UNIVERSITY OF CALIFORNIA, MERCED

Biochar-composting of dairy manure as a greenhouse gas and air pollutant emission mitigation strategy for dairies

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Environmental Systems

in

Environmental Systems

by

Brendan Harrison

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2023

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Published journal articles:

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2023 S. Gao, **B. Harrison**, T. Thao, M. Gonzales, D. An, T. Ghezzehei, G. Diaz, R. Ryals, Biochar co-compost improves nitrogen retention and reduces carbon emissions in a winter wheat cropping system. *Global Change Biology - Bioenergy*, DOI: 10.1111/gcbb.13028.

2022 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, A.A. Berhe, T. Ghezzehei, G. Diaz & R. Ryals. Dairy manure co-composting with wood biochar plays a critical role in meeting global methane goals. *Environmental Science & Technology*, 56, 10987-10996.

2020 **B. Harrison**, E. Chopra, R. Ryals, & J. E. Campbell. Quantifying the farmland application of compost to help meet California's organic waste diversion law. *Environmental Science & Technology*, 54, 4545 – 4553.

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ACADEMIC AWARDS, SCHOLARSHIPS & GRANTS

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2022 **B. Harrison**, S. Gao, T. Thao, M. Gonzales, K. Williams, L. Hale, T. Ghezzehei, G. Diaz & R. Ryals. Methane emissions during biochar co-composting are driven

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2022 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, E. Bischak, T. Ghezzehei, A.A. Berhe, G. Diaz & R. Ryals. Biochar co-composting for dairy methane mitigation. **Invited speaker** at International Biochar Initiative 2022 Annual Symposium: Raising Climate Ambitions with Biochar.

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2022 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, E. Bischak, T. Ghezzehei, A.A. Berhe, G. Diaz & R. Ryals. Dairy manure biochar-composting cuts methane emissions and enhances soil carbon sequestration. **Contributed poster** at the California Strategic Growth Council Climate Change Research Program: Research Round Table at UC Merced.

2022 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, E. Bischak, T. Ghezzehei, A.A. Berhe, G. Diaz & R. Ryals. Biochar-composting is a climate-negative solution for dairy manure management that can help meet global methane goals. **Contributed talk** at the Ecological Society of America Annual Meeting.

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2021 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, A.A. Berhe, T. Ghezzehei & R. Ryals. The effect of biochar on nitrogen losses during dairy manure composting. **Contributed poster** at the American Geophysical Union annual meeting (virtual).

2021 **B. Harrison**, S. Gao, M. Gonzales, T. Thao, A.A. Berhe, T. Ghezzehei & R. Ryals. Reducing methane emissions from dairies using biochar. **Contributed poster** at the UC Global Climate Leadership Council Spring Meeting.

2021 **B. Harrison**. Fighting climate change with a 1000-year-old technology. **Invited talk** at Valencia High School's Eco Chico's Environmental Club meeting (virtual).

2020 **B. Harrison**, E. Chopra, R. Ryals, & J.E. Campbell. Quantifying the farmland application of compost to help meet California's organic waste diversion law. **Invited talk** at BioCycle Connect West 2020 (cancelled due to Covid-19).

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Student Researchers United, UC Merced, Merced, CA, 2020 – present
2020 – present
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Eco Chicos Environmental Club, Santa Clarita, CA, 2013 – present
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Graduate Student Association Committee on Research, UC Merced, CA, 2020 – 2021
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Fossil Free UC, UC Santa Cruz, Santa Cruz, CA, 2016 – 2019
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Kresge College Garden and Food Co-op, UC Santa Cruz, Santa Cruz, CA, 2017
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Abstract of the Dissertation

Biochar-composting of dairy manure as a greenhouse gas and air pollutant emission reduction strategy for dairies

by

Brendan Harrison
Doctor of Philosophy in Environmental Systems
University of California, Merced, 2023
Dr. Rebecca Ryals, Chair

Dairy manure is one of the largest emitters of greenhouse gases (GHG) and air pollutants from agriculture. In California, the nation's leader in dairy production, dairy manure accounts for 25% of total methane (CH_4) emissions and contributes to poor air quality in agricultural regions. Recent policies such as the Global Methane Pledge and California's SB 1383 will require large reductions in CH_4 emissions from dairies. While anaerobic digesters can mitigate emissions from liquid manure, very few management strategies exist to reduce emissions from solid manure. Recently, biochar-composting has been proposed as a strategy to cut emissions during the composting of organic materials. However, limited information exists on whether biochar could reduce emissions during the composting of dairy manure. Here, we investigated the potential of dairy manure biochar-composting to reduce both GHG and air pollutant emissions from dairies. In the first project, we measured GHG emissions during the full-scale composting of dairy manure with or without biochar, and we found that biochar-composting reduced CH_4 emissions by 84%. Using life-cycle assessment (LCA), we also estimated the net climate impact of managing solid dairy manure through biochar-composting, composting, or stockpiling, and we found that biochar-composting was a climate-negative dairy manure management strategy. In the second project, we investigated whether biochar-composting could also reduce the emission of air pollutants from dairy manure. We found that biochar-composting cut the emission of hydrogen sulfide, volatile organic compounds, and nitrogen oxides by 70%, 61% and 67%, respectively. Using an integrated assessment model, we estimated that this reduction in air pollution would reduce health-related social costs by $66,000 annually per dairy farm. In the third project, we conducted a laboratory composting experiment to test the effect of biochar feedstock (walnut shells, almond shells, and almond clippings) and application rate (5% and 20%, by mass) on composting emissions. While there was no difference in emissions between biochar type, we found that high application rates increased CH_4 emissions and reduced N_2O emissions. We ascribe this pollution swapping to an increase in compost aggregation with biochar application, as aggregates likely acted as anoxic microsites for methanogenesis and complete denitrification. We recommend using lower biochar application rates, which reduced N_2O emissions without increasing CH_4 emissions in our study. This dissertation shows that biochar-composting of solid dairy manure is an untapped natural climate solution with a high potential to help meet climate goals and improve the health of rural, disadvantaged communities by reducing air pollution.

Chapter 1.

Introduction

While dairy is an important source of nutrition and income for people around the world, dairy manure management is a leading contributor of agricultural greenhouse gas and air pollutant emissions [1-5]. Due to high stocking densities of dairy cattle at concentrated animal feeding operations, manure accumulates onsite and is typically stored in anerobic lagoons and stockpiles until it can be land applied [1, 6]. The anaerobic conditions present in both lagoons and stockpiles result in high methane (CH_4) emissions as well as the emission of air pollutants such as hydrogen sulfide (H_2S), volatile organic compounds (VOCs), ammonia (NH_3), and nitrogen oxides (NO_x) [7-9]. Recent policies such as California's SB 1383 and the Global Methane Pledge will require large reductions in dairy CH_4 emissions by the end of the decade [10-11]. Novel, sustainable dairy manure management strategies offer an opportunity to make significant progress on these climate goals while improving public health by reducing air pollution from dairies [10-11].

Anaerobic lagoons are the largest source of CH_4 emissions from manure, but converting lagoons into anaerobic digesters can mitigate CH_4 by capturing it to produce renewable energy [5, 7, 12]. However, solids separated from anaerobic lagoons and digesters are typically stockpiled and remain a large source of GHG and air pollutant emissions [8-9]. Composting dairy manure solids can reduce CH_4 emissions relative to stockpiling, while transforming manure into a valuable organic amendment [5, 8]. However, anaerobic microsites that form during composting can generate significant CH_4, H_2S, and VOC emissions and reduce the environmental benefit of composting [13]. Furthermore, the composting of nitrogen-rich manures can result in high nitrous oxide, NH_3 and NO_x emissions [5, 8, 14].

Amending compost with biochar, a charcoal-like organic material produced through the pyrolysis of biomass, has recently been proposed as a strategy to reduce emissions during composting [14-16]. Evidence suggests that the high porosity of biochar can reduce the formation of anaerobic microsites during composting, while the high surface area and reactivity of biochar can reduce gaseous nitrogen emissions through the adsorption of gases and their precursors [14-16]. However, to our knowledge, no study had tested whether biochar-composting could reduce GHG and air pollutant emissions from dairy manure. This dissertation addresses this knowledge gap by exploring the potential of biochar-composting of dairy manure as a GHG and air pollution mitigation strategy.

In Chapter 2, we investigated whether dairy manure biochar-composting can reduce CH_4 emissions relative to composting or stockpiling manure. We conducted a full-scale biochar-composting experiment at a dairy farm and measured greenhouse gas emissions from composing dairy manure amended with or without biochar. Emission data from the composting experiment was then incorporated into a life-cycle assessment (LCA) model to compare the net global warming potential of managing dairy manure through either biochar-composting, composting, or stockpiling. Results from our LCA were then used along with the Tier 2 strategy from IPCC to estimate the role that biochar-

composting could play in helping to meet California's SB 1383 law and the Global Methane Pledge [17].

While Chapter 2 examined the potential of biochar-composting to help mitigate climate change, it remained unclear if this practice could also improve public health by reducing air pollutants emitted from dairies. In Chapter 3, we addressed this by carrying out a second full-scale dairy manure biochar-composting experiment in which we measured H_2S, VOCs, NH_3, and NO_x emissions, in addition to GHG emissions. We then used an integrated assessment model to compare the estimated health-related social costs associated with managing dairy manure through either biochar-composting or composting [18].

While the composting experiments in Chapters 2 and 3 provided valuable data and promising results, they tested only one type of biochar applied at a single application rate. In Chapter 4, we investigated the effect of different biochar feedstocks and application rates on composting emissions. We tested biochars made from either walnut shells, almond shells, or almond clippings, and applied them at a rate of 5% or 20%, by mass. These biochar-manure mixtures, along with a no-biochar control, were composted in aerated, insulated bioreactors in the lab, and GHG and NH_3 emissions were measured from each bioreactor over the 42-day experiment. Based on the results of this experiment, we provided recommendations for optimizing dairy manure biochar-composting for emission reduction as well as opportunities for future research.

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Chapter 2.

Dairy manure co-composting with wood biochar plays a critical role in meeting global methane goals

Abstract

Livestock are the largest source of anthropogenic methane (CH_4) emissions, and in intensive dairy systems, manure management can contribute half of livestock CH_4. Recent policies such as California's short-lived climate pollutant reduction law (SB 1383) and the Global Methane Pledge call for cuts to livestock CH_4 by 2030. However, investments in CH_4 reduction strategies are primarily aimed at liquid dairy manure, whereas stockpiled solids remain a large source of CH_4. Here we measure the CH_4 and net greenhouse gas reduction potential of dairy manure biochar-composting, a novel manure management strategy, through a composting experiment and life-cycle analysis. We found that biochar-composting reduces CH_4 by 84%, compared to composting without biochar. In addition to reducing CH_4 during composting, we show that the added climate benefit from biochar production and application contributes to a substantially reduced life-cycle global warming potential for biochar-composting: -535 kg CO_2e Mg^{-1} manure compared to -194 kg CO_2e Mg^{-1} for composting and 102 kg CO_2e Mg^{-1} for stockpiling. If biochar-composting replaces manure stockpiling and complements anaerobic digestion, California could meet SB 1383 with 132 less digesters. When scaled up globally, biochar-composting could mitigate 1.59 Tg CH_4 yr^{-1} while doubling the climate change mitigation potential from dairy manure management.

2.1 Introduction

Agriculture is responsible for one-third of global greenhouse gas (GHG) emissions, and methane (CH_4) from agriculture accounts for 35% of food-system emissions [1]. Livestock are the leading source of anthropogenic CH_4. In developed countries, the industrialization of animal agriculture has concentrated emissions, pollution, and manure into feedlots with relatively small physical footprints [2-4]. Dairy feedlots in particular present a significant nutrient recycling and GHG mitigation opportunity due to their large stocking densities, high rate of manure production, and spatial decoupling of livestock from feed production [5-6]. Optimizing the treatment and reuse of dairy manure could help prevent nutrient loss while substantially reducing CH_4 emissions. This is especially relevant in dairy-intensive regions such as California, where dairy manure accounts for 25% of total CH_4 emissions [6-9].

In 2016, California enacted SB 1383 which requires CH_4 from dairies to be reduced by 40% below 2014 levels by 2030 [10]. More recently, The Global Methane Pledge, which was signed by 110 countries at Conference of the Parties 26 (COP26), calls for a 30% reduction in CH_4 from 2020 levels by 2030 [11]. While most Global

Methane Pledge signatories do not yet have detailed plans for reducing CH_4 from manure, California plans to meet its dairy CH_4 reduction goal primarily through the deployment of anaerobic digesters which capture CH_4 from liquid manure lagoons for energy production [8]. However, California is not currently on track to meet this goal, in part due to economic barriers to constructing anaerobic digestion systems [12-13].

Additionally, CH_4 mitigation at dairies with digesters is limited to the liquid portion of manure while separated solids are often stockpiled in large, static piles favorable for CH_4 production [6, 14-15]. An effective strategy to reduce CH_4 from separated solid manure could increase the CH_4 mitigation potential for every digester installed and reduce the number of digesters needed to achieve CH_4 reduction goals.

One alternative to stockpiling is aerobic composting. While composting can reduce CH_4, eliminate pathogens and create a valuable soil amendment, it can still be a significant source of nitrous oxide (N_2O) and CH_4 [16-18]. Some studies have shown that when added to compost, biochar, a carbon-rich material produced through biomass pyrolysis, can reduce GHGs by improving aeration, adsorbing gases, and stimulating key microorganisms [19-22]. Combining biochar with organic waste is an agricultural technique that is practiced by numerous Indigenous Peoples, but only a few studies have quantified the GHG benefit of biochar-composting at the field-scale, and none have used separated dairy manure solids as a feedstock [23-26]. It also remains unclear whether scaling up this technology can play a significant role in meeting CH_4 mitigation goals [10, 27].

Here, we conducted a field-scale composting experiment to measure GHG emissions during the composting of separated solid dairy manure with and without biochar. We hypothesize that CH_4 is reduced from biochar-amended piles due to improved pile aeration [20]. GHG results from the composting experiment are incorporated into a life-cycle assessment (LCA) of solid manure management systems. Finally, LCA results are used to estimate the role that biochar-composting can play in meeting CH_4 reduction goals in California and globally.

2.2 Materials and Methods

2.2.1 Site description and experimental set-up

The composting experiment was conducted at Philip Verwey Dairy in Madera, California (36˚56’03’’N, 120˚23’09’’W) from August to September 2021. Biochar used in the experiment was Rogue Biochar from Oregon Biochar Solutions (White City, OR). Biochar feedstock was composed of approximately 85% Douglas fir (*Pseudotsuga menziesii L.*) and Ponderosa pine (*Pinus ponderosa L.)* wood waste mixture, 14-15% almond and walnut tree pruning, and < 1% nutshells. The maximum pyrolysis temperature was reported to be 900˚C (K. Strahl, pers. comm.). The characteristics of biochar, composts, and compost feedstocks are listed in Tables S2-1 and S2-2.

A manure-only compost windrow pile and a biochar-compost windrow pile were prepared on-site on August 10th, 2021. Each pile was trapezoidal in shape and approximately 30 m in length, 3 m in width, and 1 m in height. The manure-only pile consisted of approximately 15.34 t fresh solid manure and 1.32 t orchard clipping

residues (3.37 t dry manure and 1.2 t dry clippings residues). Biochar-compost pile consisted of 15.35 t fresh solid manure, 1.32 t orchard clipping residues, and 1.0 t biochar (3.37 t dry manure, 1.2 t dry clippings, and 0.91 t dry biochar). Both piles were turned weekly for a total of four times (on days 8, 15, 22, and 29) throughout the 35-d experiment.

2.2.2 Greenhouse gas flux measurement and compost characterization

Compost greenhouse gas fluxes (CO_2, N_2O, and CH_4) were measured daily over the 35-day experiment using a cavity ring-down laser spectrometer (Picarro G2508, Picarro Inc., Santa Clara, CA) connected to a closed system static chamber (made from polyvinyl chloride and 26 cm diameter by 13 cm tall). Collars (made from polyvinyl chloride and 25.5 cm diameter by 15 cm tall) were inserted 3 cm into the compost pile and allowed to sit for one hour before measurement. Gas was sampled daily from nine locations (3 South side, 3 top and 3 North side) on each windrow, as shown in Figure S2-1, by fitting the chamber lid over a collar (creating a total chamber volume of 12271.9 cm^3) and sampling for 5 minutes. After taking a measurement, gas concentrations were allowed to return to ambient concentrations before the next measurement. Gas fluxes (nmol m^{-2} s^{-1}) were calculated in the Picarro Soil Flux Processor program using the exponential model developed by Hutchinson & Mosier (1981) to account for non-linear changes in headspace concentration [28]. To account for the "chimney effect" and the spatial variation within the pile, we considered each pile's dimensions when calculating gas fluxes and emission factors at the scale of the compost pile following Anderson et al. (2010) and Sánchez et al. (2015) [29-30]. Specifically, the average pile flux was calculated as: (North side flux * North side surface area + top side flux * top side surface area + South side flux * south side surface area) / compost pile base area. Surface area and base area were measured and estimated weekly to ensure the temporal changes in pile dimensions were taken into account over the course of the experiment. The average pile fluxes (nmol m^{-2} s^{-1}) were later converted to daily emission factors presented as g or mg trace gas or C or N kg^{-1} dry feedstock d^{-1} using the feedstock mass data.

For each flux measurement, compost surface temperature was measured with a digital probe thermometer (PDT650, UEi Test Instruments, Indianapolis, IN), and chamber temperature was measured with a suction cup thermometer (Taylor Precision Products, Oak Brook, IL) attached to the top of the chamber. Pile temperature was measured daily by inserting two 5TE sensors connected to an EM50 data logger (METER Group, Pullman, WA) into the center of the pile approximately 30 cm deep at a height of 30 cm and allowing the temperature to stabilize over at least one hour.

Fresh compost samples were collected weekly after piles were turned to determine physiochemical properties. Briefly, compost moisture content was determined by weighing the fresh and dried sample before and after drying in an oven at 105˚C for 24 h. Compost pH was determined in 1:2 sample to DI water (v/v) suspension. Porosity was determined following the protocols described in Flint & Flint (2002) [31]. Compost NH_4^+-N and NO_3^--N concentrations were determined by shaking 3 g of compost in 30 ml of 2M KCl and analyzing extractions on a Lachat QuikChem 8500 Flow Injection Analyzer (Lachat Instruments, Milwaukee, WI). Total C and N were analyzed on oven-

dried samples (105˚C) using an elemental analyzer (Costech 4010, Costech Analytical Technologies Inc., Valencia, CA). Compost germination index was determined according to Luo et al. (2018) [32].

Initial biochar and manure feedstocks were analyzed for total C, total N, pH, NH_4^+-N, NO_3^--N using the same methods used for compost. Proximate analysis of feedstocks and compost was also conducted following ASTM D3172-13 [33]. Biochar surface area and pore characteristics were determined using the Brunauer, Emmett and Teller (BET) method on a TriStar II *Plus* (Micromeritics, Norcross, GA) [34]. Biochar surface images at 50x and 200x magnification were taken using scanning electron microscopy (Figure S2-2) (Gemini500 FE-SEM, ZEISS, Dublin, CA).

2.2.3 Statistical Tests

All statistical analyses were performed using the open-source statistical analytical software R. Cumulative gas emissions were estimated by calculating the area under the daily emission curves using the function auc() in package 'flux' in R [35-36]. Analysis of variance (ANOVA) and Tukey's post-hoc tests were carried out on weekly cumulative gas emissions to examine the significance of biochar treatment at $P = 0.05$. Pearson correlation tests were conducted on selected variables that were of interest to us to elucidate the relationships between gas emissions and compost characteristics throughout the experiment. In addition, we used a mixed linear regression (MLR) model to determine the dominant drivers controlling gas fluxes in our 35-d field study (Table S2-3). All data were tested for homogeneity of variance and normality of residuals before the MLR analyses and were log transformed when necessary.

2.2.4 Life-cycle Assessment

A life-cycle assessment (LCA) was conducted to estimate the climate impacts associated with each major stage of biochar-composting, composting and stockpiling.[17] The functional unit for the model is one metric ton of separated solid dairy manure, and we use manure stockpiling as a reference system to account for avoided emissions. The LCA system boundary begins with raw feedstock transportation and ends with compost application to soil. While we account for the portion of carbon in each amendment that is likely to remain stable in soil long-term, we exclude ecosystem impacts from amendment application due to the lack of field studies that measure changes in soil GHG fluxes and plant biomass after the application of biochar-compost to soil, but improvements to the model can be made when this data becomes available [37-41]. Both the 20-year and 100-year GWPs were quantified for each system. A 20-year global warming potential was included because CH_4 has a high GWP over its short 12-year lifespan, which is relevant in the context of CH_4 reduction policies like SB 1383 and the Global Methane Pledge that are designed to help mitigate the most devastating impacts from climate change over the next few decades as governments begin to transition away from fossil fuels [2, 8, 42-43]. Biogenic CO_2 emissions from composting are assumed to be climate neutral in our primary model because the carbon originates from recently photosynthesized CO_2 and has

no net climate impact [17, 44-45]; although, we do include a model version that accounts for biogenic CO_2 emissions in the supplementary material (Figure S2-3a).

In our LCA, we use our experimental cumulative GHG fluxes for the composting and biochar-composting stages. In order to estimate GHG fluxes from stockpiling, we use our compost emission data and assume an average reduction in CH_4 and N_2O by 71% and 50%, respectively, when manure is composted instead of stockpiled [18]. The portion of C in compost that can be sequestered in soil long-term is assumed to be 9%, which is the mid-range value presented in a review by Martinez-Blanco et al. (2013) [38]. We use a 97% C sequestration rate for the biochar fraction of biochar-compost, which is based on results of a meta-analysis by Wang et al. (2016) [37]. Avoided fossil fuel emissions from the energy produced from pyrolysis is estimated using a net energy production value for pyrolysis of 4043 MJ/feedstock and a 28.8% biochar yield from Roberts et al. (2010) as well as IPCC default emission factors for coal and natural gas (assuming a 50/50 mix in the baseline scenario) [46-47]. We assume that gases produced during pyrolysis are combusted and the only GHGs released are biogenic CO_2 [46]. Biochar production can also reduce GHG emissions from biomass burning of crop residues and forestry waste, and we assume that 10% of the woody feedstock used in composting and biochar production would have otherwise been burned [48-50]. This value is based on the percent of wheat and corn residue (the two largest sources of crop residue in the U.S.) burned in the United States annually [51-52]. Feedstock and composts are transported by 36-ton diesel trucks and are distributed locally (5-40 km) in each strategy's baseline scenario [53-54].

2.2.5 Sensitivity and uncertainty analyses

Since the LCA model has nonlinearities, we performed a global sensitivity analysis [55]. First order (S1) indices measure the singular effect of a parameter on variance in the output, and total order (S.T.) indices measure the total effect, or first and higher order effects (multiplicative effects) of a parameter [56]. We used a variance-based Sobol analysis method, given its easy computation and interpretation [56]. The ranges applied to each variable are shown in Table S2-4. The LCA was first programmed in Python, and the experiment was performed using the SALib library [57]. 2048 samples were generated from the given parameter space (Table S2-4) using a Saltelli sampler. This number of samples was enough to ensure convergence in the index's values. From the sensitivity analysis experiment, we analyzed the output space from each management strategy to characterize their uncertainty.

2.2.6 Methane reduction from biochar-composting in California

For our California analysis, we estimate the number of additional anaerobic digesters needed to meet California's 40% CH_4 reduction goal without biochar-composting (digester + stockpiling scenario), with biochar-composting (digester + biochar-composting scenario), and with biochar-composting along with a 1% annual decrease in statewide herd population (enhanced population reduction scenario). The average annual CH_4 reduction rate per digester was calculated according to IPCC Tier 2

guidelines [58]. We used California specific values for the average number of lactating cows per dairy and the mass of volatile solids produced per head, as well as the maximum methane production capacity (B_0) and methane conversion factors (MCF) for both anaerobic lagoons and anaerobic digesters [59] (Table S2-5). We account for the CH_4 emissions avoided from converting an anaerobic lagoon into an anaerobic digester, as well as the direct CH_4 emissions from anaerobic digesters due to leakages and from incomplete combustion 59-60. The net dairy manure CH_4 reduction associated with biochar-composting was calculated by subtracting the CH_4 emitted during biochar-composting from the CH_4 avoided by not stockpiling, which are both taken from our LCA.

CH_4 reductions for anaerobic digestion and biochar-composting are relative to a baseline system similar to the model in Owen & Silver (2015) in which dairy manure from mature and lactating cows is separated into a solid fraction, which is stockpiled, and a liquid fraction, which is stored in an anaerobic lagoon [5]. We assume a 50% solid separation rate, which is the average efficiency of the four solid-liquid separation technologies reviewed in Hjorth et al. (2010) [61]. We do not consider any manure managed from heifers or calves because manure from immature and non-milking cows are typically managed through alternative methods such as daily spread or dry lot systems that yield little CH_4, and according to an analysis by Marklein et al. (2021), account for less than 2% of total dairy CH_4 emissions [9]. Current progress on SB 1383, which we use as a baseline in our model, is based on a recent CARB report that estimates that by 2022, the state will have reduced dairy CH_4 emissions by 3.5 MMT and will have 130 anaerobic digestors operating [8]. Our model also accounts for CH_4 reduction contributions from CARB projected reductions in statewide herd population (0.5% in digester + stockpiling and digester + biochar-composting scenarios, and 1% in enhanced population reduction scenario), as well as CARB projected increases in the number of other alternative manure management projects (assuming a rate of 1 AAMP project implemented per digester project) likely to be done at smaller farms unable to install anaerobic digesters [8]. We incorporate the CH_4 mitigation from annual herd population reduction by assuming that the 40% CH_4 reduction goal is achieved in 2030 in each scenario, and the total CH_4 savings from herd population reduction from 2022 to 2030 is distributed equally over the number of new digesters built from 2022 to 2030. A 100-year GWP is used in this estimate because the state's goal of 9 MMT CO_2e reduction in CH_4 is based on a 100-year CH_4 conversion factor.

