A. Project Information:

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Project Leaders:

Suduan Gao, Research Soil Scientist
USDA-ARS, San Joaquin Valley Agricultural Sciences Center (SJVASC)
9611 S. Riverbend Ave.
Parlier, CA, USA 93648
Tel: (559) 596-2870
Fax: (559) 596-2851
e-mail: suduan.gao@usda.gov

Co-Project Investigator:

Dong Wang, Research Soil Scientist
USDA-ARS, SJVASC
9611 S. Riverbend Ave.
Parlier, CA, USA 93648
Tel: (559) 596-2852
Fax: (559) 596-2851
e-mail: dong.wang@usda.gov

Project Cooperators:

Tom Turini, Farm Advisor, Cooperative Extension Fresno County, Fresno, CA USA 93710. (559) 241-7515; taturini@ucanr.edu

Kurt Hembree, Weed Management Farm Advisor, Cooperative Extension Fresno County, Fresno, CA, USA 93710. (559) 241-7520; kjhembree@ucanr.edu

Niles Brinton, Charborn, LLC, Salinas, CA, USA 93902. (510) 457-0482; info@charborn.com

Project participants/supporting staff:

Robert Shenk, Aileen Hendratna, Julio Perez, Diana Camarena, Tom Pflaum, Yinghua Duan (visiting scientist), Ruijun Qin, Sadikshya Dangi, Stella Zambrzuski, Jim Gartung, USDA-ARS, San Joaquin Valley Agricultural Sciences Center, Water Management Research, Parlier, CA, USA.

B. Abstract:

Soil amended with biochar has shown many environmental benefits, but its effects on the fate of nitrogen (N) has not been clear. The aim of this research was to examine the interaction between biochar and N in laboratory and evaluate its influence on crop yield, N uptake, changes in soil, and environmental losses under field conditions. Two laboratory experiments were conducted to determine adsorption capacity of ammonium and nitrate by seven biochar products and to evaluate effects on N fertilizer transformation in soil. Two field experiments were carried out. The first one evaluated the effects of biochar and interactions with irrigation on N dynamics (movement in soil, gas emissions, and leaching) in an onion field for three years. The second one investigated the effects of biochar and combination with manure on N dynamics for two years with processing tomato followed by garlic using microplots. Laboratory data showed that biochar has some capacity to adsorb NH_4^+ (at the maximum 1000 mg N kg^{-1} at pH 8-9), but the ability to retain N was insignificant (<10% total N applied). This was also because NH_4^+ is not stable unless in flooded soil and was quickly oxidized to NO_3^-, which adsorption to biochar was extremely low. The lab data support field findings that biochar did not reduce ammonia volatilization or nitrate leaching. The first field experiment demonstrated dominant irrigation effect on crop production and interaction with biochar on soil NO_3^-. The second field experiment confirmed similar findings that soil amendments with biochar did not show direct link to crop yield, biomass production, N uptake, and N losses as ammonia volatilization or leaching. However, biochar shows undeniable benefits to increase SOC and supply nutrients especially potassium to improve soil productivity that can be important for most California soils.

C. Introduction:

Input of inorganic (synthetic) fertilizers continues to increase over time, but N use efficiency (NUE) has declined accompanied by detrimental environmental impact. In the US, NUE decreased in majority of regions from 1987-97 and 2002-12 (Swaney et al., 2018). Agricultural fields have been identified as the major source for the statewide nitrate pollution in groundwater in California. Other large mass loss of N is ammonia (NH_3) volatilization that has detrimental effects on air quality and human health. Effective N management is needed to increase NUE and minimize environmental loses.

Biochar, a carbon rich material produced by heating organic materials at high temperature under no or limited oxygen, has been shown to improve soil physical, chemical, and biological properties, and mitigate some environmental contamination problems (Glaser et al., 2002; Lehmann and Joseph, 2009). Studies have indicated that biochar increased N retention, reduced N leaching, and decreased gas emissions (Ahmad et al., 2013; Steiner et al., 2010). However, variabilities in observed biochar effects are large among studies with many showing no benefits for reducing or even increasing N loss to the environment (e.g., Liu et al., 2017; Sánchez-García et al. 2014). We hypothesize that adsorption is one of the important mechanisms to increase N retention or the amount of available N in soil for plant uptake that can increase N uptake or NUE and reduce leaching or gas emissions. There are significant gaps in understanding of mechanisms biochar products possess to interact with N or alter the dynamics, and what properties of biochar determine positive effects on soil productivity. This project was designed to examine the mechanisms of biochar to interact with N and investigate effects on plant growth and the fate of N fertilizers under field conditions.

