentrations, such as different crops, proximity to older homes, or potential contamination from previous site history. Soil was sampled using the incremental sampling method (ISM) to ensure a representative sample, and HWG partners were trained in ISM technique. The presence of metal refining slag was identified in one residential site by an HWG member. Therefore, this site was sampled heavily due to the unknown nature of soil contamination and potential for elevated heavy metals. Slag samples from this site were also analyzed separately from the soil. Samples were analyzed with x-ray fluorescence (XRF). The mean 95% upper confidence limits (UCL) of each DU and site were compared using a T test. Overall UCL means were compared between rural, urban, and slag sites. Finally, UCL means were compared between different types of beds that generally had non-native, amended soil present as well as actively growing versus not growing sites to ascertain how practices affect soil concentrations of heavy metals. Methods such as new top soil, raised beds, or soil amendments have been shown to ameliorate the impacts of heavy metal contaminated soil[58,59].

Risk from soil contamination in the United States is typically analyzed through the lens of the Environmental Protection Agency's (EPA) regional screening levels (RSL) for residential soil[60]. However, there are other agencies, including the University of Georgia, with lower risk levels (LRLs) than the EPA for agricultural soils due to the increased human interaction compared to residential soil[61,62,63]. There are no studies comparing the EPA RSLs to other risk levels that account for increased interaction in agricultural soils on the same set of urban soil samples. To assess how a risk framework with lower concentration limits compares to EPA RSLs, all UCLs were compared to the University of Georgia's LRLs for agricultural soils to determine if this changed the number of samples and sites deemed as low risk. Finally, potential best practices for reducing exposure such as raised beds were compared in the context of the two risk levels.

## Specific Aims

The detailed specific aims for each study are as follows:

Study 1

1. Examine any significant differences in soil GHG or $NH_3$ fluxes between white clover living mulch, two suppressed cover crop, and bare soil systems for growing corn in northern Georgia
2. Measure soil parameters in each system to determine potential mechanisms contributing to differences in soil trace gas fluxes

Study 2

1. Examine any significant differences in soil GHG or $NH_3$ fluxes between five different nitrogen sources and with/without biochar amendment in corn cropping systems in northeastern Brazil
2. Determine the net carbon equivalence of these cropping systems taking into account other agricultural inputs including the production of biochar

Study 3

1. Measure baseline soil heavy metal concentration and bioavailability in agricultural and residential spaces in west Atlanta using community engaged research throughout to promote inclusion and sustainability
2. Analyze heavy metal concentrations in the context of two different regulatory risk levels, one with agricultural routes of exposure and one without, across sample location and growing practices

## Chapter 2: Soil Trace Gas Fluxes in Living Mulch and Conventional Agricultural Systems

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## Abstract

Row crop agriculture is a significant source of two major greenhouse gases (GHG), carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), and the air pollutant precursor, ammonia ($NH_3$). Fluxes of these naturally-occurring trace gases are often augmented by agricultural practices, such as fertilizer application, tillage, and crop systems management. A living mulch system (LMS) maintains a live cover crop year-round and are an emerging agricultural system that can minimize environmental impacts (e.g. reduced pesticides), while maintaining yields. Corn grown in a white clover LMS has the potential to reduce GHG and $NH_3$ emissions through soil carbon sequestration and lower fertilization rates. This study compared soil gas fluxes in a white clover LMS with two other cover crop and a no cover crop agricultural system. Infrared and gas chromatography measurements were taken over two years in northern Georgia, USA. $CO_2$ and $N_2O$ mean fluxes (5.78 µmol $m^{-2}$ $sec^{-1}$ and 2.60 µmol $m^{-2}$ $hr^{-1}$, respectively) from between corn rows in LMS plots exceeded those from other treatments. Soil temperature, moisture, potentially mineralizable nitrogen, and nitrate partially explained these flux differences. Mean $NH_3$ emissions were higher in the LMS (497 µg $m^{-2}$ $hr^{-1}$) compared to the no cover crop system (210 µg $m^{-2}$ $hr^{-1}$). Increased $N_2O$ and $NH_3$ fluxes could be from extended nitrogen release through clover decomposition. These results do not indicate a strong soil trace gas mitigation potential for LMS. However, the LMS significantly increased labile carbon, offsetting soil GHG emissions and improving soil health.

## Key Terms

Living mulch, soil trace gas flux, greenhouse gas

## Abbreviations

Abbreviations: Living mulch system (LMS), greenhouse gas (GHG), climate-smart agriculture (CSA), potentially mineralizable nitrogen (PMN), soil organic carbon (SOC), infrared gas analyzer (IRGA), gas chromatography (GC), permanganate oxidizable carbon (POXC), white clover (WC), crimson clover (CC), cereal rye (CR), traditional bare soil (Tr)

## Introduction

Carbon dioxide ($CO_2$), and nitrous oxide ($N_2O$) are two key greenhouse gases (GHG) that make up the majority of anthropogenic contributions to climate change[64]. Over 20% (10-12 Gt $CO_2$ eq $yr^{-1}$) of anthropogenic GHG emissions come from agriculture, forestry, and land use change[3]. Within those three sectors, agriculture has become the largest contributor since 2010, emitting 11.2% of total GHG emissions annually (5.4 Gt $CO_2$ eq $yr^{-1}$ in 2012)[4]. Approximately 30-38% of agricultural GHGs and the largest anthropogenic contributions of $N_2O$ come from soils in response to inputs such as manure and synthetic nitrogen (N) fertilizer application[3,5,6,7]. Agricultural practices that mitigate GHG emissions have the potential to reduce overall GHG emissions and increase the feasibility of meeting the 2°C increase limit outlined in the Paris Agreement within the United Nations Framework Convention on Climate Change[65,66].

N-based fertilizer application is also estimated to contribute 10-20% of the US total of anthropogenic ammonia ($NH_3$) emissions[8]. $NH_3$ emissions contribute to increased levels of fine particulate matter ($PM_{2.5}$) through the formation of secondary inorganic aerosols (SIA). $PM_{2.5}$, including SIAs, cause respiratory, cardiovascular, and other health issues[9]. Using agricultural systems that reduce soil $NH_3$ emissions could decrease surface SIA formation and $PM_{2.5}$ concentrations[67].

Climate-Smart Agriculture (CSA) is a new paradigm for climate-risk management in agriculture that seeks to mitigate climate change, promote adaptation to climate change impacts, and enhance farm productivity and food security [68]. Using a cover crop, i.e. replacing bare fallow in the winter with crops that are suppressed and plowed as green manure in the spring, is a CSA management technique that increases soil organic carbon (SOC), offsetting GHG emissions and improving soil health[69]. Studies have shown reduced soil GHG's in cover crops compared to traditional tillage and no-till agricultural systems[70,13,14]. However, a meta-analysis demonstrates that $N_2O$ reductions are only present in experiments lasting less than a year, so further long-term studies are needed to determine overall effects of cover crops on $N_2O$[15].

A living mulch system (LMS) is a modified cover crop system where a legume cover crop is only suppressed where the cash crop is planted. The remaining cover crop actively grows throughout the cash crop's growing season[16]. LMSs have been shown to provide a variety of benefits including reduced erosion, reduced pesticide and fertilizer use, improved soil organism biodiversity, and reduced nitrate leaching, and function best in areas with ample available water[16,17,18,19,20].

To date, only one study has measured soil gas flux in an LMS, examining $N_2O$ emissions in a kura clover (*Trifolium ambiguum*) and corn (*Zea mays*) production system[21]. This study found that cumulative area-scaled $N_2O$ emissions were higher in the LMS ($2.3 \pm 0.1$ kg N $ha^{-1}$) despite lower fertilizer inputs, compared to conventional corn production ($1.3 \pm 0.1$ kg N $ha^{-1}$). The majority of this increase came later in the growing season due to kura mineralization[21].

Quantification of other GHG emissions using a variety of legume cover crops need to be measured to assess the broader environmental impact of LMSs. For example, the kura clover used in the Turner et al. (2016) study is slower growing than white clover[71,16], which could affect gaseous N loss. Soil differences between Minnesota[21] and Georgia could also affect $N_2O$ fluxes. Additionally, flux values should be measured with concurrently measured soil parameters to understand the soil processes contributing to GHG fluxes.

This study measured the $CO_2$, $N_2O$, and $NH_3$ soil fluxes and potential causal parameters in a white clover and corn LMS. We compared these fluxes to two other no-till systems (crimson clover and cereal rye) and a no cover crop system over two growing seasons. We hypothesized that in LMS plots: 1. $CO_2$ fluxes would be increased but would be offset by increased SOC; 2. Overall $N_2O$ fluxes would be greater than other systems as found in Turner et al. (2016), but lower than kura clover, as white clover grows faster; and, 3. $NH_3$ fluxes would be the lowest of all management systems due to reduced urea fertilizer application.

## Materials and Methods

### Site Description and Field Preparation

Over the 2016 and 2017 summer growing seasons, we measured the $CO_2$, $N_2O$, and $NH_3$ soil fluxes associated with four different management systems for growing corn: 1) a no-till system with crimson clover as the cover crop (CC), 2) a no-till system with cereal rye as the cover crop (CR), 3) a no-till white clover LMS (WC), and 4) a no cover crop system (Tr) (Figure 2.S1). Three 6.1 × 7.3 m plots of each management technique were located at the West Unit of the University of Georgia's J. Phil Campbell Sr. Resource and Education Center in Watkinsville, GA, USA, on a soil classified as a Cecil sandy loam (fine, kaolinitic, thermic type Kanhapludults) (Figure 2.1). Details regarding field treatment can be found in the Supplementary Material (Table 2.S1). 15 mm irrigation was applied using a Kifco (Havana, IL) T200L portable water wheel. Each irrigation event applied 20 mm water when water-filled pore space (WFPS) dropped to 40% or lower to replenish soil to 90% WFPS.

### Static Chamber Measurements of GHGs

Gaseous $CO_2$ and $N_2O$ fluxes were measured weekly over each growing season in opaque PVC static chambers according to previously used methods[72,73] with size and material modifications explained in Figure 2.S2. Three chambers were inserted in March, 2016 into each plot (Figure 2.1). In WC chambers, there was living clover biomass, but biomass in CC and CR chambers had been previously killed by herbicides (Roundup for crimson clover and Dicamba for cereal rye) and was on the surface of the soil. One chamber from each of the 12 plots was sampled weekly by extracting five 10 mL samples midmorning via syringe. Samples were drawn from chambers over 30 minutes at 7.5 minute intervals for the 2016 season and over 15 minutes at 3.75 minute intervals for the 2017 season. The time interval changed in 2017 to save time and reduce potential temperature effects on the chambers after initial analysis of 2016 data showed a 15-minute measurement would provide an accurate estimate of the flux. To account for heterogeneity in soil fluxes, each week we randomly selected one of the three collars to sample. Gas samples were analyzed using a Shimadzu Gas Chromatograph (GC)-2014 GHG, using a flame ionizing detector and methanizer for $CO_2$ and an electron capture detector for $N_2O$.

Background flux samples were taken on August 12th, November 5th, and December 28th, 2016 and February 1st, 2017 in the same 12 plots and with the same sampling techniques as in the growing season. During this time, there was no corn planted, and the data was assumed to be minimally affected by management techniques and used as a reference to control for baseline fluxes in regression analysis.

Following GC analysis, we plotted concentrations of each gas species over time and calculated fluxes using the following formula:

$$F = m \times V/A \quad [1]$$

Where F is soil flux in μmol $m^{-2}$ $sec^{-1}$ or μmol $m^{-2}$ $hr^{-1}$ for $CO_2$ and $N_2O$ respectively, m is the rate of GHG concentration change over 30 or 15 minutes in μmol $m^{-3}$ $sec^{-1}$ or μmol $m^{-3}$ $hr^{-1}$, V represents chamber volume in $m^3$, and A is the chamber surface area in $m^2$. Only fluxes with a positive or negative slope with an $R^2$ of 0.75 or greater were included for analysis.

### $CO_2$ In-Field Infrared Gas Analyzer Measurements

A Licor-6400XT Portable Photosynthesis System Infrared Gas Analyzer (IRGA) was used to measure $CO_2$ and to verify the GC static chamber measurements in 2016[74]. IRGA samples were not taken directly in PVC chambers, but next to them, to allow for simultaneous sampling.

IRGA measurements were taken from every plot each week and recorded as an average of continuous individual measurements over a minimum change of 10 ppm $CO_2$. IRGA measurements were collected directly within corn rows (areas with no cover crop biomass) and half way between corn rows (areas with cover crop biomass) to determine if there were differences in respiration. Three replicates of both in row and between row measurements were taken in all 12 plots every week during the 2016 growing season. The average of these three replicates was used for data analysis, providing one value for each plot each week.

### $NH_3$ Acid Trap Measurements

$NH_3$ fluxes were measured with a static chamber and a vacuum pump acid trap in an open system configuration. Acid trap designs came from previously tested methods[75], with modifications including a Balston ammonia filter replacing an additional tube of acid before the chamber inlet for the ambient air, as well as using a reduced flow rate of 2 L $min^{-1}$ to match different chamber volume. Sampled air came from inside the chamber and was then bubbled through a fritted Midget impinger for two hours. WC and Tr plots were sampled each week, rotating chambers and plots randomly. Samples were analyzed colorimetrically in duplicate using

EPA method 350.1[76]. Due to only having two acid traps, only WC and Tr plots were sampled to obtain a high sample size for the two systems hypothesized to be most different.

### Soil and Environmental Parameters

Soil water content and temperature were measured using CS625 reflectometers (Campbell Scientific, Logan, UT) placed at two different soil depths (0-15 cm and 15-30 cm) between the corn rows. The rods were 30 cm in length and installed at an angle of 30 degrees from the surface. Water content data and temperature were measured and recorded on 10-min intervals, stored on data loggers, and downloaded weekly. A soil moisture release curve based on the van Genuchten equation[77] was created using the evaporation method[78] with a HYPROP device (Decagon, Pullman, WA) from soil collected from the plot area.

Corn canopy light interception was measured weekly until the tasseling (VT) stage of corn development. A line quantum sensor (Model LI 191sb, Li-Cor, Lincoln, NE) measured the amount of light above the corn canopy and the amount of light reaching the clover canopy in the WC plots, the surface of the cover crop residue in the CC and CR plots, or the soil surface in the Tr plots, at four locations in each plot. The percentage of light intercepted by the corn canopy was calculated using the following formula:

$$\%\text{ light interception} = [1-(\text{light at lower surface} / \text{light above corn canopy})] \times 100 \quad [2]$$

Eight soil cores were randomly sampled using a 1.5 cm diameter soil probe to a 15-cm depth weekly from each plot using a 1.5-cm diameter handheld soil probe. Soil cores were taken from the center two rows of the plot, the cores combined, air-dried, and stored at 4°C. Five grams of soil from each sample was extracted at 21°C with 40 mL of 1M KCl (cold extraction) and at 100 °C with 40 mL of 2M KCl (hot extraction) for $NO_3$–N and $NH_4$–N analysis[79]. Soil extracts were analyzed for $NO_3$–N and $NH_4$–N concentration using a TL-2800 Ammonia Analyzer. Soil potentially mineralizable nitrogen (PMN) was calculated as the difference between cold and hot $NH_4$ extractions. Two soil pits were dug on the periphery of the plots and 5 × 5 cm brass rings were inserted into the top 15-cm of soil. The rings and soil were dried at 105°C and the soil bulk density was calculated. The bulk density was used to calculate per hectare mass of $NH_4$–N, $NO_3$–N, and PMN. Bulk density, saturated hydraulic conductivity (Ksat), and total porosity were measured according to the core method, constant head method, and calculation from particle and bulk densities respectively[80,81,82]. Labile C was quantified measuring permanganate oxidizable carbon (POXC)[83].

$NO_3^-$, $NH_4^+$, and PMN were measured in paired plots with those where gas fluxes were measured in 2016 due to previous placement of soil sampling equipment before this experiment. In 2016, soil $NO_3^-$, $NH_4^+$, and PMN were averaged over all plots within two days of flux sampling and paired with the flux measurements from the same management technique on that day. In 2017, all soil N properties were measured in the same plots as flux samples. Finally, clover biomass data was measured weekly in all WC plots. Biomass measurements were used along with soil temperature to estimate the amount of respiration coming from clover versus soil in an attempt to infer soil only respiration in following analysis.

## Statistics and Missing Data

All statistical analyses were carried out in R version 3.4.1 using the packages aov, TukeyHSD, and lm. An initial ANOVA of all individual flux observations determined that there were significant differences in $CO_2$ and $N_2O$ fluxes between treatments. To specify these differences, mean GHG fluxes were compared between all four management techniques using Tukey's pair-wise comparison[84]. $N_2O$ comparisons used static chamber GC data for all time points.

$CO_2$ comparisons used between row IRGA data for 2016 and GC data for 2017. A student's T-test compared mean $NH_3$ fluxes in WC and Tr plots. Seasonal sums were also calculated using the average of all fluxes measured from a system on a sampling data. These averages were extrapolated over the time period between sampling times to estimate fluxes when not sampling.

A multiple linear regression of log-transformed (after normality testing with a Shapiro-Wilks test) individual observations of flux was performed to determine which soil and climatic parameters were related to differences in soil GHG fluxes found in the pair-wise comparisons, or which management techniques were still significantly different after controlling for these parameters. Management technique was included as a categorical variable in part, to control for differences in fertilizer application. Single variable, season specific, and management technique specific regressions were conducted initially to develop the final model for $N_2O$ and $CO_2$ as displayed below:

$$Y_s = \beta_0 + \beta_1 Tech_1 + \beta_2 Tech_2 + \beta_3 Tech_3 + \beta_4 Season_{2016} + \beta_5 Season_{2017} + \beta_6 Temp + \beta_7 Mois + \beta_8 LightInt + \beta_9 NO_3 + \beta_{10} NH_4 + \beta_{11} PMN + \varepsilon \quad [3]$$

**$Y_s$** denotes soil trace gas emissions with s for separate log transformed gas species ($N_2O$ or $CO_2$). The independent variables are as follows: **$Tech_1$** is CC, **$Tech_2$** is CR, **$Tech_3$** is WC compared to Tr as a reference, **$Season_{2016}$** and **$Season_{2017}$** compared to background measurements as a reference, **Temp** is soil temperature in °C at 15 cm, **Mois** is soil moisture between corn rows at 15 cm depth in volumetric water content, **LightInt** is light interception as the inverse of the percentage of light reaching the soil, **$NO_3$** is soil nitrate in μg/g, **$NH_4$** is soil ammonium in μg/g, and **PMN** is potentially mineralizable N in μg/g. Multicollinearity was tested for with a correlation matrix in all final models and was not found.

Percent change for each coefficient was calculated using the following formula:

$$\% \, Change = 100 * (e^{\beta - 1}) \quad [4]$$

Where $e$ is Euler's number and β is the coefficient for each term given by the linear regression.

For all final $CO_2$ and $N_2O$ models (N=292 and 203 respectively), soil temperature, moisture, and N compound surrogates were calculated for Tr plots from the average of all CR plots over the same time period. This was because instrumentation for these parameters was set up from previous experiments before Tr plots were created for this one. Tr plots had similar labile C to CR plots (Table 2.S2) and had equivalent fertilization amounts each year (Table 2.S1). Missing values for soil temperature, moisture, and N compound data were replaced with averages of the measurements taken the week before and the week after in plots with the same corn production system. This could bias results towards the null through misclassification, and underestimate the effects of these parameters in the linear regression.

Model parameters other than soil temperature and moisture were not measured during background sampling. Averages from the end of the 2016 season and the beginning of the 2017 season were paired with observed background fluxes. Light interception was considered to be zero during background periods, as no corn was present to shade the soil. $CO_2$ data from IRGA (2016) and GC (2017) measurements were combined for the $CO_2$ model.

In order to estimate $CO_2$ fluxes from soil without clover respiration, emissions due to heterotrophic respiration were estimated by subtracting clover respiration rates from total $CO_2$ flux observed. The clover respiration rates were derived using measured clover biomass and soil temperature and a previously developed curve of clover respiration over various temperatures[85]. The formula for the clover respiration estimation is shown below:

$$CO_2Clover = \frac{BM * 0.24 * \frac{b+m*T}{43,200}}{44} * 1,000,000 \quad [5]$$

Where **$CO_2$Clover** is the estimated $CO_2$ flux from clover in µmol $sec^{-1}$, **BM** is the clover biomass in mg within the chamber, **b** and **m** are the intercept in °C respiration rate in mg $CO_2$ $sec^{-1}$ and slope in respiration rate of respiration function derived from Beinhart (1962), and **T** is soil temperature in °C.

## Results

After analyzing means by management technique for all soil parameter measurements, porosity, Ksat, and labile C were all higher in WC plots, while bulk density was lower (Table 2.S2).

### $CO_2$

In between row GC and IRGA measurements correlated well ($R^2$=0.73) in 2016, with IRGA measurements greater than GC measurements in the same plot. Mean $CO_2$ fluxes for both 2016 and 2017 from between corn row measurements were higher in WC plots compared to other systems with differences of 2.99, 3.00, and 3.80 µmol $m^{-2}$ $sec^{-1}$ for WC-CC, WC-CR, and WC-TR, respectively (p-value <0.001 for all). This effect was not found in corn rows in 2016, where clover biomass was not present in the chamber (Table 2.1). However, the heterotrophic $CO_2$ flux estimation that subtracted clover respiration still showed significantly higher emissions compared to other techniques (Figure 2.2). This was likely because the heterotrophic estimates overestimated $CO_2$ flux early in the growing season compared to in row measurements (Figure S4). However, they matched well with in row fluxes in 2016 in the mid and late growing season (Figure 2.S4). The $CO_2$ fluxes in corn rows and between rows in WC plots differed significantly, unlike for other plots (Figure 2.S3), indicating clover respiration was indeed occurring when the clover switched from photosynthesis to respiration in the opaque sampling chambers. Higher $CO_2$ fluxes were observed in the WC plots in the early and middle of the growing season, before decreasing to background levels. Fluxes for all other treatments had smaller peaks in the middle of the growing season and decreased towards background levels (Figure 2.2). Cumulative sums for between row $CO_2$ fluxes were higher in WC plots for both growing seasons (Table 2.1) and were greater than total SOC sequestered per year in WC plots (Table 2.S2, 2.27 kg $m^{-2}$ versus 0.62 kg $m^{-2}$).

The multiple linear regression of individual log-transformed in between row $CO_2$ fluxes showed greater flux in CC, CR, and WC plots compared to Tr plots (p-value<0.001), with WC plots having the greatest increase (Table 2.2), confirming the results of the post-hoc ANOVA analysis. Soil temperature, moisture, and $NO_3$ were correlated with higher $CO_2$ flux (p-value <0.001, <0.001, 0.085 respectively). PMN was correlated with a decrease in $CO_2$ flux (p-value=0.026). Light interception and soil $NH_4$ did not have significant relationships with $CO_2$ flux (Table 2.2).

Using the estimated heterotrophic only respiration, there were no changes in significance, except for 2017 growing season compared to the background, soil $NO_3$, and soil $NH_4$ (Table 2.2). Importantly, WC plots still had significantly higher flux after removing the autotrophic contributions, indicating that soil microbial respiration increased beyond clover contributions between rows of corn.