2.2.7 Global GHG mitigation potential of biochar-composting

For our global analysis, we quantify the total GHG and CH_4 mitigation of anaerobic digestion and biochar-composting dairy manure management systems when scaled up to their global potential. Like Höglund-Isaksson et al. (2020), we assume that it is only economically feasible to install anaerobic digesters at dairies with herd sizes greater than 100 heads [2]. An estimate of the number of dairy cattle kept on farms with greater than 100 head is taken from Höglund-Isaksson et al. (2020) [2]. We then calculate a per head GHG mitigation rate for anaerobic digestion and biochar-composting and assume a 50% solid-liquid separation efficiency [61]. The annual mass of manure volatile

solids produced per head is estimated using average values for total animal mass and volatile solids produced per total animal mass from North America, Europe, and Asia, the regions most likely to be suitable for anaerobic digestion projects due to their intensive dairy systems (Table S2-5) [2, 58]. IPCC default emission factors are used to estimate anaerobic digestion CH_4 reduction per head, and we use EPA's guidelines for estimating the avoided fossil fuel emissions from biogas electricity production [58, 62]. Emission reductions from biochar-composting are taken from our LCA results, and we consider different rates (0-100%) of on-farm biochar-composting where it is assumed that any manure solids not biochar-composted are stockpiled.

2.3 Results and Discussion

2.3.1 Dairy manure biochar-composting experiment

We conducted a 35-day field-scale composting experiment to measure differences in daily GHG fluxes during the composting of dairy manure solids amended with or without biochar. Over the course of the experiment, the manure-only pile emitted 5.03 g CH_4 kg^{-1} dry feedstock, 451 g CO_2 kg^{-1} dry feedstock, and 0.060 mg N_2O kg^{-1} dry feedstock (Figure 2-1, Figure S2-4). In contrast, cumulative emissions from the biochar-compost pile were 0.81 g CH_4 kg^{-1} dry feedstock, 280 g CO_2 kg^{-1} dry feedstock, and 0.119 mg N_2O kg^{-1} dry feedstock (Figure 2-1, Figure S2-4).

Differences in cumulative CO_2 and N_2O emissions for each pile were not statistically significant (Figure 2-1, Figure S2-4). Similar to Vergara & Silver (2019), both piles had very low N_2O fluxes which may be due to low initial nitrate (NO_3^-) concentration in both composts (Figure S2-5) as well as potential nitrification inhibition from the high temperatures maintained throughout the composting experiment [17].

There was a significant reduction in CH_4 emissions when biochar was added in the composting process ($P > 0.001$, Figure 2-1). The biochar-compost CH_4 emission factor was 84% less than that of the manure-only pile. The majority of CH_4 was emitted during the first three weeks of composting for both piles (81% for manure-only and 91% for biochar-compost), which is consistent with other manure composting studies [14, 17] (Figures S2-6 and S2-7).

We find that CH_4 mitigation in the biochar-compost pile is highly correlated with moisture content, which was significantly lower than the manure-only pile (Figures S2-8 and S2-9; Table S2-3). This is consistent with previous findings that suggest adding biochar to compost can decrease CH_4 emissions by increasing pile aeration and O_2 diffusion due to biochar's high micro and macroporosity [19-20]. An increase in O_2 from biochar addition could reduce CH_4 production by methanogens and increase CH_4 consumption by methanotrophs, reducing the net CH_4 flux from the biochar-compost pile [19-20, 63]. Biochar could have advantages over other compost bulking agents because it provides very little labile C compared to biomass that has not been pyrolyzed, and labile C can drive CH_4 emissions. Biochar may also reduce CH_4 emissions through the adsorption of manure labile C and CH_4 during composting [21]. Though the biochar-compost pile had a higher pH than the manure-only pile, the pH of both composts was in the range suitable for methanogenesis (Table S2-1) [64]. Additional studies are needed

that isolate and investigate other potential biological and physiochemical mechanisms through which biochar could mitigate composting CH_4 emissions [20].

Excluding turning days when compost temperature dropped by 5-10˚C for approximately 24 hours, temperature for both piles ranged from 65-73˚C (Figure S2-8). While the biochar-compost pile reached peak temperature faster, there was no significant biochar treatment effect for temperature throughout the experiment ($P > 0.10$). The biochar-compost pile had a lower moisture content than the manure-only pile throughout the experiment, and the moisture content of both piles dropped by week 5 (Figure S2-8). Both composts reached maturity at the end of week 5 which was demonstrated by a germination index above 50, NH_4^+-N less than 0.4 g/kg, and a C/N ratio less than 25 (Table S2-1) [65]. While the composting process can be done over a much longer period, we found that 35 days was suitable for our compost to reach maturity and be suitable for use as a soil amendment in agroecosystems. Shorter composting times are likely needed in intensive dairy systems that have high daily rates of manure production and limited space for composting given that compost maturity indices are met, and compost temperatures reach a minimum of 55°C for three days as required by the USDA [65-67].

While our study shows that biochar-composting has substantial CH_4 mitigation potential when implemented in dairy systems, our experiment used only one type of biochar applied at a single rate. Biochar physiochemical properties can vary greatly depending on the initial feedstock used and on the temperature and duration of pyrolysis. Different biochars applied at different rates may thus result in different capacities for biochar-composting to mitigate GHG emissions from dairy manure. For example, Pascual et al. (2020) found that soils amended with different types of biochars had different rates of CH_4 emissions, likely due to differences in the physiochemical properties of the biochars [68]. Therefore, research is needed that tests multiple types of biochars, applied at multiple rates, to optimize biochar feedstocks and application rates for the greatest GHG reduction during biochar-composting. This would allow for researchers to make specific recommendations to dairy farmers interested in adding biochar to their manure compost [25].

2.3.2 Life-Cycle Assessment

We incorporated our GHG data from the composting experiment into an LCA of solid dairy manure management strategies. Results show a significant reduction in net global warming potential (GWP) when a functional unit of one metric ton of fresh solid dairy manure is managed through composting or biochar-composting compared to a reference system in which separated solid manure is stockpiled (Figure S2-10). Results from our 100-year GWP model are -535 kg CO_2e, -194 kg CO_2e, and 102 kg CO_2e for biochar-composting, composting, and stockpiling, respectively (Figure 2-2). Using a 20-year GWP, which some argue is appropriate when considering CH_4 mitigation policies designed to reduce warming over the next few decades, the net climate impact of biochar-composting, composting, and stockpiling is -870 kg CO_2e, -441 kg CO_2e and 446 kg CO_2e, respectively (Figure S2-3b) [42-43].

The life-cycle stage with the largest reduction in GWP for biochar-composting and composting is the avoided CH_4 emissions that would have occurred if the manure had

been stockpiled. The largest source of emissions for biochar-composting and composting systems is from direct composting emissions; however, biochar-composting had lower direct emissions (10 kg CO_2e) compared to composting (50 kg CO_2e) due to an 84% reduction in CH_4 emissions (Figure 2-1). Compost carbon (C) sequestration from soil application is a large sink of emissions for composting (-71 kg CO_2e) and biochar-composting (-77 kg CO_2e), but the persistent biochar C in biochar-compost resulted in the additional sequestration of -215 kg CO_2e (Figure 2-2; Figure S2-11). The avoided fossil fuel emissions from the electricity generated through biochar production also reduced the GWP of biochar-composting by -76 kg CO_2e (Figure 2-2). When using a 20-year GWP and accounting only for direct emissions from each system by excluding the avoided emissions from stockpiling, biomass burning, and fossil fuel displacement, biochar-composting remains a net sink of emissions (-261 kg CO_2e) while compost becomes a net source (79 kg CO_2e) (Figure S2-12a).

Our LCA suggests that adding biochar to compost can enhance CH_4 mitigation from solid dairy manure management systems while offering co-benefits such as electricity production, soil C sequestration, and sustainable woody biomass management. Unlike composting, biochar-composting has a negative GWP when excluding avoided emissions in the 20-year GWP model (Figure S2-12b). This is a significant finding as we work toward managing agroecosystems to function as a net sink of GHGs rather than a source. While our study is the first to use LCA to examine the climate change impact of biochar-composting as a solid dairy manure management strategy, our analysis is limited in that it does not include direct measurements of stockpiling emissions or agroecological impacts (e.g., changes in crop biomass or soil N_2O fluxes) from compost and biochar-compost when it is used as a soil amendment. To better quantify the GWP of biochar-composting compared to other manure management systems, future studies are needed that examine the long-term climate change and agronomic impacts associated with the addition of dairy manure biochar-composts to soil. Studies are especially needed that compare biochar-composting to other soil amendments or compare biochar-composts with different biochar feedstocks or biochar application rates.

2.3.3 Sensitivity and uncertainty analyses

Results from a global sensitivity analysis show the net GWP of each management strategy is most sensitive to parameters that affect the net CH_4 output, such as CH_4 GWP and CH_4 emission factors for manure stockpiling and composting (Figure S2-13). Our uncertainty analysis shows that stockpiling manure almost always results in a net source of emissions, with a minimum of -6.62 kg CO_2e Mg^{-1} manure and a maximum of 684.26 kg CO_2e Mg^{-1} manure (Figure S2-14). Composting always results in a net sink with a minimum of -618.60 kg CO_2e Mg^{-1} manure and a maximum of -96.16 kg CO_2e Mg^{-1} manure. Biochar-composting almost always results in the largest net sink with a minimum of -920.87 kg CO_2e Mg^{-1} manure and maximum of -443.99 kg CO_2e Mg^{-1} manure.

2.3.4 Methane reduction from biochar-composting in California

California aims to meet its 40% dairy methane reduction goal primarily using anaerobic digesters, but the state is currently not on track to meet this target [8]. We estimate the role that biochar-composting could play in reducing CH_4 when it is used to manage solid dairy manure separated from anaerobic digester systems in California (Figure 2-3). Average per farm CH_4 reduction is estimated using our LCA results for biochar-composting and using IPCC Tier 2 guidelines with California specific values for anaerobic digestion [58-59]. We also assume a 0.5% annual reduction in dairy cow population, which the California Air Resources Board (CARB) projects for 2022-2030, and account for additional Alternative Manure Management Projects that would be implemented on farms not eligible for anaerobic digesters [8].

Our model shows that total CH_4 mitigation on farms with existing anaerobic digesters increases by 29% when biochar-composting replaces solid manure stockpiling. The additional CH_4 mitigation in the digester + biochar-composting scenario allows the state to meet its CH_4 goal with 598 digesters, or 132 fewer digesters, than it would take in the digester + stockpiling scenario — a number nearly equivalent to the 130 digesters currently built or cited in California [8]. However, the EPA's AgSTAR anaerobic digester program has identified only 799 dairy farms that would be suitable for anaerobic digester projects in California because it is not economically feasible for smaller dairies to build digesters [62]. Under the digester + stockpiling scenario, our model shows the state needing 91% of eligible dairy farm owners to build anaerobic digestion systems on their farms to meet SB 1383. Even under the digester + biochar-composting scenario, 74% of eligible dairies would need digesters. While anaerobic digestion could provide an additional revenue stream for dairy farmers, there are high upfront costs associated with installing digesters. High adoption rates may, therefore, be unlikely without additional funding in programs that reduce financial risk for farmers [8]. Under our enhanced population reduction scenario, which includes biochar-composting and increases the current annual rate of dairy cow population reduction from 0.5% to 1%, California can meet SB 1383 with 483 digesters or a 60% adoption rate. This additional population reduction could allow California to meet its CH_4 goal without having to rely on the high digester adoption rates required under the digester + biochar-composting or digester + stockpiling scenarios.

2.3.5 Global GHG mitigation potential of biochar-composting

We estimate the maximum technical CH_4 and net GHG mitigation potential of biochar-composting when it is added to anaerobic digestion systems at the global scale using IPCC Tier 1 guidelines for anaerobic digestion, EPA estimates for fossil fuel emission offsets from energy produced through anaerobic digestion, and our LCA model for biochar-composting [58, 62]. Due to the logistical and economic barriers facing small-scale dairies, we limit our analysis to the number of dairy cows kept in intensive systems with at least 100 head [2-3]. We find that when solid manure is biochar-composted instead of stockpiled, the technical annual GHG mitigation potential nearly doubles, increasing from 154 Tg CO_2e yr^{-1} to 297 Tg CO_2e yr^{-1} (using 100-year GWPs) (Figure 2-4a). When using 20-year GWPs, biochar-composting increases the technical annual GHG mitigation from dairies from 409 Tg CO_2e yr^{-1} to 640 Tg CO_2e yr^{-1}. Annual

technical CH_4 mitigation potential increases from 4.54 Tg CH_4 yr^{-1} to 6.13 Tg CH_4 yr^{-1} when biochar-composting is implemented (Figure 2-4b). An annual reduction of 6.13 Tg CH_4 would account for a 26% reduction in total dairy CH_4 relative to 23.4 Tg CH_4 yr^{-1}, the current GAINS model estimate of CH_4 emissions from dairies globally [2]. However, the GAINS model projects annual baseline dairy CH_4 emissions to increase by 4.5 Tg CH_4 yr^{-1} to a total of 27.9 Tg CH_4 yr^{-1} [2]. This is primarily due to the growth of the dairy industry in developing regions where a lack of effective policy and/or socioeconomic barriers to implementing technical mitigation strategies may limit CH_4 reduction potential [2-3, 69]. In order to offset increases in dairy CH_4 from developing countries, developed countries will likely need to ramp up the implementation of manure CH_4 mitigation strategies along with techniques to reduce enteric fermentation, such as improved feed quality and feed additives, and at the same time, encourage the adoption of low-dairy diets [3, 70].

While our analysis shows the benefit of biochar-composting relative to digester-only systems, there are also large uncertainties associated with this estimate due to a ± 30% uncertainty in emission factors when using Tier 1 guidelines as well as a ± 20% uncertainty when estimating livestock population [58]. Assumptions made about the proportion of manure in liquid and solid systems is also a source of uncertainty as this ratio can vary greatly depending on region [5].

Other estimates of global livestock manure CH_4 mitigation are also highly variable and depend largely on model assumptions. For example, CH_4 mitigation potential estimates by Höglund-Isaksson et al. (2020) and Frank et al. (2018) for 2030, the deadline to meet the Global Methane Pledge, are lower at 1.21 Tg CH_4 yr^{-1} and 1.43 - 3.57 Tg CH_4 yr^{-1}, respectively, while Beach et al. (2015) predict a much larger reduction of 9.64 Tg CH_4 yr^{-1} [2, 71-72]. The EPA estimates a manure CH_4 reduction potential for the U.S. dairy industry of 1.64 Tg CH_4 yr^{-1}, which is larger than some of the estimates for global livestock manure mitigation [62]. Despite the range in estimates, each of these models assumes anaerobic digestion to be the sole manure management strategy. Our analysis suggests that when biochar-composting is combined with anaerobic digestion, the maximum technical manure CH_4 mitigation potential could increase significantly. While the maximum economic mitigation potential will likely be much lower than our maximum technical mitigation potential due to economic barriers facing dairy farmers, adding biochar-composting to existing anaerobic digestion systems may be a low-cost way to enhance manure CH_4 mitigation on these farms relative to the high cost of constructing and maintaining digesters [2-3]. However, the widespread adoption of biochar for use in dairy systems is dependent on a functioning biochar market along with the existence of infrastructure needed to harvest and pyrolyze biomass [48].

We show that there is substantial additional CH_4 mitigation potential when solid dairy manure separated from anaerobic digesters is biochar-composted, instead of stockpiled. Incorporating this novel strategy into CH_4 mitigation models could increase maximum mitigation potentials from the livestock sector and provide governments with an additional strategy to help meet CH_4 reduction targets. Despite the potential climate benefits of biochar-composting, significant additional cuts to livestock and dairy CH_4 are likely needed if animal agriculture is to contribute its fair share to the 30% reduction in total CH_4 required by signees of the Global Methane Pledge. While growth in the dairy

industry has slowed in developed countries, it is expected to continue to rapidly expand in developing countries where widescale adoption of manure management practices may be less likely [2-3, 69-73]. To ensure that global dairy CH_4 emissions decrease over time, developed countries will likely need to further reduce their dairy consumption, in addition to implementing mitigation strategies that target both solid and liquid manure and enteric fermentation.

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2.6 Figures

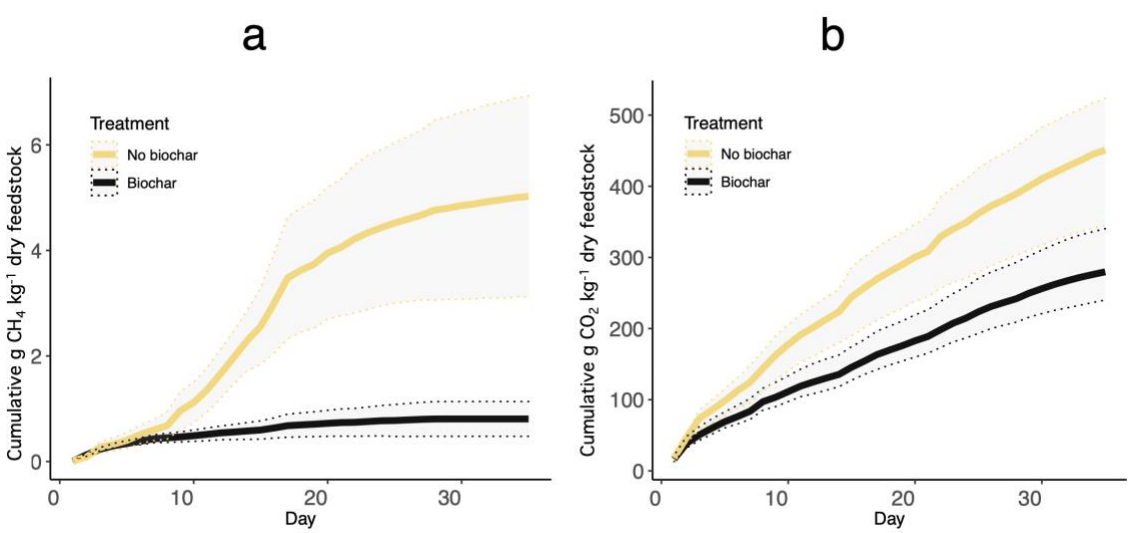

Figure 2-1. Cumulative CH_4 (a) and CO_2 (b) emissions over the 35-day composting experiment. CH_4 emissions are expressed in units of g CH_4 kg^{-1} dry feedstock. CO_2 emissions are expressed in units of g CO_2 kg^{-1} dry feedstock. The black curve shows cumulative emissions from biochar-composting, and the yellow curve shows cumulative emissions from composting. The shaded region for each curve shows the 95% confidence interval for each pile's gas flux measurements.

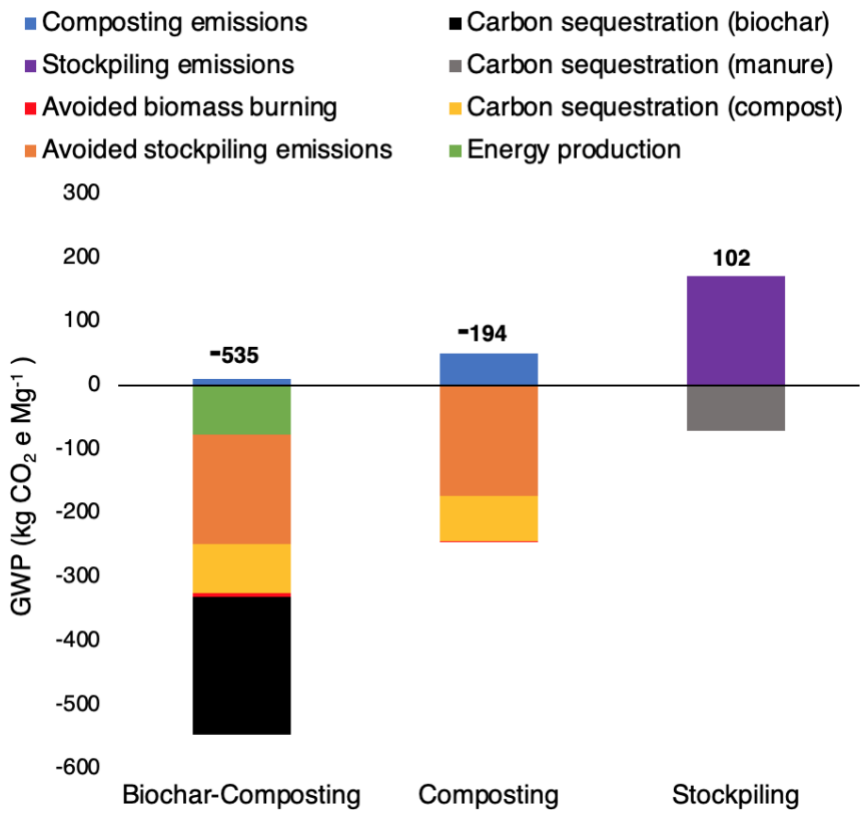

Figure 2-2. Life-cycle assessment of management strategies for separated solid dairy manure using 100-year GWPs. The number above each strategy is the net GWP in kg CO2e Mg-1 manure. Each color represents a different life-cycle stage and is referenced in the legend above. The transportation stages are removed from the figure due to their minuscule contribution to the total GWP of each strategy.

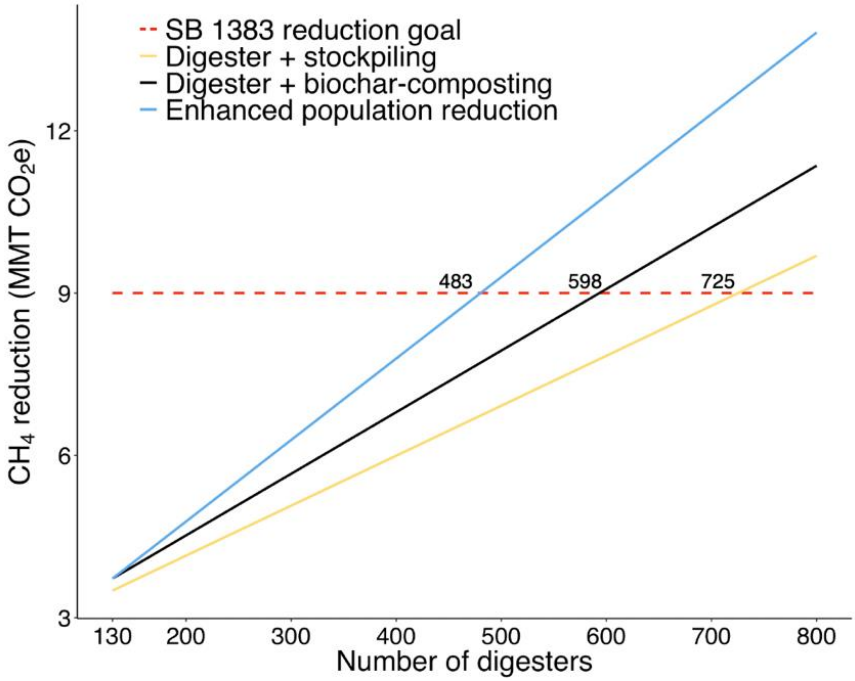

Figure 2-3. The number of anaerobic digesters needed to meet California's 40% dairy CH_4 reduction goal mandated by SB 1383 under different scenarios. The digester + stockpiling scenario assumes that dairies with anaerobic digesters stockpile their separated solid manure. The digester + biochar-composting scenario assumes that dairies with anaerobic digesters biochar-compost their separated solid manure. The enhanced population reduction scenario assumes that dairies with anaerobic digesters biochar-compost their separated solid manure and that the statewide herd population declines at an annual rate of 1% instead of the California Air Resources Board's (CARB) projected annual reduction of 0.5%, which is used in the other scenarios. In addition to assumed population reduction rates, each scenario assumes CARB projected rates for implementing new alternative manure management projects at dairies not large enough for anaerobic digesters.

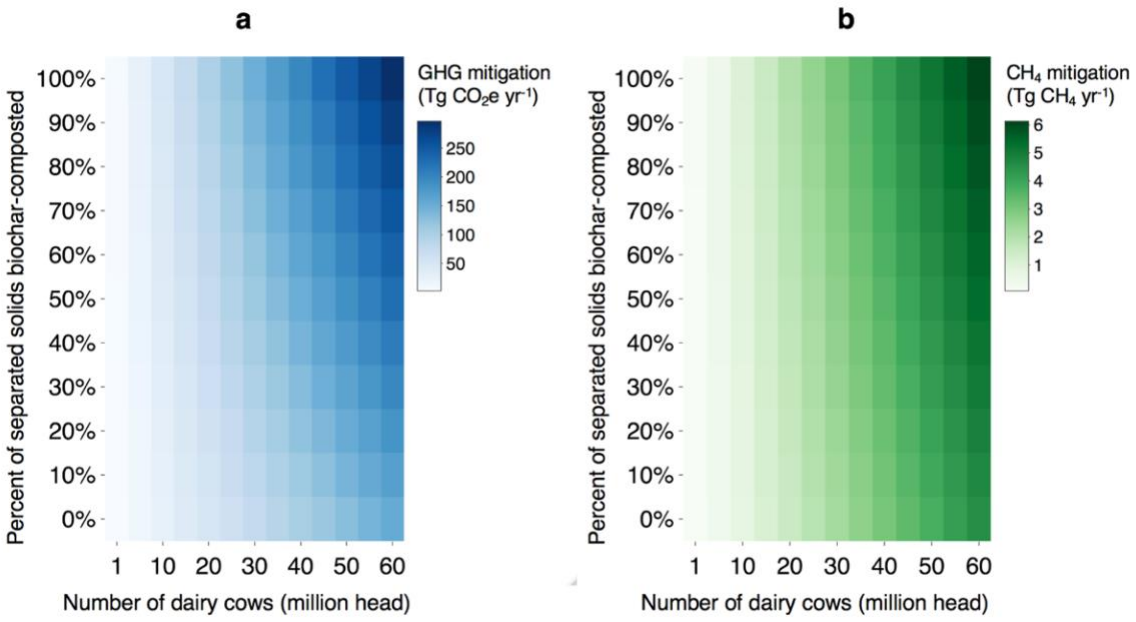

Figure 2-4. Technical GHG and CH_4 global mitigation potential from dairy manure management. **a**. The net life-cycle GHG mitigation from dairy manure management consisting of anaerobic digestion of dairy manure and varying degrees of biochar-composting of separated solid manure. **b**. The CH_4 mitigation from dairy manure management consisting of anaerobic digestion of dairy manure and varying degrees of biochar-composting of separated solid manure. For each figure, the x-axis shows the hypothetical number of dairy cows (in million head) managed in systems with anaerobic digesters. We limit our analysis to the number of dairy cows kept in intensive systems globally. The y-axis shows the percent of solid manure separated from digesters that is managed through biochar-composting. Solid manure that is not biochar-composted is assumed to be stockpiled.

Chapter 3.