D. Objectives:

1. To determine effects of soil amendment with biochars produced from different feedstocks found in the San Joaquin Valley of California, USA on adsorption capacity for NH_4^+ and NO_3^- and N transformation (urea hydrolysis and nitrification) rates as well as soil-water retention.
2. To determine effective amendment rate of biochar products and irrigation rates on crop response and N fate under field conditions.

E. Methods:

Both laboratory and field studies were conducted to achieve the project objectives. For objective 1, laboratory studies were carried out to characterize biochar products made from different feed stocks, determined adsorption capacity for major mineral N species (ammonium or NH_4^+ and nitrate NO_3^-) onto biochar, and evaluated N transformation (urea hydrolysis and nitrification) affected by biochar. Total seven biochar products were selected for characterization and they included two freshly made from almond shells at two pyrolysis temperatures (~550°C and ~900°C), two from softwood (500°C and 540°C pyrolysis temperature), and one each from wood/tree trimming (green waste, 900°C), bamboo or coconut shells (550°C). Adsorption capacity for NH_4^+ and NO_3^- was determined for all seven products. Selected biochar products with high adoption potential were selected and tested in the field experiments. To accomplish Objective 2, two field experiments were conducted to investigate the effects of biochar incorporation into soil on N dynamics or the fate of N fertilizers including N uptake, movement or changes in soil, and environmental losses via ammonia (NH_3) volatilization and nitrate leaching. The first field experiment investigated effects of biochar application rate and interaction with irrigation level in producing processing bulb onions. The second field experiment evaluated the effects of biochar, manure, and their combination on the fate of N with processing tomato followed by garlic plants. Soil, plant, and leaching loss of N as well as yield and uptake were determined.

Because major findings from both field experiments have been either published or summarized in a manuscript submitted to journal for publication, the full papers are included in **Appendix 1** and **Appendix 2** for the two experiments, respectively. The **Methods** and **Data/Results** sections in the following sections only report information about the laboratory experiments. The **Discussion and Conclusions,** however, integrate information and findings from all experiments.

Table 1. Selected properties of biochar produced from various feedstocks and pyrolysis temperature

Biochar feedstock (pyrolysis T °C)[1]	H_2O (% fresh wt)	Org-C (% dry mass)	H:C Molar Ratio	Total Ash (% dry mass)	Total N (% dry mass)	pH	EC_{20} (mS/cm)	Liming (neut. Value) (% CaCO3)	Carbonates (% CaCO3)	Butane Act. (g/100 g dry)	Surface Area (m^2/g dry)	Total K (g/kg)	Total P (mg/kg)	Ammonia (NH4-N) (mg/kg)	Nitrate (NO3-N) (mg/kg)	Organic (Org-N) (mg/kg)
CB Softwood (500)	39	56	0.53	43.6	0.5	9.5	2.96	29.1	16.6	3	229	31.1	7,965	25.9	24.5	4,780
Almond shell (900°)	0.2	23.4	0.5	65.2	0.54	12.0	30.7	51.7	33.9	4.1	262	280.6	12,491	57.8	7.3	5,363
Almond shell (550)	28.8	56.6	0.70	19.5	0.96	9.8	5.32	10.5	1.5	0.5	150	24.3	1,146	23.9	12.9	9,526
AG Softwood (540)	15.2	62	0.43	20.2	0.64	10.3	2.31	22.5	13.3	5.8	317	27.7	4,208	16.6	25.7	6,362
Green waste (>900)	7.7	56.8	0.66	11.5	2.19	7.3	0.223	9.6	2.6	0.5	149	5.8	576	23.5	0.5	21,914
Bamboo[2] (Blue Sky)	14.3	75.9	0.46	19.8	0.99	9.2	0.351	5.2	0.6	0.6	153	12.5	767	21.7	1	9,852
Coconut shell - Cool Terra (<550°)	14.1	74.1	0.49	5.1	0.7	6.5	0.197	3.9	0.4	0.5	149	7.9	731	18.7	0.5	6,975

[1] CB softwood char was obtained from Charborn, LLC (Salinas, CA). Both almond shell chars and coconut shell char were prepared by Cool Terra (Camarillo, CA). AG softwood char (540 °C) was from AG Biochar, LLC (Modesto, CA). The Green waste (wood/tree trimming) char was from CA Greenest (San Jose, CA) and the bamboo char was provided by Blue Sky (Thousand Oaks, CA).
[2] Pyrolysis temperature for the bamboo is not confirmed but believed to be ≤550°C based on its water content, org-C content, and other parameters.