## $N_2O$

Mean $N_2O$ flux was higher in WC plots with differences of 1.81, 1.71, and 1.65 µmol $m^{-2}$ $hr^{-1}$ for WC-CC, WC-CR, and WC-Tr, respectively (Table 2.1, p-value 0.001 for all). $N_2O$ fluxes were near background levels at the beginning and end of the growing season with increases following fertilizer application. The largest fluxes observed were in the WC plots for both years and in Tr plots following fertilizer application in 2016. There were smaller increased fluxes in CC, CR, and Tr plots in 2017 in the weeks following fertilizer application (Figure 2.3). Cumulative sums for $N_2O$ were also higher in WC plots for both growing seasons compared to all other techniques (Table 2.1).

The multiple linear regression of individual log-transformed $N_2O$ fluxes indicated that WC plots had a larger $N_2O$ flux than Tr plots (Table 2.3, p-value<0.001), confirming the results of the post-hoc ANOVA analysis. Higher $N_2O$ fluxes compared to Tr plots were not observed in CC and CR plots (Table 2.3). Soil moisture and soil $NO_3$ were correlated at the $\alpha$=0.05 level with higher $N_2O$ fluxes (p-values of <0.001 and 0.016 respectively) and soil $NH_4$ was corelated at the $\alpha$=0.10 level (p-value of 0.063). Soil temperature, PMN, and light interception did not have statistically significant relationships with $N_2O$ flux (Table 2.3).

## $NH_3$

Mean $NH_3$ fluxes were significantly higher in the WC plots (497 µg $m^{-2}$ $hr^{-1}$, 95% CI (316, 678)) compared to the Tr plots (210 µg $m^{-2}$ $hr^{-1}$, 95% CI (142, 278)) during the 2017 growing season. $NH_3$ fluxes were higher towards the middle of the growing season (Figure 2.4) in both Tr and WC plots with large increases in the weeks following fertilizer application (maximum flux of 1697 µg $m^{-2}$ $hr^{-1}$). Fluxes were reduced in the early and late growing season (~100 to 200 µg $m^{-2}$ $hr^{-1}$ in WC and Tr plots).

# Discussion

## $CO_2$

Higher $CO_2$ fluxes in WC plots was observed in between rows where clover biomass was present but was not within corn rows where no clover biomass was present in 2016. This indicates a large amount of the flux between corn rows could be due to clover respiration. After estimating clover respiration using biomass and soil temperature and subtracting it from the total $CO_2$ flux, results still indicated significantly higher fluxes in WC plots compared to Tr plots, suggesting that the WC LMS increased heterotrophic soil respiration between corn rows. The discrepancy between estimated heterotrophic respiration and measurements in corn rows likely arose from an underestimation of clover respiration in the early growing season. Importantly, an increase in soil labile C over the duration of the experiment suggests that LMS may be an overall sink for terrestrial carbon (Table 2.S2). Future studies should increase in row measurements to avoid clover respiration masking responses in heterotrophic soil respiration.

WC plots had increased soil porosity and reduced soil bulk density (Table 2.S2). These changes in soil structure could have caused the observed increase in soil respiration. Additionally, plant decomposition can increase soil respiration[86]. However, increases in soil respiration are influenced more by substrate affinity to producing or consuming organic matter than the differences in vegetation[87]. Future studies should determine differences in bacteria species that are involved in organic matter decomposition.

Soil moisture was the most highly correlated parameter with $CO_2$ flux in the linear model. This soil moisture–$CO_2$ relationship has been shown to be an important factor altering $CO_2$ flux within no-till systems[88,89,90]. Soil temperature was also positively correlated with increasing $CO_2$

flux, a commonly observed response[90]. As PMN decreased, there was a small but significantly higher $CO_2$ flux, contrary to other research which has shown the two parameters to be positively correlated[91]. In Chirinda et al. (2010)[91], soil samples were sieved and did not include organic matter on top of the soil as this present study did. All systems except Tr had higher PMN (organic N) than cold extract $NH_4^+$ (Table 2.S2). This indicates a large portion of N in the samples was in the organic form, which decomposes slower and is less available for respiration, which could explain this inverse relationship, contrary to the results from Chirinda et al. (2010). However, this relationship was not significant after correcting for clover respiration in the regression (Table 2.2), so clover respiration may have confounded the true relationship between soil $CO_2$ flux and PMN.

Previous studies have shown that systems with N-rich legume biomass residue have higher soil respiration compared to systems without residue on the soil surface[92]. This effect could be amplified in the WC plots, with clover depositing biomass throughout the entire growing season. Future studies should measure the carbon added from clover deposition to determine if added C outweighs the carbon loss through respiration. Additionally, WC plots had a higher labile C content, which has been associated with higher $CO_2$ flux in previous studies[93]. This study showed that a WC LMS had higher soil heterotrophic respiration in between corn rows compared to three other systems after subtracting estimated autotrophic clover respiration and controlling for relevant soil parameters. However, the greater labile C for in WC plots indicates an overall sequestration of C into the soil. Future studies should calculate a complete net carbon equivalence using inputs and outputs including irrigation, fertilizer production, and soil respiration.

## $N_2O$ and $NH_3$

$N_2O$ and $NH_3$ fluxes between rows were significantly higher in WC plots compared to the other cover crops and no cover crop systems. Higher $NH_3$ fluxes in WC plots compared to Tr plots was contrary to the original hypothesis, based on the fact that a lower amount of urea-based fertilizer was applied on WC plots versus Tr plots (Table 2.S1). Cereal grain cover crops have been shown to decrease $NH_3$ and $N_2O$ emissions due to enhanced N retention[94]. However, soils with higher SOC (as observed in WC plots) can have greater overall $N_2O$ emissions compared to less fertile soils[95]. The difference in LMS versus common cover crop practices could be related to the timing of N fertilization in between rows from the clover biomass. $NH_3$ flux spikes tend to be restricted to short time periods after fertilizer application in ryegrass and clover only systems[96]. $N_2O$ fluxes tend to increase following fertilizer application, then decrease to a level greater than pre-fertilizer application[97]. In LMS, more of the N is supplied from cover crop decomposition versus inorganic fertilizer, which is the main N source for the other plots[98] (Table 2.S1). The release of gaseous N from cover crops in LMSs is not limited to the weeks following an inorganic fertilizer application, potentially causing the overall increases in N species fluxes in WC plots. In row measurements of $N_2O$ and $NH_3$ fluxes should be sampled in future studies to account for potential effects of clover on flux.

Soil moisture, $NO_3^-$, and $NH_4^+$ have all been proven as drivers of $N_2O$ flux [99]. The correlations presented here with $N_2O$ and $NO_3^-/NH_4^+$ suggest both nitrification and denitrification are contributing to $N_2O$ fluxes[100]. The stronger relationship with $NO_3^-$, which is converted into $N_2O$ through denitrification, indicates that denitrification could be the more prominent pathway compared to nitrification of $NH_4^+$ in this study. Soils with higher SOC (as observed in WC plots) can have greater overall $N_2O$ emissions compared to less fertile soils[95]. However, denitrification and nitrification are complex processes, so techniques such as stable isotope and acetylene inhibition[101] could be used in future studies to quantify the amount of $N_2O$ from both processes[102]. One limitation of this study is that the 2016 soil N compound data is in paired plots, rather than in the same plots as flux measurements. Regressions with only 2017 data showed $NH_4^+$ as a stronger driving force than $NO_3^-$ for $N_2O$ fluxes (Table 2.S3), so future studies should maintain consistency in measurement locations.

The higher $N_2O$ flux in WC plots compared to Tr plots supports the findings in Turner et al. (2016)[21]. Additionally, cumulative sums for LMS systems were similar between the two studies (220.2 mg N $m^{-2}$ in 2016 and 229.9 mg N $m^{-2}$ in 2017 versus 226.5 mg N $m^{-2}$ in Turner et al. (2016)[21]), indicating that white clover and kura clover affect soil fluxes similarly despite different growth rates. Both studies observed the largest $N_2O$ fluxes late in the growing season, likely due to clover decomposition and mineralization. While the current study originally hypothesized that $NH_3$ fluxes would be decreased in WC plots due to a lower fertilizer application rate, the results suggest that the continuous release of N outweighed the reduced fertilizer amount.

## Conclusion

This study found greater mean $CO_2$, $N_2O$, and $NH_3$ soil fluxes in WC plots compared to three commonly used agricultural management techniques. However, for $CO_2$ these increased fluxes were not observed from measurements in the corn rows, indicating further study is necessary to elucidate if the increased respiration is autotrophic, heterotrophic, or a combination. Heterotrophic estimates in this study matched well with in row measurements late in the growing season, but not earlier on. Spikes in $N_2O$ and $NH_3$ fluxes were often observed following fertilizer application, but lasted longer in LMS plots. Nitrification and denitrification rates should be explored to better understand the specific sources of $N_2O$ fluxes.

The WC LMS investigated here was not a strong mitigator of GHG or $NH_3$. However, higher labile C measured in WC plots along with greater respiration could indicate improved C storage capacity and a net GHG benefit. Future studies should use soil flux data from this study and others such as Turner et al. (2016) combined with carbon equivalence of agricultural inputs to elucidate a more wholistic assessment of the impacts of LMSs on the environment.

# Tables and Figures

Figure 2.1:

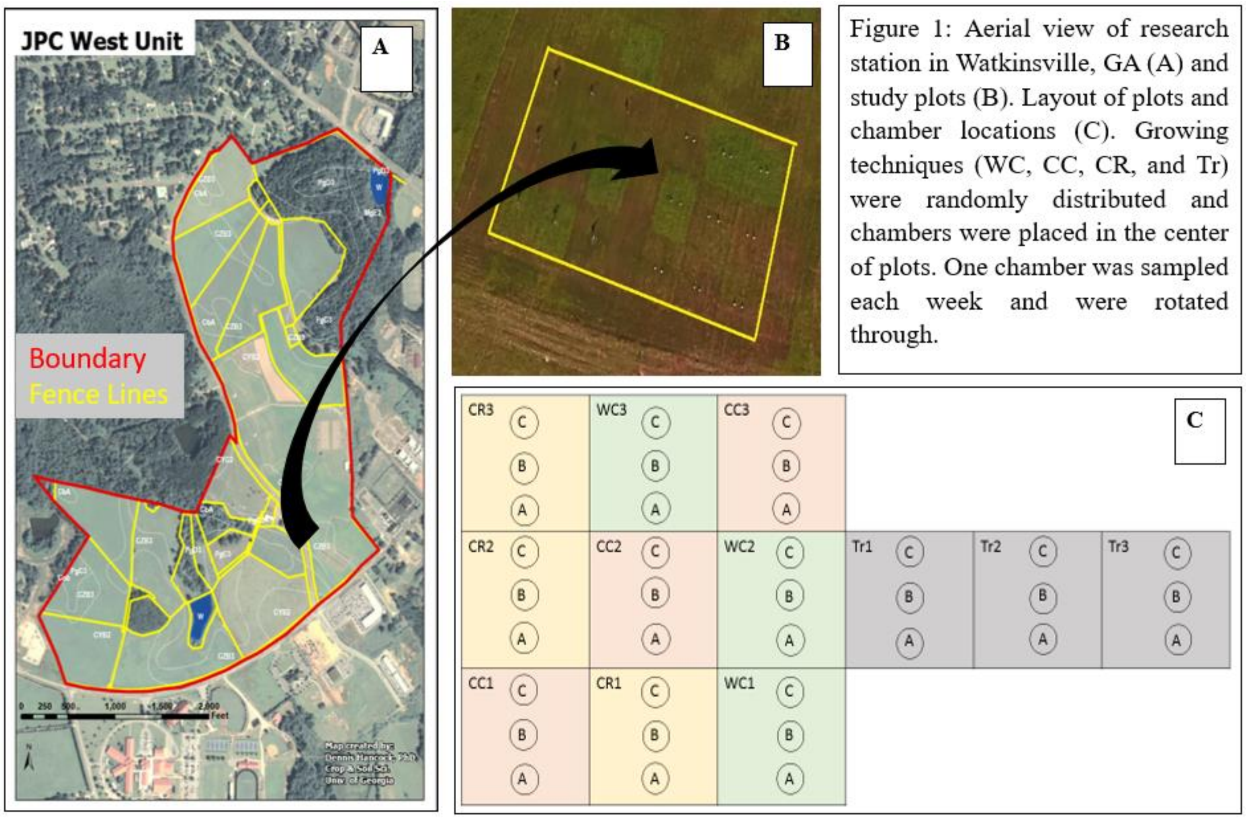


Figure 2.1: Location of research station (A), study plot design (B), and layout of plots and chamber locations (C). Chambers were placed in the center of plots. One chamber was chosen in rotation (A, B, or C) and was sampled in repeating order each week to address heterogeneity across the soil. Athens, GA, USA. Georgia road map taken from The National Atlas of the USA. Management techniques were white living mulch (WC), traditional bare soil (Tr), cereal rye cover crop (CR), crimson clover cover crop (CC).

Figure 2.2:

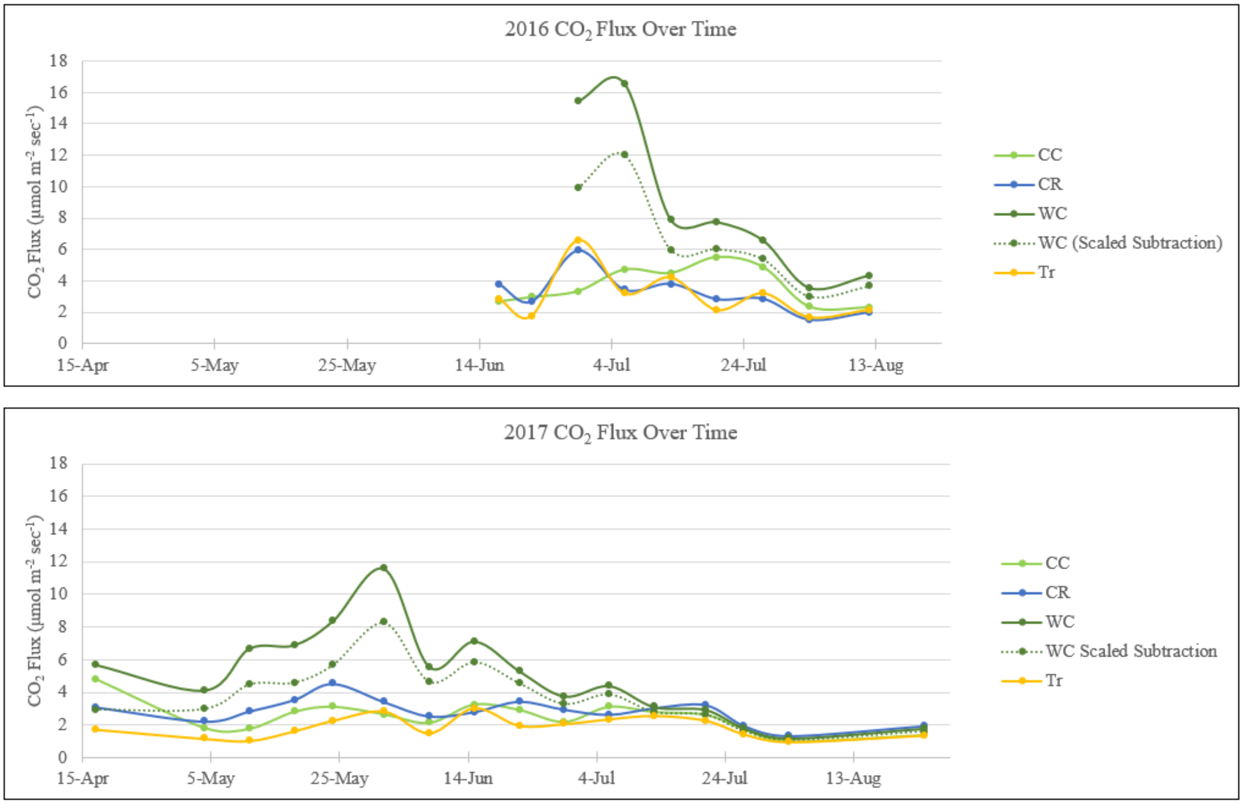


Figure 2.2: Time series of flux measurements between the corn rows of $CO_2$ in µmol m$^{-2}$ sec$^{-1}$ during the 2016 (A) and 2017 (B) growing seasons for crimson clover (CC), cereal rye (CR), white clover living mulch (WC), and traditional (Tr) treatments. Also includes WC measurements with scaled autotrophic effects subtracted. Overall $CO_2$ flux was higher in WC plots for both seasons.

Figure 2.3:

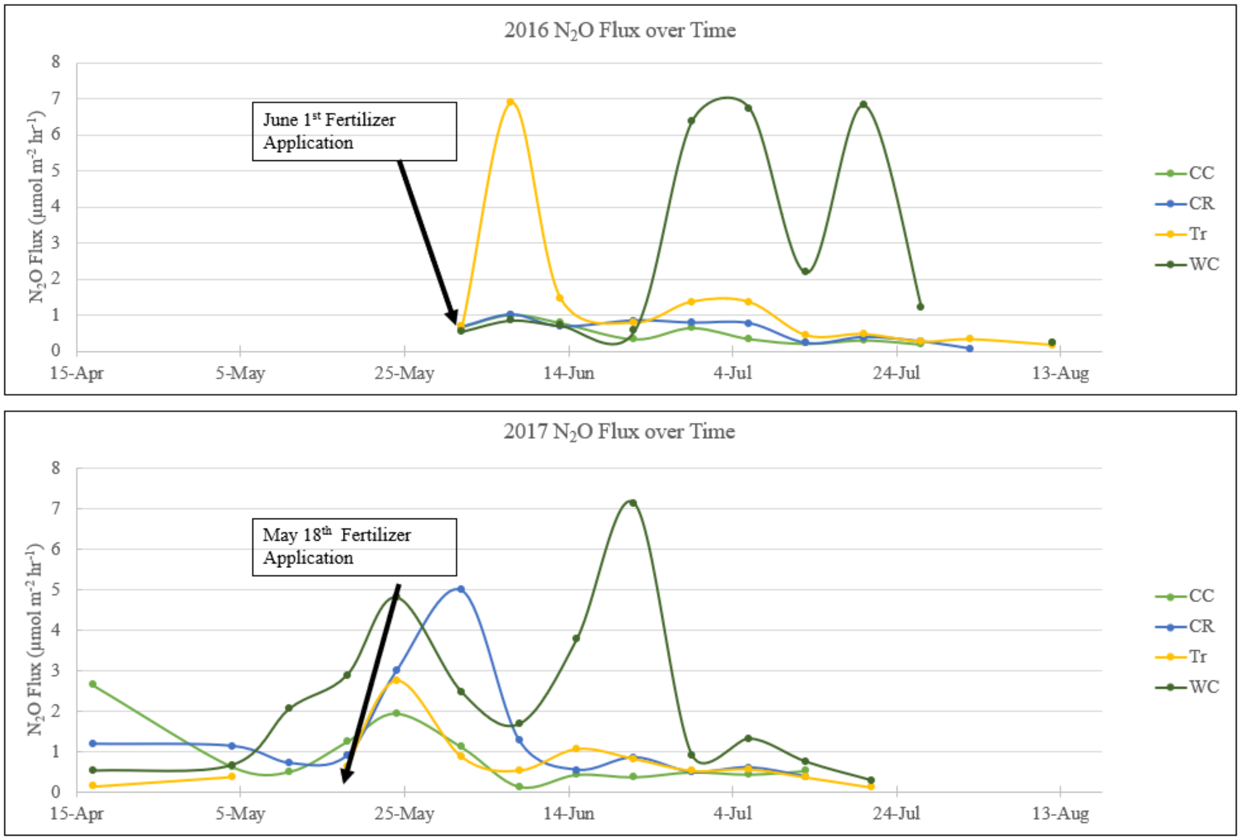


Figure 2.3: Time series of flux measurements between the corn rows of $N_2O$ in µmol $m^{-2}$ $hr^{-1}$ during the 2016 (A) and 2017 (B) growing seasons for crimson clover (CC), cereal rye (CR), white clover living mulch (WC), and traditional (Tr) treatments Following fertilizer application, there was a spike in $N_2O$ flux in Tr plots in 2016 and spikes in all systems in 2017. Overall $N_2O$ flux was higher in WC plots for both seasons.

Figure 2.4:

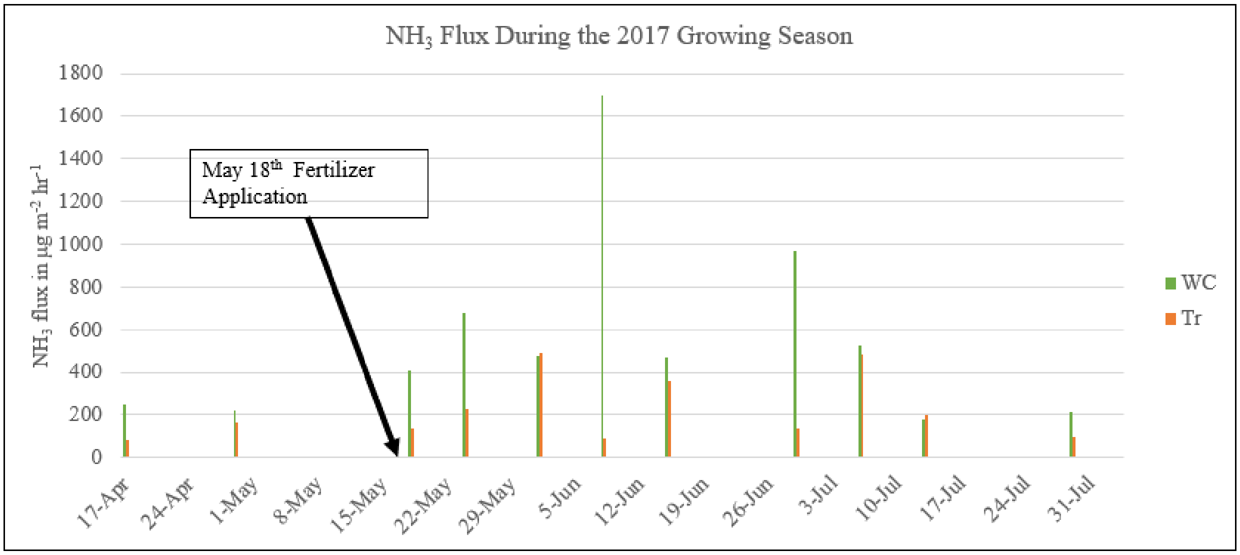


Figure 2.4: $NH_3$ flux measurements in white clover living mulch (WC) and traditional (Tr) treatments over the 2017 growing season. Fertilizer was applied on May 1st.