Biochar-composting substantially reduces methane and air pollutant emissions from dairy manure

Abstract

Dairy manure is one of the largest sources of methane (CH_4) emissions and air pollution from agriculture. In a previous study, we showed that composting dairy manure with biochar substantially reduces CH_4 emissions and could help the dairy industry meet climate goals. However, it remained unclear whether biochar could also mitigate the emission of air pollutants and odor during composting. Here, we conducted a full-scale composting study at a dairy farm and monitored the emission of greenhouse gases (CO_2, CH_4, N_2O) and air pollutants (H_2S, VOCs, NO_x, NH_3) from compost piles amended with or without biochar. We found that amending compost with biochar significantly reduced total CH_4 emissions by 58% and cut H_2S, VOCs, and NO_x emissions by 70%, 61% and 67%, respectively. We attribute this reduction in emissions to improved oxygen diffusion from the porous biochar and the adsorption of gas precursors to the biochar surface. Interestingly, NO_x fluxes from the composting dairy manure were much higher than the few values reported in the literature, suggesting that dairy manure could also be a significant source of NO_x emissions. We estimate that biochar-composting of dairy manure would reduce the social cost from dairy emissions by over $66,000 annually per farm. Results from this study show that in addition to being a powerful CH_4 mitigation strategy, biochar-composting could play an important role in improving air quality and the health and wellbeing of rural communities.

3.1 Introduction

Livestock manure is a leading source of anthropogenic methane (CH_4) emissions and air pollution from agriculture [1-6]. In the U.S., manure accounts for 9% of total CH_4 emissions and is responsible for 43% of all premature deaths from food-related air pollution – nearly 7,000 people per year [7-8]. As the global demand for animal products rises, there is an increasing need for novel strategies that mitigate emissions from manure as governments work to fight climate change and improve rural air quality [8-10]. The dairy industry represents a large opportunity to mitigate both CH_4 and air pollutant emissions due to the large amount of manure produced and stored on-site in anaerobic lagoons and stockpiles at intensive dairies [11-14]. Due to the low oxygen present in these environments, manure managed through these strategies generates substantial CH_4 emissions and is also a large source of odorous air pollutants such as ammonia (NH_3), volatile organic compounds (VOCs), and hydrogen sulfide (H_2S) [15-17]. In California,

approximately 45% of total anthropogenic CH_4 emissions come from dairies, and the state's short-lived climate pollution reduction law (SB 1383) will require a 40% reduction in dairy methane by 2030 [18-19]. Alternatives to traditional manure management practices are desperately needed that can cut CH_4 emissions, reduce air pollution and transform dairy manure from a polluting waste into a valuable organic resource [18].

Anaerobic digestion is one strategy that can mitigate CH_4 by capturing it from anaerobic lagoons for use in renewable energy production [20]. While this strategy may substantially reduce CH_4 from liquid manure, manure solids stored in stockpiles remain a large source of CH_4 [11, 13, 16-17]. In a previous study, we show that biochar-composting, which consists of composting manure together with biochar, is an effective alternative to stockpiling or composting manure solids and can reduce CH_4 emissions by 84% relative to composting without biochar [11]. If biochar-composting replaces manure stockpiling at intensive dairies globally, this strategy can increase the maximum CH_4 mitigation potential of dairy manure from 4.5 Tg CH_4 yr^{-1} to 6.1 Tg CH_4 yr^{-1} [11].

Pairing anaerobic digestion together with biochar-composting creates a system in which both liquid and solid dairy manure is managed for CH_4 mitigation [11]. However, composting organic waste, in general, can be a large source of air pollution [21]. A recent study by Nordahl et al. (2020) showed that, while composting had the lowest global warming potential of all the organic waste management strategies considered in their analysis, it also had the highest social cost due to the negative health impacts resulting from the high rate of air pollutants emitted during composting [22]. At the local scale, odor from composting, produced from air pollutants such as NH_3, VOCs, and H_2S, can act as an environmental stressor in addition to harming respiratory health [22-25]. At the regional scale, these pollutants, along with nitrogen oxides (NO_x), can react in the atmosphere to form both fine particulate matters ($PM_{2.5}$) and ozone (Figure 3-1) [22, 26-27]. In California, over 80% of dairies are located in the state's rural Central Valley which regularly exceeds federal $PM_{2.5}$ and ozone standards [14, 28]. Due to the high number of disadvantaged communities in the Central Valley, vulnerable communities may have limited capacity to cope with the potential health impacts from additional air pollution from composting [29-31].

While evidence is limited, some studies suggest that, in addition to reducing CH_4 emissions during composting, amending compost with biochar may also reduce the emission of some air pollutants [32-35]. However, we are aware of no full-scale field studies that simultaneously measure both greenhouse gases (GHGs) and air pollutants during biochar-composting of dairy manure. If biochar-composting can reduce air pollution from dairies, this would result in a significant co-benefit of this powerful CH_4 mitigation strategy.

In this study, we test whether biochar-composting can function as both a CH_4 mitigation and air pollution reduction strategy for dairy manure management. In a full-scale field experiment at a dairy, we measured the emission of GHGs (CO_2, CH_4, N_2O) and air pollutants (H_2S, VOCs, NO_x, NH_3) during the composting of separated solid dairy manure with and without biochar. We hypothesized that incorporating biochar into the composting process would mitigate both CH_4 and air pollutant emissions primarily through an increase in pile aeration and the adsorption of gases and/or their precursors on the surface of biochar. We also use the emission data from our composting experiment,

along with an integrated assessment model, to estimate the social cost of each composting strategy to assess their potential impact on public health.

3.2 Methods

3.2.1 Site Description and Experimental Design

The composting experiment was conducted over 35 days from October 24 to November 27, 2022, at a dairy in Madera, California. While composting can take place over much longer periods of time, intensive dairies are limited in space for composting and have high rates of manure production, so shorter on-farm composting times may be necessary [11, 36]. In our previous study, we determined that 35 days of composting allowed dairy manure compost to reach maturity and to achieve thermophilic temperatures long enough to kill most pathogens [11, 37-38].

Two full-scale windrows (10 m long, 2 m wide, 1 m tall) were prepared from separated dairy manure solids, and biochar was applied to one pile at a rate of 20% by volume or 13% by mass. The manure-only pile was composed of approximately 10.23 t fresh manure (2.66 t dry weight) while the biochar-compost pile had the same amount of manure amended with 1.36 t biochar (1.32 t dry weight). Biochar was produced from almond shells through slow pyrolysis at 475°C and characteristics of the biochar are listed in Table S3-1. Both piles were aerated and homogenized using a mechanical compost turner 4 times over the course of the experiment (days 1, 8, 23, and 31).

3.2.2 Greenhouse Gas and Air Pollutant Flux Measurements

Gas fluxes from the compost piles were measured using a static chamber system connected to several gas analyzers. For each pile, fluxes were measured from three locations (south side, top, and north side) daily for the first week, when pile conditions were most dynamic, and every other day for the remainder of the experiment. The collar for each chamber was inserted 3 cm into the compost and left to sit for at least 30 minutes before measurement to allow the initial pulse of gas released from the compost after chamber installation to dissipate. Measurements were made by placing a chamber (12271.9 cm^3) that was connected to the gas analyzer and circulation pump.

GHGs (CO_2 CH_4, N_2O) and NH_3 were sampled for three minutes from each chamber and measured using a cavity ring-down laser spectrometer (Picarro G2508, Picarro Inc. Santa Clara, CA). GHG and NH_3 fluxes were calculated using Picarro's Soil Flux Processor program using a linear model or the Hutchinson and Mosier exponential model when changes in concentration were nonlinear. Using an identical sampling strategy, NO_x ($NO + NO_2$) was measured using a chemiluminescent NO_x analyzer (Serinus 40 Oxides of Nitrogen Analyzer, Acoem, Richmond, VA), and H_2S was measured with a portable gas analyzer equipped with an electrochemical H_2S sensor (Analytical Technology Inc., D-16 PortaSens III, Collegeville, PA). Changes in NO_x and H_2S concentration were determined through linear regression, and fluxes were calculated using the change in concentration and the chamber temperature and dimensions [39-40]. Non-methane VOCs were sampled by drawing air from each chamber at a rate of 0.1 L

min^{-1} for 7 minutes into VOC sorbent tubes (Markes International, Bridgend, UK), which were capped and later analyzed using a thermal desorption system (UNITY-xr, Markes International, Bridgend, UK) coupled to a gas chromatography mass spectrometer (G7077BA, Agilent), see details given in the Supplement.

Gas fluxes were converted from a per area basis to a per dry feedstock mass basis by multiplying each flux by the area of the compost pile and dividing by the dry mass of the compost pile. Flux measurements on the sides of the compost pile were multiplied by a correction factor to account for the difference in the mass of compost below side measurements and top measurements. The cumulative emission of each gas from each pile over the course of the experiment was estimated by calculating the area under each average flux curve.

3.2.3 Social cost analysis

We used the Air Pollution Emission Experiments and Policy (APEEP, version 3) integrated assessment model to quantify the social cost from the emission of GHGs and air pollutants during dairy manure composting and biochar-composting [41]. We also use the Biden administration's recommended social costs for CH_4 and N_2O emissions [42]. While H_2S is an odorous and toxic air pollutant, the social cost of H_2S is not reported in environmental or public health literature, so it is not included in this analysis. The social cost multipliers we used for each gas are listed in Table S3-2. Social costs were calculated in U.S. dollars per metric ton of compost and were scaled up to the farm scale using average per farm manure production for California dairies [13-14].

3.2.4 Compost and Biochar Characterization

Compost samples were taken weekly after compost piles were homogenized through turning of the windrows. Samples were taken from a minimum of six locations on the sides and top of the windrow at depths ranging from 0 to 20 cm. Compost moisture was determined gravimetrically through oven drying at 55°C for 72 h. Oven dried samples were ground and analyzed on an elemental analyzer (Costech 4010, Costech Analytical Technologies Inc., Valencia, CA) to determine total carbon (C) and nitrogen (N). The NH_4^+-N and NO_3^--N concentration of compost samples were measured by analyzing 2M KCl compost extracts through colorimetry on a microplate reader (Synergy HTX Multimode Reader, Agilent Technologies Inc., Santa Clara, CA). Compost pH and EC was determined in a 1:5 (w/v) compost to DI water suspension. Proximate analysis of feedstocks and final compost was performed according to ASTM D3172-13 and compost germination indexes of final compost samples were determined following recommendations by Luo et al. (2018) [43-44].

Biochar samples were characterized using the same methods detailed above for moisture, total C and N, NH_4^+-N and NO_3^--N, pH and EC, and proximate analysis. The specific surface area of biochar was determined through the Brunauer, Emmett, and Teller (BET) method on a TriStar II Plus (Micromeritics, Norcross, GA) [45]. Total O and H of biochar were also measured on a thermal conversion elemental analyzer (TC/EA High Temperature Conversion Elemental Analyzer Thermo Scientific, Waltham, MA).

3.2.5 Statistical Tests

All statistical analyses were performed in R [46]. Differences in physical and chemical properties between compost and biochar-compost over the course of the experiment were tested for significance using general linear models with treatment and time used as fixed factors. Differences in cumulative gas emissions were tested for significance using Welch's t-test. Pearson correlation coefficients were used to analyze the relationship between compost characteristics and gas emissions. Significance for all analyses was set at $p < 0.05$. Assumptions of normality and homoscedasticity were checked before each analysis and non-normal data was transformed if necessary.

3.3 Results

3.3.1 Compost physical and chemical characteristics

After achieving thermophilic temperatures, both composts remained above 55°C for the remainder of the experiment, except for turning days when compost temperature dropped substantially for both piles for approximately 24 h (Figure 3-2a). The biochar-compost pile had significantly lower moisture content ($p = 1.4 \times 10^{-8}$) and higher porosity ($p = 0.0016$) compared to the manure-only pile (Figure 3-2b, 3-2c). NO_3^- in both composts were relatively low and remained similar throughout the composting process, but the biochar-compost had significantly less NH_4^+ than the manure-only compost ($p = 0.00491$) (Figure 3-2g, 3-2h). Both composts were determined to be mature at the end of the experiment which was demonstrated by a C/N ratio less than 25, a germination index above 50 and NH_4^+-N less than 400 mg kg^{-1} (Table S3-3) [37].

3.3.2 Greenhouse gas emissions

Over the course of the experiment, the biochar-compost pile emitted 421 g CO_2 kg^{-1} TS, 4.44 g CH_4 kg^{-1} TS, and 18.6 mg N_2O kg^{-1} TS. The manure-only pile emitted 711 g CO_2 kg^{-1} TS, 10.60 g CH_4 kg^{-1} TS and 3.65 mg N_2O kg^{-1} TS (Figure 3-3). The difference in cumulative N_2O emitted was not statistically significant ($p = 0.2857$). However, biochar did significantly reduce total CO_2 ($p = 0.0371$) and CH_4 ($p = 0.0479$) emitted during composting by 41% and 58%, respectively.

3.3.3 Air pollutant emissions

Total air pollutant emissions from the biochar-compost pile were 78.4 mg H_2S kg^{-1} TS, 0.11 mg VOCs kg^{-1} TS, 0.12 mg NO_x kg^{-1} TS, and 0.64 mg NH_3 kg^{-1} TS. The total air pollutants emitted from the manure-only pile were 239 mg H_2S kg^{-1} TS, 0.29 mg VOCs kg^{-1} TS, 0.40 mg NO_x kg^{-1} TS, and 0.51 mg NH_3 kg^{-1} TS (Figure 3-4). While the difference in cumulative NH_3 emitted was not statistically significant between the two piles ($p = 0.567$), the biochar-compost treatment significantly reduced VOCs ($p = 0.0369$), NO_x ($p = 0.0281$) and H_2S ($p = 0.0466$) by 61%, 70% and 67%, respectively.

3.3.4 Social cost analysis

Results from our social cost analysis show that the public health damages from composting and biochar-composting are \$47.21 t TS^{-1} and \$37.6 t TS^{-1}, respectively. The annual social cost per farm for composting and biochar-composting was found to be \$325,670 yr^{-1} and \$259,455 yr^{-1}, respectively. Based on this analysis, dairies that use biochar-composting instead of composting to manage their manure could reduce social costs by \$66,215 per farm annually.

3.4 Discussion

3.4.1 Greenhouse gas emissions

Biogenic CO_2 released during composting is considered to have no net climate impact, but it is an important composting metric that provides insight into decomposition rates, aeration, and stability [37]. Over the course of the experiment, the biochar-compost pile emitted 41% less CO_2 than the manure-only pile (Figure 3-3e). This could be due to the adsorption of labile C on the biochar surface, the precipitation of CO_2 onto the high pH biochar, or the absorption of CO_2 into the biochar's extensive pore network (Table S3-1) [47]. Despite a reduction in CO_2 emissions, the biochar-compost pile reached thermophilic temperatures faster than the manure-only pile, suggesting that biochar likely enhanced microbial activity.

We found that the biochar-compost pile emitted 58% less CH_4 than the control over the course of the experiment, which is consistent with previous biochar-composting studies (Figure 3-3d) [11, 34, 48-49]. The primary mechanism driving this reduction is likely an increase in oxygen diffusion in the biochar-compost. We observed significantly higher porosity and lower moisture in the biochar-compost, which could reduce anaerobic hotspots and potentially increase CH_4 oxidation by methanotrophs [50-52] (Figure 3-2b, 2c). Though not statistically significant, CH_4 was positively correlated with moisture (p = 0.246) and negatively correlated with porosity (p = 0.202), which agrees with our understanding of the drivers behind CH_4 emissions during composting (Figure S3-1) [50-51]. While other compost bulking agents may also improve aeration, biomass that is not pyrolyzed can provide a readily available source of C for methanogenesis, whereas biochar likely provides very little, further restricting CH_4 production [11].

Cumulative N_2O emissions from both piles were very low, and differences between piles were not statistically significant (Figure 3-3f). We previously reported very low N_2O fluxes during the composting of dairy manure with or without biochar, and we attribute this to the inhibition of nitrification due to the high temperatures maintained over the composting experiment [11, 53]. Interestingly, N_2O emissions were mostly negative for both composts during the first half of the experiment when the majority of CH_4 was emitted, which suggests complete denitrification under very anaerobic conditions. While the biochar-compost pile emitted slightly more N_2O, total N_2O emissions were still very low, and the climate benefit of the reduction in CH_4 was much larger.

In addition to reducing GHG emissions during biochar-composting, the production of biochar and the application of biochar-compost to soils offer additional climate benefits (Figure 3-1) [11]. For example, facilities that produce biochar often also generate renewable energy from the pyrolysis process, which can displace fossil fuel use [54]. Biochar production also serves as a sustainable management strategy for biomass that may have otherwise generated additional GHG emissions though burning or landfilling [11, 55]. While the pyrolysis process requires energy and generates some GHGs, emissions from this stage are typically negligible compared to other lifecycle stages because pyrolysis is an exothermic reaction that requires little initial energy and releases mostly biogenic CO_2, which has no net climate impact [56]. Incorporating biochar into the composting process also enhances its soil carbon sequestration potential as the majority of biochar carbon is likely to persist in soils long-term [57].

3.4.2 Air pollutant emissions

While some studies have shown that biochar-composting can reduce CH_4 emissions, there are very few studies that have investigated how biochar influences H_2S during composting, despite both gases forming under similar, anaerobic conditions [32, 50-51]. We found that biochar significantly reduced H_2S during composting by 67%, likely through the same mechanisms through which it mitigated CH_4 emissions (Figure 3-4d). This odorous gas is toxic and can act as an environmental stressor, so H_2S mitigation from dairies could improve the health and wellbeing of farmworkers and rural communities living near dairies [58-60]. A reduction in H_2S emissions may have also reduced the number of stable flies (*Stomoxys calcitrans*), a harmful cattle pest attracted to decomposing manure, which we observed in fewer numbers on the biochar-compost (Figure 3-5) [61].

VOCs released during composting are rarely reported in the literature, despite their potential toxicity and contribution to both malodor and tropospheric ozone formation [21]. We found that total non-CH_4 VOCs were significantly reduced by 61% in the biochar-compost treatment, suggesting that biochar application may be an effective strategy to reduce VOCs during composting, which could benefit both farmworker and community health [26]. Biochar has been shown to be an effective sorbent for VOCs, which could explain their reduction in the biochar-compost treatment [35, 62-63]. Anaerobic hotspots in the compost pile can also be a source of VOCs, so biochar's aeration effect may also limit VOC formation by increasing oxygen diffusion in the compost [64-65]. While different VOCs can have varying environmental impacts, and different composts may produce different types of VOCs, we report the total mass of thirty VOCs identified by GCMS to provide an emission factor that can be used to compare with other emission factors in the literature [21]. We also provide emission data for individual VOCs in the supplementary material (Table S3-4).

NO_x emissions from composting are typically assumed to be negligible, and there exist very few measurements of NO_x fluxes during composting [66-70]. However, in our study, NO_x emissions from both compost piles were surprisingly high. When considered on an area basis, the peak NO_x flux from the manure-only pile was 101 ng NO_x-N m^{-2} s^{-1} while the peak flux for the biochar-compost pile was 43 ng NO_x-N m^{-2} s^{-1} (Figure 3-4b).

This is comparable to large NO_x fluxes observed from agricultural and arid soils, suggesting that manure management and composting could be a significant source of NO_x, which should be investigated further [39-40, 71-72].

Although NO_x emissions were relatively high from both piles, the biochar-compost pile emitted 70% less NO_x than the manure-only pile (Figure 3-4g). While this is the first time that biochar has been found to reduce NO_x emissions during composting, some studies have reported that biochar mitigated NO_x emissions when applied to soils [73-76]. In our study, NO_x fluxes from both piles peaked after piles were aerated and cooled through mechanical turning, suggesting that nitrification was the dominate NO_x production pathway. This hypothesis is also supported by the very low NO_x fluxes we recorded when compost piles reached thermophilic temperatures and when CH_4 emissions were high, as high temperatures and low oxygen can inhibit nitrification [11, 53]. Interestingly, the biochar-compost pile had much lower NH_4^+ concentrations than the compost pile throughout the experiment, while NO_3^- concentration in both piles were similar (Figure 3-2g, 3-2h). This suggests that electrostatic adsorption of NH_4^+ onto the biochar surface did not play a significant role in NO_x mitigation. Instead, we suggest that biochar chemisorption of NH_4^+ was the dominate NO_x mitigation mechanism. Chemisorption of NH_4^+ through covalent bond formation has been found to be an important process for N retention on biochar surfaces and would explain the lower KCl-extractable NH_4^+ in the biochar-compost [77-79].

While amending compost with biochar significantly reduced NO_x emissions, it surprisingly did not mitigate NH_3 emissions (Figure 3-4h). Multiple studies have reported lower NH_3 emissions during biochar-composting compared to composting without biochar [32, 51, 80-81]. However, biochar has also been found to increase NH_3 emissions from soils and composts by increasing pH [75, 82-84]. Even though biochar may have adsorbed NH_4^+ during composting, it may have increased the rate of volatilization of non-adsorbed NH_4^+ by increasing the pH of the compost. This tradeoff may explain why differences in NH_3 emissions between the biochar-compost pile and the manure-only pile were not statistically significant. NH_3 is an important air pollutant released during composting, so further research that tests which biochar feedstocks and production techniques optimize NH_3 mitigation during composting is needed to improve the potential of biochar-composting to reduce air pollution.

Biochar production may also mitigate air pollution by providing an alternative to the burning of agricultural biomass, a common waste management strategy on farms (Figure 3-1). Biomass burning is a large source of $PM_{2.5}$ pollution and is a significant contributor to poor air quality in rural regions [6]. Compared to combustion, pyrolysis emits far less $PM_{2.5}$ and $PM_{2.5}$ precursors, especially when gases are trapped for renewable energy production [85-86]. In order to improve rural air quality, California plans to ban nearly all biomass burning of agricultural residues in the San Joaquin Valley by 2025 [87]. Biochar production offers a sustainable management pathway for this agricultural waste that adds value to the biomass and could help develop a circular economy based on biomass transformation and reuse in agriculture (Figure 3-1) [88]. Biochar use in dairy manure management would further the air pollution reduction potential of this system and could provide a reliable market for biochar companies.

3.4.3 Social cost analysis

We found that biochar-composting could reduce the annual social cost from dairy manure composting emissions by over $66,000 per farm. This is likely a conservative estimate since we do not consider the public health damages from H_2S emissions, which was the largest source of non-GHG air pollution during the experiment and which was reduced by 67% in the biochar-compost treatment. There are also other air pollution and climate benefits in the biochar-composting lifecycle that are not quantified in this analysis, such as reduced biomass burning, that would further reduce social cost. We also acknowledge the limitations of using social cost to quantify public health impact, as communities vary in their capacity to cope with pollution. For example, rural areas tend to have a higher proportion of socioeconomically disadvantaged communities, and members of these communities are much more likely to lack the economic and social means to deal with air pollution compared to members of middle class or affluent communities [29-31].

3.5 Conclusion

Biochar-composting of dairy manure solids is an untapped CH_4 mitigation strategy that serves as a complement to the anaerobic digestion of liquid manure and offers multiple climate benefits over its lifecycle. Here, we confirm biochar's capacity to reduce CH_4 from dairy manure and highlight a significant co-benefit of this strategy – its potential to reduce air pollution from dairies. In addition to substantially mitigating CH_4 emissions, biochar-composting could improve the health of rural, disadvantaged communities, especially in California's Central Valley which suffers from poor air quality and where many of the nation's dairies are concentrated. Sourcing biochar feedstock from agricultural biomass that would have otherwise been burned offers an additional opportunity to reduce air pollution from agriculture. Biochar-composting offers governments and farmers a rare chance to tackle both climate change and air pollution simultaneously. However, further research is needed that optimizes biochar production and application for NH_3 mitigation during composting.

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3.7 Figures

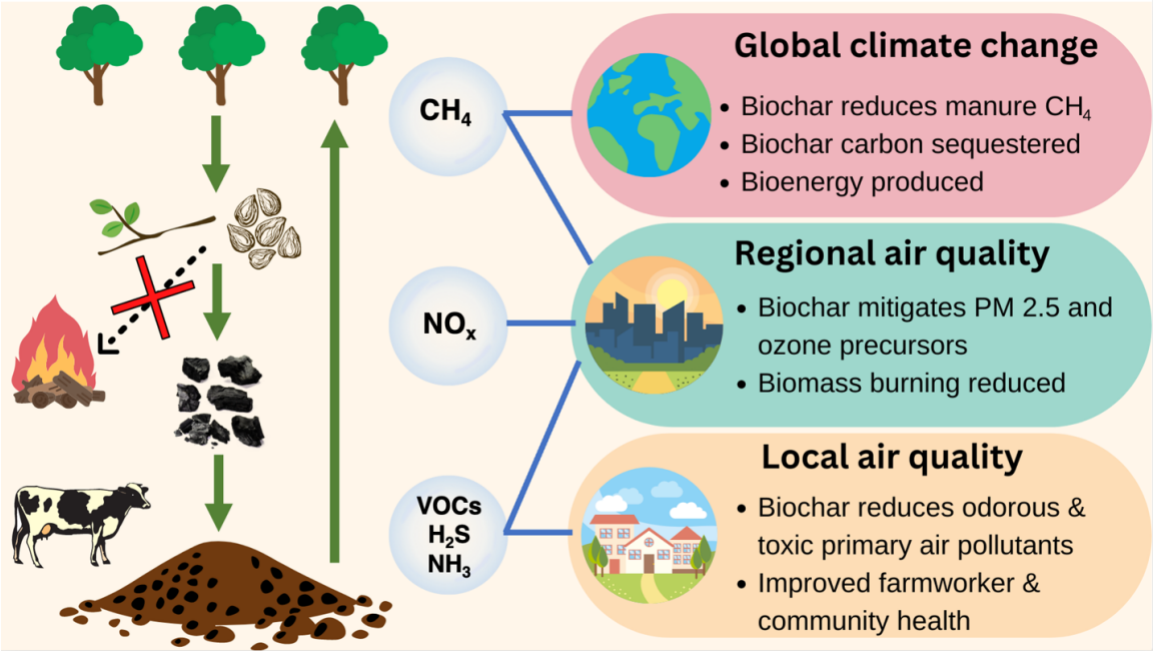

Figure 3-1. Conceptual model showing the flow of orchard biomass to a biochar production facility, biochar to a dairy farm, and biochar-compost back to the orchard for use as an organic soil amendment. The impacts at the local, regional, and global scale from the reduction in the emission of CH_4 and air pollutants during composting are also reported.