Table 2.1: Flux Rate Means and Comparisons for $CO_2$ and $N_2O$

| Overall Means | | | | |
|---|---|---|---|---|
| *Mean Gas Flux* | *CC (95% CI)* | *CR (95% CI)* | *WC (95% CI)* | *Tr (95% CI)* |
| $CO_2$ (μmol $m^{-2}$ $sec^{-1}$) | 2.79 (2.43, 3.15) | 2.78 (2.50, 3.06) | 5.78 (4.82, 6.74) | 1.98 (1.73, 2.24) |
| $N_2O$ (μmol $m^{-2}$ $hr^{-1}$) | 0.79 (0.57, 1.00) | 0.89 (0.62, 1.15) | 2.60 (1.71, 3.48) | 0.95 (0.51, 1.39) |
| $NH_3$ (μmol $m^{-2}$ $hr^{-1}$) | NA | NA | 29.2 (18.6, 40.4) | 12.4 (8.35, 16.4) |

Cumulative Flux Sums (in kg $ha^{-1}$ $yr^{-1}$)

| Gas | CC-2016 | CC-2017 | CR-2016 | CR-2017 | WC-2016 | WC-2017 | Tr-2016 | Tr-2017 |
|---|---|---|---|---|---|---|---|---|
| $CO_2$ | 8,010 | 12,000 | 6,830 | 12,800 | 22,700 | 23,100 | 6,620 | 8,320 |
| $N_2O$ | 0.37 | 1.11 | .41 | 1.40 | 2.20 | 2.30 | .99 | .74 |

Mean $CO_2$ Flux Comparisons from Between Row Measurements (2016 & 2017)

| *Comparison* | *Difference in μmol $m^{-2}$ $sec^{-1}$* | *95% CI Lower Bound* | *95% CI Upper Bound* | *P-value* |
|---|---|---|---|---|
| WC-Tr | 3.80 | 2.72 | 4.87 | <0.001* |
| WC-CR | 3.00 | 2.01 | 4.00 | <0.001* |
| WC-CC | 2.99 | 1.99 | 3.99 | <0.001* |
| Tr-CR | -0.79 | -1.85 | 0.26 | 0.21 |
| CR-CC | -0.013 | -0.99 | 0.97 | 0.99 |
| Tr-CC | -0.81 | -1.87 | 0.26 | 0.21 |

Mean $CO_2$ Flux Comparisons from In Row Measurements (2016)

| *Comparison* | *Difference in μmol $m^{-2}$ $sec^{-1}$* | *95% CI Lower Bound* | *95% CI Upper Bound* | *P-value* |
|---|---|---|---|---|
| WC-Tr | 1.19 | -0.82 | 3.21 | 0.41 |
| WC-CR | 0.99 | -0.39 | 2.37 | 0.25 |
| WC-CC | 1.17 | -0.21 | 2.55 | 0.12 |
| Tr-CR | -0.21 | -2.28 | 1.86 | 0.99 |
| CR-CC | 0.18 | -1.28 | 1.65 | 0.99 |
| Tr-CC | -0.02 | -2.10 | 2.05 | 0.99 |

Mean Between Row $N_2O$ Flux Comparisons

| *Comparison* | *Difference in μmol $m^{-2}$ $hr^{-1}$* | *95% CI Lower Bound* | *95% CI Upper Bound* | *P-value* |
|---|---|---|---|---|
| WC-Tr | 1.65 | 0.55 | 2.74 | 0.001* |
| WC-CR | 1.71 | 0.72 | 2.70 | <0.001* |
| WC-CC | 1.81 | 0.78 | 2.83 | <0.001* |
| Tr-CR | 0.065 | -1.04 | 1.17 | 0.99 |
| CR-CC | 0.094 | -0.95 | 1.13 | 0.98 |
| Tr-CC | 0.16 | -0.98 | 1.30 | 0.99 |

* Significant differences at $\alpha$=0.05 level using Tukey's pairwise comparisons.
White living mulch (WC), traditional bare soil (Tr), cereal rye cover crop (CR), crimson clover cover crop (CC)

Table 2.2: Linear Regression of Weekly Log Transformed $CO_2$ Flux

| Without Autotrophic Scaled Subtraction (N=292, $R^2$=0.62) | | | | |
|---|---|---|---|---|
| *Variable* | *Estimate (β) (95% CI)* | *Standard Error of Estimate* | *Percent Change (%) (95% CI)* | *P-value* |
| Intercept | -1.30 | 0.25 | NA | <0.001*** |
| CC | 0.37 (0.22, 0.52) | 0.074 | 44.9 (24.6, 68.2) | <0.001*** |
| CR | 0.32 (0.18, 0.47) | 0.073 | 38.0 (19.7, 60.0) | <0.001*** |
| WC | 1.00 (0.85, 1.15) | 0.076 | 172.5 (134.0, 215.8) | <0.001*** |
| Season 2016 | 0.67 (0.47, 0.87 | 0.10 | 95.4 (60.0, 138.7) | <0.001*** |
| Season 2017 | 0.19 (-0.005, 0.39) | 0.10 | 20.8 (-0.50, 47.7) | 0.056# |
| Temp | 0.032 (0.015, 0.05) | 0.0089 | 3.27 (1.51, 5.13) | <0.001*** |
| Soil Moisture | 5.96 (4.63, 7.28) | 0.67 | 6.14 (4.74, 7.55) | <0.001*** |
| Light Interception | 0.070 (-0.10, 0.24) | 0.087 | 7.26 (-9.52, 27.12) | 0.42 |
| Soil $NO_3$ | 0.0050 (-0.0007, 0.011) | 0.0029 | 0.50 (-0.070, 1.11) | 0.085# |
| Soil $NH_4$ | -0.0020 (-0.0056, 0.0015) | 0.0018 | -0.20 (-0.56, 0.15) | 0.26 |
| PMN | -0.021 (-0.04, -0.0026) | 0.0095 | -2.12 (-3.92, -0.26) | 0.026* |
| With Autotrophic Scaled Subtraction (N=282, $R^2$=0.41) | | | | |
| *Variable* | *Estimate (β) (95% CI)* | *Standard Error of Estimate* | *Percent Change (%) (95% CI)* | *P-value* |
| Intercept | -1.35 | 0.32 | NA | <0.001*** |
| CC | 0.36 (0.18, 0.53) | 0.090 | 43.1 (19.9, 70.7) | <0.001*** |
| CR | 0.31 (0.13, 0.48) | 0.089 | 35.7 (13.9, 61.7) | <0.001*** |
| WC | 0.53 (0.34, 0.72) | 0.095 | 69.8 (40.8, 104.8) | <0.001*** |
| Season 2016 | 0.55 (0.30, 0.80) | 0.13 | 72.8 (34.6, 121.7) | <0.001*** |
| Season 2017 | 0.044 (-0.20, 0.28) | 0.12 | 4.55 (-17.8, 32.9) | 0.72 |
| Temp | 0.034 (0.012, 0.056) | 0.011 | 3.46 (1.17, 5.80) | 0.003** |
| Soil Moisture | 6.24 (4.59, 7.90) | 0.84 | 6.44 (4.69, 8.22) | <0.001*** |
| Light Interception | 0.14 (-0.072, 0.35) | 0.11 | 15.0 (-6.93, 42.1) | 0.19 |
| Soil $NO_3$ | 0.0050 (-0.002, 0.012) | 0.0035 | 0.50 (-0.20, 1.20) | 0.16 |
| Soil $NH_4$ | -0.0020 (-0.0062, 0.0023) | 0.0022 | -0.20 (-0.62, 0.23) | 0.37 |
| PMN | -0.018 (-0.041, 0.0049) | 0.012 | -1.78 (-4.00, 0.49) | 0.12 |

***p<0.001, **p< 0.01, *p< 0.05, #p<0.10

White living mulch (WC), traditional bare soil (Tr), cereal rye cover crop (CR), crimson clover cover crop (CC)

Table 2.3: Linear Regression of Weekly Log Transformed $N_2O$ Flux, (N=203, $R^2$=0.48)

| *Variable* | *Estimate (β) (95% CI)* | *Standard Error of Estimate* | *Percent Change (%) (95% CI)* | *P-value* |
|---|---|---|---|---|
| Intercept | -4.58 | 0.76 | NA | <0.001*** |
| CC | 0.12 (-0.21, 0.45) | 0.17 | 12.8 (-18.9, 56.8) | 0.47 |
| CR | 0.092 (-0.23, 0.41) | 0.16 | 9.66 (-20.5, 50.7) | 0.57 |
| WC | 1.19 (0.86, 1.52) | 0.17 | 228.5 (136.3, 357.2) | <0.001*** |
| Season 2016 | 0.75 (0.15, 1.36) | 0.31 | 112.4 (16.2, 289.6) | 0.015* |
| Season 2017 | 0.68 (0.079, 1.28) | 0.31 | 97.4 (8.22, 259.7) | 0.027* |
| Temp | 0.03 (-0.029, 0.089) | 0.030 | 3.07 (-2.86, 9.31) | 0.31 |
| Soil Moisture | 11.94 (8.73, 15.2) | 1.63 | 12.69 (9.12, 16.4) | <0.001*** |
| Light Interception | -0.12 (-0.46, 0.23) | 0.17 | -10.0 (-36.9, 25.9) | 0.50 |
| Soil $NO_3$ | 0.014 (0.0025, 0.025) | 0.0056 | 1.38 (0.25, 2.53) | 0.016* |
| Soil $NH_4$ | 0.0062 (-0.00034, 0.013) | 0.0033 | 0.62 (-0.034, 1.31) | 0.063[#] |
| PMN | 0.0024 (-0.008, 0.13) | 0.0053 | 0.24 (-0.80, 13.9) | 0.65 |

***p<0.001, **p< 0.01, *p< 0.05, [#]p<0.10

White living mulch (WC), traditional bare soil (Tr), cereal rye cover crop (CR), crimson clover cover crop (CC)

## Supplementary Material

Supplemental Figure 1:

Figure 2.S1: Appearance of corn from top to bottom at V6 (6 leaf), V12 (12 leaf), and VT (tassel) growing stages under four growing techniques. Left to right: Crimson clover (CC), cereal rye (CR), white clover living mulch (WC), and traditional bare-soil (Tr). Watkinsville, GA, USA. Photo credit: Samuel Peters.

Supplemental Figure 2:

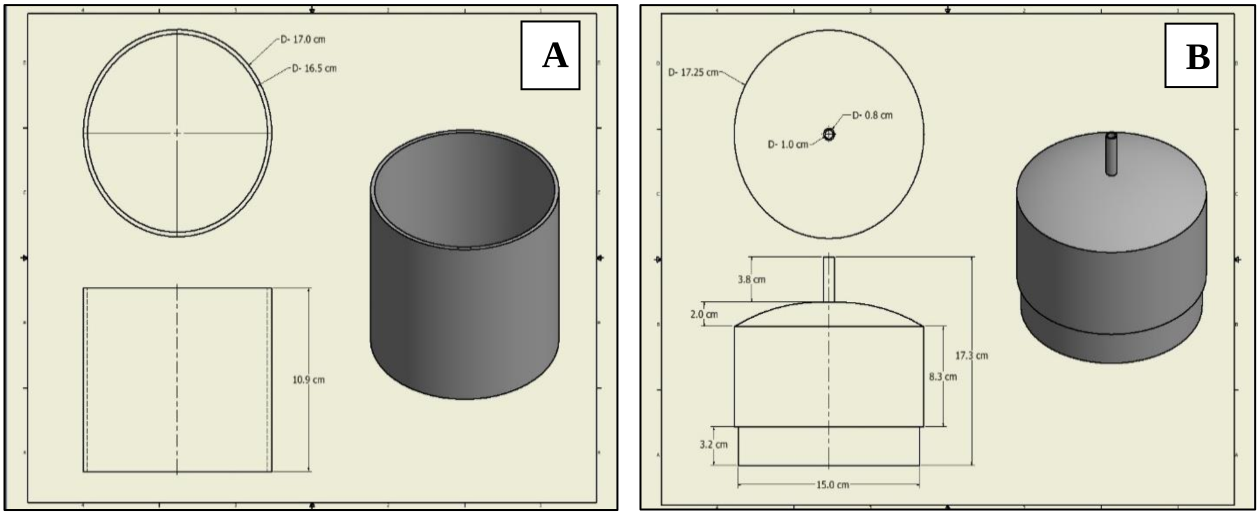


Figure 2.S2: Schematic and measurements of chamber base (A) and chamber top (B). Chambers had a surface area of 0.0182 $m^2$ and a volume of 2.92 L. White PVC pipe was used as opposed to previous designs[72,73] to maintain an airtight seal, have non-disruptive insertion into the soil, reflect sunlight to reduce temperature changes in the chamber, and maintain atmospheric pressure at the beginning of sampling. Chamber design was modified to the above size from Strahm (Personal communication, 2015).

Supplemental Figure 3:

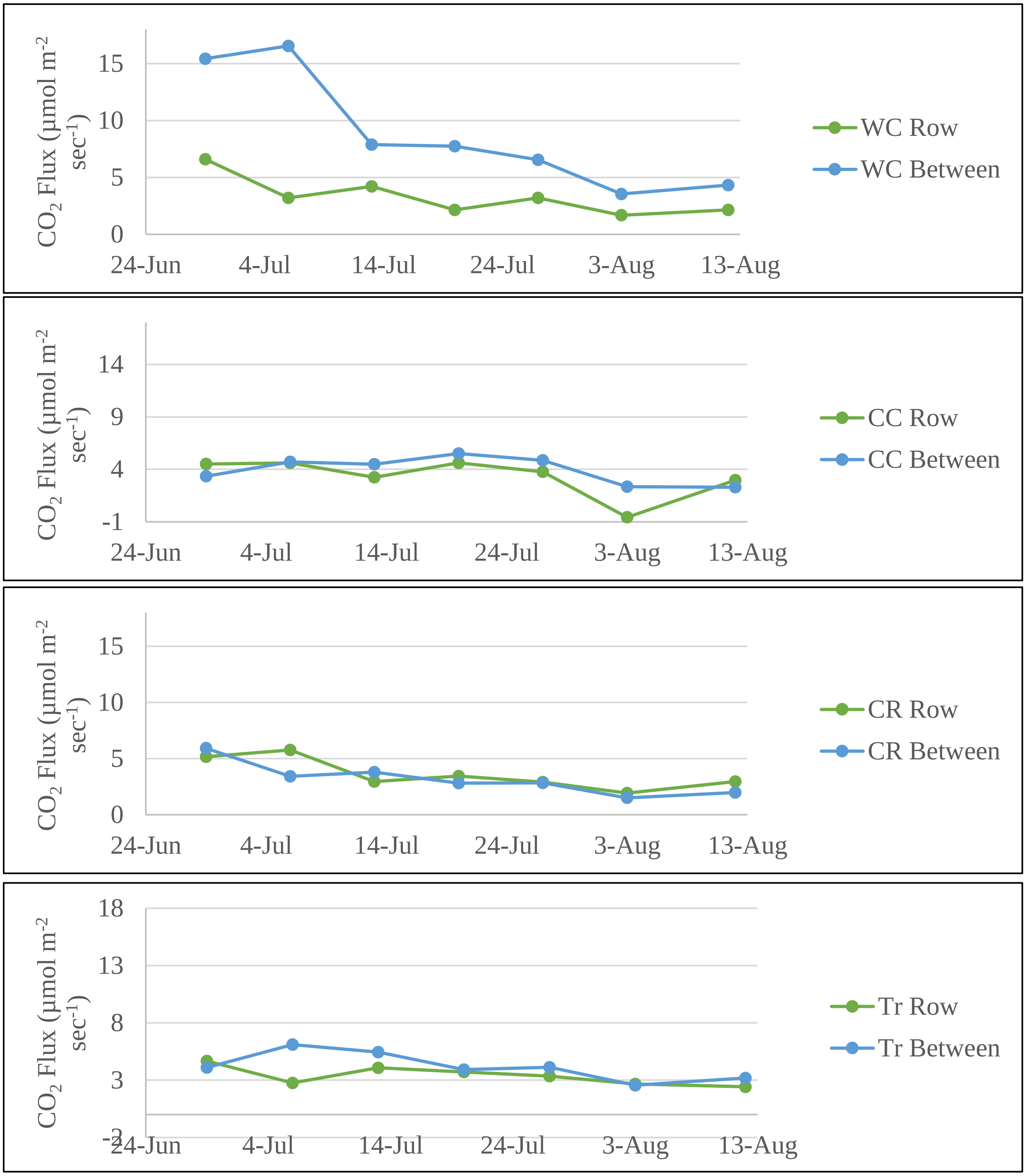


Figure 2.S3: Time series of all growing techniques comparing in row and between row measurements from 2016 Licor infrared gas analyzer (IRGA) data. From top to bottom: Crimson white clover living mulch (WC), clover (CC), cereal rye (CR), and traditional bare-soil (Tr).

Supplemental Figure 4:

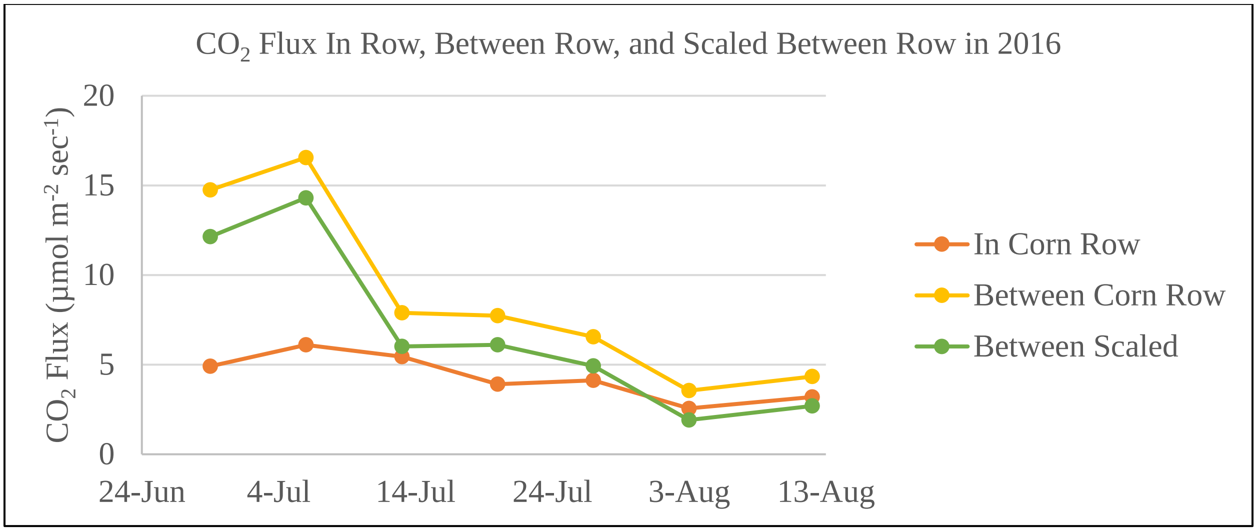


Figure 2.S4: Time series of $CO_2$ flux measurements for white clover living mulch from the Licor Infrared Gas Analyzer (IRGA) from 2016 comparing in corn rows, between corn rows, and between corn rows scaled to account for clover respiration. Scaled approximations match well with in row measurements (where no clover is present) later in the growing season.

Supplemental Table 2.S1: Field Planting and Treatment Timeline

| 2016 | | | | | |
|---|---|---|---|---|---|
| Technique | Cover Crop Suppression | Corn Planted | Starter Fertilizer | Additional Fertilizer | Harvest |
| WC | NA | Apr. 28 | NA | NA | Aug. 8 |
| CR | Mar. 23 | Apr. 28 | May 10-56 kg $ha^{-1}$ | Jun. 2-168 kg $ha^{-1}$ | Aug. 8 |
| CC | Mar. 23 | Apr. 28 | NA | Jun. 2-56 kg $ha^{-1}$ | Aug. 8 |
| Tr | NA | Apr. 28 | May 10-56 kg $ha^{-1}$ | Jun. 2-168 kg $ha^{-1}$ | Aug. 8 |
| 2017 | | | | | |
| Technique | | Corn Planted | Starter Fertilizer | Additional Fertilizer | Harvest |
| WC | NA | Apr. 21 | May 1-50.9 kg $ha^{-1}$ | NA | Aug. 15 |
| CR | Mar. 26 | Apr. 21 | May 1-50.9 kg $ha^{-1}$ | May 18-224 kg $ha^{-1}$ | Aug. 15 |
| CC | Mar. 26 | Apr. 21 | May 1-50.9 kg $ha^{-1}$ | May 18-112 kg $ha^{-1}$ | Aug. 15 |
| Tr | NA | Apr. 21 | May 1-50.9 kg $ha^{-1}$ | May 18-224 kg $ha^{-1}$ | Aug. 15 |

Crimson clover cover crop (CC), cereal rye cover crop (CR), white clover living mulch (WC), traditional bare soil (Tr)

WC cover crop was established in October of 2014, then re-established itself for other growing seasons. CR and CC cover crops were established in October of 2014, 2015, and 2016. CR and CC cover crops were completely suppressed shortly before planting dates. WC plants were only partially suppressed at this time to keep clover alive throughout the growing season. Fertilizer for all plots was urea-based.

Supplemental Table 2.S2: Soil Parameter Means by Management Technique (95% CI)

| *Soil Parameter* | *CC* | *CR* | *WC* | *Tr* |
|---|---|---|---|---|
| Soil Mois. (%WFPS) | 17 (17, 18) | 18 (17, 19) | 18 (17, 19) | 19 (18, 20) |
| Soil Temp. (°C) | 23.2 (22.4, 23.9) | 22.7 (21.8, 23.5) | 22.7 (21.7, 23.7) | 22.5 (21.5, 23.4) |
| $NO_3$ (ppm) | 9.85 (7.27, 12.4) | 9.53 (7.46, 11.6) | 8.61 (6.79, 10.4) | 16.7 (12.4, 21.1) |
| $NH_4$ (ppm) | 8.32 (5.19, 11.5) | 9.14 (5.92, 12.4) | 5.56 (4.26, 6.87) | 13.7 (6.53, 20.9) |
| PMN (ppm) | 14.7 (13.9, 15.5) | 14.8 (13.9, 15.7) | 14.2 (13.2, 15.1) | 13.3 (12.3, 14.3) |
| Bulk Density (g/cm$^3$) | 1.36a | 1.40a | 1.25b | 1.41a |
| Porosity (%) | 48.7a | 47.0a | 52.3b | 47.0a |
| Ksat (mm/hr) | 353a | 307a | 1523b | 161a |
| Water held (cm$^3$/cm$^3$) | 46.3 | 46.3 | 47.0 | 46.7 |
| Labile C (mg/kg) | 641a | 550a | 788b | 576a |

Letters a and b denote significant differences at $\alpha$=0.05

Crimson clover cover crop (CC), cereal rye cover crop (CR), white clover living mulch (WC), traditional bare soil (Tr)

Supplemental Table 2.S3: Linear Regression of Log-Transformed $N_2O$ Fluxes Without 2016 Data

| Variable | *Estimate (β) (95% CI)* | *Standard Error of Estimate* | *Percent Change (%) (95% CI)* | *P-value* |
|---|---|---|---|---|
| Intercept | -4.61 | 0.85 | NA | <0.001*** |
| CC | 0.30 (-0.01, 0.7) | 0.20 | 35.0 ( -1.00, 101.4) | 0.14 |
| CR | 0.36(-0.028, 0.74) | 0.19 | 43.3 (-2.76, 109.6) | 0.07# |
| WC | 1.14 (0.75, 1.53) | 0.20 | 212.7 (111.7, 361.8) | <0.001*** |
| Season 2017 | 0.93 (0.28, 1.57) | 0.32 | 153.5 (32.3, 380.7) | 0.005** |
| Temp | 0.04 (-0.027, 0.11) | 0.03 | 4.08 (-2.66, 11.6) | 0.24 |
| Soil Moisture | 10.28 (5.98, 14.6) | 2.17 | 10.8 (6.16, 15.7) | <0.001*** |
| Light Interception | -0.33 (-0.74, 0.087) | 0.21 | -28.1 (52.3, 9.09) | 0.12 |
| Soil $NO_3$ | 0.004 (-0.0086, 0.017) | 0.007 | 0.40 (-0.86, 1.71) | 0.50 |
| Soil $NH_4$ | 0.01 (0.003, 0.2) | 0.004 | 1.01 (0.30, 22.1) | 0.008** |
| PMN | 0.001 (-0.01, 0.13) | 0.006 | 0.10 (-0.10, 13.9) | 0.82 |

***p<0.001, **p< 0.01, *p< 0.05, #p<0.10

White living mulch (WC), traditional bare soil (Tr), cereal rye cover crop (CR), crimson clover cover crop (CC)

# Chapter 3: The Effects of Intercropping and Biochar on Soil Trace Gas Fluxes and Net Carbon Equivalence in Semiarid Brazil

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## Abstract

Agricultural soils are sources of greenhouse gases (GHG) and ammonia ($NH_3$), which can result in climate change and air pollution. Using sources of nitrogen (N) alternative to inorganic fertilizers, or soil amendments such as biochar, have been proposed as methods to reduce these soil trace gas fluxes, which could lower net carbon equivalent (CE) of agricultural systems. This study explored soil carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), methane ($CH_4$), and $NH_3$ fluxes and net CE of five different N sources in corn-cropping systems at two sites in the semiarid Caatinga region of Brazil. The N sources were cowpea intercropping, urea fertilizer, two bacterial inoculants, and a control with no N added. Half of the plots were amended with mango branch biochar. When controlling for soil temperature and moisture, $CO_2$ fluxes were higher in plots with cowpea and urea fertilizer as the N source compared to controls. $CO_2$ and $NH_3$ fluxes were lower in plots with biochar compared to those without. All N sources were net CE sources over the growing season, with cowpea and urea fertilizer having the largest. Plots with biochar had a lower net CE than those without biochar, but when factoring in the CE of biochar production, the plots with biochar had a higher net CE. More robust measurements of soil parameters such as carbon, soil texture, and microbes should be paired with soil trace gas flux measurements in these systems in future studies to expand the net CE analysis and elucidate soil processes contributing to any differences in flux.

## Key Terms

Biochar, intercropping, greenhouse gas, soil flux, net carbon equivalent

## Abbreviations

Greenhouse gas (GHG), carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), methane ($CH_4$), ammonia ($NH_3$), particulate matter ($PM_{2.5}$), carbon (C), soil organic carbon (SOC), nitrogen (N), biological nitrogen fixation (BNF), carbon equivalent (CE), global warming potential (GWP), Intergovernmental Panel on Climate Change (IPCC)

## Introduction

Anthropogenic sources of the three major greenhouse gases (GHG), carbon dioxide ($CO_2$), nitrous oxide ($N_2O$), and methane ($CH_4$), have contributed to global warming in the atmosphere[64]. Almost a quarter of these GHGs come from agriculture, forestry, and land use change[3]. Agriculture is now the largest of these three sectors with 11.2% of total GHG (5.4 Gt $CO_2$ eq $yr^{-1}$ in 2012)[4]. Soil inputs, such as synthetic fertilizer and manure, account for 30-38% of agricultural GHGs and are the largest source of anthropogenic $N_2O$in the world[3,5,6,7]. GHG-mitigating agricultural practices are therefore essential to meet the goal of a 2°C increase limit outlined in the Paris Agreement within the United Nations Framework Convention on Climate Change[65,66] (Paustian et al., 2016, Wollenberg et al., 2016). Climate-Smart Agriculture (CSA) is a new approach to growing food that aims to lower the impacts on the climate while improving adaptability and productivity[68]. Specifically, increasing soil organic carbon (SOC) sequestration through recommended agricultural strategies, such as no-till and cover cropping, could offset global fossil fuel emissions by 5 to 15%, while improving soil fertility[103]. Calculating net growing season carbon equivalence (CE), the overall positive or negative effect on the atmosphere in terms of kg of C, of agricultural systems, is an effective method to determine the overall climatic impact of agricultural systems rather than soil fluxes alone[104].

Additionally, N-based fertilizer application contributes to ammonia ($NH_3$) emissions, which form particulate matter ($PM_{2.5}$)[8]. Soil processes separate from fertilizer application could also be an important source of $NH_3$ in the United States, but there is high uncertainty in these estimates[8]. $PM_{2.5}$ can be damaging to respiratory and cardiovascular health[9]. $PM_{2.5}$ concentrations could potentially be lowered by employing agricultural practices that reduce $NH_3$ fluxes such as reduced fertilizer amounts[67].

48.2 % of GHGs in Brazil come from agriculture and 34% of those emissions are from soils[105]. $NH_3$ emissions from agriculture continue to increase in South America and Brazil in particular[106]. However, the country could be a key contributor to improved global food security and environmental agricultural practices[22]. Northeast Brazil, or the Caatinga region, is one area where poor land and soil management has led to degraded SOC stocks and desertification[24], making it an ideal location to improve soil health and lower net CE at the same time. Growing corn decreases the SOC pools in the Caatinga region more than other cropping systems, and is a key crop to target for improving sequestration of carbon (C)[107]. Climate change is predicted to be more variable and make growing food more difficult in this semi-arid region through increased temperatures, decreased precipitation, and longer drought conditions[25,26,27]. Investigating potential CSA corn cropping systems that can retain or increase yields in the semi-arid environment under climate change stressors, while lowering net CE is important going forward for the region.

One system that can increase SOC, and is commonly used in the Caatinga region, is corn-cowpea intercropping, where corn and cowpea are planted at the same time and location. The cowpea supplies the corn with nitrogen (N) throughout the growing season by fixing N from the atmosphere into the soil. In the semiarid northeast of Brazil, these intercropping systems are on average 41% more productive than growing corn alone[28]. Adding legume crops like cowpea can increase the SOC pool, biological nitrogen fixation (BNF), and the capacity of the management system to improve soil quality[29,108]. Systems that increase SOC, such as no-till, have been shown to lower net CE, even if soil emissions increase[109,110].

Two studies have measured higher $N_2O$ fluxes in a living mulch system, where corn was planted into clover throughout the growing season[21,111], similar to a corn-cowpea system but with a perennial forage cover crop instead of an annual one. Studies on the GHG fluxes of other corn/legume intercropping systems indicate that these systems are net sources of $CO_2$, but are contradictory as to whether $N_2O$ fluxes increase or decrease compared to monocultures[32,33]. Intercropping systems have been shown to be a $CH_4$ sink in wet soil with readily available carbon[32]. Corn-soybean intercropping systems have potentially lower GHG soil emissions but may be smaller net CE sinks than when each crop is grown separately[32,112]. The lowest net CE for intercropping systems may arise when no fertilizer is applied[113]. One study to date has measured $NH_3$ fluxes in a corn intercropping system, but did not compare to conventional agricultural systems[114]. No study to date has explored all three major GHGs and $NH_3$ in the same study location over the same growing season, and few have assessed the net CE of these systems[113,112]. Studies have examined the soil trace gas fluxes of cowpea cover crop residue on the soil[30] and corn/cowpea separately[31], but no study to date has explored soil GHG or $NH_3$ flux while these two specific crops are actively growing together or assessed the net CE of the system. Particularly, further investigation on the net CE of CSA systems is necessary to assess the true potential for contributions to global warming.

Amending soil with biochar, or the C-rich product produced by burning biomass with limited oxygen, also has the potential to be a CSA technique through increased soil C sequestration[36]. A meta-analysis suggests that biochar reduces $N_2O$ soil fluxes, increases $CO_2$ fluxes, and has no significant effect on $CH_4$ fluxes[36]. Some studies present contradictory findings, with increased $CO_2$ fluxes in some agricultural settings with low soil organic matter content[37] or increased $N_2O$ fluxes with biochar depending on the soil type and $N_2O$ formation pathway[39]. Biochar has also been shown to enhance $NH_3$ fluxes in agricultural soil[37,38]. Studies on the trace gas fluxes of biochar amended soil in the Caatinga region are limited, and biochar has never been studied in tandem with corn-cowpea intercropping.

Biochar systems have been estimated to decrease[115] or increase[116] net CE. Studies measuring GHG's in potential CSA systems don't always calculate a net CE including a variety of agricultural inputs, even though these inputs can affect overall conclusions and determine if a system is a sink or a source[117,110]. In particular, no study to date factors the C loss of the production of biochar itself before field application into the net CE calculation. Studies on the climate impact of different agricultural systems also rarely analyze net CE in the context of yields, an important factor for producers to consider.

This study measured soil GHG and $NH_3$ fluxes in and estimated a net CE for corn cropping systems in two different soil types in the Caatinga region of Brazil. Plots with five different N sources including cowpea were planted with and without biochar amendments. A study with comparisons between ten total systems (five N sources with and without biochar) is rarely done. The present study had three aims: 1) Measure the trace gas fluxes in a corn system using cowpea intercropping as a source of N and compare to other widely-used methods; 2) Explore how biochar amendments affect the soil trace gas fluxes in corn treated with cowpea and other N sources; and 3) Use the fluxes measured and other agricultural inputs including biochar production to estimate a net CE for each system, specifically the potential CSA techniques of intercropping and biochar.

## Materials and Methods

### Site Description and Field Preparation

Experiments were located at the Brazilian Agricultural Research Corporation (EMBRAPA) Semiarido test sites Campo Experimental de Bebedouro (-9.138° N, -40.300° W) and Campo Experimental de Mandacaru (-9.394° N, -40.416° W). Ten plots of each N source; urea fertilizer (UF), government-recommended bacterial inoculant (GI, Abv5), bacterial inoculant from the Fernandes lab (FI, mixture of BS24, BS7, and 6.2), cowpea intercropping (CP), and a control with no nitrogen source added (CT), were planted at each site (Figure 3.1). Plots were randomized within four blocks, each block with two plots of each N source. Four plots of each N source at each site were amended with biochar before planting. Biochar was created through pyrolysis of mango branches within a barrel surrounding by high temperature fire. On January 16th, 2018 with 137.5 kg $ha^{-2}$ of potassium, 437.5 kg $ha^{-2}$ of phosphorus, and 10,000 kg $ha^{-2}$ of biochar were applied at the Mandacaru site. Corn was planted on January 17th, 2018. Bebedouro was field dressed identically on March 12th, 2018 and planted on March 13th, 2018. UF plots were dressed with 100 kg $ha^{-1}$ of urea fertilizer at each site two weeks following planting. Pesticides were applied to each site as needed.

## Static Chamber Measurements of GHG

Chamber construction and sampling protocol followed previous methods[72,73] with some material and size modifications, as explained below. Chambers were inserted at the Mandacaru site on January 17th, 2018. These chambers were made of PVC pipe and caps. One chamber was inserted 5 cm into the soil in the center row of each plot with an internal above soil volume of 3.5 L. At Bebedouro, chambers were inserted on March 12th, 2018, again one per plot in the center row. These chambers were made of sheet metal covered in reflective aluminum with an internal above soil volume of 77 L. Different chambers were used at each site due to construction and transportation limitations at the Mandacaru site, which was farther from the central research station. Chambers were sampled every two weeks until corn was harvested, with one extra measurement the week following urea fertilizer application. At Mandacaru, 20 mL samples were taken in the mid-morning at 5-minute intervals over a total of 20 minutes. At Bebedouro, samples were taken at 10-minute intervals over 40 total minutes due to the larger chamber size. All samples were analyzed via gas chromatography (GC) with a flame ionizing detector for carbon species and an electron capture device for $N_2O$.

Fluxes for each gas were calculated using the following formula:

$$F = m \times V/A \quad [1]$$

Where **F** is soil flux in μmol $m^{-2}$ $sec^{-1}$ or μmol $m^{-2}$ $hr^{-1}$ for $CO_2$ and $N_2O/CH_4$ respectively, **m** is the rate of GHG concentration changed over 20 or 40 minutes in μmol $m^{-3}$ $sec^{-1}$ or μmol $m^{-3}$ $hr^{-1}$, **V** is chamber volume in $m^3$, and **A** is the chamber surface area in $m^2$. Only slopes with $R^2$ values of 0.75 or greater were included for analysis to only assess fluxes with strong trends.

## $NH_3$ Flux Measurements

Soil $NH_3$ fluxes were measured at the Bebedouro site over the entire growing season. Two methods were used: a vacuum pump acid trap and static bottle methods, both with 0.05 M sulfuric acid. For the vacuum pump acid trap, previous methods were modified with a Balston filter replacing the inlet acid trap to remove ambient $NH_3$, reduced flow rate of 1.5 L $min^{-1}$, and use of a fritted Midget impinger in the acid trap to increase diffusion of gas[75]. For the static bottle method, semi-static chamber designs were based off of other studies and intended to be low cost for comparison with the acid trap[118,119]. Chambers were 2 L soda bottles with the bottoms removed. The bottoms were attached to the top of the bottle to prevent rain or particle intrusion into the bottle. For each sampling, a 15 cm by 2.5 cm strip of foam was soaked in 20 mL of 0.05 M sulfuric acid and hung in the bottle with the bottom of the strip resting in the remaining acid. Bottles were left for 24 hours, and washed with acid to remove all captured ammonia. All acid samples for both methods were analyzed using the indophenol blue method[76].

## Soil Parameters

Soil moisture and temperature were measured in each plot as GHGs were being sampled. Two soil moisture readings per plot were taken within 1 cm of chamber walls using a Campbell Scientific Hydrosense II instrument, and were recorded as volumetric water content. Soil temperature was taken using a Spectrum digital soil thermometer (product number 6300), as was air temperature for flux calculations. Soil at the Bebedouro site was sandy and soil at the Mandacaru site had a heavy clay content.

## Plant Growth and Yield

Five full corn plants were randomly sampled at the V6 stage from each plot on March 7$^{th}$ from Mandacaru and on April 20$^{th}$ from Bebedouro. These plants were then dried in an oven at 70° C for 24 to 48 hours until dry and weighed to determine plant growth at the middle point of the growing season. At the end of the growing season (April 16$^{th}$ for Mandacaru and June 11$^{th}$ for Bebedouro), 10 cobs from 10 plants were randomly sampled and dried from each plot. Ear, kernel, and cob weight were recorded to assess yield.

## Theory/Calculation

All statistics were carried out using R version 3.5.1. Mean comparisons were done with an initial ANOVA test and further explored with a Tukey's comparison when there were more than two pairs[84]. Cumulative sums for each gas were calculated over the growing season by assuming the average fluxes for a given treatment applied to the days following until the next sampling date.

Additionally, a linear regression of individual log-transformed (after a Shapiro-Wilks test showed increased normality after transformation) fluxes controlling for soil temperature and moisture was performed for each of the GHGs. The regression assessed significance at the $\alpha$=0.05 level and allowed for expansion of the Tukey's comparisons to understand why N sources or biochar application could affect fluxes and if differences remained or changed after controlling for soil parameters. The equation for the linear regression is as follows:

$$Y_s = \beta_0 + \beta_1 N\ Source_1 + \beta_2 N\ Source_2 + \beta_3 N\ Source_3 + \beta_4 N\ Source_4 + \beta_5 Biochar + \beta_6 Mois + \beta_7 Temp + \varepsilon \quad [2]$$

Where **$Y_s$** is soil trace gas emissions with s for separate log transformed gas species, **N Source** variables indicate the existence of urea fertilizer, government recommended inoculant, Fernandes lab inoculant, and cowpea (all with control plots as a reference for N Source), **Biochar** indicates the addition of biochar compared to no biochar as a reference, **Mois** is percent soil volumetric water content, and **Temp** is soil temperature in degrees centigrade.

Finally, a net CE was calculated for each N-source and plots with or without biochar amendment using the seasonal sums of GHG's calculated and estimates of other agricultural inputs. Seasonal sums were calculated by extrapolating the flux measured on a sampling date to the days between sampling. GHG CEs were calculated for $N_2O$ and $CH_4$ fluxes in reference to the global warming potential (GWP) of 1 kg of $CO_2$[120]. The Intergovernmental Panel on Climate Change (IPCC) has determined that 1 kg of $N_2O$ has the GWP of 298 kg $N_2O$ in a 100-year horizon and 1 kg of $CH_4$ has a GWP equivalent to 25 kg $CO_2$[121]. Previously estimated CE's for various agricultural practices were used to determine the effects beyond soil emissions of each system tested[122]. In the present study, hand tilling was used, which was not included in Lal et al. (2004)[122]. Tillage is assumed to be half of the rotary hoeing estimate from Lal et al. (the tillage system most similar in soil disturbance to hand tilling) for a total of 1.0 kg CE ha$^{-1}$. The C loss of biochar production was assumed to be 85%, according to previous studies of high temperature, low technology biochar production[40,41]. This amounted to 8,500 kg of C lost for 1 hectare of biochar application at a rate of 1kg m$^{-2}$. This assumes that the tree was already going to be cut down, because if the tree were to be planted with the intention of being used for biochar, the carbon sequestration from growth would have to be accounted for as well. The CEs of all soil fluxes and agricultural practices were summed to estimate a net CE of each system. Net CEs were then calculated in reference to grain yield data by dividing net CE by kg $ha^{-1}$ of grain for each system. One cob per plant and a plant every 20 cm as planted for a total of 75 cobs in each 12 $m^2$ plot was assumed.

## Missing Data

Soil temperature and moisture data were available for all days that GHG fluxes were measured, except on April 9th at Bebedouro due to an equipment malfunction. For that date, averages from the two sampling periods before and after the 9th were used. For $CO_2$ flux data, the only N-source that had missing data was with the government recommended inoculant plot on January 31st at Mandacaru. $N_2O$ data are missing in all plots on four sampling dates (Jan. 31st, Feb. 8th, Feb. 21st, Mar. 2nd) at Mandacaru due to a failure of the electron capture device in the GC. Additionally, if no fluxes were detected with an $R^2$ above 0.75 for a given N source of a sampling date, those data are also missing. In total, 22 of 40 possible $N_2O$ fluxes across N sources at Mandacaru were missing and 11 out of 40 were missing at Bebedouro. 14 of 40 possible $CH_4$ fluxes were missing at Mandacaru and 5 out of 40 were missing at Bebedouro. Data on plots with and without biochar were available on all sampling dates except for $N_2O$ during the instrument malfunction at Mandacaru (Jan. 31st, Feb. 8th, Feb. 21st, Mar. 2nd).

For cumulative sums, if any N-sources had missing data (with/out biochar plots had data for every sampling day), a surrogate of the average of the sample date before and after the missing data was used to calculate the sums between sampling dates. This interpolation could bias results towards false negative, or potential differences between systems may not be discernible.

Soil temperature and moisture values were not always taken on the same days as $NH_3$ collection. For days without direct measurements, $NH_3$ fluxes were paired with the soil parameter data from measurements within two days of $NH_3$ sampling. $NH_3$ data from both bottles and the acid trap were used for the regression. On days where data from both methods is available, an average of both is used for the regression. Cumulative sums of $NH_3$ were calculated by extrapolating the average from each N-source over the days between sampling.

## Results

### GHG's

ANOVA and Tukey's comparisons tests between GHG fluxes by N source and biochar amendment did not show any significant differences at either site (Figure 3.2). Daily means at the did not show any strong difference (Figure 3.S1). At Bebedouro, increases in $CO_2$ and $N_2O$ were observed early in the growing season in fertilized plots, as well as a large increase in $CH_4$ in cowpea plots in the middle of the growing season (Figure 3.S2). All fluxes were of greater magnitude at Bebedouro compared to Mandacaru (Figure 3.2).

At Mandacaru, cumulative growing season sums of $CO_2$ were the largest in plots with cowpea (0.58 kg $m^{-2}$) and urea fertilizer (0.44 kg $m^{-2}$) as an N source and lower in biochar amended plots (0.34 kg $m^{-2}$), compared to ones without (0.46 kg $m^{-2}$). Cumulative sums of $N_2O$ were somewhat lower in plots with urea fertilized (0.16 g $m^{-2}$) and FI plots (0.14 g $m^{-2}$). Cumulative sums for $CH_4$ varied greatly, with CT and FI plots acting as overall sinks (-0.26 g $m^{-2}$ and -0.76 g $m^{-2}$ respectively). Plots with biochar (-0.31 g $m^{-2}$) were greater cumulative $CH_4$ sinks than those without (-0.05 g $m^{-2}$).

At Bebedouro, cumulative $CO_2$ sums in plots with urea fertilizer (3.06 kg $m^{-2}$) and government recommended inoculant (3.08 kg $m^{-2}$) were higher than other treatments. Cumulative $N_2O$ sums were higher in control (2.35 g $m^{-2}$) and urea fertilizer plots (2.34 g $m^{-2}$) compared to other N sources, and plots without biochar (2.88 g $m^{-2}$) were higher compared to those with biochar (1.72 g $m^{-2}$). Only control plots acted as a cumulative sink for $CH_4$ at the Bebedouro site (-6.60 g $m^{-2}$), with urea fertilized plots as the largest $CH_4$ source (4.53 g $m^{-2}$) (Figure 3.3).

The multiple linear regression for $CO_2$ at Mandacaru indicated that biochar-amended plots decreased fluxes by -20.1% (95% CI=-35.3, -1.30) (p-value=0.04), compared to those without. Cowpea and urea fertilizer N sources had 55.0 (95% CI=12.0, 114.6) (p-value=0.001) and 41.3% (95% CI=1.30, 97.0) (p-value=0.04) higher $CO_2$ fluxes, respectively, than the control plot (Table 3.1). Regressions for $N_2O$ and $CH_4$ emissions did not have any significant N-source or biochar coefficients at the $\alpha$=0.05 level (data not shown).

### $NH_3$

Initial mean comparisons and ANOVA testing between $NH_3$ fluxes by N source and biochar amendment did not show any significant differences at either site (Figure 3.S3). Mean $NH_3$ fluxes from bottle measurements were much lower than measurements from the acid trap (0.43, (95% CI=0.40, 0.47) and 6.61 (95% CI=5.98, 7.24) respectively). Acid trap fluxes did not correlate well with averages of bottle measurements from the same plots ($R^2$=0.11). The multiple linear regression of log-transformed $NH_3$ fluxes showed a -19.9% (95% CI=-0.43, -0.014) decrease in flux in biochar amended plots significant at the $\alpha$=0.10 level (Table 3.1). $N_2O$ and $NH_3$ did not have a significant linear relationship ($R^2$=0.03). Cumulative sums of $NH_3$ were highest in control plots and lowest in government recommended inoculant plots (Figure 3.3).

## Plant Biomass and Yield

All plant biomass and kernel yield measurements were not significantly different across N sources or biochar amendments (Table 3.S1), except for plots with government-recommended inoculants (0.53 kg (95% CI=0.39, 0.68)), which had lower average grain yields per plant than plots treated with urea fertilizer (0.86 kg (95% CI=0.73, 0.99)). Yields were significantly higher at Mandacaru compared to Bebedouro for plots with cowpea and both bacterial inoculants as the N source.

## Net CE

When taking into account the CE for all three GHG's and a variety of agricultural practices employed in this experiment, all treatments were net sources of CE at both sites (Table 3.2). Net CE was highest in plots with cowpea (2,499 kg C $ha^{-1}$) and urea fertilizer (1,819 kg C $ha^{-1}$) as an N source at the Mandacaru site. Plots with urea fertilizer (16,585 kg C $ha^{-1}$) had the highest net CE at the Bebedouro site. Control plots had the lowest net GWP at both sites.