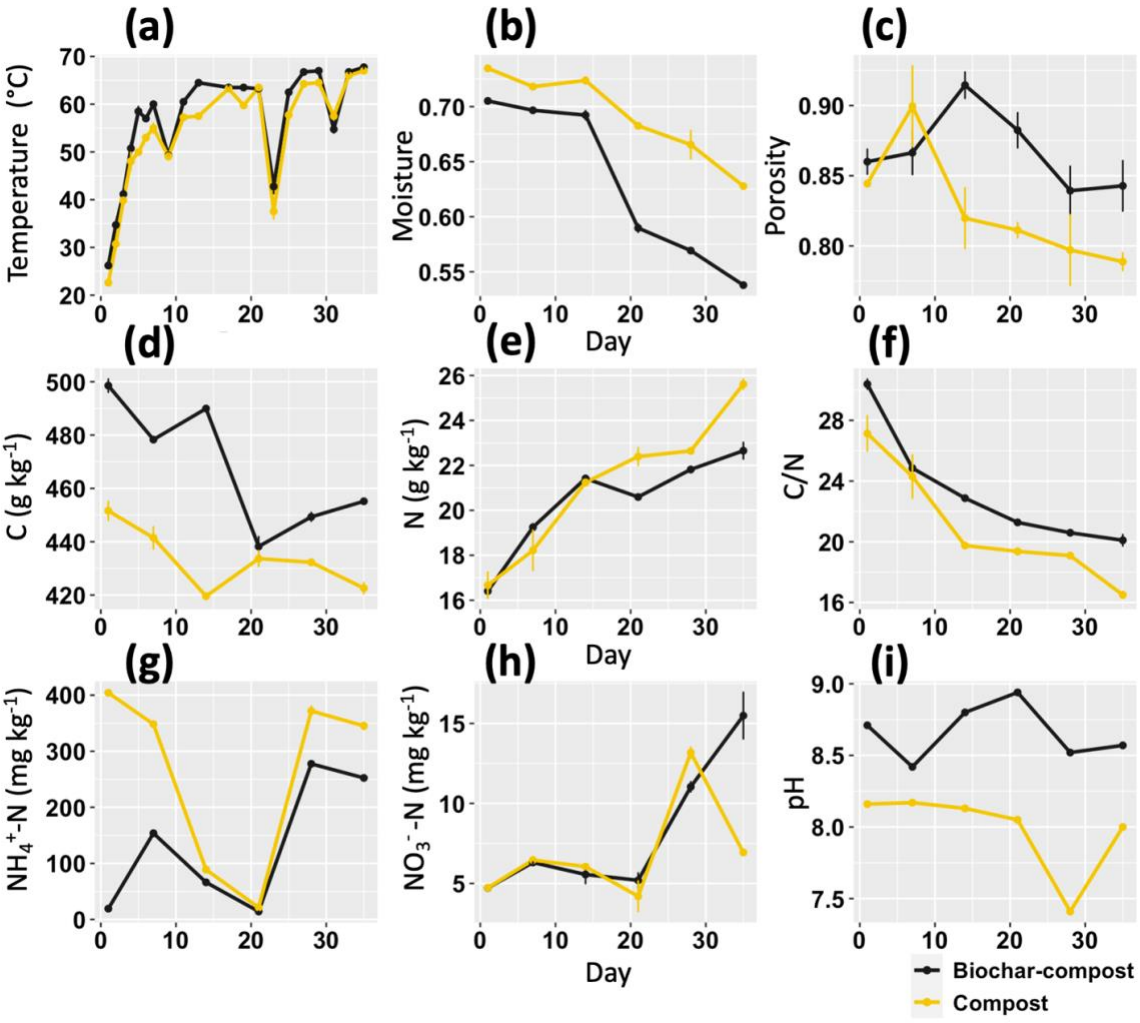

Figure 3-2. Physical and chemical characteristics of the composts over the course of the experiment including (a) temperature in °C (b) moisture content (c) porosity (d) C in g kg^{-1} (e) N in g kg^{-1} (f) C/N ratio (g) NH_4^+-N in mg kg^{-1} (h) NO_3^--N in mg kg^{-1} (i) pH. The black lines are the biochar-compost treatment, and the yellow lines are the manure-only compost. Error bars are ± 1 standard error.

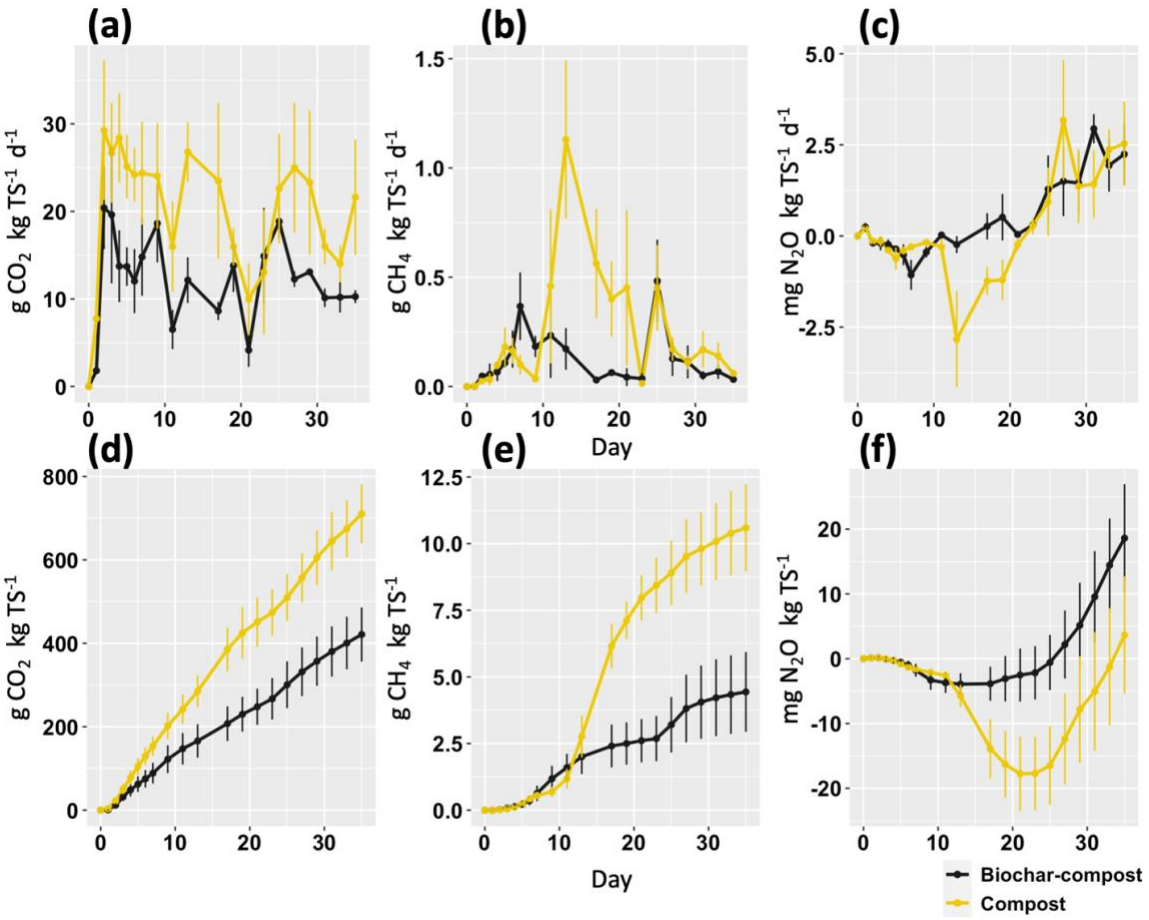

Figure 3-3. Daily average flux emission of (a) CO_2 in g CO_2 kg TS^{-1} d^{-1} (b) CH_4 in g CH_4 kg TS^{-1} d^{-1} (c) N_2O in mg N_2O kg TS^{-1} d^{-1} and cumulative emission of (d) CO_2 in g CO_2 kg TS^{-1} (e) CH_4 in g CH_4 kg TS^{-1} (f) N_2O in mg N_2O kg TS^{-1}. The black lines are the biochar-compost treatment, and the yellow lines are the manure-only compost. Error bars are ± 1 standard error.

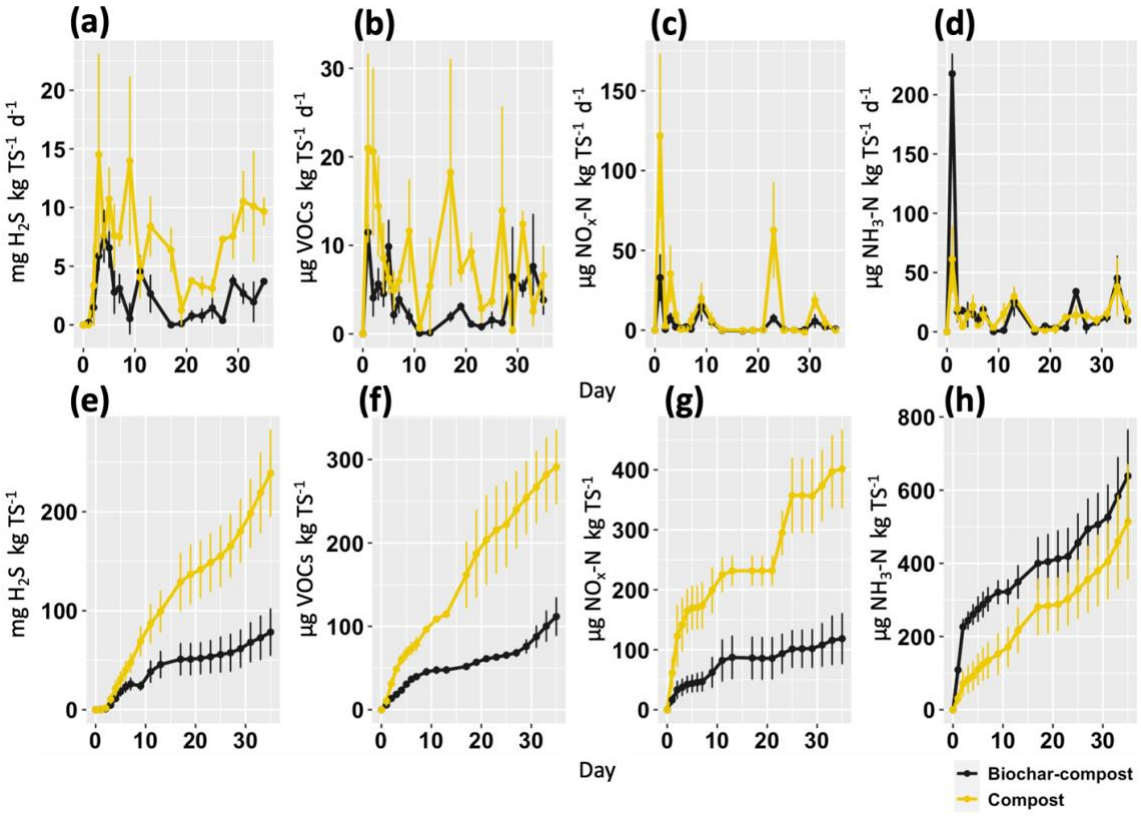

Figure 3-4. Daily average flux emission of (a) H_2S in mg H_2S kg TS^{-1} d^{-1} (b) VOCs in µg VOCs kg TS^{-1} d^{-1} (c) NO_x in mg NO_x-N kg TS^{-1} d^{-1} (d) NH_3 in µg NH_3-N kg TS^{-1} d^{-1} and cumulative emission of (e) H_2S in mg H_2S kg TS^{-1} (f) VOCs in µg VOCs kg TS^{-1} (g) NO_x in mg NO_x-N kg TS^{-1} (h) NH_3 in µg NH_3-N kg TS^{-1} d^{-1}. The black lines are the biochar-compost treatment, and the yellow lines are the manure-only compost. Error bars are ± 1 standard error.

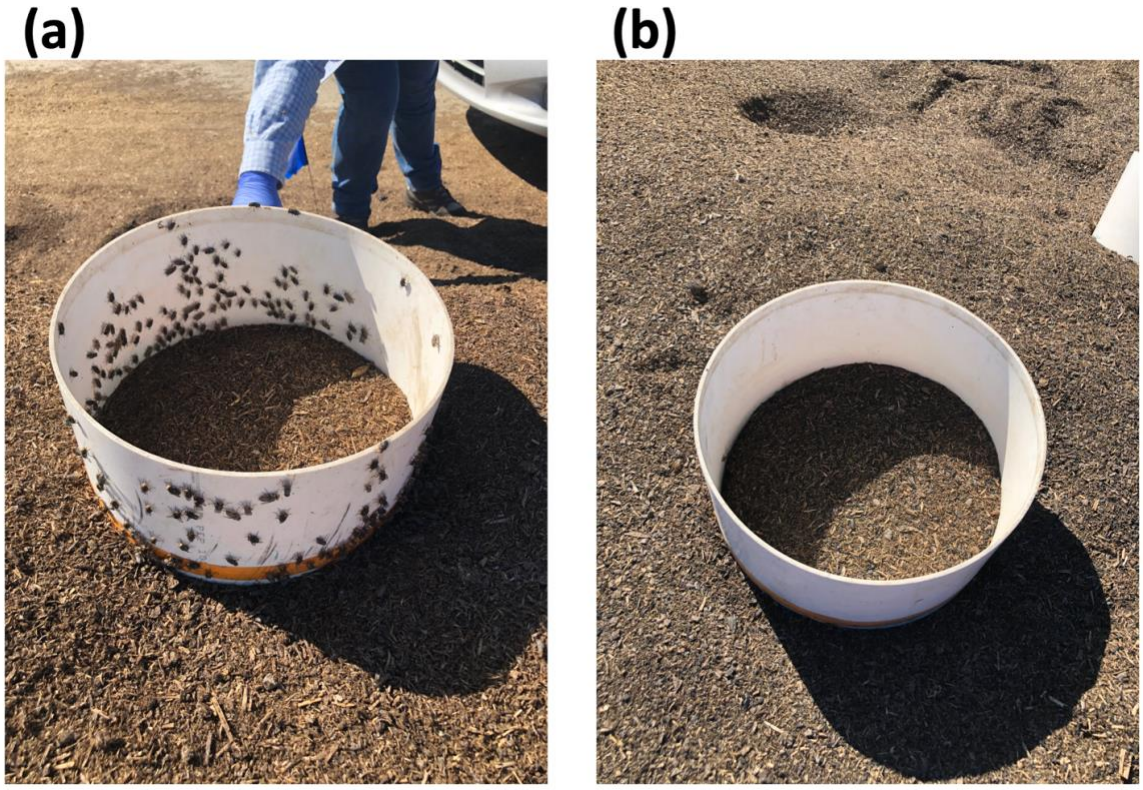

Figure 3-5. Photographs of (a) a gas sampling collar on the manure-only compost and (b) a gas sampling collar on the biochar-compost. The photographs were taken on the same day, moments apart from each other. We observed substantially fewer stable flies (*Stomoxys calcitrans*) on the biochar-compost, which could be due to the reduction of H_2S emissions following biochar application.

Chapter 4

Methane and nitrous oxide emissions during biochar-composting are driven by biochar application rate and aggregate formation

Abstract

Manure is a leading source of methane (CH_4), nitrous oxide (N_2O), and ammonia (NH_3) emissions, and alternative manure management practices can help society meet climate goals and mitigate air pollution. Recent studies show that biochar-composting can substantially reduce emissions from manure. However, most studies test only one type of biochar applied at a single application rate, leading to high variation in emission reductions between studies. Here, we measured greenhouse gas and NH_3 emissions during biochar-composting of dairy manure with biochar applied at 5% or 20%, by mass, and made from walnut shells, almond shells, or almond clippings. We found little difference in emissions between biochar type. However, we found that the 20% application rates increased CH_4 emissions and decreased N_2O and NH_3 emissions, resulting in a net reduction in global warming potential (GWP). We attribute this result to biochar increasing the formation of compost aggregates, which likely acted as anaerobic reactors for methanogenesis and complete denitrification. Biochar may have further fueled CH_4 production and N_2O consumption by acting as an electron shuttle within aggregates. We recommend lower application rates, as we found that the 5% treatments in our study led to a similar reduction in GWP without increasing CH_4 emissions.

4.1 Introduction

Manure management is a leading source of anthropogenic methane (CH_4) and nitrous oxide (N_2O), and ammonia (NH_3) emissions. In the U.S., manure management accounts for 9% of CH_4 emissions and 4% of N_2O emissions, while in California, the nation's leader in dairy production, manure contributes 26% and 12% of statewide CH_4 and N_2O emissions, respectively [1-3]. Because the 100-year global warming potential (GWP) of CH_4 and N_2O are 28 and 264 times that of carbon dioxide (CO_2), respectively, reducing the emission of these gases from manure is a low hanging fruit when it comes to climate change mitigation and can help society make significant progress on rapidly approaching climate goals [4-7].

Recent efforts to curb emissions from livestock manure have focused on the use of anaerobic digesters, which trap CH_4 emissions from manure lagoons for use in energy

production [8-10]. While this strategy can lead to large reductions in CH_4 emissions from liquid manure, solid manure that is separated from digesters is often stockpiled and can remain a significant source of both CH_4 and N_2O [11-12]. Aerobically composting these manure solids, rather than stockpiling them, can reduce CH_4 emissions while producing a valuable organic fertilizer [13-14]. However, composting nitrogen (N) rich manure can lead to high N_2O emissions, which risks reducing the climate benefit of composting by essentially "pollution swapping" CH_4 for N_2O [11, 13, 15]. Furthermore, manure composting can result in large losses of reactive N to the environment through the volatilization of ammonia (NH_3), an odorous gas and an important precursor to $PM_{2.5}$ pollution [16-17]. In order to improve the effectiveness of manure composting as a climate change mitigation strategy, novel composting techniques are needed that can minimize the emission of greenhouse gases (GHG) and NH_3 from solid manure while transforming this polluting waste into a valuable organic resource.

Biochar-composting is one strategy that has been recently proposed for reducing the emission of CH_4, N_2O and NH_3 from manure [18-20]. While the technique of combining charcoal and organic waste to improve soil fertility has been practiced by multiple Indigenous Peoples for millennia, biochar-composting for emission mitigation is a novel manure management strategy that has only recently been investigated [18, 21-23]. Several studies suggest that the high porosity of biochar can improve compost pile aeration and help prevent the formation of anaerobic microsites where CH_4 is produced [24-27]. In a recent study, we found that biochar-composting reduced CH_4 emissions by 84% relative to composting without biochar, resulting in a climate-negative dairy manure management strategy [28]. Biochar has also been found to substantially cut N_2O and NH_3 emissions from soils and composts, likely by adsorbing precursors to these gases on the surface of biochar and by promoting N_2O reduction to N_2 through the shuttling of electrons to denitrifiers [29-32].

Despite the promising potential of biochar to reduce emissions during composting, most biochar-composting studies have tested only one type of biochar applied at a single application rate, leading to a wide range in reported emission reductions between studies [18, 20, 28]. Biochar can be made from essentially any organic material, and it retains many of the original properties of the feedstock from which it is made. Because of this, key physical and chemical characteristics of biochars such as porosity, surface area, and functionality, can vary greatly depending on their feedstock, and this can influence a particular biochar's capacity to reduce emissions [18, 33-34]. Furthermore, different application rates of biochar to manure could lead to a wide range of composting environments, differing in physical structure, redox conditions, and nutrient compositions, all of which can lead to dramatic changes in the composting process and its associated emissions [18, 20, 32]. Therefore, an investigation into the optimal biochar feedstocks and application rates for emission mitigation during composting, as well as the mechanisms driving these potential reductions, is desperately needed to provide farmers with specific recommendations for biochar-composting. Testing biochars made from locally abundant sources of organic resources is especially needed in order to strategically harness biomass streams in agricultural regions to help develop circular, climate-smart economies [35].

Here we conducted a laboratory scale biochar-composting experiment to investigate the optimal biochar feedstocks and application rates for mitigating GHG and NH_3 emissions from dairy manure. We tested biochars made from either walnut shells, almond shells, or almond clippings and applied biochar at a rate of 5% or 20% by mass. We hypothesized that higher application rates of biochar would result in the greatest reductions in emissions and that biochars with the highest porosity would be most effective in mitigating CH_4 emissions through enhanced pile aeration. We also hypothesized that biochars with the highest surface area would result in the greatest reduction in N_2O and NH_3 emissions, through the absorption of gas precursors and NH_3 on the biochar surface.

4.2 Methods

4.2.1 Compost experiment design

We conducted a composting experiment in aerated, insulated bioreactors over six weeks in the laboratory. Our experimental design consisted of a no-biochar control and six biochar treatments, each tested in triplicate. Treatments consisted of biochars applied at a rate of 5% or 20% by dry mass, and produced from either almond shells, almond clippings, or walnut shells. These feedstocks were used because orchard biomass has been identified as a large source of available feedstock for biochar production in California's Central Valley where the majority of the state's dairies are also located [35-36]. Biochars were produced at approximately 350°C in a mobile, continuous feed pyrolizer (AC Fox, Incorporated, Groton, MA).

Compost bioreactors were constructed from a polyethylene drum (38.1 cm inner diameter, 53.4 cm height, 0.06 m^3 volume) and covered with a removable, air-tight lid (Figure 4-1a). Each drum was insulated with 7.62 cm of polyurethane foam to ensure that thermophilic composting temperatures were met [29]. Each experimental block had its own compressed air source, which was controlled by a pressure regulator, while the volume of air flowing into each bioreactor was regulated with a mechanical flowmeter set at a rate of 0.6 l min^{-1} (0.5 l min^{-1} kg VS^{-1}) [29, 37]. Air was dispersed at the bottom of each reactor through a coiled, 167 cm long tube, with 20 evenly spaced 4 mm wide holes. The compost feedstock sat 7.62 cm above the tube on a perforated steel plate. Out gas was allowed to pass out of the top of the bioreactor through a 5.1 cm wide hole in the middle of the air-tight lid.

Fresh solid dairy manure was obtained from a solids separator at a local dairy farm the day before the experiment began. Each treatment and the control received 15 kg of fresh dairy manure, and the 5% and 20% treatments also received 0.17 kg and 0.83 kg of biochar, respectively. Due to the very low moisture content of the biochars, the 5% and 20% treatments also received 0.6 and 2.9 kg of deionized water, respectively, to bring the overall gravimetric moisture content of the manure and biochar mixtures up to approximately 74%, the same as the no-biochar control. Before the feedstocks were loaded in the bioreactor, the contents of each treatment and the no-biochar control were mixed thoroughly in a mechanical mixer, lined with a clean plastic bag, for three minutes at a rate of 36 rotations per minute (rpm). Similarly, composting feedstocks were mixed

weekly by emptying the contents of each bioreactor into the lined mixer and rotating for one minute at 36 rpm. Each bioreactor was assigned to a random position within each block, and new positions were randomly assigned after compost mixing each week.

4.2.2 Compost and biochar characterization

In one of the three experimental blocks, each bioreactor was equipped with an oxygen sensor (Apogee SO-110, Apogee Instruments, Logan, UT) connected to a data logger (CR 1000, Campbell Scientific, Logan, UT) and a temperature sensor (5TE, Campbell Scientific, Logan, UT) connected to a separate data logger (ZL6 Basic, Meter Group, Pullman, WA) (Figure 4-1a). Oxygen sensors were calibrated before the experiment and weekly during the experiment according to the manufacturer's instructions. Sensor data was logged hourly and daily averages are reported.

Each week, compost samples were taken after homogenization through mechanical mixing. Compost moisture was measured through oven drying at 55°C for 72 h and total carbon (C) and nitrogen (N) were measured from the dried samples on an elemental analyzer (Costech 4010, Costech Analytical Technologies Inc., Valencia, CA) in the Stable Isotope Ecosystem Laboratory of UC Merced. Compost ammonium (NH_4^+-N) and nitrate (NO_3^--N) were extracted in 2M KCl and analyzed on a microplate reader (Synergy HTX Multimode Reader, Agilent Technologies Inc., Santa Clara, CA) through colorimetry. Compost dissolved organic carbon (DOC) was extracted in 0.5 M K_2SO_4, filtered through a 0.45 µm syringe filter, and measured on a TOC analyzer (Shimadzu TOC-Vcsh Total Organic Carbon Analyzer, Shimadzu Scientific Instruments, Kyoto, Japan). The pH and electrical conductivity (EC) of the composts were measured in a 1:5 (w/v) compost to DI water suspension. Volatile solids and ash contents of the composts and feedstocks were determined through proximate analysis according to ASTM D3172-13 [38]. Maturity of the final compost was tested by determining the germination index of each sample according to Luo et al (2018) (Table S4-1) [39]. Aggregates in the final composts were measured by first sifting the contents of each bioreactor through a 25.4 mm screen, and then by sifting the material that passed through the first screen through a second, 6.35 mm screen. The mass of compost aggregates in each of the three size fractions (>25.4 mm, 6.35 - 25.4 mm, and < 6.35 mm) was then measured for each bioreactor (Table S4-1).

Each of the three biochar types were also analyzed for total C and N, NH_4^+-N and NO_3^--N, pH and EC, and volatile solids and ash content using the same methods used for the composts (Table S4-2). The total O and H of each biochar was determined using a thermal conversion elemental analyzer (TC/EA High Temperature Conversion Elemental Analyzer Thermo Scientific, Waltham, MA). Each biochar's specific surface area and pore size was also measured on a TriStar II Plus (Micromeritics, Norcross, GA) using the Brunauer, Emmett, and Teller (BET) method [40].

4.2.3 Gas flux measurements

GHGs (CO_2, CH_4 and N_2O) and NH_3 were measured daily for the first 16 days, when the composting conditions were most dynamic, and then approximately every other

day for the 42-day experiment. All gases were measured using a closed-circuit, static chamber connected to a cavity ring-down laser spectrometer (Picarro G2508, Picarro Inc. Santa Clara, CA). A chamber was created by removing the lid of the bioreactor and replacing it with a separate, air-tight lid with two 1/4" tube fittings connected to the inlet and outlet ports of the gas analyzer with FEP tubing (Figure 4-1b). Gas was sampled from each reactor for 5 minutes and fluxes were calculated in the Picarro Soil Flux Processor program using a linear model or the Hutchinson and Mosier exponential model when nonlinear changes in concentration were observed [41]. As the composting process proceeded, the headspace above the compost increased as mass was lost, and this change in headspace was accounted for before each flux measurement and calculation. Cumulative emissions were estimated by calculating the area under each flux curve using the trapezoid rule.