Plots with biochar had a lower net CE than those without at both sites without factoring in the production of biochar as an input. However, once production was included, plots with biochar had a higher net CE than those without (Table 3.2). For example, at Mandacaru, plots with biochar had an initial net CE of 1,588 kg C $ha^{-1}$ compared to those without (1,996 kg C ha $^{-1}$) but this increased to 10,008 kg C $ha^{-1-}$ when factoring the production of biochar.

When calculating per kg grain yield, the N sources of cowpea (0.046 kg CE $kg_{grain}^{-1}$) and urea (0.033 kg CE $kg_{corn}^{-1}$) fertilizer were the largest net CE at the Mandacaru site (Table 3.2). At Bebedouro, plots with cowpea (0.29 kg CE $kg_{corn}^{-1}$) and urea fertilizer (0.31 kg CE $kg_{corn}^{-1}$) had the largest net CE of all N sources. Plots with biochar had a lower net CE per kg of corn (0.029 kg

C ha $^{-1}$) than those without before factoring in biochar production (0.034 kg C ha $^{-1}$), but increased after accounting for biochar production (0.183 kg C ha$^{-1}$, Table 3.2).

## Discussion

### $CO_2$

Cowpea and urea-based fertilizer as an N-source were associated with increased $CO_2$ fluxes at the Mandacaru site after controlling for soil moisture and temperature and had the highest $CO_2$ contributions to net CE. When urea is applied, there is higher microbial biomass and plant growth, potentially causing this increase in $CO_2$ flux[123,124]. For plots containing cowpea intercropped with corn, adding cowpea could potentially increase soil respiration through increased soil porosity, microbial activity, or SOC[87,124,125]. These increased $CO_2$ fluxes were not found at the Bebedouro site. Higher overall respiration from the sandier soil due to increased porosity[126], potentially masked the differences. This study provides the first known measurements of soil GHG fluxes in cowpea and corn intercropping systems, but was limited in soil parameter measurements that could explain this potential increase in $CO_2$ flux in these potential CSA systems. The magnitude of $CO_2$ fluxes was greater at Bebedouro, potentially because the chambers used there were made of metal and therefore more likely to have an increased internal temperature. Neither inoculant showed significant differences in seasonal means compared to other N-sources, potentially because of a low population of growth-promoting bacteria which would otherwise increase respiration[127,35].

Biochar was significantly associated with a decrease in $CO_2$ flux at the Mandacaru site when controlling for soil parameters and N sources in the linear regression. Plots with biochar had a lower $CO_2$ contribution to net CE at both sites compared to unamended plots. Previous studies regarding the effect of biochar on $CO_2$ fluxes vary in their conclusions[116], but at least one meta-analysis suggests that $CO_2$ flux is increased[36]. However, when soil is high in soil organic matter (SOM), $CO_2$ can be decreased with application of biochar due to shifts in the microbial community towards fungi[37]. The soil at Bebedouro has a higher sand content, which has been shown to be associated with increased soil $CO_2$ flux when amended with biochar, but lower SOM may have prevented a measurable difference in flux in the current study[37]. Additionally, biochar application rates of 10 t $ha^{-1}$, the rate in the present study, might not be enough to affect $CO_2$ emissions[128]. Future studies should measure SOM, soil microbe populations, and soil porosity to better understand the effects of biochar on $CO_2$ fluxes in these corn cropping systems to better assess net CE. This study contributes data to the body of literature regarding soil fluxes in biochar amended soils, specifically being the first study to look at biochar with cowpea and corn intercropping.

$CO_2$ was the largest GHG contributor to net CE at both sites for all systems, as seen in previous studies[109,110]. This indicates soil respiration is a key component in intercropping and other systems in assessing overall climatic impact. However, accounting for the SOC added to the soil, especially in the cowpea intercropping system, could offset some $CO_2$ fluxes and change the net CE of these systems. Assessment of SOC, soil texture, and soil microbes would provide a better estimate of $CO_2$ fluxes and contributions to net CE in future studies.

## $N_2O$

ANOVA and Tukey's comparisons and linear regressions did not show any significant differences in soil $N_2O$ flux between N sources or with/without biochar application. Living mulch intercropping systems have been shown to increase seasonal $N_2O$ flux[21,111], However, this effect could be reduced in the present study, because the nitrogen fixing crop is not located in the chamber bases releasing N into the soil, as was the case in Turner et al. 2016 and the first study of this dissertation. While plots with urea-based fertilizer were not significantly higher than other N sources when comparing means, despite that relationship being a well-documented phenomenon[97]. Higher $N_2O$ fluxes from urea fertilizer might not have occurred in the present study because of the coarse temporal scale of measurements, and potentially missing large $N_2O$ fluxes caused by fertilizer application. The CE of $N_2O$ fluxes among N sources varied greatly between the two sites, further emphasizing the uncertainty when measuring these fluxes at such coarse temporal scale and the need to measure these agricultural systems with more robust sampling.

$N_2O$ fluxes did not differ between plots with biochar and those without. One lab-based study has demonstrated that the effects of biochar on $N_2O$ might not occur until after multiple wetting and drying cycles over five months[129]. The current study only took place over one three month growing season, and longer-term studies may yield stronger effects for daily measurements, mean comparisons, and linear regressions. $N_2O$ reduction by biochar has been demonstrated in multiple studies, and is often attributed to adsorption of $NH_4^+$ and $NO_3^-$[36]. However, this effect is not as prominent in field-based studies due to lower mixing rates of biochar with the soil[36]. Finally, the effects of biochar on $N_2O$ can be affected in different ways by nitrification and denitrification depending on soil type[39]. Future studies should take more frequent samples, measure $NH_4^+$, $NO_3^-$, soil pH, and explore denitrification/nitrification pathways to potentially observe and explain reductions in $N_2O$ flux at a finer scale than the seasonal CE differences observed here.

All systems were net sources of $N_2O$, which contributed to a positive net CE, an effect that has been seen in previous studies[109,110]. While the magnitude of CE was lower than $CO_2$, $N_2O$ is an important gas to consider when assessing the climate impacts of an agricultural system, as it does not have a direct offsetting relationship with SOC like $CO_2$ does.

## $CH_4$

Mean comparisons and linear regressions did not show any significant differences in soil $CH_4$ flux between N sources or with/without biochar application. Intercropping systems, such as corn and cowpea, have been shown to be sinks for $CH_4$[32]. This effect may not be present in the current study if there are not enough methane oxidizing bacteria in the soil[130]. Urea fertilizer has been correlated with increased $CH_4$ fluxes, potentially through competition between $NH_4^+$ and $CH_4$ methanotrophic enzyme systems[131]. While this effect was seen at a seasonal level at Bebedouro, it might not have been observed between daily means because of gaps in sample dates or different soil enzymes compared to Venterea et al (2005)[131]. The effects on net CE contributions from $CH_4$ varied between N sources and sites, indicating the variability of these fluxes and the need for future studies to include more frequent sampling and assessments of soil bacteria involved in methane oxidation.

A meta-analysis of biochar effects on $CH_4$ found inconclusive results[36], indicating that this process is not well understood, supported by the variability between sites in the present study. Individual studies have shown that biochar can reduce $CH_4$ oxidation[132] or small reductions in the CE of $CH_4$ following application[128]. More investigation into the $CH_4$ oxidizing potential of bacteria in biochar/non-biochar plots could help explain the processes affecting the CE of $CH_4$ in these systems.

### $NH_3$

There were no significant differences in mean $NH_3$ fluxes when comparing N-sources or biochar amendment. One of the only previous studies measuring soil $NH_3$ flux in intercropping systems observed mostly negative $NH_3$ fluxes, potentially due to a water film on soil and several intercropped plants' surfaces from a humid environment, which increases $NH_3$ deposition[114]. The positive fluxes in the current study could be due to a much more arid environment and bare soil, both conducive to $NH_3$ emissions rather than deposition[114]. There was a reduction in $NH_3$ fluxes with biochar application at the $\alpha=0.10$ level in the linear regression at Bebedouro. In soil with low clay content like found at this site, $NH_3$ emissions have been reduced by biochar amendments, potentially due to adsorption of $NH_3$ in soil or a low potential to increase respiration in sandy soil compared to more compact, clay-based soil[37,38]. More frequent sampling and laboratory-based assessments of adsorption in soil from field tests in future studies could help confirm or refute the $NH_3$ reductions indicated in this study. Compared to GHG, $NH_3$ fluxes are understudied from biochar amended soils.

### Yields & Net Global Warming Potential

Dry plant mass and yields were similar across N-sources and biochar application. This indicates if these alternative sources of N to conventional fertilizer can reduce environmental impact, they may not harm yields. Higher yields at the Mandacaru site for the cowpea and inoculant N-sources compared to the same plots at the Bebedouro site indicate that higher clay content could be particularly important for these non-conventional methods of agriculture that do not use urea fertilizer.

This study was the first to calculate the net CE of a cowpea and corn intercropping system and a net CE of biochar factoring in production of the biochar. The net CE potential of agricultural inputs other than biochar production were fractional compared to the impact of the soil fluxes measured in this study. Using urea fertilizer as an N-source had the largest CE at Bebedouro and the second highest at Mandacaru, corroborating previous studies[131]. Cowpea had the highest CE at Mandacaru and the highest net CE per kg of corn at both sites, indicating that it may not be a potential GHG mitigating technique due mostly to increased soil respiration. However, intercropping systems have been shown to increase SOM in previous studies[133,125], which can offset increased soil GHG flues and create a system with an overall negative CE[109,110]. Future studies should measure SOM in conjunction with GHG fluxes, especially to expand on the novel measurements in cowpea and corn intercropping systems.

Net CE was higher for all N sources at Bebedouro compared to Mandacaru, due to the increased $CO_2$ and $N_2O$ fluxes potentially from larger chambers generating more heat from aluminum coverings or soil properties not measured in the present study. At both sites, the net CE of plots with biochar was lower than those without before factoring in the biochar production, but higher when the production was factored in. The C lost in biochar production far outweighed the potential reductions in soil GHG fluxes. This finding indicates that biochar may not be a successful CSA option when viewed holistically. Biochar production should be taken into account in all future studies regarding the potential climate benefits of biochar.

## Conclusion

This study examined the soil GHG and $NH_3$ fluxes in agricultural systems with five different N sources both with and without biochar soil amendments. Increases in soil $CO_2$ flux were associated with cowpea and urea fertilizer as N sources. Cowpea and urea-based fertilizer had the highest net CE of all N sources. However, increased soil SOC from cowpea should be measured in future studies to see if C sequestration could offset increased fluxes and indicate intercropping as a potential CSA system. The absences of effects of other N sources on GHG's could be explained by a variety of soil parameters in future studies. Biochar amendment was associated with reductions in $CO_2$ and $NH_3$. Plots with biochar incorporated into the soil had a lower net CE when not accounting for biochar production. When accounting for biochar production, plots with biochar had a much higher net CE, indicating that biochar amendments may not be as beneficial to the climate as previous studies have indicated. Future studies investigating the GHG mitigating potential of biochar should factor in the carbon cost of biochar production in this possible CSA system.

The lack of certain soil data, the most important being SOC, soil texture, and microbes, limits this study's ability to assess microbial or physical processes. However, the multiple soil trace gases and agricultural inputs provided an initial assessment of overall climatic impact and net CE of cowpea and corn intercropping systems and added to the literature on the potential of biochar to reduce climatic impacts. Future studies should take more frequent samples, include relevant soil parameter measurements, and include agricultural inputs in net CE calculations.

# Tables and Figures

Table 3.1: Significant Results from Linear Regressions of Log-Transformed Fluxes

| Mandacaru $CO_2$ | | | | |
|---|---|---|---|---|
| Variable | Estimate (β) (95% CI) | Standard Error of Estimate | Percent Change (%) (95% CI) | P-value |
| Intercept | 0.11 | 0.58 | NA | 0.85 |
| Soil Temperature | 0.002 (-0.03, 0.04) | 0.02 | 0.23 (-3.09, 3.67) | 0.89 |
| Soil Moisture | -0.009 (-0.02, 0.002) | 0.005 | -0.009 (-1.89, 0.16) | 0.10# |
| Cowpea | 0.44 (0.11, 0.76) | 0.16 | 55.0 (12.0, 114.6) | 0.01* |
| Urea Fertilizer | 0.35 (0.01, 0.68) | 0.17 | 41.3 (1.30, 97.0) | 0.04* |
| Gov. Inoculant | 0.19 (-0.17, 0.54) | 0.18 | 20.4 (-15.7, 71.8) | 0.30 |
| Fernandes Inoculant | 0.18 (-0.15, 0.52) | 0.17 | 20.3 (-14.2, 68.6) | 0.28 |
| With Biochar | -0.22 (-0.44, -0.01) | 0.11 | -20.1 (-35.3, -1.30) | 0.04* |

| Bebedouro $NH_3$ | | | | |
|---|---|---|---|---|
| Variable | Estimate (β) (95% CI) | Standard Error of Estimate | Percent Change (%) (95% CI) | P-value |
| Intercept | 1.22 | 1.40 | NA | 0.38 |
| Soil Temperature | 0.003 (-0.10, 0.10) | 0.05 | 0.30 (-9.21, 10.8) | 0.95 |
| Soil Moisture | 0.03 (-0.04, 0.10) | 0.04 | 0.03 (-4.27, 10.2) | 0.45 |
| Cowpea | 0.25 (-0.15, 0.65) | 0.20 | 28.4 (-14.2, 92.1) | 0.22 |
| Urea. Fertilizer | 0.18 (0.20, 0.57) | 0.19 | 20.3 (-18.3, 77.0) | 0.35 |
| Gov. Inoculant | 0.19 (-0.17, 0.54) | 0.18 | 20.4 (-15.7, 71.8) | 0.30 |
| Fernandes Inoculant | 0.30 (-0.08, 0.69) | 0.19 | 35.2 (-8.11, 98.9) | 0.12 |
| With Biochar | -0.22 (-0.47, 0.03) | 0.13 | -19.9 (-37.6, 2.75) | 0.08# |

*$p< 0.05$, #$p<0.10$

Inoculants are government recommended bacterial inoculant (Gov. Inoculant), and Fernandes laboratory bacterial inoculant (Fernandes Inoculant). Reference for N source categorical variable is control plots and no biochar amendments is reference for plots with biochar.

Table 3.2: Net Carbon Equivalent (CE) for All Treatments

Table S1: Net Carbon Equivalent (CE) for All Treatments

CE by Treatment for Various Agricultural Inputs (kg C $ha^{-1}$)

| Treatment | Irrigation | $NH_3$ Fertilizer | No-till Planting | Forage Harvesting | Tillage | Biochar Prod. |
|---|---|---|---|---|---|---|
| CP | 84.9 | NA | 3.8 | 13.6 | 1.0 | NA |
| UF | 84.9 | 10.1 | 3.8 | 13.6 | 1.0 | NA |
| GI | 84.9 | NA | 3.8 | 13.6 | 1.0 | NA |
| FI | 84.9 | NA | 3.8 | 13.6 | 1.0 | NA |
| CT | 84.9 | NA | 3.8 | 13.6 | 1.0 | NA |
| BC Y | 84.9 | NA | 3.8 | 13.6 | 1.0 | 8500 |
| BC N | 84.9 | NA | 3.8 | 13.6 | 1.0 | NA |

Mandacaru CE by Treatment for All Greenhouse Gases (GHG) (kg C $ha^{-1}$)

| Treatment | $CO_2$ | $N_2O$ | $CH_4$ | Total GHG | Net CE | Net CE per kg of corn |
|---|---|---|---|---|---|---|
| CP | 1520 | 820 | 57 | 2397 | 2499 | 0.046 |
| UF | 1208 | 477 | 22 | 1707 | 1819 | 0.033 |
| GI | 935 | 633 | 96 | 1663 | 1766 | 0.031 |
| FI | 1022 | 425 | -189 | 1258 | 1360 | 0.023 |
| CT | 866 | 637 | -65 | 1438 | 1540 | 0.024 |
| BC Y | 937 | 627 | -78 | 1486 | 1588 (10,008*) | 0.029 (0.183*) |
| BC N | 1259 | 648 | -13 | 1894 | 1996 | 0.034 |

Bebedouro CE by Treatment for All Greenhouse Gases (GHG) (kg C $ha^{-1}$)

| Treatment | $CO_2$ | $N_2O$ | $CH_4$ | Total GHG | Net CE | Net CE per kg of corn |
|---|---|---|---|---|---|---|
| CP | 7395 | 2613 | 539 | 10546 | 10648 | 0.29 |
| UF | 8357 | 6982 | 1133 | 16472 | 16585 | 0.31 |
| GI | 8401 | 1031 | 758 | 10190 | 10292 | 0.22 |
| FI | 6771 | 1414 | 408 | 8594 | 8696 | 0.26 |
| CT | 5022 | 7011 | -1651 | 10381 | 10484 | 0.25 |
| BC Y | 6760 | 5130 | 227 | 12117 | 12220 (20720*) | 0.29 (0.49*) |
| BC N | 7893 | 8574 | 95 | 16562 | 16664 | 0.39 |

N sources cowpea intercropping (CP), urea fertilizer (UF), government recommended bacterial inoculant (GI), Fernandes laboratory bacterial inoculant (FI) and control (CT). Plots were either amended with biochar (BC Y) or not (BC N). All values are reported as kg C $ha^{-1}$.

*Includes biochar production in net CE calculation

Figure 3.1: Layout of Plots

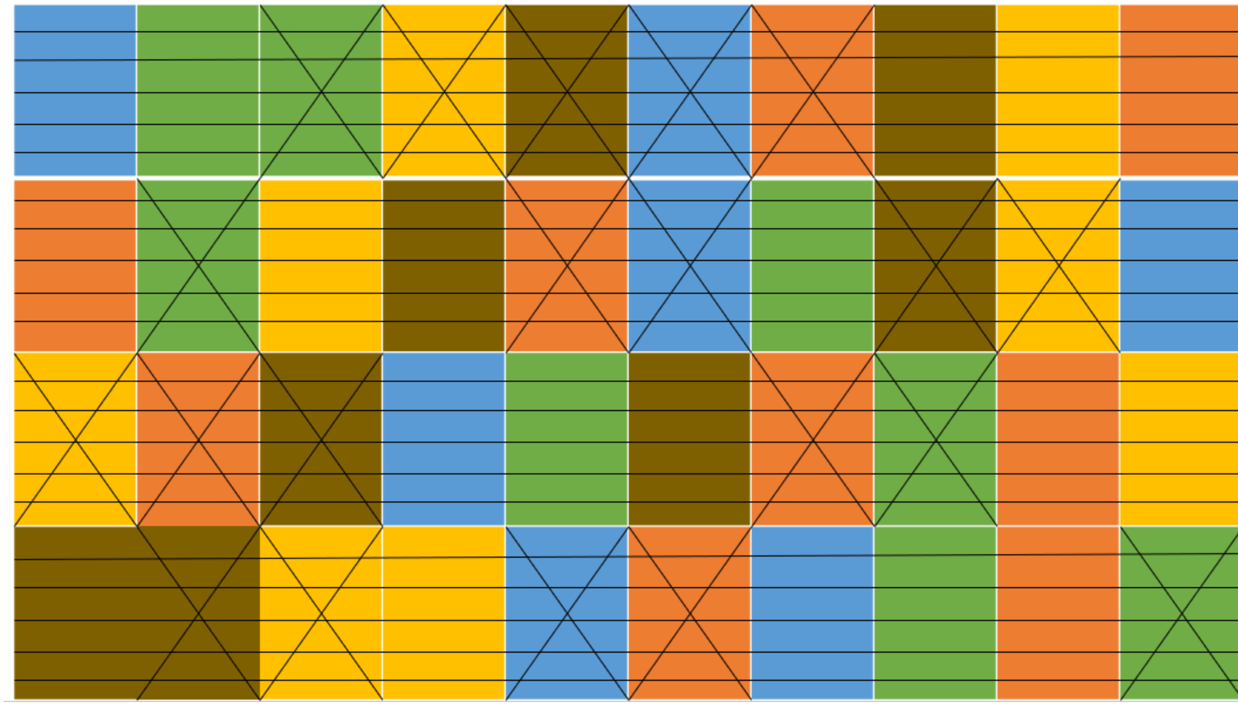

Figure 3.1: Plots were laid out in the same locations at each site. The colors correspond to N sources and are as follows: cowpea (green), urea fertilizer (red), government-recommended inoculant (yellow), Fernandes-developed inoculant (blue), and control (brown). Plots with an X on them were amended with biochar and those without were not. Each plot was 3 m x 4 m with five lines of irrigation spaced 80 cm apart represented by the horizontal lines above.

Figure 3.2: GHG Means by N-Source and Biochar Amendment

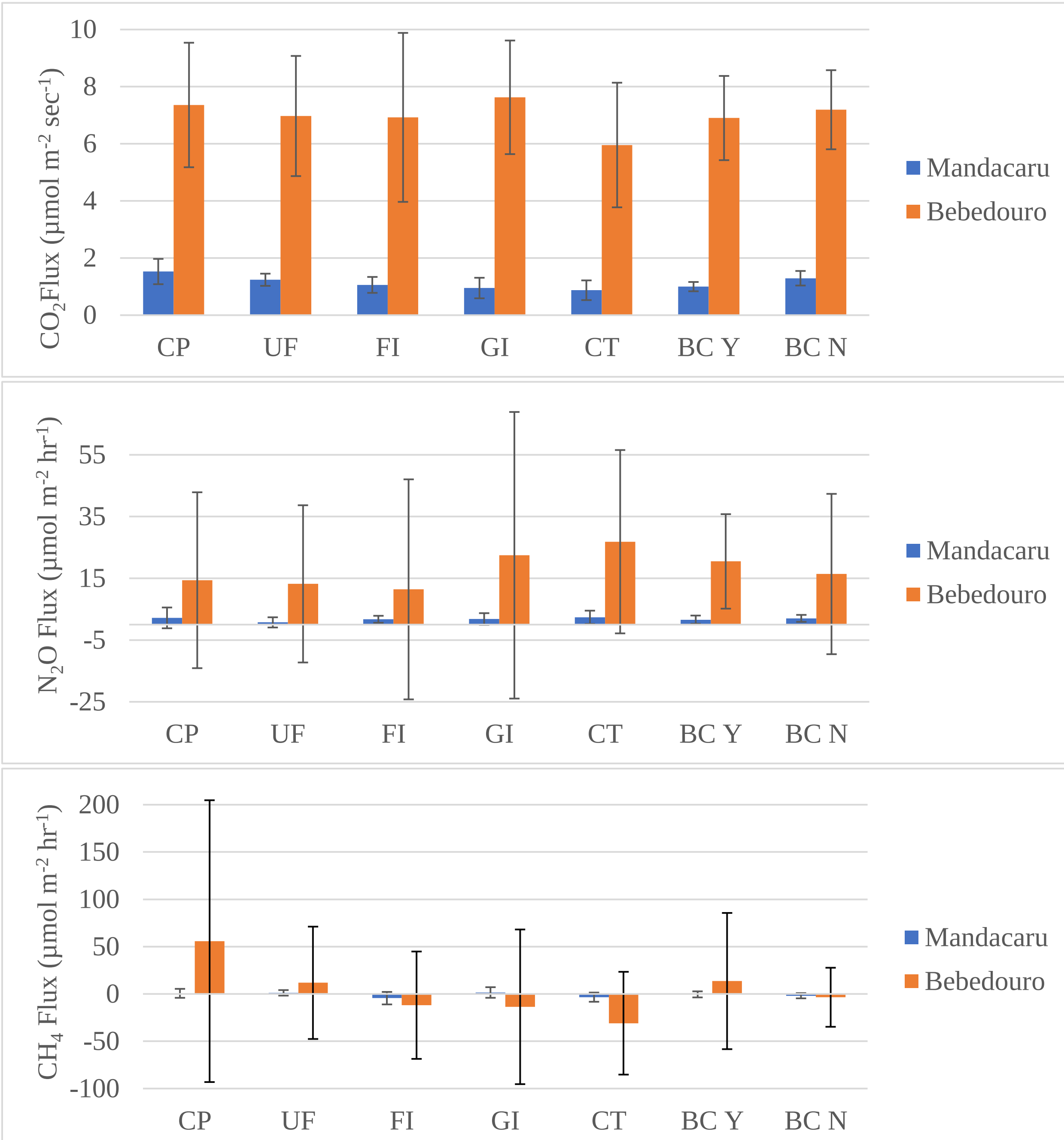


Figure 3.2: Mean soil greenhouse gas (GHG) fluxes by N-source and biochar amendment. N sources are cowpea intercropping (CP), urea fertilizer (UF), Fernandes laboratory bacterial inoculant (FI), government recommended bacterial inoculant (GI), or control (CT). Plots were either amended with biochar (BC Y) or not (BC N). 95% CI error bars are displayed.

Figure 3.3: Seasonal Cumulative Sums of all Gases

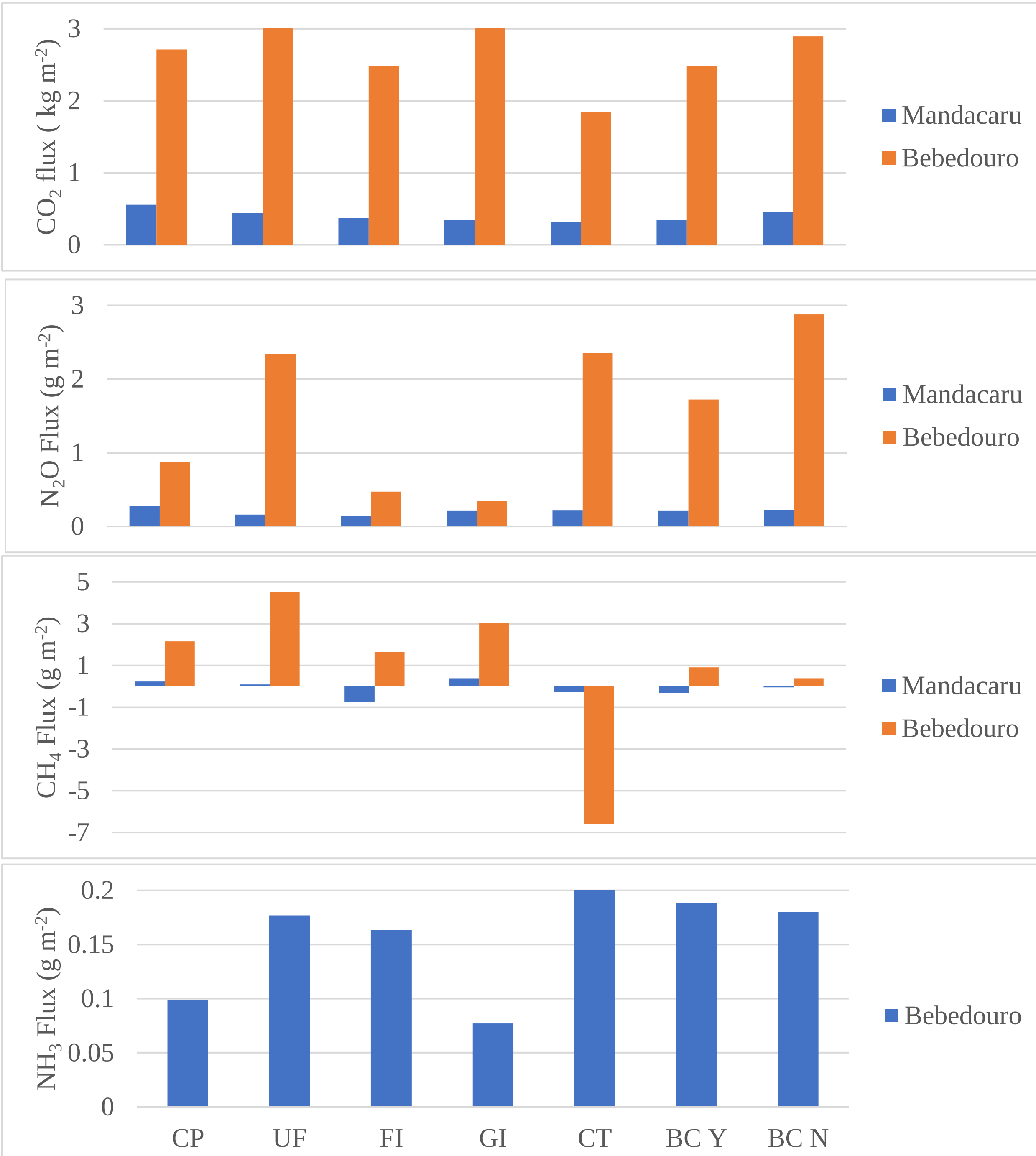


Figure 3.3: Cumulative sums for all gases over the entire growing season at each test location. From top to bottom; $CO_2$, $N_2O$, $CH_4$, and $NH_3$. $CO_2$ fluxes are reported in kg $m^{-2}$, while the other three gases are reported in mg $m^{-2}$. N sources are cowpea intercropping (CP), urea fertilizer (UF),

government recommended bacterial inoculant (GI), Fernandes laboratory bacterial inoculant (FI) and control (CT). Plots were either amended with biochar (BC Y) or not (BC N).

# Supplementary Material

Supplementary Table 3.S1: Plant Weights and Yields

| Table S1: Mean Plant Dry Weight and Yield (Kernel Weight) | | |
|---|---|---|
| Mandacaru | | |
| N-Source | Plant Dry Weight (g) | Kernel Weight (kg) |
| CP | 255 (157, 353) | 0.87 (0.56, 1.18) |
| UF | 263 (206, 319) | 0.89 (0.38, 1.40) |
| FI | 296 (244, 348) | 0.92 (0.76, 1.07) |
| GI | 264 (180, 349) | 0.93 (0.64, 1.24) |
| CT | 269 (172, 367) | 1.03 |
| Biochar Amendment | Plant Dry Weight (g) | Kernel Weight (kg) |
| With Biochar | 287 (256, 318) | 0.88 (0.81, 0.95) |
| Without Biochar | 254 (221, 286) | 0.94 (0.69, 1.19) |
| Bebedouro | | |
| N-Source | Plant Dry Weight (g) | Kernel Weight (kg) |
| CP | 102 (34.5, 170) | 0.58 (0.36, 0.80) |
| UF | 128 (61.6, 194) | 0.86 (0.73, 0.99) |
| FI | 170 (84.8, 256) | 0.76 (0.60, 0.92) |
| GI | 163 (68.2, 258) | 0.53 (0.39, 0.68) |
| CT | 128 (18.6, 237) | 0.66 (0.57, 0.76) |
| Biochar Amendment | Plant Dry Weight (g) | Kernel Weight (kg) |
| With Biochar | 133 (86.2, 180) | 0.67 (0.57, 0.76) |
| Without Biochar | 143 (94.6, 192) | 0.69 (0.58, 0.80) |

N sources are cowpea intercropping (CP), urea fertilizer (UF), government recommended bacterial inoculant (GI), Fernandes laboratory bacterial inoculant (FI) and control (CT). Plots were either amended with biochar (BC Y) or not (BC N).

95% confidence intervals are presented after means when enough data was available.

Supplementary Figure 3.S1: Time Series of Mandacaru GHG Emissions

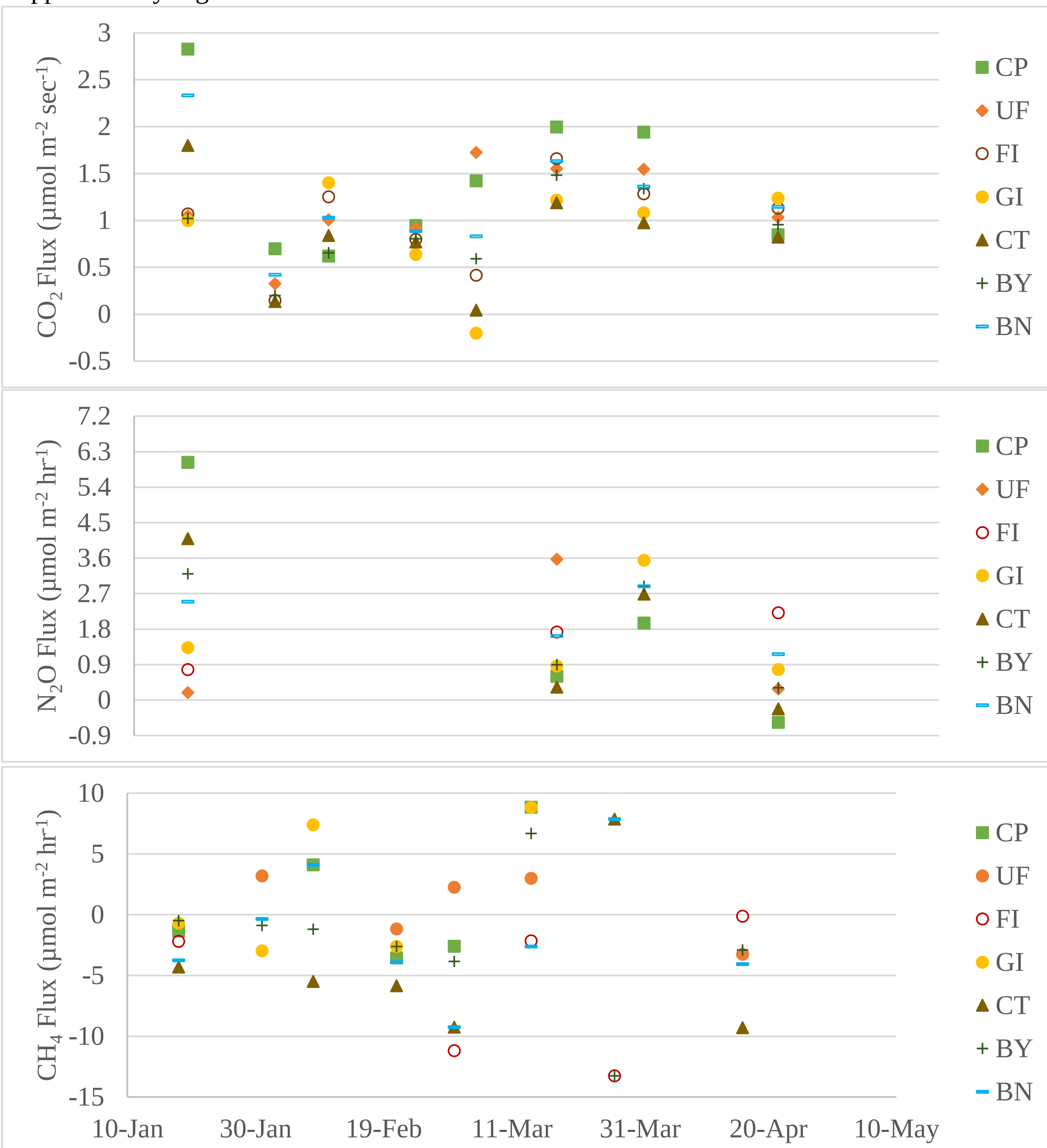


Figure 3.S1: Time series of GHG's over the growing season at Mandacaru. Fluxes are in µmol $m^{-2}$ $hr^{-1}$ for $N_2O$ and $CH_4$ and in µmol $m^{-2}$ $sec^{-1}$ for $CO_2$. $CO_2$ fluxes are generally higher in plots without biochar and plots with cowpea or urea fertilizer compared to other N sources. N sources are cowpea intercropping (CP), urea fertilizer (UF), Fernandes laboratory bacterial inoculant (FI),

government recommended bacterial inoculant (GI), or control (CT). Plots were either amended with biochar (BC Y) or not (BC N).

Supplementary Figure 3.S2: Time Series of GHG at Bebedouro

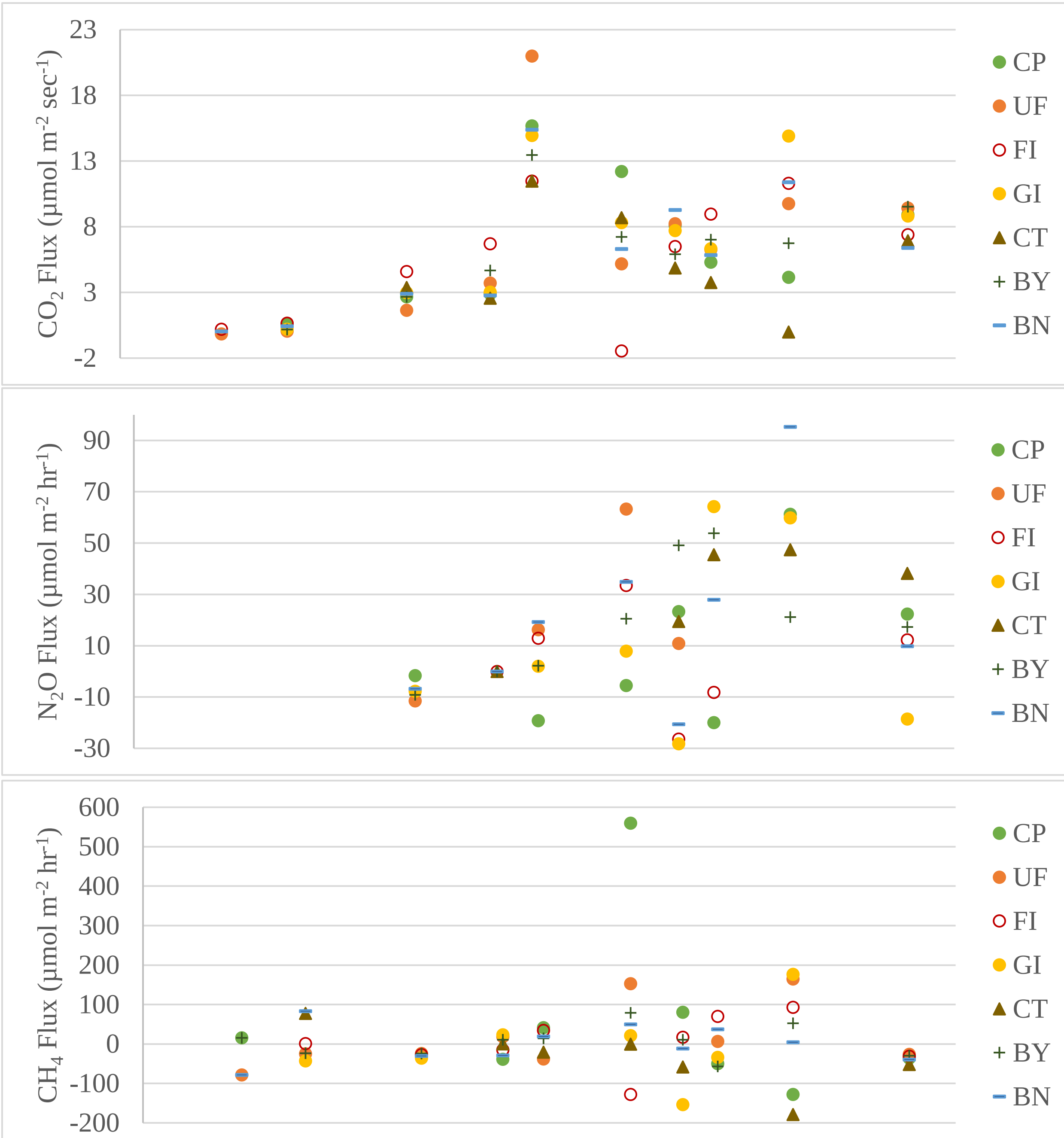


Figure 3.S2: Time series of GHG's over the growing season at Bebedouro. Fluxes are in µmol $m^{-2}$ $hr^{-1}$ for $N_2O$ and $CH_4$ and in µmol $m^{-2}$ $sec^{-1}$ for $CO_2$. N sources are cowpea intercropping (CP), urea fertilizer (UF), Fernandes laboratory bacterial inoculant (FI), government recommended

bacterial inoculant (GI), or control (CT). Plots were either amended with biochar (BC Y) or not (BC N).

Supplementary Figure 3.S3: Times Series of $NH_3$ Fluxes and Comparison Between Bottle and Trap Measurements

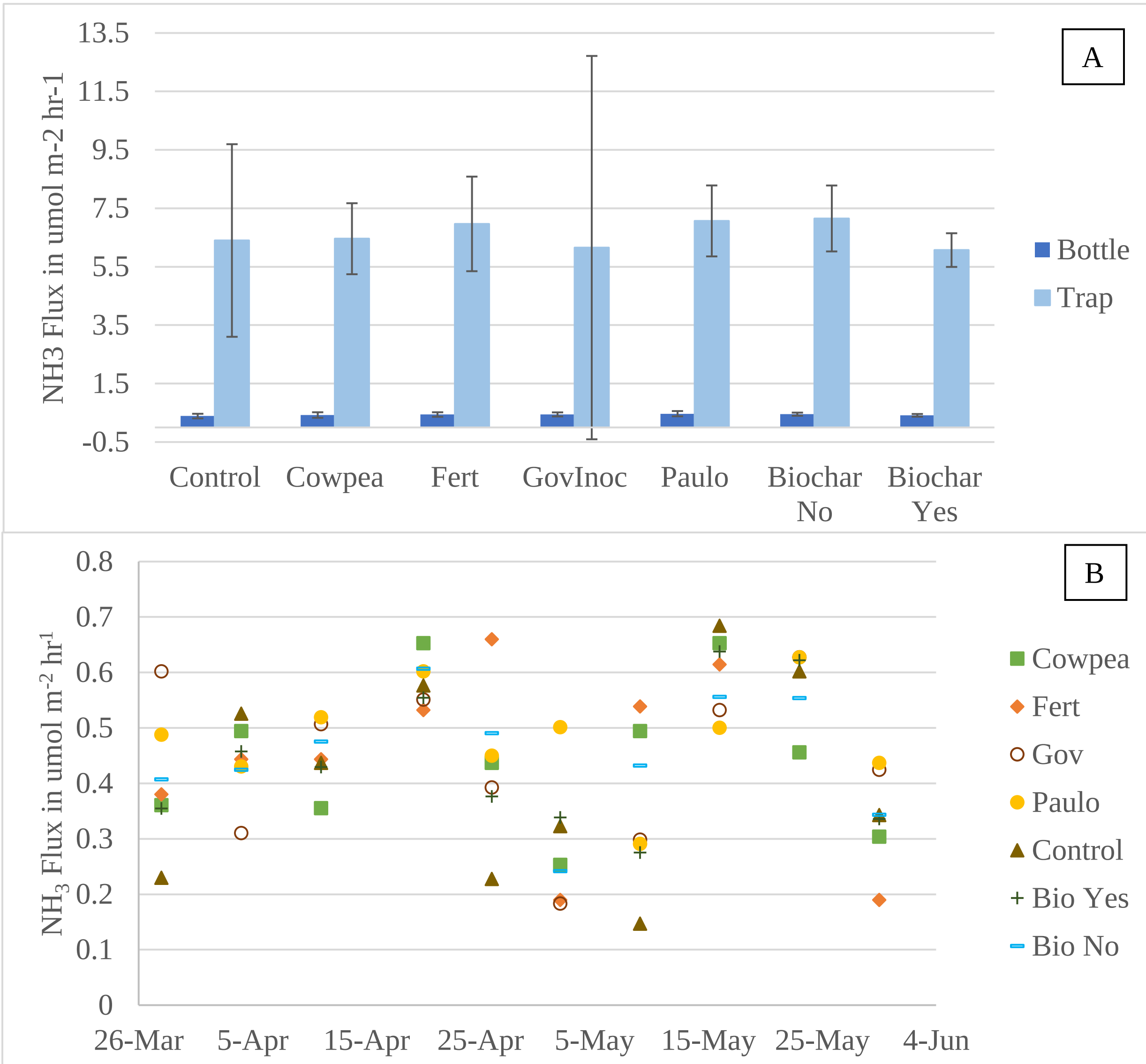


Figure 3.S3: A-Comparison of $NH_3$ fluxes measured using the bottle method and the acid trap across different N sources and biochar use. Acid trap fluxes are significantly higher for all treatments, indicating large loss to evaporation in bottle method. B-Time series of $NH_3$ fluxes from bottle method across different N-sources and biochar use.

# Chapter 4: Community-Engaged Assessment of Soil Heavy Metal Contamination Under Two Risk Frameworks in Atlanta Urban Growing Spaces

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Abstract

Urban agriculture is emerging as a method to improve food security and public health in cities across the United States. However, there is potentially an increased risk of exposure to heavy metals through consumption of contaminated soil, especially for children. There is also debate on what concentrations of heavy metals in soil constitute a low risk for those engaged in urban agricultural activities. This community-engaged study measured the concentrations of 25 metals including lead (Pb), arsenic (As), chromium (Cr), and cadmium (Cd) in 19 urban agricultural and residential sites in West Atlanta and compared them to three rural background sites. Heavy metal concentrations were compared in the context of the Environmental Protection Agency's (EPA) regional screening levels (RSL) and University of Georgia's (UGA) extension service low risk levels (LRLs). The majority of sites were below EPA RSLs for most metals. For Pb, As, Cr, and Cd, there were several sites that were above the UGA LRL but below the EPA RSL. Using concentrations lower than EPA RSLs to assess risk highlights a more endemic problem of long-term exposure to a larger population. A slag dump site was discovered with community and regulatory partners, which greatly exceeded both low risk levels. This study reaffirmed best practices for growing food in contaminated soil that can lower the potential risk within both risk frameworks which should be promoted in future policies.

## Key Words

Urban agriculture, heavy metals, regional screening levels, soil

## Abbreviations

Environmental Protection Agency (EPA), regional screening level (RSL), community-engaged research (CER), Historic Westside Gardens (HWG), incremental sampling method (ISM), x-ray fluorescence (XRF), lead (Pb), arsenic (As), chromium (Cr), and cadmium (Cd), barium (Ba), silver (Ag), calcium (Ca), copper (Cu), iron (Fe), mercury (Hg), potassium (K), manganese (Mg), nickel (Ni), rubidium (Rb), antimony (Sb), strontium (Sr), thorium (Th), titanium (Ti), zinc (Zn), cesium (Cs), sulfur (S), tin, (Sn), tellurium (Te), uranium (U)

## Introduction

Urban agriculture and gardening can improve food security, build community capacity, and provide education regarding food and agriculture to community members[43]. There are numerous public health benefits to urban agriculture, including increased consumption of fruits and vegetables[44,134], decreased chronic disease[45,135], decreased body mass index in overweight children[136], and improved mental health[137]. Accordingly, urban agriculture is increasing in popularity across the United States with an estimated 18,000 community gardens in 2018[138]. In one country-wide study, 46% of urban farms were classified as start-up farms in 2014, or less than 10 years old[139]. In Atlanta, there were over 350 community gardens and 90 urban farms as of 2018[140].