4.2.4 Data analysis

All statistical tests were performed in R [42]. Differences in compost characteristics between treatments over the course of the experiment were analyzed using two-way mixed analysis of variance (ANOVA), with application rate (0%, 5%, or 20%) and amendment type (none, walnut shell, almond shell, or almond clippings), and their interaction as fixed effects and block and time as random effects. Pairwise comparisons of means using Tukey's HSD test were then performed to test for significance differences between treatments. Two-way ANOVA and Tukey's HSD post-hoc tests were used to test whether differences in cumulative gas emissions between application rate, biochar type, and their interaction, were significant. Significance for all statistical analyses was set at $p < 0.05$. Data was checked for normality and homogeneity before conducting all statistical analyses, and non-normal data was transformed using Box-Cox transformations [43]. Linear regression was also used to investigate the relationship between compost properties and gas emissions.

4.3 Results

4.3.1 Compost physical and chemical characteristics

The gravimetric moisture contents of the composts slightly increased over the course of the experiment, or remained nearly constant, and there was no significant difference between amendment type or application rate (Figure 4-2c). Compost temperatures peaked on days 2 and 3 of the experiment, and maximum temperatures were consistent, ranging from 66-68°C (Figure 4-2a). All composts were at thermophilic temperatures (> 55°C) for three days, which meets the USDA requirement for pathogen control during thermophilic composting [44]. The mesophilic stage (< 55°C) was reached by all composts by day 5, and temperatures cooled to slightly above ambient temperatures shortly thereafter, where they remained for the duration of the experiment. The oxygen concentration for all composts at the start of the experiment were below 10%, but all biochar treatments reached ideal aerobic composting conditions (15-20%) by

day 3 [45] (Figure 4-2b). However, the no-biochar treatment remained at very low oxygen concentrations (< 4%) until day 7.

Total C concentrations remained stable over the course of the experiment for all composts while total N concentrations increased, and there was a significant difference in C between amendment type ($p < 0.001$), application rate ($p < 0.001$), and their interaction ($p < 0.001$) and a significant difference in N between amendment type ($p < 0.001$), application rate ($p < 0.001$), but not their interaction ($p = 0.105$) (Figure 4-2d, 4-2e). All biochar treatments had significantly higher concentrations of C relative to the no-biochar control, and all 20% biochar application treatments had significantly lower N concentrations compared to the 5% application treatments and the no-biochar control. There was no significant difference in NO_3^- or NH_4^+ content between treatments, which both declined as compost matured (Figure 4-2f, 4-2g). DOC content peaked in week 2 and declined thereafter, and there was a significant difference between amendment type ($p < 0.001$), application rate ($p < 0.001$), and their interaction ($p < 0.001$), with almond clippings 20% and walnut shell 20% having lower DOC concentrations than the other biochar treatments and the no-biochar control (Figure 4-2h). We also observed a significant difference in pH between amendment type ($p < 0.01$) as the almond shell 20% treatment had significantly higher pH compared to the no-biochar control Figure 4-2i).

At the end of the experiment, the final composts were sifted to determine the fraction of compost mass in aggregates (Table S4-1). There was a significant difference between application rates in the fraction of compost mass in total aggregates (> 6.5 mm) ($p < 0.001$), medium aggregates (6.5 - 25.4 mm) ($p < 0.01$), and large aggregates (>25.4 mm) ($p < 0.05$). The 20% biochar application treatments had a significantly greater proportion of their mass in total and medium aggregates than the 5% and no-biochar control, as well as significantly more large aggregates than the no-biochar control. Differences in aggregate mass between the 5% treatments and the control were not statistically significant for any of the size fractions. The final composts were determined to be mature by the end of the experiment as they had an NH_4^+ content below 400 mg kg^{-1}, a DOC content below 4 g kg^{-1}, and a germination index above 50 (Table S4-1) [45].

4.3.2 Greenhouse gas and ammonia emissions

A peak in CO_2 emissions occurred for all treatments and the control during the thermophilic stage when compost temperatures were highest, and there was a significant difference in CO_2 emissions between application rate ($p < 0.001$) (Figure 4-3a, 4-3e). The 5% ($p < 0.05$) and 20% ($p < 0.001$) biochar application treatments significantly reduced cumulative CO_2 emissions relative to the no-biochar control (Table 4-1). There was also a significant difference in cumulative CO_2 emissions between amendment type ($p < 0.001$) and the interaction between amendment type and application rate ($p < 0.05$) (Table S4-3). Almond shell biochar treatments had significantly higher CO_2 emissions than almond clippings biochar ($p < 0.01$) and walnut shell biochar treatments ($p < 0.01$), but there was no significant difference between almond shell biochar and no biochar ($p = 0.119$).

CH_4 fluxes from all composts peaked during the thermophilic stage of composting (Figure 4-3b, 4-3f). There was no significant difference in cumulative CH_4 emissions between amendment types ($p = 0.721$), but there was a significant difference between

application rates ($p = 1.56 \times 10^{-9}$). While there was no significant difference between the no-biochar control and the 5% application treatments ($p = 0.972$), the 20% application treatments significantly increased CH_4 emissions relative to the control ($p < 0.001$) and the 5% treatments ($p < 0.001$), by an order of magnitude (Table 4-1).

Nearly all N_2O and NH_3 was emitted on day 2 of the experiment (Figure 4-3c, 4-3g, 4-3d, 4-3h). There was no significant difference in cumulative N_2O ($p = 0.949$) or NH_3 ($p = 0.735$) emissions between amendment type. However, the difference in N_2O ($p < 0.01$) and NH_3 ($p < 0.01$) between application rates was significant (Table 4-1). Though not statistically significant, the 5% biochar application treatments, on average, reduced N_2O ($p = 0.0895$) and NH_3 ($p = 0.354$) emissions by 64% and 33%, relative to the no-biochar control, respectively. The 20% application treatments, on average, significantly reduced N_2O ($p < 0.01$) by 84% and NH_3 ($p < 0.01$) by 65%, relative to the control, respectively.

Differences in net 100-year GWP between amendment types were not statistically significant ($p = 0.944$). However, biochar application rate had a significant effect on GWP ($p < 0.01$) (Table 4-1). The 5% application treatments significantly reduced GWP by 63%, on average, relative to the no-biochar control ($p < 0.05$), while the 20% application treatments reduced GWP by 70%, on average, relative to the control ($p < 0.01$). Differences in GWP between the 5% and 20% application treatments were not significant ($p = 0.874$).

4.4 Discussion

4.4.1 Greenhouse gas and ammonia emissions

4.4.1.1 CO_2 emissions

CO_2 emissions released during composting are biogenic in origin and are a part of the fast carbon cycle, so they do not have an overall impact on the climate [13]. However, CO_2 emissions indicate the rate of aerobic decomposition, and they are useful in determining the stability of the final compost produced [45]. While the overall trend in CO_2 emissions was consistent between treatments and the control, we found that all biochar treatments significantly reduced CO_2 emissions. Some biochar-composting studies observed an increase in CO_2 emissions following the application of biochar, likely due to the capacity of biochar to increase microbial activity during composting through enhanced aeration [46-47]. However, in a previous study, we also found that biochar suppressed CO_2 emissions during composting [28]. While all biochar treatments increased compost O_2 concentrations in our study, biochar may have reduced CO_2 fluxes by limiting respiration through the adsorption of labile C onto its surface [48]. We find evidence for this hypothesis in the significantly lower DOC concentrations of the walnut shell 20% and almond clippings 20% treatments, which also had the lowest cumulative CO_2 emissions (Figure 4-2f, 4-3e). However, we did not find a significant correlation between CO_2 emissions and DOC (Figure S4-1).

4.4.1.2 CH_4 emissions

In a previous field study, we found that a 6% (w/w) application rate of biochar to composting dairy manure reduced CH_4 emissions by 84% [28]. Surprisingly, we did not observe a significant difference in CH_4 emissions between the no-biochar control and the 5% biochar treatments in this study. Even more surprising, we found that the 20% biochar application treatments significantly increased CH_4 emissions by an order of magnitude. The no-biochar control and the 5% application treatments had a peak in CH_4 emissions on the first day of the experiment, when O_2 concentrations were low (Figure 4-2b, 4-3b). However, the 20% application treatments had a peak in CH_4 emissions on day 3, when all biochar treatments had high O_2 concentrations, and the no biochar control remained anaerobic. Despite increasing O_2 concentrations relative to the no-biochar control, the 20% biochar treatments increased CH_4 emissions.

This puzzling result led us to investigate whether biochar could be driving CH_4 emissions by providing a significant source of labile organic carbon, but differences in DOC between treatments were not statistically significant, except for the walnut shell 20% and almond clippings 20% treatments, which each had significantly lower DOC than the no-biochar control (Figure 4-2f). However, we did find a significant correlation between CH_4 emissions and the amount of compost mass in aggregates ($R^2 = 0.75$, $p < 0.001$) (Figure 4-4a, 4-4b). We hypothesize that biochar acted as a binding agent in the compost, enhancing aggregation through cation bridging between cations adsorbed to the biochar surface and the negatively charged compost (Figure 4-5). Previous analyses of the surface of co-composted biochars have found that composting enhances biochar surface oxidation and forms a mixed-charge organo-mineral layer on the surface of biochar [49-53]. The increase in biochar's reactivity through surface oxidation during composting may play an important role in enhancing biochar's ability to help form aggregates. Furthermore, the formation of an organo-mineral layer on the surface of biochar provides evidence for the capacity of biochar to adsorb composting organic matter through cation bridging.

While our sensors measured high O_2 concentrations in the bulk compost of the 20% biochar application treatments, the compost aggregates may have acted as anaerobic microsites that were undetectable by our bulk O_2 sensors. In soils, aggregates are known to be anaerobic hotspots, with O_2 diffusion to the core of aggregates limited by pore connectivity and microbial consumption [54-56]. This anoxic environment allows for aggregates to function as biogeochemical reactors for methanogenesis and denitrification [56-61]. Compost aggregates, though largely unexplored, may serve a similar role in the production of CH_4 emissions during composting.

In addition to creating this anoxic environment, biochar may have also increased CH_4 emissions by acting as an electron donor for methanogenesis within aggregates (Figure 4-5). Biochars have been found to play a direct role in redox reactions through the transfer of electrons facilitated by (hydro)quinone functional groups and/or polyaromatic hydrocarbons [62-63]. While previous studies have found that biochar can reduce CH_4 emissions through improved pile aeration when applied during aerobic composting, other studies have found that biochar can increase CH_4 emissions by mediating the transfer of electrons within anaerobic environments [18, 28, 64-67]. Aggregates in the 20% application treatments likely had more biochar available for

electron shuttling than aggregates in the 5% application treatments. This may help explain why a relatively modest increase in aggregation from the 5% to the 20% application treatments led to a large difference in the amount of CH_4 emitted (Figure 4-4a, 4-4b).

It is also important to note that the average CH_4 emission factor for the 20% application treatments was still approximately an order of magnitude lower than that of the compost windrows in our previous field study [28]. This shows the large variation in emissions between composting practices. For example, our bioreactors, which had forced air flowing through the composting feedstock, likely had much more aerobic conditions relative to the large windrows from our field experiment. In composting conditions with limited air flow, such as windrows, the aeration effect by biochar may play a more important role, which may have led to the large reduction in CH_4 emissions from biochar-composting in the field experiment [28]. Different compost turning practices may also help explain why we did not see a reduction in CH_4 emissions from the biochar-compost treatments in this study, as the slow rotating tumbler may have helped biochar form aggregates whereas the mechanical windrow turners used in the field study may have helped break up aggregates formed by biochar.

4.4.1.3 N_2O emissions

Nearly all N_2O was emitted from the treatments and control on days 2 and 3 of the experiment, when temperatures approached their maximum and O_2 concentrations were very low (Figures 4-2a, 4-2b, 4-3c). This suggests that N_2O was produced primarily through denitrification. We found that N_2O emissions were reduced on average by 64% and 84%, by the 5% and 20% biochar application treatments, respectively. In this anoxic environment, biochar likely reduced N_2O emissions by facilitating electron shuttling to promote complete denitrification to N_2 [31, 68-71]. Biochar may also reduce N_2O emissions by slowing down the rate of denitrification through N immobilization, NO_3^- and DOC adsorption, and improved aeration, but we found no significant difference in NH_4^+ or NO_3^- concentrations, suggesting similar rates of denitrification (and nitrification) between biochar treatments and the control [31, 71]. We also found a significant negative correlation between compost aggregates and N_2O emissions ($R^2 = 0.21$, $p < 0.05$) (Figure 4-4c, 4-4d). Aggregates can be hotspots for denitrification in soils [56, 58-59, 60-61]. We found evidence that aggregation contributed to lower N_2O emissions, suggesting that aggregates may have functioned as reactors for complete denitrification, due to the very low O_2 concentrations at their core. Aggregates with biochar pieces in them may have further fueled N_2O consumption by promoting complete denitrification through electron shuttling (Figure 4-5).

4.4.1.4 NH_3 emissions

Biochar's capacity to reduce NH_3 emissions from soils and composts through the adsorption of NH_4^+ and NH_3 has been well documented [18, 29, 32, 72-75]. In agreement with previous work, we found that the 5% and 20% biochar application treatments reduced NH_3 emissions by 33% and 65%, on average, respectively, although only the

reduction by the 20% treatments was statistically significant (Table 4-1). Nearly all NH_3 emissions occurred in the first three days of composting for all treatments and the control, when temperatures were rising rapidly and O_2 concentrations were low (Figure 4-2a, 4-2b, 4-3d). This high rate of NH_3 volatilization is likely the result of an accumulation of NH_4^+ from rapid ammonification and low nitrification rates, which were likely inhibited due to high temperatures and low O_2 concentrations in the compost [28, 76]. Despite lower NH_3 emissions in the biochar treatments, there was no significant difference in NH_4^+ content during composting (Figure 4-2h). While we do not find direct evidence for the adsorption of NH_4^+ by biochar, it is possible that biochar reduced NH_3 emissions through the chemisorption of NH_4^+ through covalent bond formation. Chemisorbed NH_4^+ would be retained on the biochar surface and would explain why there was no difference in KCl-extractable NH_4^+ between biochar treatments and the control. Chemisorption has recently been shown to be an important and previously overlooked mechanism through which biochar can retain NH_4^+ [77-79].

4.4.2 Optimizing biochar-composting for emission mitigation

It is interesting that differences in CH_4, N_2O, and NH_3 emissions between biochar type were not significant. This could be because differences in key biochar properties such as surface area, total pore volume, and pH were fairly consistent between biochar types and because biochar surface reactivity and redox potential, which likely acted as the primary controls on emissions in this experiment, are largely regulated by pyrolysis conditions [62, 69-70, 80-81]. The low pyrolysis temperature of 350°C used to produce the biochars in this study likely led to similarities in reactivity and redox potential. These low temperature biochars each had high H:C and O:C ratios, which indicate a high proportion of oxygen-containing functional groups that are important for adsorption and electron shuttling by biochar (Table S4-2) [62]. In order to better understand which biochar properties are key to optimizing biochar-composting for emission mitigation, future research is needed that compares biochars with distinct properties. This could be done by producing biochars at varying temperatures or by comparing contrasting feedstocks, such as manure, wood and grass.

We did, however, find that biochar application rate has a significant impact on composting emissions. While the 5% application treatments did not affect CH_4 emissions, the 20% application treatments emitted over 10 times more CH_4 than the control. On the other hand, greater application rates led to a greater reduction in N_2O and NH_3 emissions. Due to the higher N_2O emission mitigation from the 20% application treatments, the average climate mitigation potential of the 5% and 20% treatments were similar, reducing net GWP by 63% and 70%, respectively (Table 4-1). However, higher application rates come at a higher financial cost to farmers and compost managers, and similar reductions in emissions could be achieved at lower, more cost-effective application rates. Furthermore, we found that high application rates risk increasing CH_4 emissions. While the increase in CH_4 emissions was offset by the large reduction in N_2O emissions by the 20% application treatments in this study, this may not always be the case. Therefore, we recommend using lower biochar application rates to optimize the reduction of emissions during biochar-composting.

In this study, we found, for the first time, a strong relationship between compost aggregation and CH_4 emissions. In the composting literature, the term "anaerobic microsites" is often used to refer to the source of CH_4 emissions during aerobic composting [13, 16, 18, 28, 76]. However, here we link CH_4 emissions to a physical property of compost piles that could be measured relatively easily by compost managers, which is a significant finding as we work toward optimizing manure composting for CH_4 mitigation. We propose that composting and biochar-composting should be managed to reduce aggregation in order to maximize aerobic conditions. This could be done by using turning practices that break up and destroy aggregates, such as mechanical windrow turners, and by avoiding turning methods that could promote aggregation, such as slow rotating drums or tumblers for in-vessel composting. In the case of biochar-composting, lower biochar application rates may reduce the risk of excessive aggregate formation. Finally, using biochars produced at higher temperatures, which typically have low surface reactivity and greater aromatization, may also reduce the potential of biochar to bind with compost to help form aggregates, although, this could reduce the potential of biochar to adsorb gases, such as NH_3, and their precursors [81].

In summary, we show that biochar-composting with low and high rates of biochar results in a similar reduction in net GWP during dairy manure composting, but high application rates risk "pollution swapping" N_2O emissions for CH_4 emissions. While we did not find a significant difference in emissions between biochar types, this was likely because the biochars tested had similar characteristics, and future research should test biochars produced at different temperatures and from contrasting feedstocks. We also found that aggregates formed during composting may act as anoxic biogeochemical reactors for methanogenesis and complete denitrification. Furthermore, the surface reactivity of biochar may help form aggregates while the electron shuttling capacity of biochar may drive redox reactions within aggregates. Because compost aggregates may be a significant source of CH_4 emissions, we recommend that compost managers take measures to reduce aggregate formation during manure composting.

4.5 References

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4.6 Figures

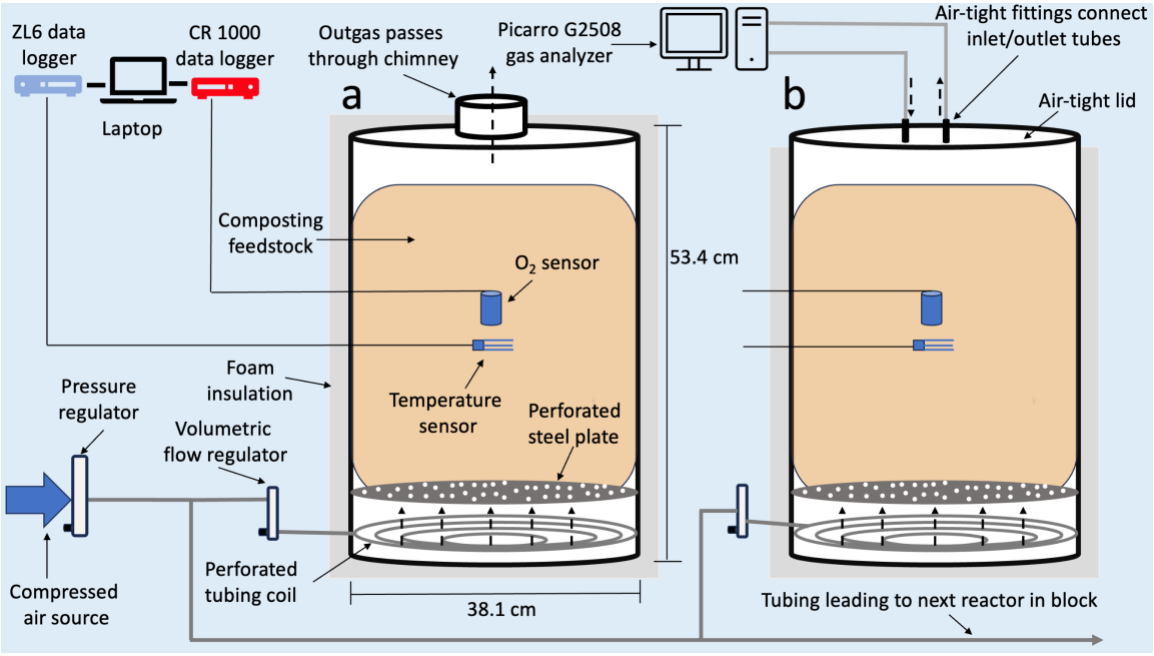

Figure 4-1. Compost reactor design showing sensor sensor set up and aeration system of (a) a reactor that is not being measured for gas emissions and (b) a reactor being measured for gas emissions. Dotted arrows indicate the direction of air flow.

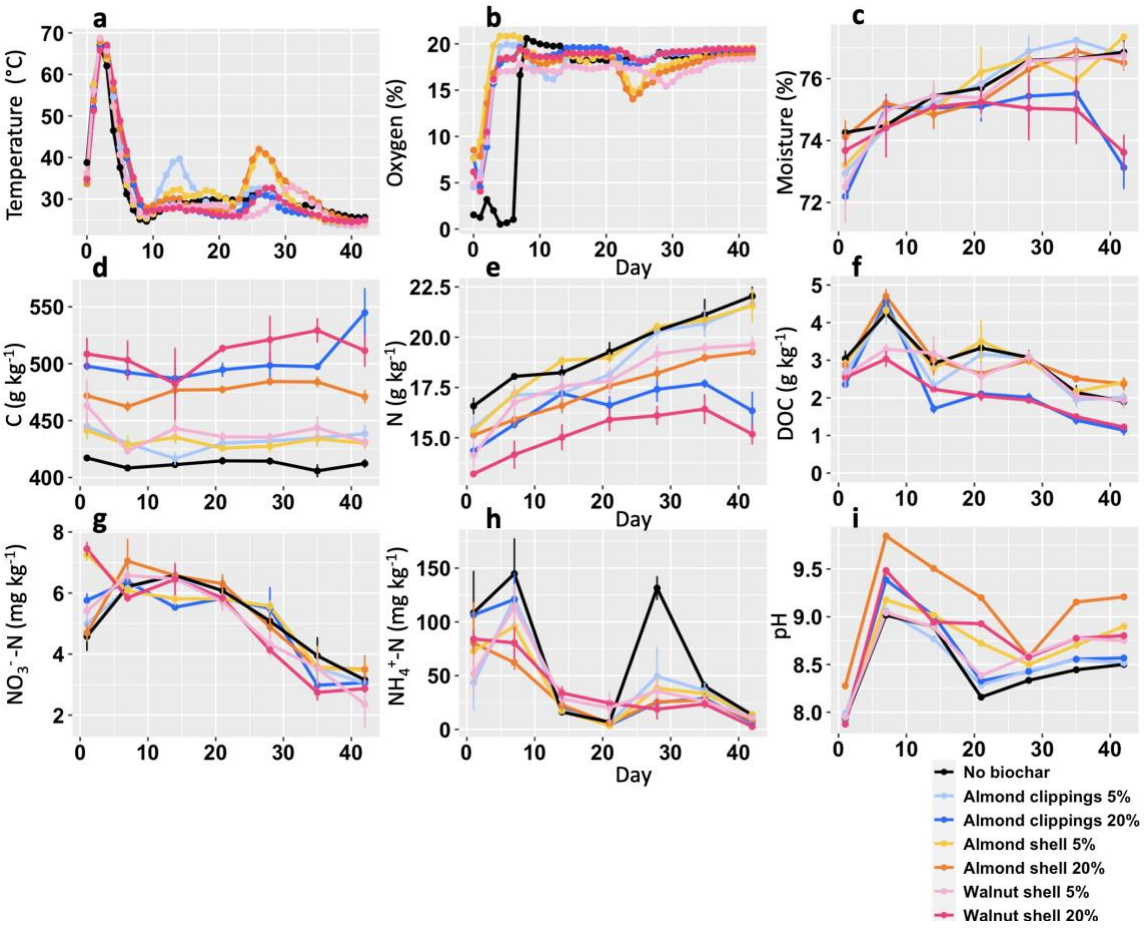

Figure 4-2. Physical and chemical properties of each biochar-compost treatment and the control over the course of the experiment showing (a) temperature in °C (b) percent oxygen concentration (c) percent gravimetric moisture (d) C in g kg^{-1} (e) N in g kg^{-1} (f) DOC in g kg^{-1} (g) NO_3^--N in mg kg^{-1} (h) NH_4^+-N in mg kg^{-1} (i) pH. Error bars are ± 1 standard error.

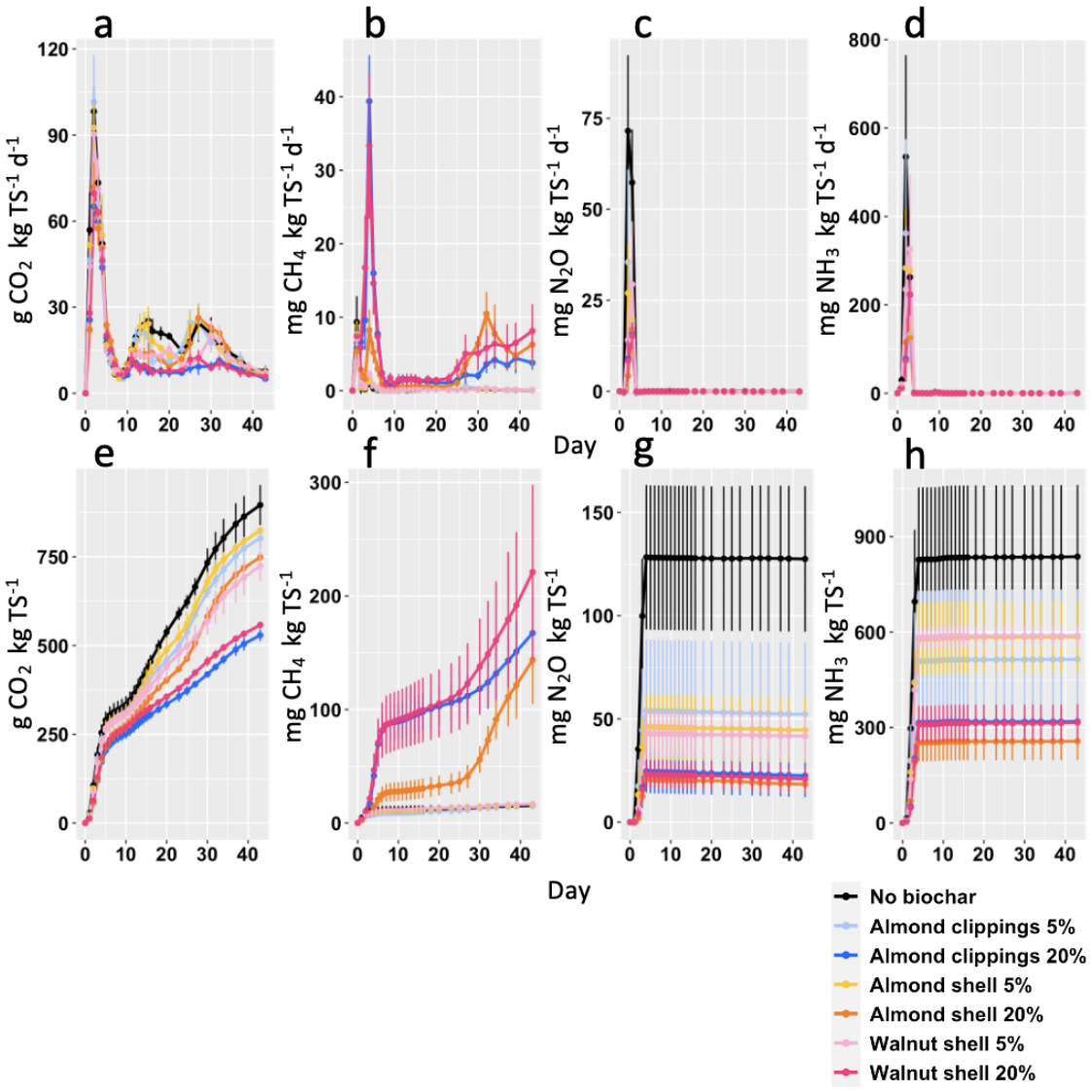

Figure 4-3. Daily average flux emission of (a) CO_2 in g CO_2 kg TS^{-1} d^{-1} (b) CH_4 in mg CH_4 kg TS^{-1} d^{-1} (c) N_2O in mg N_2O kg TS^{-1} d^{-1} (d) NH_3 in mg NH_3 kg TS^{-1} d^{-1} and cumulative emission of (e) CO_2 in g CO_2 kg TS^{-1} (f) CH_4 in mg CH_4 kg TS^{-1} (g) N_2O in mg N_2O kg TS^{-1} and (h) NH_3 in mg NH_3 kg TS^{-1}. Error bars are ± 1 standard error.

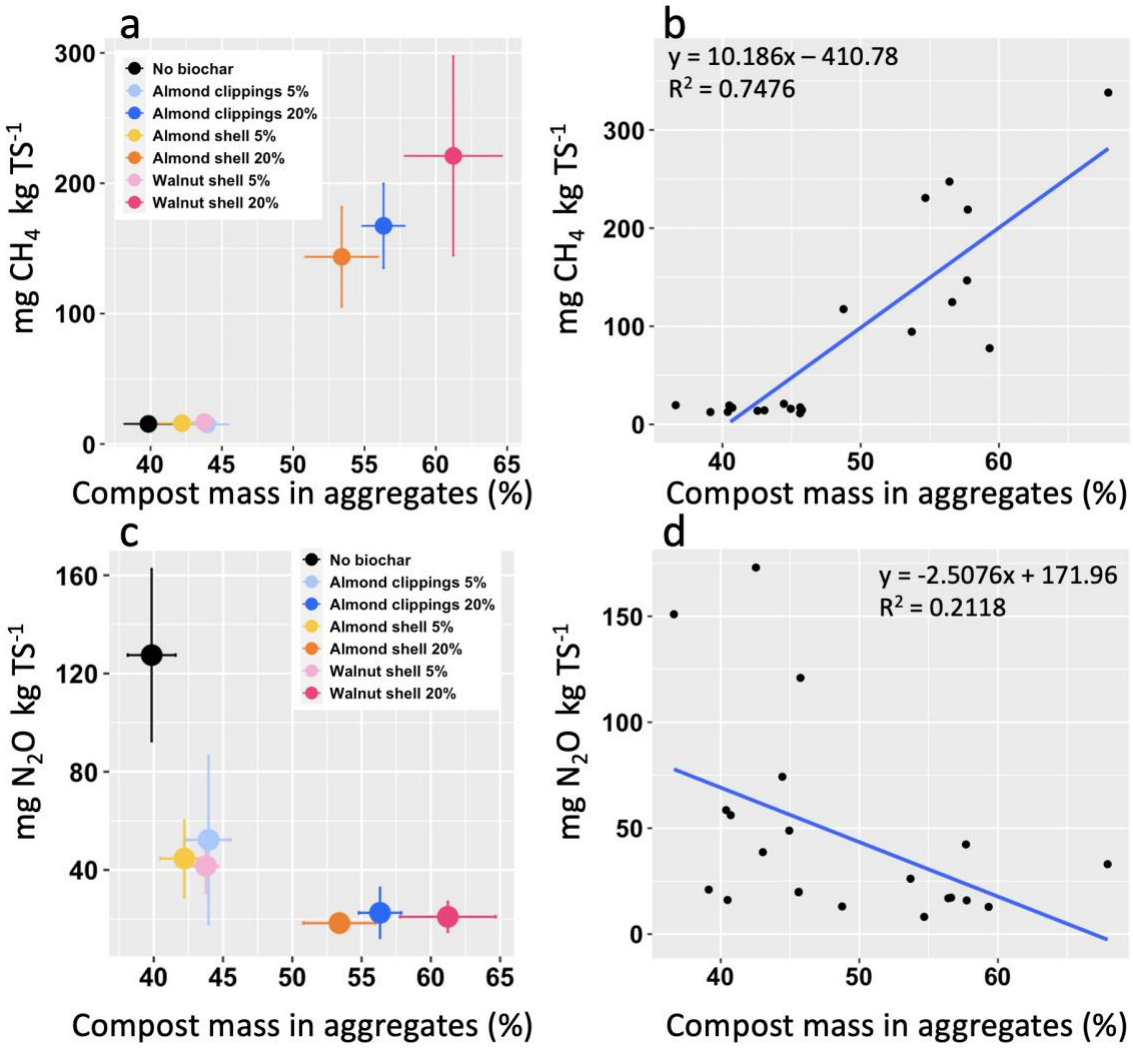

Figure 4-4. (a) Relationship between cumulative CH_4 emissions and the percent of compost mass in aggregates (> 6.35 mm), grouped by treatment. Error bars are ± 1 standard error. (b) Linear regression plot of cumulative CH_4 emissions and the percent of compost mass in aggregates (> 6.35 mm). (c) Relationship between cumulative N_2O emissions and the percent of compost mass in aggregates (> 6.35 mm), grouped by treatment. Error bars are ± 1 standard error. (d) Linear regression plot of cumulative N_2O emissions and the percent of compost mass in aggregates (> 6.35 mm).

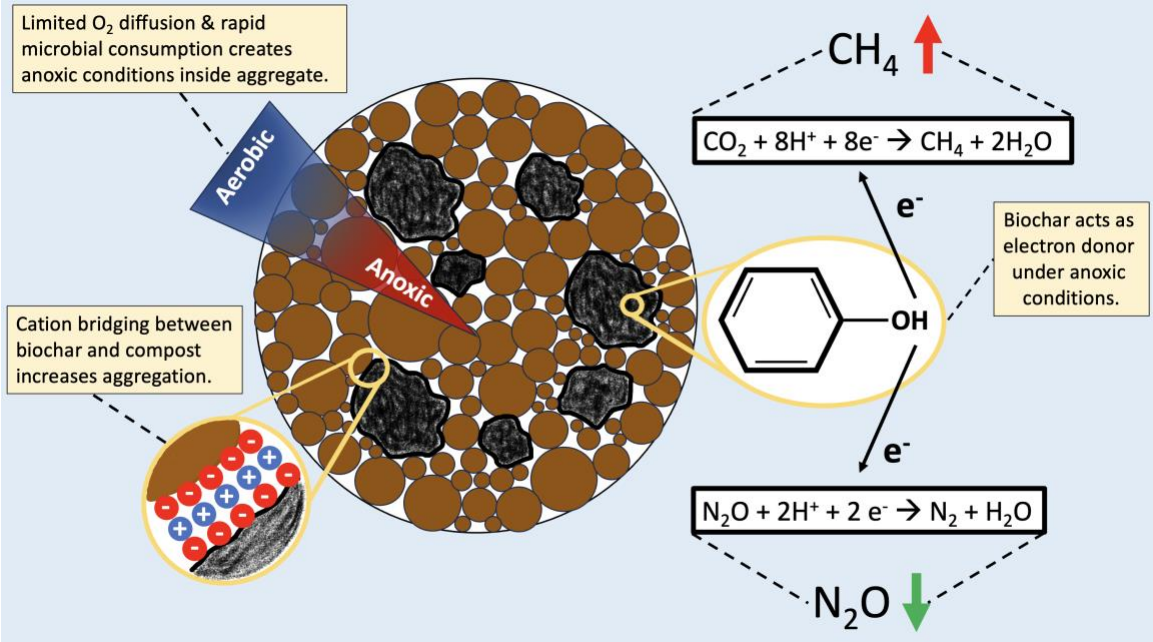

Figure 4-5. Conceptual model of the interaction between biochar and compost aggregates. Biochar increases aggregate formation through cation bridging. Aggregates likely have anoxic cores due to limited O_2 diffusion and rapid microbial consumption. In this anoxic environment, biochar pieces within aggregates likely drive CH_4 production and N_2O consumption by acting as an electron donor during methanogenesis and complete denitrification to N_2.

Tables

Table 4-1. Mean (± standard error) cumulative CO_2, CH_4, N_2O NH_3 and 100-year GWP for treatments grouped by application rate. The 0% application rate is the same as the no-biochar control. Letters denote statistical significance between application rates ($p < 0.05$).

	0% biochar (control)	**5% biochar**	**20% biochar**
Cumulative CO_2 (g CO_2 kg TS^{-1})	896 ± 55.3 a	784 ± 21.3 b	612 ± 35.1 c
Cumulative CH_4 (mg CH_4 kg TS^{-1})	15.4 ± 2.13 a	15.9 ± 1.80 a	177 ± 28.7 b
Cumulative N_2O (mg N_2O kg TS^{-1})	127 ± 35.1 a	46.2 ± 11.5 ab	20.6 ± 3.68 b
Cumulative NH_3 (mg NH_3 kg TS^{-1})	837 ± 224 a	563 ± 72.6 a	297 ± 25.6 b
GWP (g CO2e kg TS^{-1})	34.2 ± 9.32 a	12.7 ± 3.04 b	10.4 ± 4.07 b

Chapter 5.

Conclusion

This dissertation shows that biochar-composting of dairy manure solids is an effective complement to the anaerobic digestion of liquid manure and offers a powerful climate change mitigation opportunity for dairies. We found that in addition to substantially reducing manure CH_4 emissions relative to composting or stockpiling, biochar-composting also offers several other climate benefits over its life-cycle that result in a large, negative global warming potential. Despite the large potential of anaerobic digestion and biochar-composting to reduce emissions, these mitigation strategies may not be enough for the dairy industry to meet upcoming climate goals as developing countries are rapidly increasing their consumption of dairy products. To offset this increase in consumption, additional measures may need to be taken, as anaerobic digestion and biochar-composting alone will likely not be enough to offset dairy industry emissions and meet climate goals . In addition to its climate benefits, we also found that biochar-composting can substantially reduce the emission of air pollutants from dairy manure while providing a sustainable alternative to biomass burning, which offers an opportunity to improve air quality in rural regions and reduce public health costs in disadvantaged communities. Finally, in our laboratory composting experiment, we observed an increase in CH_4 emissions when high rates of biochar are used during composting. We found that high biochar application rates may risk increasing CH_4 emissions by increasing the formation of compost aggregates, creating anaerobic microsites that act as hotspots for methanogenesis. Potential strategies to reduce compost aggregation during biochar-composting could include using lower biochar application rates, using turning practices that destroy aggregates, and using biochar produced at high temperatures. While biochar-composting has considerable potential for use in climate-smart dairy systems, future research is needed to optimize biochar pyrolysis conditions for emission mitigation during composting, with special attention given to reducing NH_3 emissions and aggregate formation during composting.

Appendices

Appendix A: Supplemental Information for Chapter 2

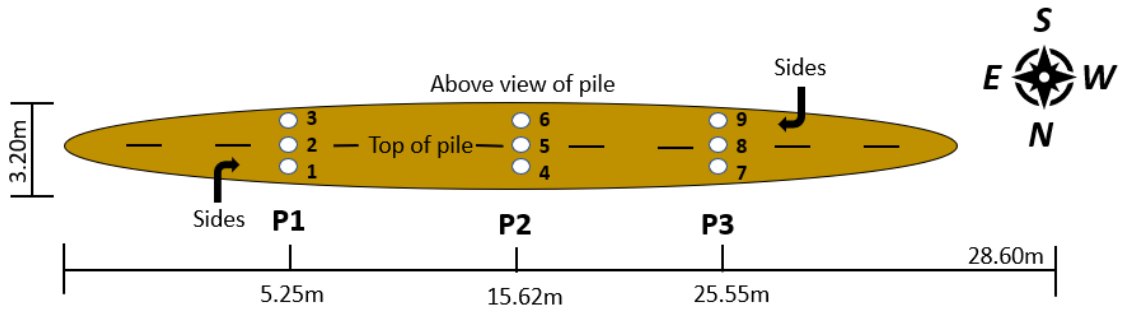

Figure S2-1. GHG sampling design for daily compost pile measurements. GHGs were sampled from the North side, South side, and top of each pile at three sections for a total of nine measurements (P1, P2, P3). The nine sampling locations are marked by a white circle with a corresponding number. The pile was approximately 30 m long, 3 m wide and 1 m tall.

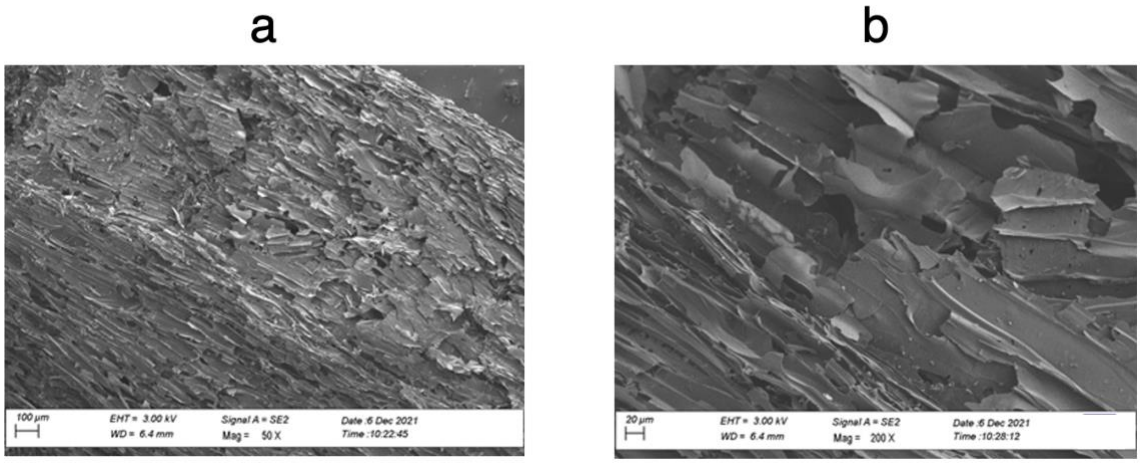

Figure S2-2. **a.** Low magnification (50x) biochar surface image taken through scanning electron microscopy (SEM). **b.** High magnification (200x) biochar surface image taken through SEM.

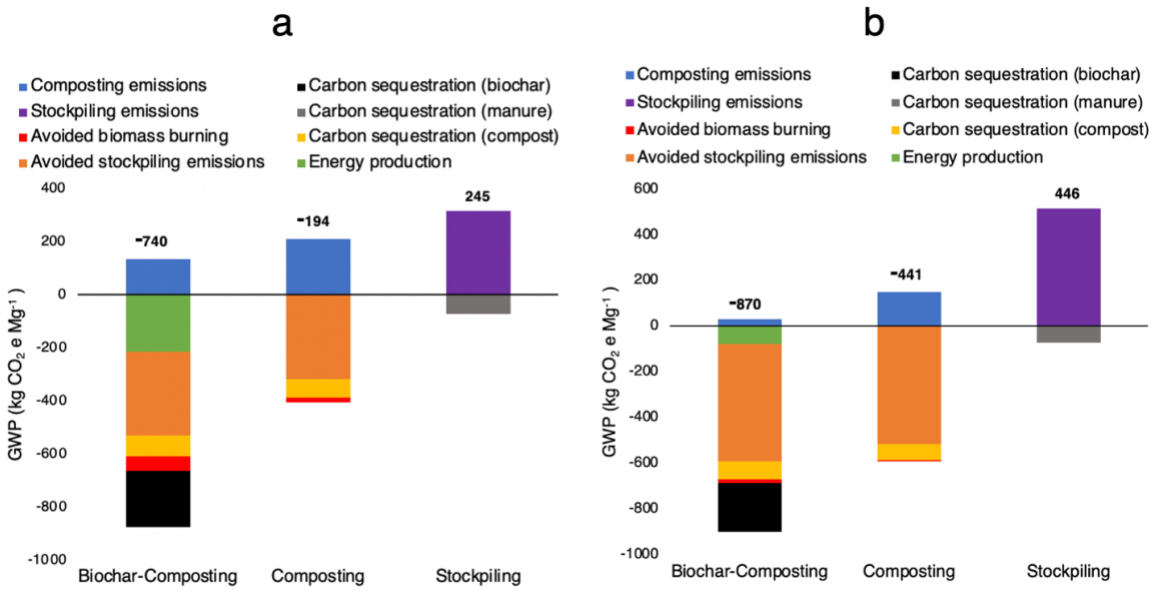

Figure S2-3. a. Life-cycle assessment of management strategies for separated solid dairy manure using 100-year GWPs and including biogenic CO_2 emissions. **b.** Life-cycle assessment of management strategies for separated solid dairy manure using 20-year GWPs. The number above each strategy is the net GWP in kg CO_2e Mg^{-1} manure. Each color represents a different life-cycle stage and is referenced in the legend. The transportation stages are removed from the figures due to their minuscule contribution to the total GWP of each strategy.

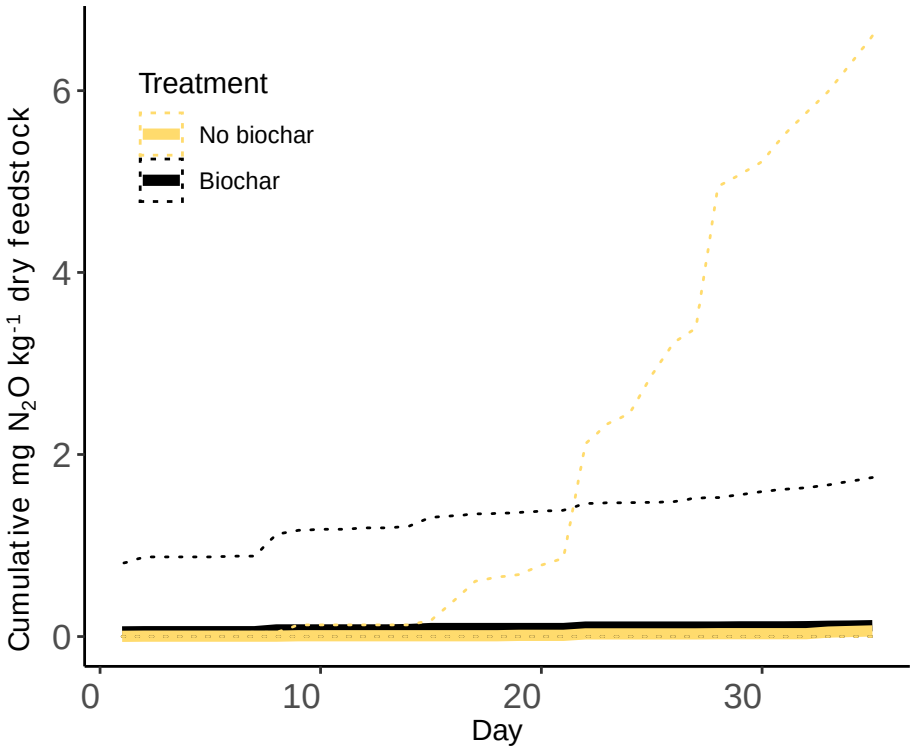

Figure S2-4. Cumulative N_2O emission (mg N_2O kg^{-1} dry feedstock) in a 35-d dairy manure composting field experiment with or without biochar treatment. Shaded area represents 95% confidence interval.

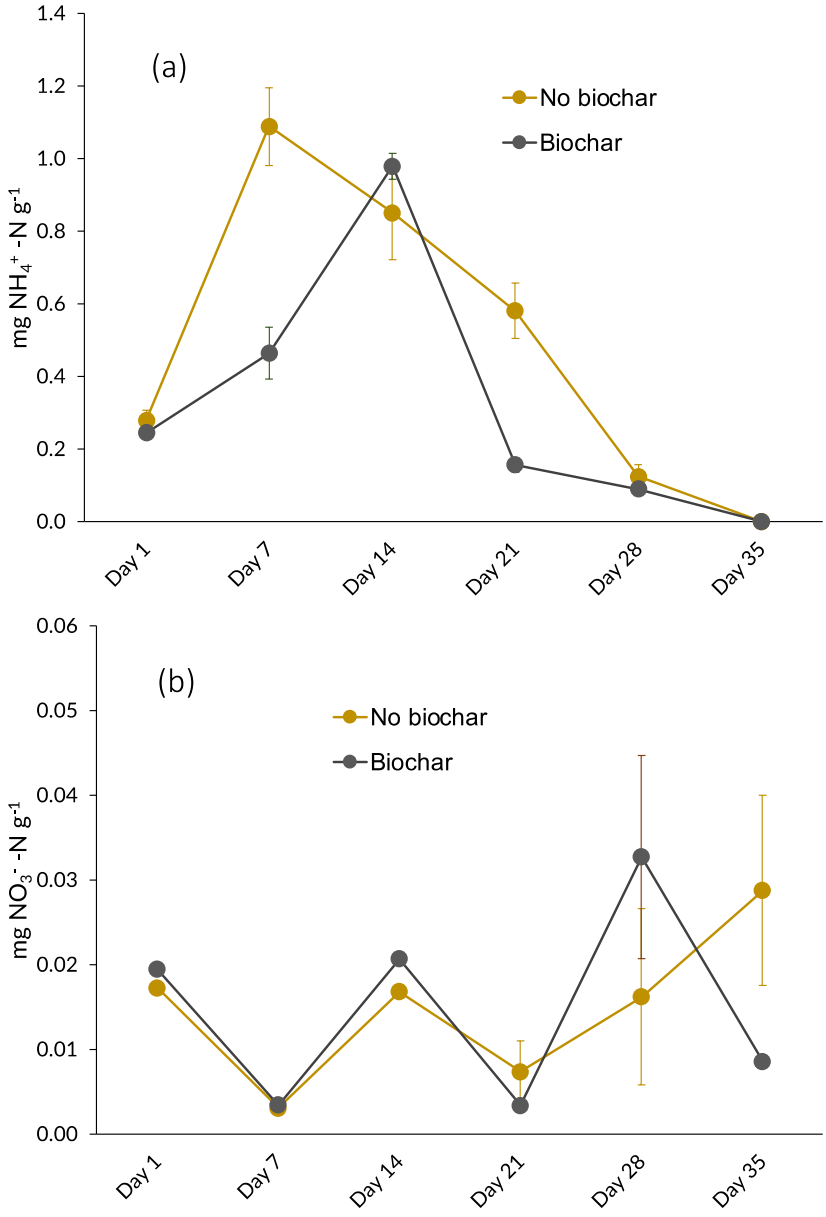

Figure S2-5. Compost (a) NH_4^+ and (b) NO_3^- concentrations (mg N g^{-1}) on Day 1, 7, 14, 21, 28, and 35 in a 35-d dairy manure composting field experiment with or without biochar treatment. Data are presented as average ± 1x standard error (n = 3).

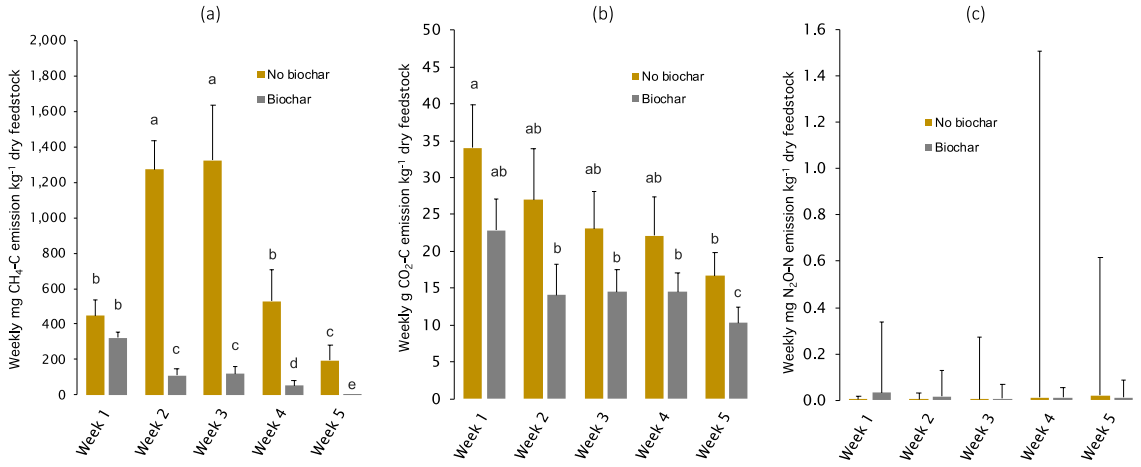

Figure S2-6. Weekly emission of (a) CH_4 (mg C kg^{-1} dry feedstock), (b) CO_2 (g C kg^{-1} dry feedstock), and (c) N_2O (mg N kg^{-1} dry feedstock) in a 35-d dairy manure composting experiment with or without biochar treatment. Data are presented as average ± 1x standard error. Data were compared using Tukey-HSD test following ANOVA. Bars with the same letter were not significantly different at $P = 0.05$.