Urban soil is often contaminated with heavy metals such as lead (Pb), arsenic (As), chromium (Cr), and cadmium (Cd) from anthropogenic sources including highways, Pb-based paint, and industrial waste[141,46,142]. Metal refining waste (slag), disposed of improperly, cause very high concentrations of heavy metals in soil[143,144]. These heavy metals can cause serious health problems, even from long term exposure at low levels and especially in children[145,146,147,148]. The risks of long-term exposure to heavy metals are not as well documented or understood as acute exposures[149]. Heavy metal concentrations in soil are often higher in urban[46], low income, and minority neighborhoods[49], potentially leading to a greater risk from chronic exposure in these areas. Heavy metal concentrations may also exceed regulatory limits in urban gardens[47,48]. While consumption of food grown in contaminated soil is not thought to be a serious exposure risk[150,151], there is a potential risk for children through hand-to-mouth-behavior[50]. Heavy metals such as Pb can also decrease nutritional value of crops, exacerbating malnutrition in areas where fresh food is scarce[152]. The benefits of urban agriculture likely outweigh the risks of contaminated soil[51].

However, the difference in risk from city to city or within neighborhoods is unknown, and working to further quantify that risk is important in promoting and creating safe urban growing spaces[58].

Traditionally, the health risks associated with heavy metals in soil in the United States have been assessed using the Environmental Protection Agency (EPA)'s residential soil regional screening levels (RSL)[60]. Other agencies have suggested lower values for soils used in agriculture due to increased interaction with the soil[61,62] and the EPA states that, "Alternative approaches for risk assessment may be found to be more appropriate at specific sites[60]." The University of Georgia (UGA) Extension office advises "low risk" levels (LRL) for urban gardening based on the Georgia Environmental Protection Division's Rules for Hazardous Site Response[63]. EPA RSLs factor in incidental ingestion of soil, dermal contact with soil, and inhalation of volatiles and particulates emitted from soil[153]. The UGA LRLs also factor in ingested soil attached to vegetables and produce that may have absorbed contaminants[63]. The differences in risk assessment between the two agencies results in UGA LRLs being up to 75% lower than EPA RSLs, which could affect how risk is determined at a given site. No studies to our knowledge have explored how these different risk frameworks apply to the same set of urban soil samples.

The goal of this study was to measure heavy metal concentrations in current and potential urban growing spaces in Atlanta and determine the risk potential as defined by the US EPA and UGA Extension service guidelines. There is a growing body of literature that suggests urban agriculture activities, including academic research, need to take a broader view and address issues surrounding food in urban areas through more diverse lenses[43,52,53]. This includes focusing on social inclusion, access in underprivileged neighborhoods, and informational accessibility[54]. Community-engaged research (CER), which aims to include marginalized community residents as valued participants in decision-making and community solution-building processes around issues that concern their lives, is one method that can promote social inclusion in science[55]. Citizen science through CER has been successful in urban agricultural settings and can increase community knowledge and participation[56,57]. CER studies on soil contamination and urban agriculture are very limited despite the potential benefits, and have not provided strong quantitative results[154].

This study sought to use CER to gather soil samples and measure heavy metal concentrations in West Atlanta, partnering with Historic Westside Gardens (HWG), a non-profit working to “plant home food gardens to cultivate relationship with the community and to encourage equitable development[155].” Soil samples were gathered from 19 urban sites, including two with slag present, using the incremental sampling method (ISM). The samples were analyzed for heavy metal concentrations with x-ray fluorescence (XRF). All data was then assessed in two risk frameworks and explored how different practices could affect interpretations of risk. The study had two specific goals; 1) Assess baseline levels and sources of heavy metal soil contamination through affordable and accessible sampling/analysis techniques while engaging with community members and 2) Explore how differences between the EPA RSL’s for heavy metals and the UGA Extension “low risk” concentrations could affect risk interpretations, best practices, and policy decisions.

## Methods and Materials

### Site Descriptions and Soil Sampling

A total of 355 samples from 19 urban sites and three rural background sites (which were at least 30 miles from the center of Atlanta with no known industrial or other potential anthropogenic contaminations) were analyzed (Figures 4.1 & 4.2, Table 4.1). Community partners provided insight for site selection. Sites were chosen due to importance to current food production or future garden locations with some snowball sampling with neighbors of initial sites. Two sites were added after a community partner discovered slag waste from metal refining (Figure 4.1). A conceptual site model (CSM) was developed with input from site owners and gardeners for each site,[156] dividing the location into decision units (DU) with potentially different levels of soil contamination due to site history.

Each site was sampled according to the incremental sampling method (ISM), which uses a robust subsampling protocol for each DU[157]. Three composite samples of 30 subsamples were taken from each DU. Subsamples were taken from random locations in a 30 square that encompassed the entire size of the DU. Four community partners working for HWG were trained in ISM protocol and took samples with and without student researchers. ISM has been shown to provide an accurate mean and 95% upper confidence level (UCL) with three replicates of combined samples if the sampling area is divided into a grid of 30 sections[157]. Each composite sample was disaggregated, oven-dried, and sieved at 100 µm. Additionally, 34 pieces of slag were sampled for analysis. Slag was crushed via sledge hammer, subsampled randomly, and crushed to a fine powder with a mill before analysis.

## Soil and Slag Analysis

All soil and slag samples were first analyzed for 25 heavy metals using XRF. Each sample was measured a minimum of four times with the XRF, and only samples with a mean relative standard deviation (RSD) of 35% or lower, which is the EPA 4 quality objective outlined in their Field Operations Guide, were used for analysis.

## Statistics

All statistics were carried out in Microsoft Excel, R version 3.5.1, and SAS 9.4. A 95% upper confidence limit (UCL) for all XRF data was calculated using the following formula:

$$\mu + Tinv(0.1, n-1) * (\frac{SD}{\sqrt{n}})$$

Where μ is the mean of all readings, *Tinv* is the inverse T-distribution, 0.1 is the 1-sided p-value for a 95% confidence interval, *n* is the number of XRF readings, and SD is the standard deviation of XRF readings. UCLs were used in place of means for all data analysis in order to compare with EPA RSLs. Overall UCLs were calculated for each site using the average of each sample UCL. All XRF data was adjusted with a five-point standard curve of metals for Pb, As, and Cr. Ba was adjusted with a curve of three points, 16 metals were adjusted by a curve with two points, and five metals had no standard curve and were unadjusted (Table 4.2). Significant differences between site locations or traits were determined using a Student's T-test with a α value of 0.05. Each site was assessed in the framework of the high and low regulatory levels; the EPA RSLs and UGA LRLs respectively. All HWG members who were involved with the project were informed on XRF protocols and statistical analyses before sharing results to be transparent about how data was acquired.

## Results and Discussion

### Priority Metals Under Different Risk Frameworks By Site

All three rural background sites had overall 95% UCLs lower than EPA RSLs and EPA LRLs for Pb, As, Cr, and Cd (four priority soil contaminants). Three of 11 urban residential sites had overall Pb UCLs above 400 ppm (the EPA RSL), but no urban agricultural sites were above the Pb RSL. Ten residential and two urban agricultural sites were above the UGA LRL of 75 ppm

Pb in agricultural soil, making for an increase of 56% compared to the number of sites above EPA RSLs. No rural or urban sites had overall UCLs above the EPA RSL for As, but five sites were over the UGA LRL of 20 ppm for an increase of 31% comparatively. All sites had overall total Cr UCLs above 30 ppm, the EPA RSL for Cr(VI),. However, none of these came close to exceeding the EPA RSL for of 350,000 ppm Cr(III).The measurements presented are total Cr, not speciated into Cr(VI) and Cr(III), which limits the conclusions that can be drawn. At one urban site, the overall Cr UCL was above the UGA LRL level of total Cr of 100 ppm. No sites were over 210 ppm Cd, the EPA RSL, but all were over 2 ppm Cd, the UGA LRL level.

Overall, there were large differences in the number of sites deemed as low risk for the priority metals of Pb, As, Cr, and Cd based on which risk framework was used. Seeing as many of these sites are used for the production of food and have children interacting with them, it is important to consider the policy implications of using other metrics besides the EPA RSL's for health risks associated with contaminated soil. However, if measurements or classification of contaminated soil are misrepresented, this can hamper the promotion and implementation of urban agriculture for those who would benefit most[158]. While benefits of urban agriculture likely outweigh the risks of contaminated soil[51], the majority of studies use EPA RSL's and conclusions could potentially change with other risk frameworks. More studies comparing these frameworks in urban agriculture settings could help lower health risk through a product certification scheme with guaranteed low levels of contamination[159]. However, a product certification scheme should be carried out with care as it could alienate gardeners or farmers who do not have the resources to remediate soil. Due to the limited number of studies comparing risk frameworks on the same data and the relative modernity of those other than the EPA's, we recommend further research.

## Location and Slag Impacts on Heavy Metal Concentrations

Heavy metal concentrations varied between urban soil and rural backgrounds, and were significantly higher in samples from sites contaminated with metal refining slag (Table 4.2, Figure 4.3). Two lots with slag were discovered by a community partner near other measured urban sites and assessed with assistance from members of EPA Region 4 and the Georgia Department of Public Health. Heavy metal concentrations were often much higher in soil at the slag sites compared to other urban samples, and were even higher in the crushed and sieved fragments of slag (Table 4.2, Figure 4.3). Pb was higher in slag soil and pieces (1,383 ppm (95% CI=557.3, 2,209) and 1,290 ppm (95% CI=813.0, 1,769) respectively) than in other urban samples (158.8 ppm (95% CI=134.8, 182.8)), and even more so than in rural background soils (34.7 ppm (95% CI=28.2, 41.1)). The overall UCL's of Pb were lower than the EPA RSL for both rural and urban soils, but above for the soil at the slag site.

As concentrations were lower in rural soil (3.31 ppm (95% CI=2.19, 4.44)) compared to those in urban samples (10.9 ppm (95% CI=8.59, 13.2)), which were lower than soil at the slag site (95.6 ppm (95% CI=53.0, 138.1)) or of slag fragments (157.6 ppm (95% CI=103.9, 221.3)). Rural and urban samples had overall As UCLs below the EPA RSL's and UGA LRLs of 67 and 20 ppm respectively. Overall As UCLs from slag soil and pieces exceeded LRLs from both frameworks.

Cr concentrations were not significantly different between rural and urban soils (58.7 ppm (95% CI=50.5, 66.9) and 61.7 ppm (95% CI=58.3, 64.5) respectively), but were higher in slag soil and pieces (119.1 ppm (95% CI=99.7, 138.4) and 254.1 ppm (95% CI=170.3, 337.9) respectively). The Cr overall UCLs exceeded UGA LRLs in slag soil and pieces, but did not in rural and other urban soils.

There were significantly higher overall Cd UCLs in non-slag urban soils (13.6 ppm (95% CI=12.2, 15.0)) compared to rural backgrounds (5.60 (95% CI=3.36, 7.83)), both of which exceeded the UGA LRL of 2 ppm but not the EPA RSL of 210 ppm. There were no significant differences in Cd between slag soils and pieces compared to other urban soils, due in part to large variability between samples. The higher variability in Cd could be due to a standard curve with less available data points than the other three priority metals in this study (Table 4.2), and future studies should use more expansive standards for all metals to better assess the impact of slag. Metals besides Pb, As, Cr, and Cd had significant differences across rural, urban, and slag sites (Table 4.2). However, there were different degrees of standard curves available for the XRF used in this study, which reduces reliability in the data beyond the priority metals.

The heavy metal concentrations at the slag sites exceeded those of other urban samples, which were already higher than rural backgrounds[46]. By focusing on social inclusion, carrying out a project in an underprivileged neighborhood, and making information available throughout the project[54], a unique partnership was formed to tackle a potential environmental justice issue. The discovery of the slag could potentially lead to a longitudinal study, which are needed to better assess the racial and income disparities in exposure to environmental dumping and pollution[160].

Slag increased concentrations of Pb and As. Pb, As, Cr, and Cd[144,143] in soil and UCLs exceeded both EPA RSLs and UGA LRLs, demonstrating how EPA regulations are designed for more severe contamination. However, the overall UCLs for all other urban sites besides those with slag were often below EPA RSLs but above UGA LRLs. Frameworks other than the EPA RSLs should be explored in regards to systemic, lower level heavy metal soil contamination. These elevated concentrations can be widespread in low-income and minority neighborhoods[49]. Frameworks such as the UGA Extension service, which take into account addition exposure pathways when soil is used to grow food, should potentially be used to assess risk in urban growing spaces. Policies should focus on how to fix widespread soil contamination beyond heavily polluted single source sites.

## Effects of Growing Practice on Heavy Metal Concentrations

Each sample was categorized into raised bed (soil generally from another location added above the native soil and contained in a four-sided structure), mound bed (soil generally from another location added above the native soil but not contained on the sides), or bare soil to assess the effect of bedding practices on overall concentrations in the context of the two risk frameworks. Pb, As, and Cr overall UCLs were significantly lower in raised and mound beds compared to bare soil throughout urban soil samples other than the slag sites (Table 4.3). For Pb, mounds beds (66.2 ppm (95% CI=59.8, 72.7)) and raised beds (104 ppm (95% CI=83.9, 125.8)), were lower than in bare soil (308.7 ppm (95% CI=247.1, 370.3)). Mound beds had overall UCLs lower than both EPA RSLs and UGA LRLs. Raised beds and bare soil were below EPA RSLs, but above UGA LRLs. As concentrations were comparable in mounds and raised beds (4.57 ppm (95% CI=1.84, 7.29) and 7.70 ppm (95% CI=5.92, 9.49) respectively), but lower than bare soil (18.9 ppm (95% CI=13.6, 24.3)). As overall UCLs within each of the three categories were below both LRLs. Overall Cr UCLs in raised beds (56.4 ppm (95% CI=52.4, 60.3)) were lower than bare soil samples (71.1 (95% CI=64.4, 77.7)), and all three bed categories were under both risk frameworks thresholds. Cd UCLs were lower in raised beds (10.5 ppm (95% CI=9.00, 11.9)) compared to bare soil (15.5 ppm (95% CI=12.5, 18.4)). All three categories had overall UCLs above the UGA LRL but below the EPA RSL for Cd. One raised bed that tested above the EPA RSL for Pb initially at 403.6 ppm (95% CI=275, 532) was tested lower than the UGA LRL to 72.7 ppm (95% CI=68.39, 77.0) after replacement of soil by the garden's owner. Several metals other than the four priority ones were lower in beds compared to bare soil (Table 4.3).

All samples were also classified as growing or non-growing to assess the impact of plants on heavy metal concentrations within the two risk frameworks. A DU was considered actively growing if there were plants intended for ingestion germinated in the soil at the time of sampling. Overall UCLs were lower for Pb, As, and Cr at sites with crops growing compared to those with no intentional growing occurring (Table 4.3). For Pb, the overall UCL was 94.4 ppm (95% CI=74.9, 113.9) at growing sites and 205.5 ppm (95% CI=167.9, 243.1) without anything growing, both of which are above the UGA LRL but below the EPA RSL. The overall As UCL at growing sites was 6.46 ppm (95% CI=4.87, 8.04) and 14.0 ppm (95% CI=10.3, 17.6) at non-growing sites, both below the two low risk limits. The overall Cr UCL was 53.4 ppm (95% CI=49.4, 57.5) at growing sites and 66.9 ppm (95% CI=62.7, 71.2) at non-growing sites, both below EPA and UGA low risk thresholds There was no significant difference in Cd overall UCL's between growing and not (Table 4.3). Overall UCLs were also lower at growing sites for several other metals including iron (Fe), potassium (K), nickel (Ni), rubidium (Rb), thorium (Th), and titanium (Ti).

This study identified some best practices for reducing soil heavy metal concentrations to below EPA RSL's or UGA LRLs. Raised and mound beds had lower concentrations than native soil, potentially from cleaner imported soil and higher organic matter[59]. Policies funding urban agricultural programs in areas at high risk for soil heavy metal contamination, such as neighborhoods with housing built before 1978[161], should focus on providing materials and clean soil for beds. One HWG grower lowered the concentration of lead in one of their beds from above the EPA RSL to below the UGA LRL by putting new soil into the bed and planting new flowers, another low-cost option for reducing exposure. Community partners were alerted to results as soon as they were analyzed, which allowed for immediate individual behavioral changes such as the integration of new soil and phytoremediating decorative plants.

Adding in new topsoil to a raised or mound bed is one potential low-cost way to reduce Pb exposure on a large scale in urban areas endemic with contamination, as long as added soil is low in Pb concentrations[162]. The way contaminated soil is classified both scientifically and socially can affect the promotion of these practices, potentially hampering urban agricultural growth once a soil is deemed "dangerous"[158]. These low-cost remediation techniques should continue to be promoted through avenues such as extension offices[63] or outreach programs regardless of which risk frameworks are used. Lower-cost remediation techniques such as raised beds and clean soil addition can lower exposure through dilution and reduced contact with contaminated soil while preventing the need for extensive regulations, which could reduce urban agriculture growth[58]. Finally, using gloves while gardening, washing hands afterwards, and changing clothes before coming into the house are other ways to reduce exposure while gardening[58]. These practices should be promoted through outreach programs in areas with potentially contaminated soil.

This study indicated that using a framework that accounts for greater exposure potential in agricultural soils versus residential increases the risk perceived over a set of urban sites. Using UGA LRLs, which are lower than EPA's RSLs, indicates there is a pervasive problem of soil contamination in urban areas in Atlanta. After further research, policies should focus on how to fix widespread soil contamination beyond heavily polluted single source sites. Several low cost, low impact interventions, such as raised/mound beds and clean soil addition, were found in the present study. Policies regarding growing food in potentially contaminated soil should focus on these options instead of extensive regulation, such as mandated testing at the cost of the grower, to continue the promotion of urban agriculture. At the same time, future research should focus on understanding the dermal/oral exposures and health impacts of lower, persistent concentrations of heavy metals in soil. Specifically, exploring bioavailability of soil samples through physiological based testing to estimate health impacts from concentrations between EPA RSLs and other frameworks that consider additional agricultural exposures. Phytoremediation using local, inexpensive plants should be explored in future community-engaged studies testing plants in community growing spaces and could be promoted through seed drives in lower income or minority communities. More in depth analysis of the slag and speciation of the metals in it could also provide information on the origin of the ore used in the slag[144], and thus the potential source.

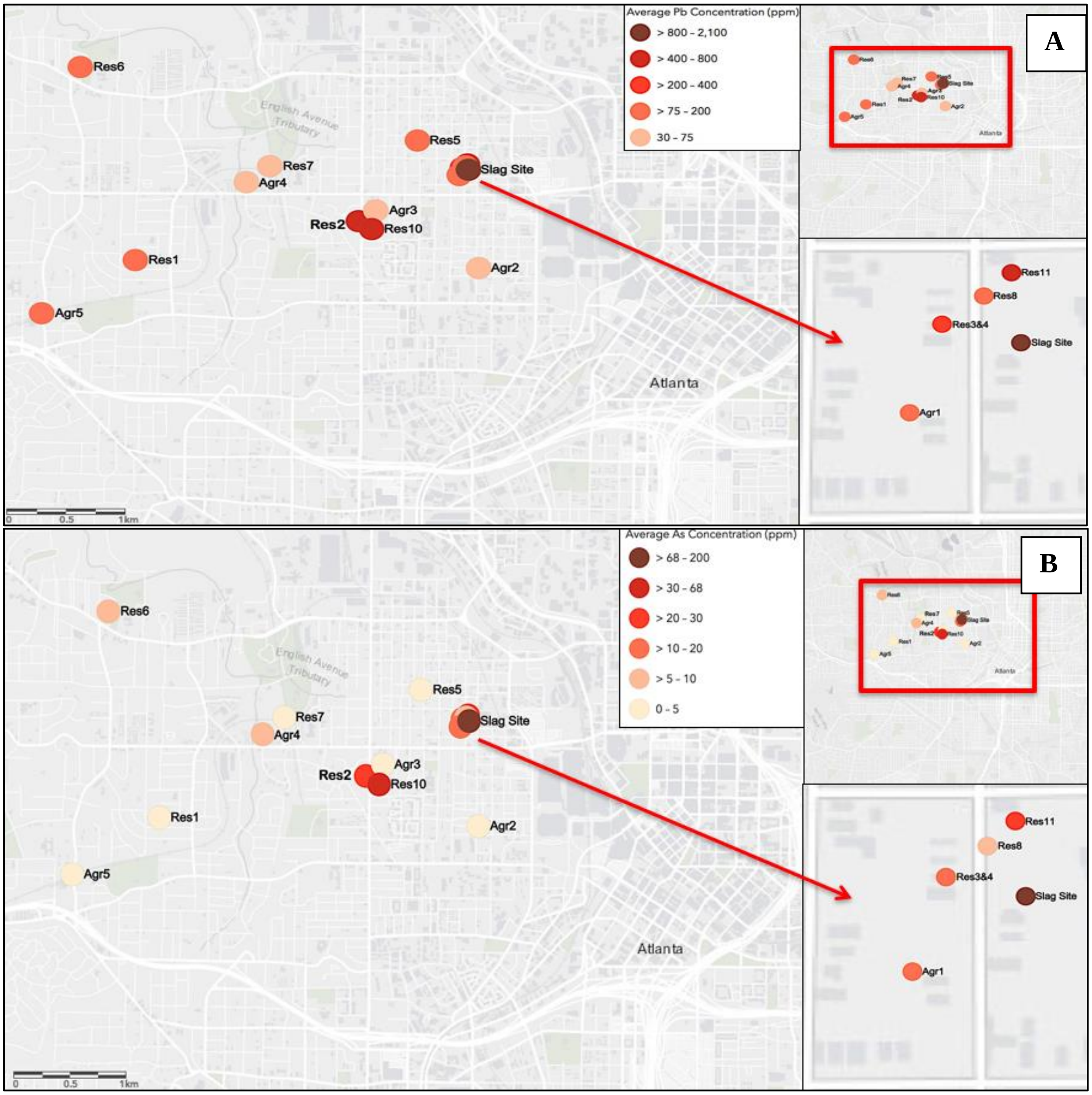
The conclusions drawn from this project were based on soil measurements, but were enhanced with feedback from community partners. The information gathered has been used to instigate outreach initiatives regarding soil testing, best practices for gardening in potentially contaminated soil, and resources on remediation for those with contaminated soil. Future projects regarding phytoremediation of soil and spatial analysis to determine potential sources of heavy metals have been initiated due to this research partnership. Results were presented by community partners and researchers together in academic settings after project completion, including the project’s funding agency’s annual retreat. This provided community partners the opportunity to share their findings with the scientific community, and create a dialogue for future research and outreach. This study showed that community engagement from project planning through data dissemination improved the scientific, behavioral, and policy implications. Future studies on soil contamination in urban spaces should focus on engaging communities as much as possible.

Tables and Figures

Figure 4.1: Lead, Arsenic, Chromium, and Cadmium Mean UCL's by Site

Figure 4.1: Means 95 % upper confidence levels (UCL) for high priority metals of lead (Pb), arsenic (As), chromium (Cr), and cadmium (Cd) in rural background (Bck), residential (Res), and urban agricultural (Agr) sites. EPA residential screening levels (RSL) are denoted by red lines and UGA low risk levels (LRLs) are denoted in orange. EPA RSL's for Cr (350,000 ppm) and Cd (210) are not displayed due to scale differences. Error bars are 95% confidence intervals of the mean of al UCL's from each site.

Figure 4.2: Spatial Distribution of Mean UCL by Site for Pb, As, Cr, and Cd



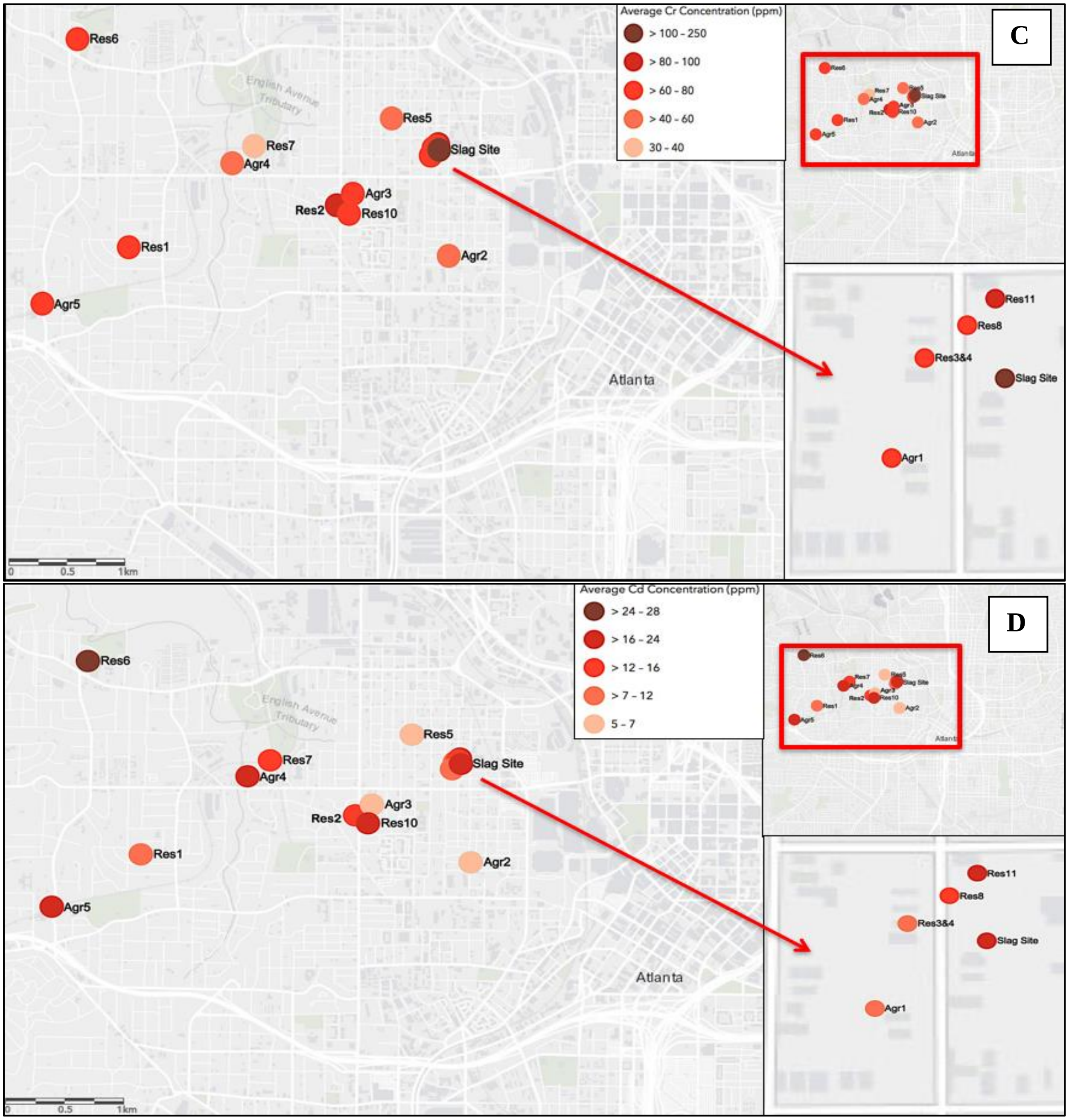



Figure 4.2: Average upper confidence limit by site for lead (Pb) (A), arsenic (As) (B), chromium (Cr) (C), and cadmium (Cd) (D). Concentrations are in parts per million (ppm) and increase as color darkens.

Figure 4.3: Concentrations of Priority Metals Between Rural, Urban, and Slag Sites

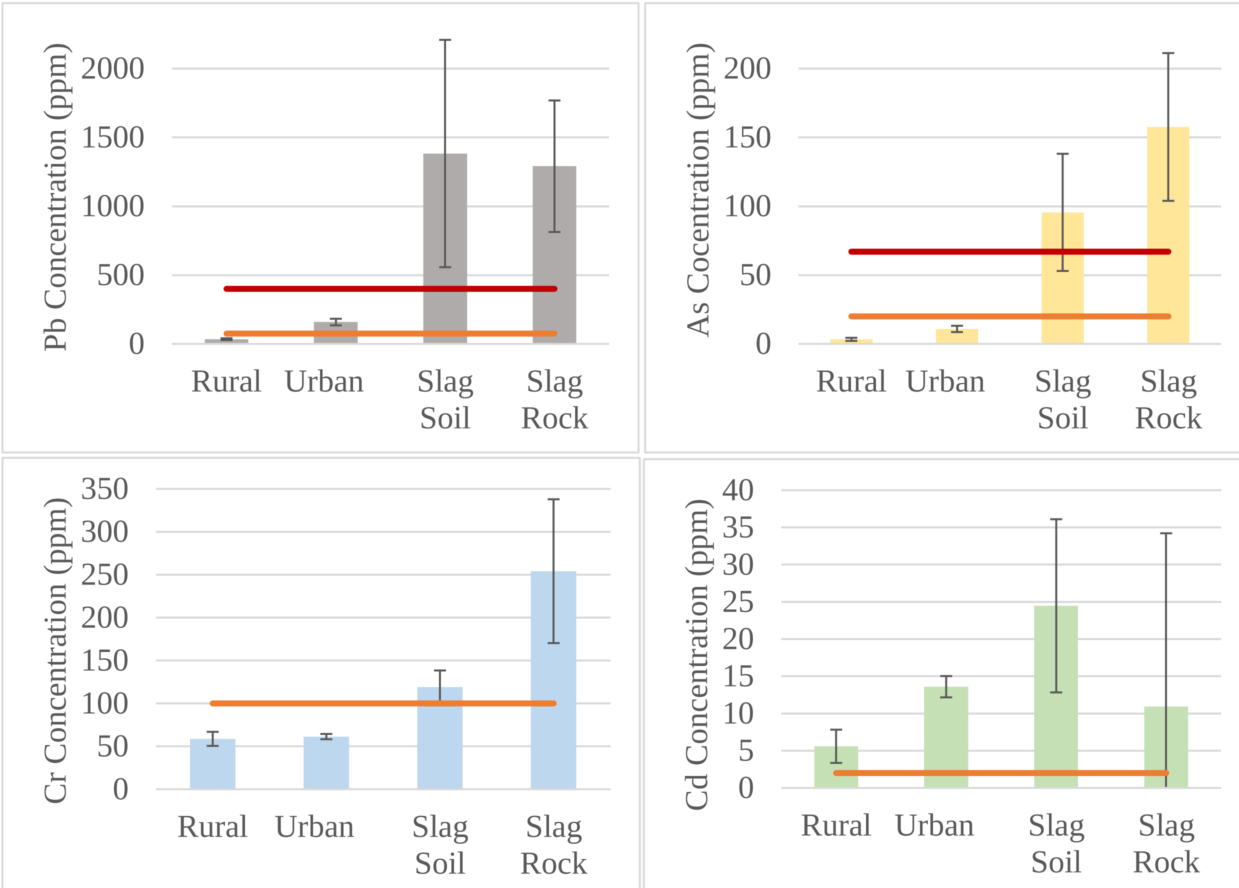



Figure 4.3: Mean upper confidence limits (UCL) of priority metals lead (Pb), arsenic (As), chromium (Cr), and cadmium (Cd) between rural background, urban samples, slag site soils, and slag pieces. All results are in parts per million (ppm). 95% confidence intervals are presented as error bars. EPA residential screening levels (RSL) are denoted by red lines and UGA low risk levels are denoted in orange. EPA RSL's for Cr (350,000 ppm) and Cd (210 ppm) are not displayed due to scale differences.

Table 4.1: Sample Counts for Different Categories

| Table 1: Sample Counts by Site and Categories | |
|---|---|
| **By Site** | |
| Site Name (Coded) | Sample Count |
| Rural Background 1 | 11 |
| Rural Background 2 | 19 |
| Rural Background 3 | 9 |
| Residential 1 | 6 |
| Residential 2 | 19 |
| Residential 3 | 3 |
| Residential 4 | 35 |
| Residential 5 | 9 |
| Residential 6 | 3 |
| Residential 7 | 9 |
| Residential 8 | 3 |
| Residential 9 | 8 |
| Residential 10 | 9 |
| Residential 11 | 3 |
| Urban Agricultural 1 | 12 |
| Urban Agricultural 2 | 44 |
| Urban Agricultural 3 | 24 |
| Urban Agricultural 4 | 106 |
| Urban Agricultural 5 | 9 |
| Slag 1 | 9 |
| Slag 2 | 5 |
| **By Category** | |
| Category | Sample Count |
| Rural Background | 39 |
| Total Urban Samples | 302 |
| Slag Soil | 14 |
| Slag Pieces | 32 |
| No Bed | 64* |
| Raised Bed | 92* |
| Mound Bed | 146* |
| Actively Growing | 127* |
| Not Actively Growing | 175* |

Sample counts from all sites and for notable categories used in mean comparisons. Each sample refers to one aggregate sample of 30 sub samples from on decision unit (DU) from a site. *Counts from a subset of data that was only the urban samples.

Table 4.2: Difference in metal UCL's in ppm between rural, urban, and slag sites

| Metal | Rural (ppm) | Urban (ppm) | Slag Soil (ppm) | Slag Pieces (ppm) |
|---|---|---|---|---|
| Lead (Pb) | 34.7a | 158.8b | 1,383c | 1,291c |
| Arsenic (As) | 3.31a | 10.9b | 95.6c | 157.6c |
| Chromium (Cr) | 58.7a | 61.4a | 119.1b | 254.1c |
| Barium (Ba) | 322.5a | 1,988c | 726.7b | 5,203c |
| Silver (Ag) | 5.56a | 8.20a | 13.8a | 18.0b |
| Calcium (Ca) | 6126a | 9697b | 14,764c | 32,651d |
| Cadmium (Cd) | 5.59a | 13.6b | 24.5b | 10.9a |
| Copper (Cu) | 45.4a | 54.1a | 470.2b | 1,523c |
| Iron (Fe) | 11,887a | 26,337b | 47,992c | 389,837d |
| Mercury (Hg) | 3.76a | 14.5a | 23.3ab | 23.5b |
| Potassium (K) | 13,601a | 15,823a | 18,979a | 13,410a |
| Manganese (Mn) | 606.3ab | 523.9a | 827.6b | 2,149c |
| Nickel (Ni) | 45.9a | 39.1a | 105.5b | 276.0c |
| Rubidium (Rb) | 54.5a | 93.7b | 117.7b | 66.6a |
| Antimony (Sb) | 453.2b | 223.1b | 63.1a | 163.5ab |
| Strontium (Sr) | 59.5a | 82.7b | 162.0c | 652.8d |
| Thorium (Th) | 19.5ab | 16.3a | 45.1ab | 27.9b |
| Titanium (Ti) | 6,803b | 4,023a | 5,252ab | 4,800ab |
| Zinc (Zn) | 61.5a | 232.7b | 1,120c | 1,371c |
| Zirconium (Zr) | 2,053c | 340.4b | 356.0b | 230.6a |
| Cesium (Cs) | 54.1a | 230.3c | 76.4b | 168.7c |
| Sulfur (S) | 940.7a | 894.3a | 2,127b | 4,163b |
| Tin (Sn) | 74.2a | 45.4a | 259.3ab | 831.6b |
| Tellurium (Te) | 117.1a | 143.4ab | 141.3ab | 170.3b |
| Uranium (U) | 123.5b | 103.6a | 137.0bc | 174.4c |

Significant differences in mean 95 % upper confidence levels (UCL) for metals across site locations (rural, urban, soil from slag sites, and slag pieces from slag sites).
Table is divided from top to bottom in descending order of confidence with standard curves that had 5, 3, 2, or 1 points of data.
Letters a, b, c, and d denote significant differences at $\alpha=0.05$ increasing in alphabetical order.
All results in parts per million (ppm).

Table 4.3: Urban Soil Concentrations Across Growing Characteristics

| Metal | No Bed | Raised Bed | Mound | Not Growing | Growing |
|---|---|---|---|---|---|
| Lead (Pb) | 308.7c | 104.9b | 66.2a | 205.5b | 94.4a |
| Arsenic (As) | 18.9b | 7.70a | 4.57a | 14.0b | 6.46a |
| Chromium (Cr) | 71.1b | 56.4a | 58.9ab | 66.9b | 53.4a |
| Barium (Ba) | 2,817b | 2,093b | 416.4a | 1,819a | 2,228a |
| Silver (Ag) | 9.08b | 6.07a | 11.9b | 8.79a | 7.36a |
| Calcium (Ca) | 6,874a | 10,007b | 12,123b | 9,273a | 10,282a |
| Cadmium (Cd) | 15.5b | 10.5a | 20.2b | 14.4a | 12.5a |
| Copper (Cu) | 63.0a | 50.0a | 50.6a | 58.0a | 48.7a |
| Iron (Fe) | 27,948ab | 26,839b | 22,875a | 27,960b | 24,100a |
| Mercury (Hg) | 22.6a | 3.26a | 15.6a | 17.1a | 4.64a |
| Potassium (K) | 17,000b | 13,900a | 18,534b | 16,732b | 14,563a |
| Manganese (Mn) | 453.8a | 557.9b | 547.2b | 500.3a | 556.5a |
| Nickel (Ni) | 47.1b | 30.0a | 47.7b | 44.5b | 30.7a |
| Rubidium (Rb) | 117.0b | 80.6a | 90.4a | 110.7b | 70.3a |
| Antimony (Sb) | 185.0a | 219.6a | 275.2a | 182.9a | 279.0a |
| Strontium (Sr) | 83.8ab | 87.8b | 69.3a | 78.7a | 88.2a |
| Thorium (Th) | 21.5b | 14.0a | 14.3a | 19.2b | 12.5a |
| Titanium (Ti) | 4,298a | 3,788b | 4,166ab | 4,257b | 3,700a |
| Zinc (Zn) | 318.7c | 212.2b | 156.0a | 256.9a | 199.5a |
| Zirconium (Zr) | 377.0b | 357.9b | 247.6a | 343.4a | 336.2a |
| Cesium (Cs) | 229.5b | 320.7b | 72.5a | 162.0a | 337.4b |
| Sulfur (S) | 881.7a | 873.3a | 1,023a | 918.7a | 862.0a |
| Tin (Sn) | 46.0a | 45.5a | 44.0a | 45.2a | 45.6a |
| Tellurium (Te) | 144.3a | 127.4a | 160.2a | 141.8a | 143.4a |
| Uranium (U) | 25.4a | 12.1a | 16.1a | 20.3a | 12.2a |

Significant differences in mean 95 % upper confidence levels (UCL) for metals across types of beds and actively growing or not.

Table is divided from top to bottom in descending order of confidence with standard curves that had 5, 3, 2, or 1 points of data.

Letters a, b, and c (for types of beds) and a and b (for actively growing or not) denote significant differences between groups at $\alpha=0.05$ increasing in alphabetical order.

All results in parts per million (ppm).

# Chapter 5: Conclusions

These three studies explored the complex relationships between growing food and the impacts on our environment and health. Each study measured the direct impacts of a specific agricultural system or systems on air and/or soil, while putting the findings in the context of the large-scale problems of climate change and soil contamination. The findings from each study highlighted the tradeoffs that arise when accounting for impacts beyond yield when assessing an agricultural system.

## Study 1 Discussion

The first study measured the GHG and $NH_3$ fluxes from four different corn cropping systems in northern Georgia, focusing on a clover LMS. Higher between row $CO_2$, $N_2O$, and $NH_3$ fluxes were observed in LMS plots compared to a bare soil system. The $CO_2$ flux was influenced by soil moisture, temperature, and potentially mineralizable nitrogen. It was determined that the larger $CO_2$ flux in LMS plots came partially from soil respiration after subtracting estimated contributions from the clover itself. However, measurements from in corn rows where no clover was present did not produce the increased $CO_2$ fluxes. Further research should expand on measurement location within plots to assess whether there is truly a difference in heterotrophic respiration. LMS plots had greater soil organic carbon, indicating that despite potentially increased respiration, the overall net effect on the atmosphere could be a sink for carbon.

$N_2O$ and $NH_3$ fluxes were likely higher in LMS plots due to sustained nitrogen deposition from the clover as biomass was deposited throughout the late growing season. Unlike gaseous nitrogen loss from fertilizer application which is robust but short-lived, the drawn-out deposition from the clover led to a greater overall impact. Soil nitrate and ammonia data indicated that nitrification and dentification are both potential pathways for these increased fluxes, and further research should focus on determining which contributes more.

Greater soil trace gas fluxes in the clover LMS could indicate a greater impact on the environment and health through climate change and air pollution. These systems, which have shown potential for improved yields and other benefits not explored in this study, might come with an increased detrimental atmospheric impact. However, increased soil organic carbon and potentially reduced runoff could offset or exceed these increased emissions. LMS's are not a largely adopted system yet, but due to the potential environmental benefits explored in this work and others from previous research, studies should continue to determine their overall impact. In particular, net CEs should be calculated for LMSs compared to other systems, using soil GHG fluxes and other inputs such as fertilizer use, carbon sequestration, and tillage.

## Study 2 Discussion

The study from Brazil measured GHG and $NH_3$ fluxes from corn cropping systems with five different N sources and with/without biochar soil amendments. $CO_2$ fluxes were higher in cowpea intercropping plots and lower in plots amended with biochar after controlling for soil temperature and moisture. Unlike measurements of LMS fluxes in the first study, the intercropping systems did not have any cover crop biomass in the chambers, indicating a change in heterotrophic respiration beyond plant contributions. Biochar may have reduced soil respiration if the soil was high in organic carbon. $NH_3$ fluxes were lower in plots at an $\alpha$=0.10 level when amended with biochar after controlling for soil temperature and moisture. Low clay content could be the cause of the reduction of $NH_3$ fluxes with biochar due to adsorption of $NH_3$ to the biochar or a low potential to increase the already high respiration in more porous sandy soil. However, further study is needed due to the lack of significance in this particular finding. Overall, this study was limited in determining potential mechanisms for increased fluxes, due to lack of data on soil parameters.

However, this study did assess the seasonal net CEs for all N sources and with/without biochar amendments over the entire growing season. Cumulative net CE was highest in plots with cowpea intercropping and urea-based fertilizer as a nitrogen source. Using an inorganic fertilizer comes with an environmental cost despite the high yields generally generated. Intercropping impacts on climate change may be offset by increased carbon in the soil, as see with LMSs in the first study, but more in-depth soil measurements are required to assess this tradeoff.

Plots with biochar had a lower net CE than those without when accounting for all fluxes and agricultural inputs except biochar production. However, this relationship reversed when including the carbon lost during the production of biochar. Most research regarding the potential GHG mitigation of biochar does not account for the production C losses, and this study showed that this crucial aspect should not be overlooked. Despite the soil health and emissions reductions of biochar amendments, there could be an overall negative impact on the environment and health when looking at the entire picture.

## Study 3 Discussion

The last study of this dissertation used community engaged research to explore how urban agriculture can affect exposure to heavy metals in soil under different risk frameworks. Overall, this study demonstrated there is potential risk from soil heavy metal contamination at some urban agricultural sites, but the severity of this risk largely depends on what regulatory metric is used. Most sites were lower than the EPA RSLs for lead, arsenic, chromium, and cadmium, four priority heavy metals in terms of health effects. However, several sites were above the UGA LRLs for the same metals. Using a different regulatory framework dramatically changed the interpretation of the data, and could have large impacts on policy and promotion of urban agriculture going forward. When agricultural routes of exposure are taken into account, as with the UGA LRLs, risk is higher across this dataset. Future studies should explore the bioavailability and health impacts using risk frameworks other than the EPA RSLs to understand how these additional routes of exposure can affect community health.

Samples from raised or mound beds had lower concentrations of lead, arsenic, chromium, and cadmium, indicating that these are good practices for farmers and gardeners to employ in potentially contaminated settings. However, soil used in the beds should be tested first before use, potentially using the inexpensive XRF methods described in this manuscript. In one case, added new top soil and replanting a bed lowered one community partners lead concentration from above the EPA RSL to below the UGA low risk level, highlighting another best practice for urban food growers. Additionally, samples from actively growing sites had lower average concentrations than those weren't growing food at the time of sampling. Potentially due to phytoremediation or incorporation of new soil, the very act of growing food has the potential to reduce the heavy metals that pose a health risk for the growers. Promotion of phytoremediating non-edible plants such as sunflowers or daisies could be a first step for urban growers to lower soil concentrations before planting edible foods.

Through community engagement, this study also led to the discovery of a metal refining slag dump site. A community partner approached the researchers with a piece of slag, concerned it could be contaminating the soil. Subsequent sampling indicated that the site had highly elevated levels of lead, arsenic, and other metals. An EPA cleanup was initiated due to this finding, helping to alleviate an instance of environmental injustice. By keeping community partners involved in all steps of the project, more of an impact at a behavioral and policy action level was achieved. Future studies regarding soil contamination and/or urban agriculture should involve the community members who are most affected.

Further research on the exposure and health effects at different risk framework concentrations should be done. There are several simple best practices that can be employed to reduce this risk, and growing itself can lower concentrations of heavy metals in soil, and these should be promoted by future policy. Community engaged research on these topics allowed for a more in-depth study and better understanding of the tradeoffs between the benefits of urban agriculture and risks of soil contamination.

## Overall Conclusions

All three studies explored the potential impacts of different agricultural systems on the environment and human health. In each case, there was a tradeoff in some capacity between the potential risks and benefits of the system. In the first study, the soil emissions of clover LMS plots were higher, potentially increasing the impact on climate change and air pollution despite other benefits such as increased soil C and reduced runoff. The second study suggests that despite the soil emission reductions often seen with biochar application, factoring in the biochar production increases the CE of the system as a whole. Finally, the third study highlighted that the risk of exposure to heavy metals should be taken into account along with the numerous benefits from urban agriculture, and that risk increases when using a framework that

Agriculture is transforming as the climate changes and populations urbanize. It is essential to acknowledge and investigate potential impacts on the environment and health as we discover new ways of growing food. This dissertation explored the impacts of emerging agricultural systems in three distinct settings and determined some of the potential factors to consider when looking at agriculture in a wholistic way. The way we grow our food matters, and we need to strive to do so in a manner that promotes a clean environment and healthy people.

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