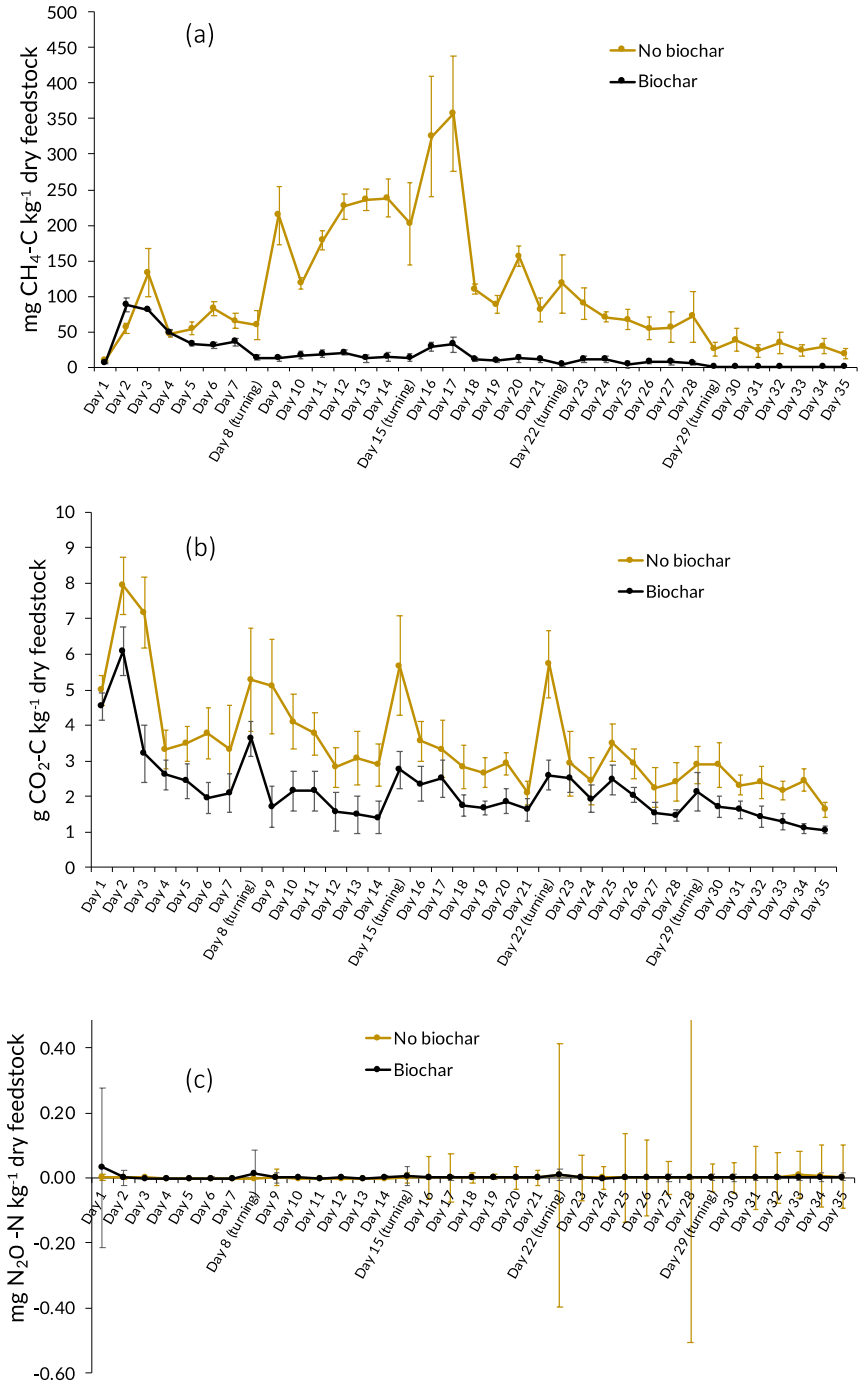

Figure S2-7. Daily (a) CH_4 (mg CH_4-C kg^{-1} dry feedstock), (b) CO_2 (g CO_2-C kg^{-1} dry feedstock), and (c) N_2O (mg N_2O-N kg^{-1} dry feedstock) emissions in a 35-d dairy manure composting field experiment with or without biochar treatment. Data are presented as average ± 1x standard error.

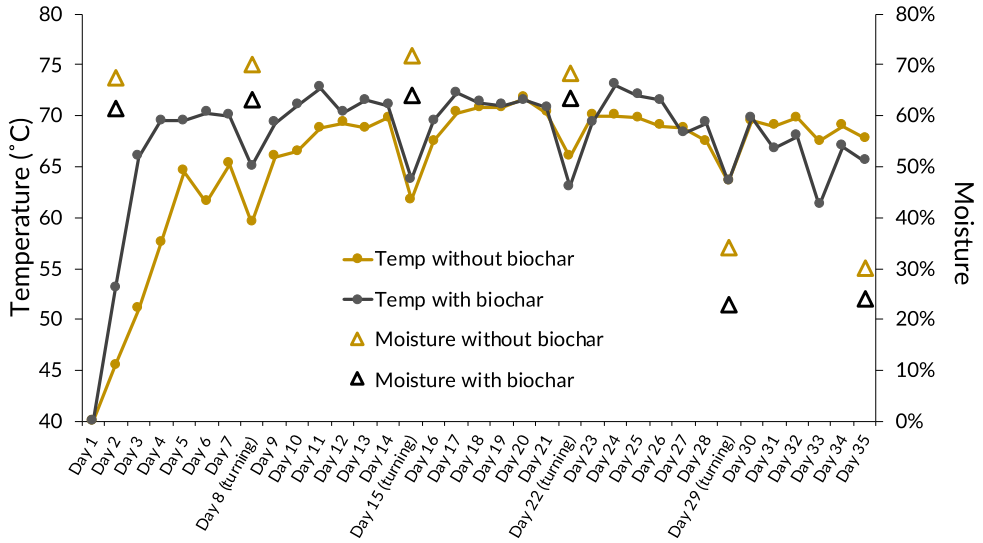

Figure S2-8. Temperature (˚C) and moisture content (%) in a 35-d dairy manure composting field experiment with or without biochar treatment. Turning events occurred on day 8, 15, 22, and 29.

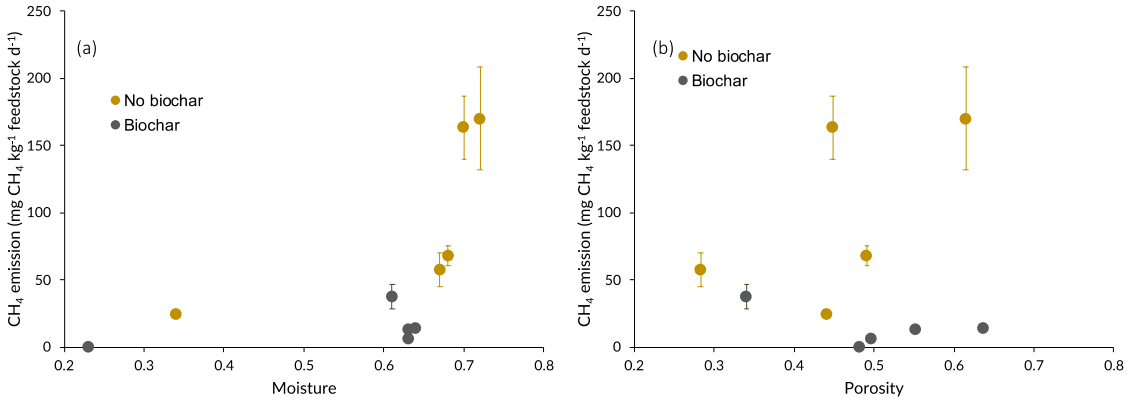

Figure S2-9. Correlation between weekly average CH_4 emission (mg CH_4 kg^{-1} dry feedstock d^{-1}) and (a) weekly pile moisture (Pearson r = 0.56, $P < 0.05$) or (b) weekly pile porosity (Pearson r = 0.10, $P > 0.05$) in a 35-d dairy manure composting field experiment with or without biochar treatment. Weekly average CH_4 emission was calculated by averaging seven daily CH_4 emissions in a week (n=7). Error bar represents 1x standard error.

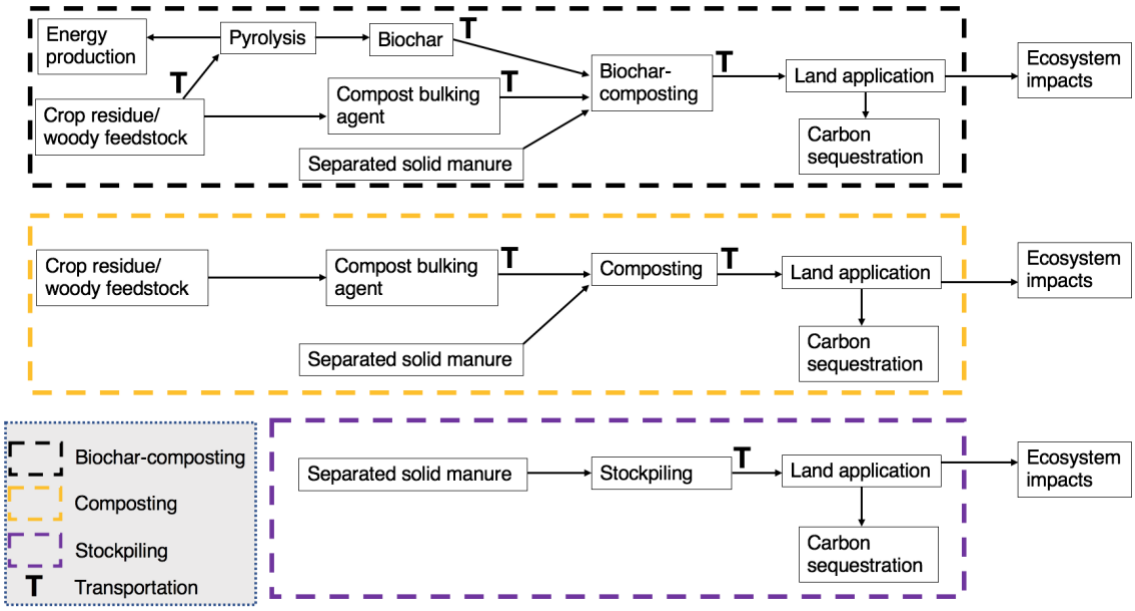

Figure S2-10. Life-cycle system boundaries for each of the three solid manure managements strategies considered in the life-cycle assessment. Ecosystem impacts (e.g. soil N_2O flux, yield increase, etc.) from applying each organic amendment are excluded from each life-cycle assessment due to limited data.

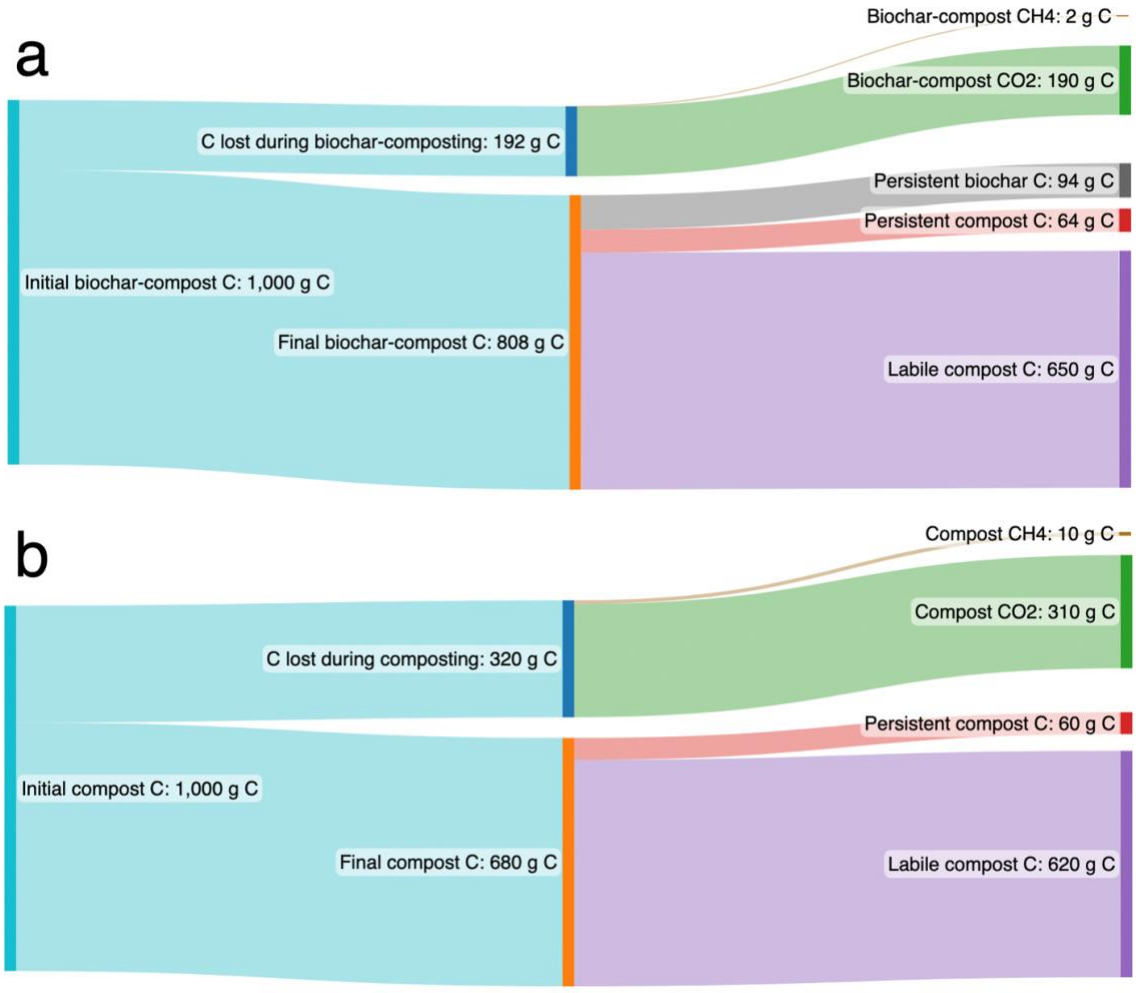

Figure S2-11. Comparative Sankey diagram showing carbon (C) flows from (a) 1 kg of biochar-compost feedstock C and (b) 1 kg of compost feedstock C. Results are based on the proportion of CO_2-C and CH_4-C lost as emissions from biochar-compost and manure-only compost piles during the composting experiment and on the C sequestration rates used in the life-cycle assessment.

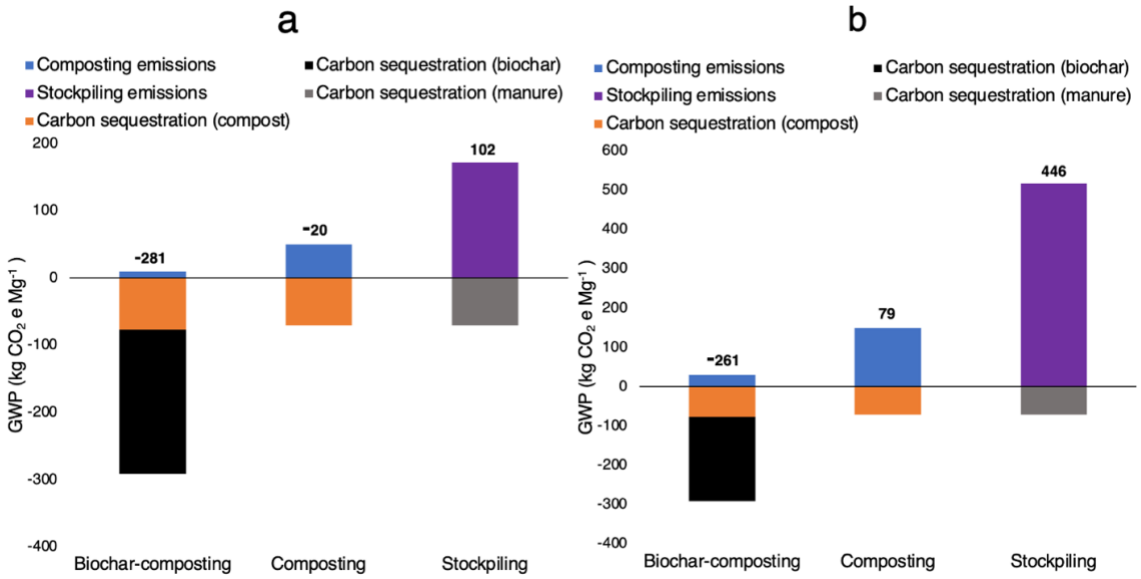

Figure S2-12. a. Life-cycle assessment of management strategies for separated solid dairy manure using 100-year GWPs and including only direct emissions (avoided emissions are excluded). **b.** Life-cycle assessment of management strategies for separated solid dairy manure using 20-year GWPs and including only direct emissions (avoided emissions are excluded). The number above each strategy is the net GWP in kg CO_2e Mg^{-1} manure. Each color represents a different life-cycle stage and is referenced in the legend. The transportation stages are removed from the figure due to their minuscule contribution to the total GWP of each strategy.

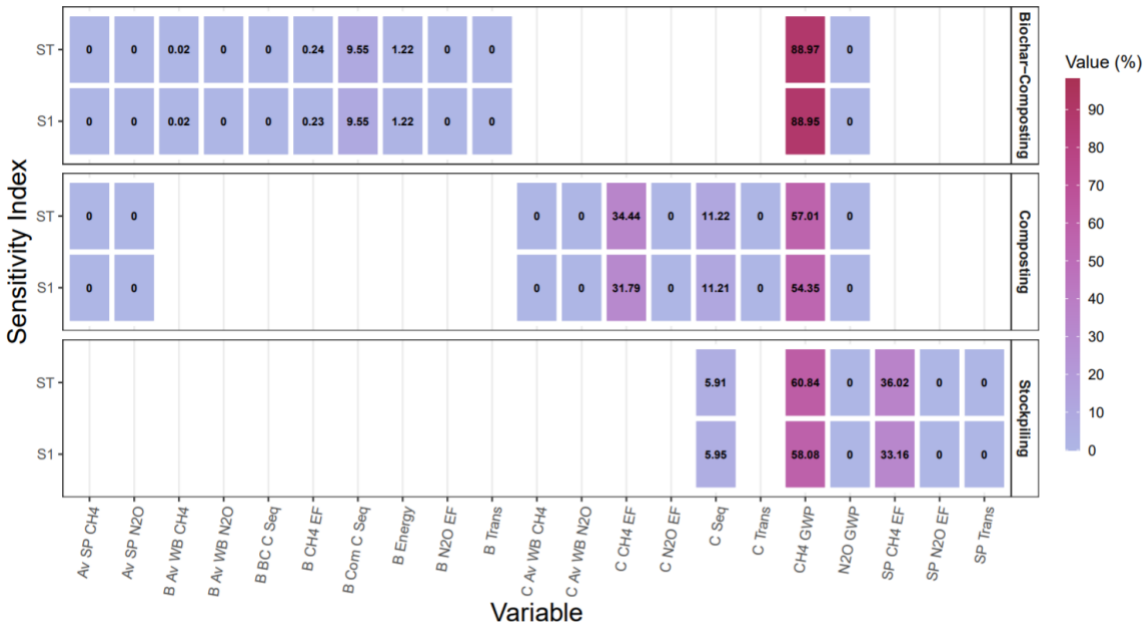

Figure S2-13. Global sensitivity analysis of the LCA for each management strategy. "ST" represents the total order sensitivity of each parameter in the given scenario, and "S1" represents the first order sensitivity. The value of the index is expressed as a percentage of the attributable variance in the output. "B" = biochar-composting, "C" = composting, "SP" = stockpiling, "Trans" = transportation, "C Seq" = manure carbon sequestration, "Av" = avoided, "WB" = woody biomass burning, "Com" = compost, "EF" = emissions factor, "GWP" = global warming potential, "Energy" = energy production from pyrolysis.

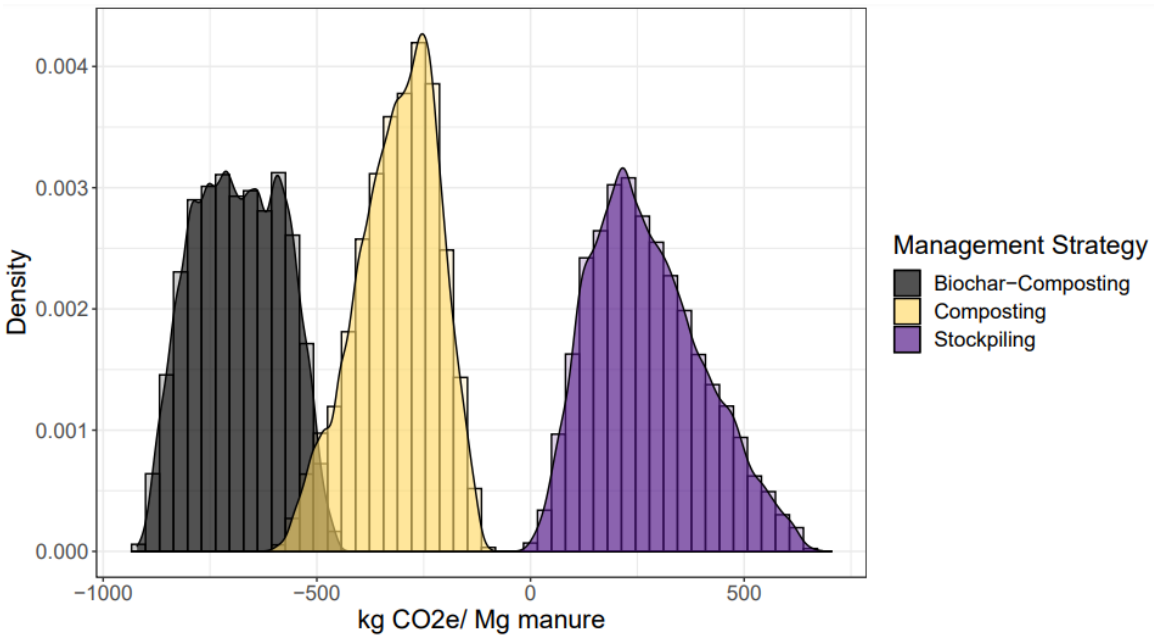

Figure S2-14. Uncertainty of management strategies contribution to net GWP. Results are expressed in kg CO_2e Mg^{-1} manure. Positive numbers indicate net emissions and negative numbers indicate net mitigation.

Table S2-1. Characteristics of dairy manure feedstock, compost, and biochar-compost in a 35-d dairy manure composting experiment with or without biochar.

**Please note: We caution against using C/N ratio as a maturity index for biochar-compost as the high C in biochar may result in a high C/N ratio, but this does not necessarily mean a biochar-compost is immature.*

	Fresh manure	Compost (final)	Biochar-compost (final)
Total C (g kg^{-1})	307	394	458
Total N (g kg^{-1})	20.2	21.6	19.4
C/N	15.2	18.2	23.6
pH	7.8	7.5	8.0
CEC (meq /100 g compost)	-	134.8	140.4
EC (dS m^{-1})	2.10	3.00	2.01
Germination index		128	133
Bulk density (g cm^{-3})	0.37	0.38	0.25
Moisture content (fresh wt. %)	78	30	24
Volatile matter (dry wt. %)	86.2	75.0	81.5
Ash (dry wt. %)	13.96	15.68	24.61
Fixed C (dry wt. %)	n.d.	n.d.	0.35
Porosity	0.377	0.491	0.496
NH_4^+-N (mg kg^{-1} dry)	223.5	55.9	10.6
NO_3^--N (mg kg^{-1} dry)	6.52	258.4	219.2
Total P (mg kg^{-1} dry)	-	2200	2400
P_2O_5 (mg kg^{-1} dry)	-	5000	5500
Total K (mg kg^{-1} dry)	-	6300	7100
K_2O (mg kg^{-1} dry)	-	7590	8550
S (mg kg^{-1} dry)	-	2700	2700
Mg (mg kg^{-1} dry)	-	4600	4700
Ca (mg kg^{-1} dry)	-	15100	15300
Na (mg kg^{-1} dry)	-	1100	1500
Fe (mg kg^{-1} dry)	-	2907	2868
Al (mg kg^{-1} dry)	-	1907	1955
Mn (mg kg^{-1} dry)	-	121	153
Cu (mg kg^{-1} dry)	-	29	36
Zn (mg kg^{-1} dry)	-	90	94
B (mg kg^{-1} dry)	-	53	63

Table S2-2. Characteristics of the biochar used in the biochar-composting experiment.

Total C (g kg^{-1})	790
Total N (g kg^{-1})	1.92
H:C (molar ratio)	0.102
O:C (molar ratio)	0.068
Particle size range (mm)	1-4 mm
pH	9.2
EC (dS m^{-1})	1.21
Bulk density (g cm^{-3})	0.08
Moisture content (fresh wt. %)	8.97
Volatile matter (dry wt. %)	55.61
Ash content (dry wt. %)	4.43
Fixed carbon content (dry wt. %)	39.96
NH_4^+-N (mg kg^{-1} dry)	Below instrument detection
NO_3^--N (mg kg^{-1} dry)	3.51
BET surface area (m^2 g^{-1})	437.17
Total pore volume (cm^3 g^{-1})	0.2549
Sorption average pore size (diameter in nm)	2.3
Cumulative surface area of pores between 0.3-1.34 nm hydraulic radius (m^2 g^{-1})	619.15
Cumulative pore volume of pores between 0.3-1.34 nm hydraulic radius (cm^3 g^{-1})	0.245

Table S2-3. Model statistics for CH_4 flux regressed against environmental and biogeochemical factors examined in this 35-d field composting study in a mixed linear model following backward variable selection (model fit R-squared = 0.845, $P < 0.001$). All data were log transformed in the model to ensure data normality and homogeneity of variance. Significant levels: *$P < 0.05$, ** $P < 0.01$, *** $P < 0.001$, ns indicates $P > 0.05$.

Coefficients	t-value	P-value	Level of significance
Intercept	0.501	0.62	ns
Biochar treatment	4.420	3.96e-05	***
Moisture	9.610	5.77e-14	***
Porosity	-5.293	1.62e-5	***
Time since composting	4.561	2.41e-5	***
CO_2 flux	3.294	0.001625	**
NO_3^- -N	3.732	0.000411	***

Table S2-4: Ranges of values used in the sensitivity and uncertainty analysis for each management strategy. "Mid" values were used in the baseline LCA models.

Parameter	Reference	Min	Mid	Max	Units
Stockpiling CH4 EF	Pardo et al 2015	3.82308846	6.146926537	8.47076462	g CH4 / kg manure
Stockpiling N2O EF	Pardo et al 2015	-0.0010408	4.13043E-05	0.00467609	g N2O / kg manure
Stockpiling CH4 GWP	IPCC	28		84	g CO2e/ g CH4
Stockpiling N2O GWP	IPCC	264		265	g CO2e / g N2O
Manure C seq.	Martinez-Blanco et al., 2013	-15.673913	-70.55434783	-125.43478	g CO2e / kg manure
Manure transportation	DeLonge et al. 2013, exp data	0.0745	0.149	0.298	g CO2e / kg manure
Parameter	**Reference**	**Min**	**Mid**	**Max**	**Units**
Composting CH4 EF	exp. data	1.10869565	1.782608696	2.45652174	g CH4 / kg manure
Composting N2O EF	exp. data	-0.0020815	2.06522E-05	0.00233804	g N2O / kg manure
Avoided Stockpiling CH4	Pardo et al 2015; exp. data	-3.8230885	-6.146926537	-8.4707646	g CH4 / kg manure
Avoided Stockpiling N2O	Pardo et al 2015; exp. data	0.00104076	-4.13043E-05	-0.0046761	g N2O / kg manure
Composting CH4 GWP	IPCC	28		84	g CO2e/ g CH4
Composting N2O GWP	IPCC	264		265	g CO2e / g N2O
Biomass burning CH4	Andreae, 2019	-0.037913	-0.049565217	-0.0612174	g CH4 / kg manure
Biomass burning N2O	Andreae, 2019	-0.0007565	-0.000782609	-0.0008087	g N2O / kg manure
Compost C seq.	Martinez-Blanco et al., 2013	-15.673913	-70.55434783	-125.43478	g CO2e / kg manure

Compost transportation	DeLonge et al. 2013, exp. data	0.08744565	0.174891304	0.34978261	g CO2e / kg manure
Parameter	**Reference**	**Min**	**Mid**	**Max**	**Units**
Biochar-composting CH4 EF	exp. data	0.20857474	0.359212051	0.50984936	g CH4 / kg manure
Biochar-composting N2O EF	exp. data	-0.0006779	5.33024E-05	0.00078447	g N2O / kg manure
Avoided stockpiling CH4	Pardo et al., 2015; exp. data	-3.8230885	-6.146926537	-8.4707646	g CH4 / kg manure
Avoided Stockpiling N2O	Pardo et al., 2015; exp. data	0.00104076	-4.13043E-05	-0.0046761	g N2O / kg manure
Biochar-composting CH4 GWP	IPCC	28		84	g CO2e/ g CH4
Biochar-composting N2O GWP	IPCC	264		265	g CO2e / g N2O
Biomass burning CH4	Andreae, 2019	-0.1465122	-0.191541136	-0.2365701	g CH4 / kg manure
Biomass burning N2O	Andreae, 2019	-0.0029235	-0.003024334	-0.0031251	g N2O / kg manure
Biochar-composting compost C seq.	Martinez-Blanco et al., 2013	-15.677868	-70.5561993	-125.42294	g CO2e / kg manure
Biochar-composting biochar C seq.	Wang et al., 2015	-200.61414	-201.8308227	-203.03592	g CO2e / kg manure
Gasification energy production	Roberts et al., 2009; IPCC, 2006	-56.639629	-76.24565469	-95.840093	g CO2e / kg manure
Biochar-compost transportation	Roberts et al., 2009; exp data	0.16483198	0.330359212	0.66071842	g CO2e / kg manure

Table S2-5. Values and equations used to estimate manure CH_4 emissions from anaerobic lagoons and anaerobic digestion for California and global scaling-up analyses. MCF = methane conversion factor. VS_{prod} = Manure volatile solids produced. B_0 = Maximum methane production capacity. EF = emission factor. TAM = Total animal mass.

Analysis	Variable	Value	Reference
California Tier 2 estimation	Anaerobic lagoon MCF (-)	0.748	CARB, 2014
	Anaerobic digestion MCF (-)	0.181	CARB, 2014
	VS_{prod} (kg VS yr^{-1} hd^{-1})	2,833	CARB, 2014
	B_0 (m^3 CH_4 kg VS^{-1})	0.24	CARB, 2014
Tier 2 equation to estimate CH_4 from a manure management strategy	CH_4 emissions (kg CH_4 hd^{-1} yr^{-1}) = MCF * VS * B_0 * 0.622 (m^3 CH_4 / kg CH_4) * fraction manure managed w/ strategy		
Global Tier 1 estimation	Anaerobic lagoon EF (g CH_4 kg VS^{-1})	100.5	IPCC, 2019 (average of cool & temperate climates)
	Anaerobic digestion EF (g CH_4 kg VS^{-1})	3.45	IPCC, 2019 (average of cool & temperate climates)
	VS_{prod} (kg VS 10^3 kg animal $mass^{-1}$ yr^{-1})	2,965.63	IPCC, 2019 (average from N.A., Europe, Asia)
	TAM (kg animal mass / animal)	526	IPCC, 2006 (average from N.A., Europe, Asia)
Tier 1 equation to estimate CH_4 from a manure management strategy	CH_4 emissions (g CH_4 hd^{-1} yr^{-1}) = EF * VS_{prod} * TAM * fraction manure managed w/ strategy		

Appendix B: Supplemental Information for Chapter 3

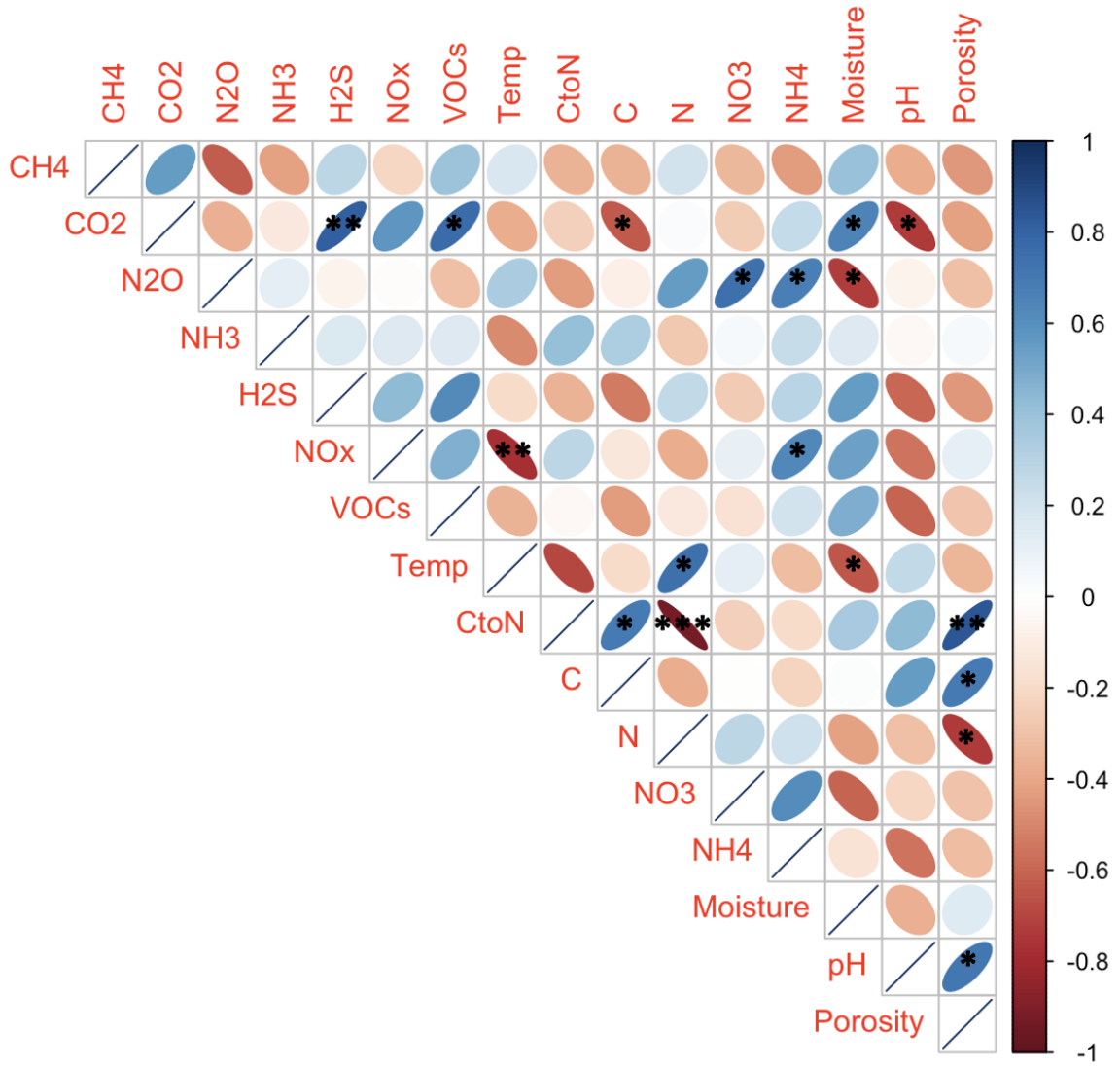

Figure S3-1. Correlation matrix of gas emissions and compost properties. The color of each ellipse represents its Pearson correlation coefficient, with blue and red representing positive and negative correlations, respectively, and darker colors representing stronger correlations. Significance levels: * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Table S3-1. Physical and chemical characteristics of the almond shell biochar used in this experiment.

Total C (g kg^{-1})	693
Total N (g kg^{-1})	14.9
C:N	46.5
H:C (molar ratio)	0.631
O:C (molar ratio	0.203
pH	9.70
EC (dS m^{-1})	4.23
Bulk density (g cm^{-3})	0.176
Moisture content (fresh wt. %)	3.2
Volatile matter (dry wt. %)	73.1
Ash (dry wt. %)	26.9
NH_4^+-N (mg kg^{-1} dry)	Below instrument detection
NO_3^--N (mg kg^{-1} dry)	3.29
BET surface area (m^2 g^{-1})	210
Total pore volume (cm^3 g^{-1})	0.170
Adsorption average pore size (diameter in nm)	3.24

Table S3-2. Social cost multipliers.

Location	Marginal Costs ($/t of emission)				
	NH_3	NOx	VOCs	N_2O	CH_4
Madera County (FIPS: 6039)	43,446.3	20,056.6	3,665	18,000	1,500

Table S3-3. Physical and chemical characteristics of fresh dairy manure and finished compost and biochar-compost.

	Fresh manure	Compost (final)	Biochar-compost (final)
Total C (g kg^{-1})	452	423	455
Total N (g kg^{-1})	16.7	25.6	22.7
C:N	27.1	16.5	20.1
pH	8.16	8.00	8.57
CEC (meq 100 g^{-1})	114	149	204
EC (dS m^{-1})	0.862	1.21	2.46
Germination index	-	89	80
Bulk density (g cm^{-3})	0.489	0.284	0.223
Moisture content (fresh wt. %)	0.757	0.612	0.514
Volatile matter (dry wt. %)	78.0	41.2	61.2
Ash (dry wt. %)	22.0	58.8	38.8
Porosity	0.844	0.789	0.843
NH_4^+-N (mg kg^{-1} dry)	404	345	252
NO_3^--N (mg kg^{-1} dry)	4.73	6.93	15.5
Total P (mg kg^{-1} dry)	2300	2900	3600
P_2O_5 (mg kg^{-1} dry)	5300	6600	8200
Total K (mg kg^{-1} dry)	5900	8100	19600
K_2O (mg kg^{-1} dry)	7110	9760	23610
S (mg kg^{-1} dry)	2800	3400	3400
Mg (mg kg^{-1} dry)	3000	3900	5500
Ca (mg kg^{-1} dry)	13900	18100	19500
Na (mg kg^{-1} dry)	1000	1300	2500
Fe (mg kg^{-1} dry)	1336	1106	1878
Al (mg kg^{-1} dry)	504	679	1094
Mn (mg kg^{-1} dry)	81	96	157
Cu (mg kg^{-1} dry)	58	64	109
Zn (mg kg^{-1} dry)	87	101	113
B (mg kg^{-1} dry)	44	54	85

Table S3-4. Cumulative emission of individual VOCs (μg VOC kg TS^{-1} ± SE) from compost and biochar-compost. Bolded values indicate a statistically significant difference at p=0.05.

Compound	Compost	Biochar-compost	Category	Environmental Impact
2,4-Dimethyl-1-heptene	16.34 ± 0.78	10.07 ± 1.83	Alkane/alkenes	Ozone precursor $PM_{2.5}$ precursor
2-Propenylidene-cyclobutene	3.78 ± 2.09	1.93 ± 0.40	Alkane/alkenes	Ozone precursor $PM_{2.5}$ precursor
d-Limonene	14.32 ± 6.77	4.54 ± 2.30	Alkane/alkenes	Ozone precursor $PM_{2.5}$ precursor
Octane	1.24 ± 0.95	0.32 ± 0.22	Alkane/alkenes	Ozone precursor $PM_{2.5}$ precursor
1,2,3-Trimethyl-benzene	0.22 ± 0.12	0.06 ± 0.06	Aromatics	Ozone precursor $PM_{2.5}$ precursor
Ethylbenzene	2.14 ± 0.59	1.27 ± 0.38	Aromatics	Ozone precursor $PM_{2.5}$ precursor
Naphthalene	5.01 ± 0.44	2.27 ± 0.91	Aromatics	Ozone precursor $PM_{2.5}$ precursor
o-Xylene	4.18 ± 0.64	2.54 ± 0.64	Aromatics	Ozone precursor $PM_{2.5}$ precursor
p-Xylene	1.09 ± 0.28	0.63 ± 0.32	Aromatics	Ozone precursor $PM_{2.5}$ precursor
Styrene	14.07 ± 1.27	8.73 ± 1.94	Aromatics	Ozone precursor $PM_{2.5}$ precursor
Toluene	**35.53 ± 0.99**	**23.61 ± 1.85**	Aromatics	Ozone precursor $PM_{2.5}$ precursor
Acetophenone	17.16 ± 4.76	10.83 ± 2.18	Carbonyls	-
Heptanal	0.97 ± 0.52	0.11 ± 0.06	Carbonyls	$PM_{2.5}$ precursor
Hexanal	3.27 ± 2.31	0.54 ± 0.20	Carbonyls	$PM_{2.5}$ precursor
Nonanal	3.88 ± 1.28	1.54 ± 0.90	Carbonyls	$PM_{2.5}$ precursor
Octanal	1.47 ± 0.51	0.17 ± 0.06	Carbonyls	$PM_{2.5}$ precursor

Butanoic acid	1.85 ± 0.82	0.00 ± 0.00	Carboxylic acids	-
Propanoic acid	**11.58 ± 2.48**	**0.85 ± 0.43**	Carboxylic acids	-
Cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate	4.29 ± 4.29	2.22 ± 2.22	Esters	-
Ethyl acetate	3.71 ± 1.26	0.63 ± 0.40	Esters	-
Isonicotinic acid, 2-phenylethyl ester	1.69 ± 0.88	0.92 ± 0.65	Esters	-
1,4-Dioxane	1.94 ± 0.98	0.36 ± 0.36	Ethers	Potential carcinogen
2-nitro-3-Pyridinecarbonitrile	0.45 ± 0.15	0.06 ± 0.03	Nitriles	-
Benzonitrile	2.07 ± 0.04	0.99 ± 0.56	Nitriles	Hazardous agent
Carbon disulfide	115.91 ± 58.34	32.57 ± 28.83	Organosulfurs	Odor
Thiophene	1.78 ± 0.76	0.78 ± 0.41	Organosulfurs	-
Dimethyl disulfide	5.42 ± 1.82	0.38 ± 0.20	Organosulfurs	Odor
Dimethyl sulfone	11.25 ± 6.62	2.12 ± 0.65	Organosulfurs	-
Butylated hydroxytoluene	2.49 ± 1.33	0.00 ± 0.00	Phenols	$PM_{2.5}$ precursor
Phenol	2.09 ± 1.70	0.65 ± 0.46	Phenols	Ozone precursor $PM_{2.5}$ precursor

Supplementary methods for VOC analysis

'Universal' sorbent tubes packed with Tenax TA, Carbograph 1TD, and Carboxen 1003 (Markes International) were used for the VOC sampling. All tubes were sealed with end caps and stored at room temperature for less than 18 hours prior to analysis. A TD-GC/MS system, which consists of a thermal desorption unit (UNITY-xr, Markes International) interfaced to a gas chromatography mass spectrometer (G7077BA, Agilent), was used for the VOC analysis. Thermal desorption of the tubes was carried out at 380 ºC with a flow rate of 50 mL min^{-1} for 20 min. Following desorption, the samples were collected on a cold trap at 25 ºC. The cold trap was purged for 2 min at 50 mL min^{-1} and then sequentially desorbed for 3 min at 320 ºC. A small fraction of the desorbed samples (split ratio 10:1) was subsequently transferred to the GC inlet for further analysis. The flow path temperature was set at 120 ºC. Chromatographic separation of VOCs was performed using a J&W HP-5ms Ultra Inert capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a flow rate of 1.2 mL min^{-1}. The temperature program was set as follows: isothermal hold at 35 °C for 3 min, temperature ramp of 10 °C min^{-1} up to 230 °C. The analyses were performed in the full scan mode, with mass ranging from m/z 40 to m/z 550. The electron ionization source was operated at an electron energy of 70 eV and temperature of 230 °C. The temperatures of the GC injector and the GC/ MS transfer line were 250 °C and 200 °C, respectively. Collected raw mass spectra were processed by the MassHunter Qualitative Analysis 10.0 software (Agilent). Compounds are further identified by validating their extracted molecular features against the standard EI spectra from the NIST-MS Library. Quantification of individual VOCs was performed by applying the GC/MS sensitivity obtained from the dimethyl disulfide standard to all identified VOCs.

Appendix C: Supplemental Information for Chapter 4

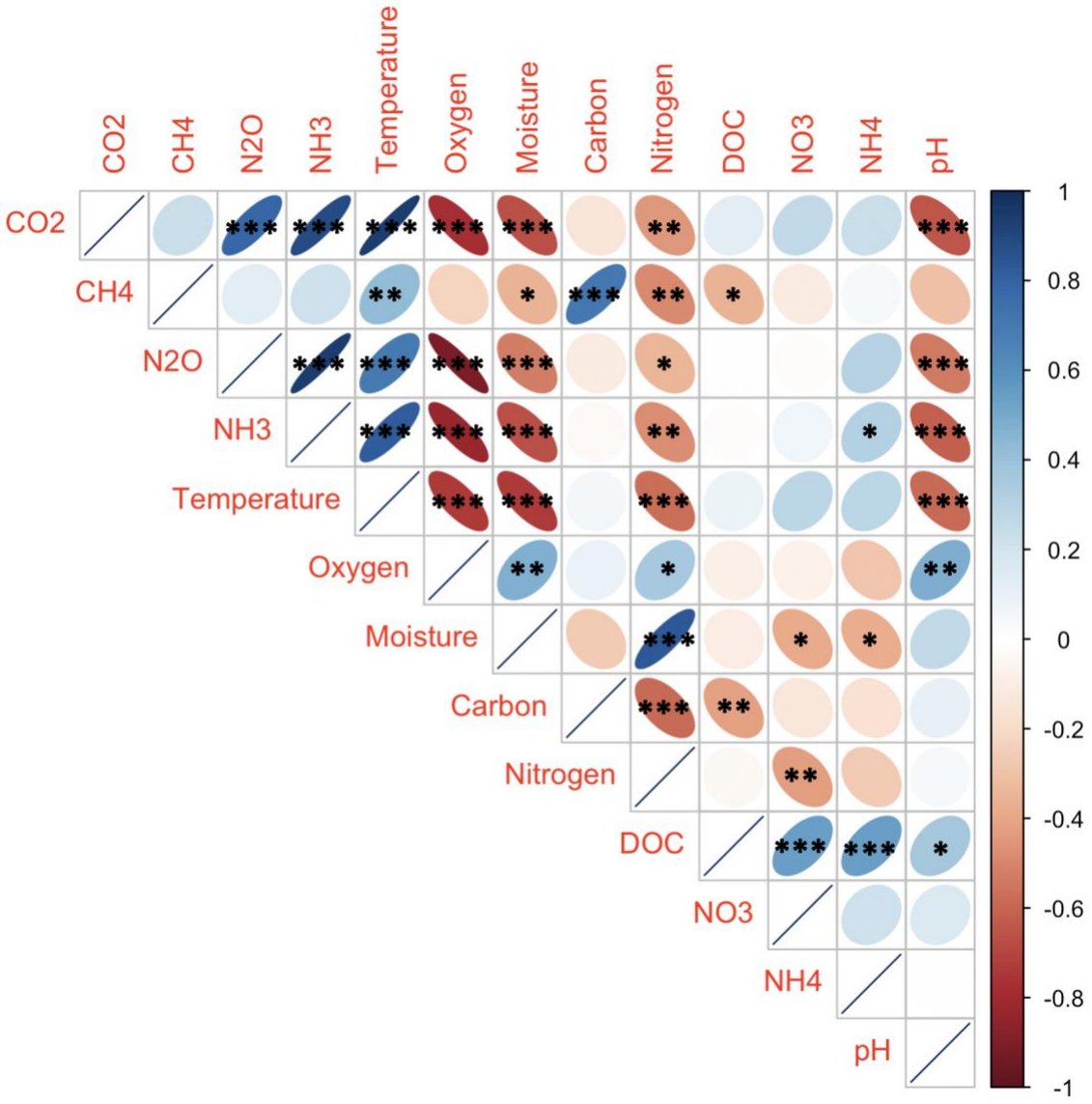

Figure S4-1. Correlation matrix of compost characteristics and cumulative gas emissions. The color of each ellipse represents its Pearson correlation coefficient, with blue representing positive correlations and red representing negative correlation, and darker colors representing stronger correlations. Significance levels: * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

Table S4-1. Mean (± standard error) characteristics of fresh manure feedstock and final compost.

	Fresh manure	No biochar (final)	Almond clipping 5% (final)	Almond clipping 20% (final)	Almond shell 5% (final)	Almond shell 20% (final)	Walnut shell 5% (final)	Walnut shell 20% (final)
Total C (g kg^{-1})	41.7 ± 0.19	41.2 ± 0.32	43.8 ± 0.72	54.5 ± 2.1	43.0 ± 0.42	47.1 ± 0.53	43.1 ± 0.58	51.1 ± 1.4
Total N (g kg^{-1})	1.66 ± 0.038	2.20 ± 0.044	2.16 ± 0.0038	1.63 ± 0.091	2.16 ± 0.081	1.93 ± 0.010	1.96 ± 0.043	1.52 ± 0.048
C:N	25.2 ± 0.49	18.7 ± 0.52	20.3 ± 0.36	33.7 ± 3.1	20.0 ± 0.72	24.4 ± 0.36	22.0 ± 0.23	33.7 ± 0.36
pH	7.93	8.50	8.52	8.57	8.90	9.21	8.75	8.80
CEC (meq 100 g^{-1})	-	155.6 ± 1.80	145.1 ± 3.92	133.1 ± 6.73	148.1 ± 4.60	154.0 ± 4.37	127.8 ± 1.57	117.9 ± 2.24
EC (dS m^{-1})	553.2	392.5	356.6	326.8	419.8	577.3	376.4	380.7
Germination index	-	84.8 ± 14.7	87.5 ± 4.20	82.7 ± 7.00	115.4 ± 3.09	92.3 ± 6.14	102.0 ± 16.9	107.2 ± 4.22
Moisture content	0.743 ± 0.0016	0.769 ± 0.0037	0.768 ± 0.0011	0.731 ± 0.0068	0.773 ± 0.0096	0.765 ± 0.0023	0.767± 0.004	0.736 ± 0.0055
Volatile matter (dry wt. %)	0.789	0.714	0.737	0.567	0.755	0.610	0.695	0.557
Ash (dry wt. %)	0.211	0.286	0.263	0.434	0.245	0.390	0.305	0.443
NO_3^--N (mg kg^{-1} dry)	4.58 ± 0.45	3.15 ± 0.21	3.04 ± 0.03	3.06 ± 0.30	3.47 ± 0.18	3.49 ± 0.45	2.35 ± 0.76	2.87 ± 0.11
NH_4^+-N (mg kg^{-1} dry)	108.50 ± 38.30	13.40 ± 1.50	8.73 ± 0.87	6.30 ± 1.82	14.04 ± 0.73	8.26 ± 1.28	10.94 ± 1.84	2.61 ± 0.79
Aggregate >6.35 mm (%)	-	39.85 ± 1.73	43.95 ± 1.73	56.33 ± 0.88	42.20 ± 1.59	53.40 ± 2.60	43.76 ± 1.53	61.22 ± 3.45
Aggregate 6.35-24.5 mm (% mass)	-	34.09 ± 1.83	35.08 ± 0.59	43.60 ± 1.96	34.74 ± 1.46	43.87 ± 3.34	34.64 ± 0.57	50.01 ± 3.79
Aggregate > 24.5 mm (% mass)	-	5.76 ± 0.35	8.87 ± 1.46	12.73 ± 2.53	7.47 ± 1.25	9.53 ± 2.06	9.12 ± 1.06	11.21 ± 0.95

Table S4-2. Characteristics of the walnut shell, almond shell, and almond clippings biochars used in the study.

	Walnut shell biochar	Almond shell biochar	Almond clippings biochar
C	80.36	64.44	75.00
N	0.53	1.23	0.85
C:N	153.01	52.32	88.64
O:C	0.114	0.205	0.157
H:C	0.436	0.562	0.479
Surface area (m^2 g^{-1})	146.90	96.69	103.93
Total pore volume (cm^3 g^{-1})	0.076	0.112	0.059
pH	10.29	9.80	8.78
EC	890	1817	234
Volatile matter	69.27	66.30	64.21
Ash	2.21	15.07	3.54
Fixed C	28.52	18.63	32.25

Table S4-3. Mean (± standard error) cumulative CO_2, CH_4, N_2O, NH_3 and GWP for biochar treatments and the control. Letters denote statistical significance between application rates ($p < 0.05$).

	No biochar	Almond clippings 5%	Almond clippings 20%	Almond shell 5%	Almond shell 20%	Walnut shell 5%	Walnut shell 20%
Cumulative CO_2 (g CO_2 kg TS^{-1})	896 ± 55.3 a	802 ± 30.1 ab	529 ± 15.8 c	824 ± 7.75 ab	749 ± 13.7 b	725 ± 41.6 b	558 ± 8.36 c
Cumulative CH_4 (mg CH_4 kg TS^{-1})	15.4 ± 2.13 a	15.1 ± 2.33 a	167 ± 32.3 b	15.9 ± 2.56 a	143 ± 38.2 b	16.8 ± 0.44 a	221 ± 76.3 b
Cumulative N_2O (mg N_2O kg TS^{-1})	127 ± 35.1	52.3 ± 34.4	22.6 ± 10.2	44.6 ± 15.7	18.4 ± 3.97	41.6 ± 11.0	20.9 ± 6.1
Cumulative NH_3 (mg NH_3 kg TS^{-1})	837 ± 224 a	515 ± 218 ab	319 ± 14.2 ab	585 ± 113 ab	257 ± 57.2 b	589 ± 31.9 ab	316 ± 56.5 ab
GWP (g CO2e kg TS^{-1})	34.2 ± 9.32	14.3 ± 9.09	10.7 ± 2.34	12.3 ± 4.22	8.9 ± 1.09	11.5 ± 2.92	11.7 ± 3.65