1. Laboratory Experiment 1 – Adsorption of N on Biochar

Selection and characterization of biochar products

Seven biochar products were collected and characterized (Table 1). The selection was based on their availability, diversity in feedstocks or pyrolysis temperature. The biochar products include two freshly made from almond shells at two pyrolysis temperatures (550°C and 900°C), two from softwood (500°C and 540°C pyrolysis temperature), and one each from wood/tree trimming (green waste, 900°C), bamboo or coconut shells (550°C). The almond shell biochar products were made by the support from Almond Board of California. The two softwood biochar products were commercially available products from different companies. The coconut shell biochar has been commercially available for long time and it is a more expensive product because of post-treatments to neutralize pH or increase its efficiency in retaining chemicals of interest. Because of more research done on this product it was used as a reference material in our testing of other biochar materials. Other two biochar products were from either high pyrolysis temperature of green waste or bamboo which has the potential to be produced in large quantity of biomass. The almond shell and softwood chars especially from ~500 ^{o}C pyrolysis temperature were considered with higher potential for adoption so they were selected in further field tests for their effects on the fate of N fertilizers.

All biochar materials were characterized for basic physiochemical properties and nutrients (NPK, total and available using established extraction methods). The characterization was done by Micromeritics Analytical Services (Norcross, GA). Parameters analyzed included surface area, pH, and chemical compositions including major nutrient NPK. Available N mineral species as ammonium or nitrate were analyzed again in our lab for the batch of materials used for laboratory studies right before use to ensure accurate values being used.

Adsorption of ammonium on biochar:

All seven biochar products were determined for adsorption capacity for NH_4^+ and NO_3^-. Prior to the experiment, all biochar materials were dried at 105°C to eliminate adsorbed water and ground to pass through 2 mm sieve. The amount of 0.200 g material was weighed in 15-mL glass screw top vials. Ten mL of 0, 25, 50, 75, 100, 150, and 200 mg L^{-1} NH_4^+-N solution (prepared from NH_4Cl in deionized water) was added to the vial. The biochar suspension was shaken for about 24 hours and then filtered through MF-Millipore™ Membrane Filter, 0.45 µm pore size using vacuum. The filtrate was analyzed for NH_4^+, which represents the concentration in the liquid phase at adsorption equilibrium. The filter membrane holding the biochar was placed into a clean 15 mL glass screw top vial and shaken with 10 mL 2M KCl for 1 h. The suspension was again filtered through the Millipore filters. The total NH_4^+ in the 2M KCl filtrate represents the concentration adsorbed on the biochar.

Adsorption isotherms were plotted (adsorbed vs concentration in solution at equilibrium) and analyzed with several models (e.g., linear, Langmuir, and Freundlich equations), but all were described well by Freundlich equation that we chose to examine and analyze adsorption characteristics or differences among the chars. Freundlich adsorption equation is expressed as (Foo and Hammed, 2010):

$$q_e = K_f\, C_e^{1/n} \qquad (1)$$

where q_e is the concentration on solid phase or adsorbed (mg kg^{-1}), C_e is the equilibrium concentration in the liquid phase (mg L^{-1}), K_f is the equilibrium constant and can be considered as the adsorption capacity at unit concentration (mg kg^{-1}) (L mg^{-1})$^{1/n}$, and 1/n is a constant (dimensionless). The linear form of Equation (1) is:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (2)$$

Equation (2) is used to obtain parameters K_f and 1/n by plotting Log C_e vs Log (q_e). The Freundlich equation is an empirical adsorption model and cannot predict an adsorption maximum. The K_f constant is considered related to adsorption capacity (Foo and Hameed, 2010). The constant 1/n is considered a correction factor, which is always ≤1. When n=1, K_f equals K_d, distribution coefficient in the linear adsorption isotherm.

To correlate the adsorption constant with biochar properties, pair-wise correlations between Kf and biochar variables were performed using both Pearson's and Kendall's correlations. Pearson's is the standard product moment correlation that assumes bivariate normality. Kendall's is based on ranks, so it is robust against extreme values. Thus, Kendall's is the better choice for the data analysis because only seven biochar products were analyzed.

Nitrate adsorption on the seven biochar products were determined following similar procedures as for the NH_4^+. The NO_3^- adsorption were determined at only two levels: low (5 mg N L^{-1}) and high (50 mg N L^{-1}) initial solution concentrations because preliminary tests showed weak adsorption on biochar. The concentrations represent the range often found in the field.

Adsorption envelopes (pH effects) of NH_4^+ on biochar

Laboratory experiments were conducted to determine the pH effects on NH_4^+ adsorption on five biochar products. The products chosen for this experiment were because of their higher potential for adoption. They included the almond shell char from pyrolysis temperature at 550°C, two softwood chars (from 500°C and 540°C pyrolysis temperature), the green waste (wood/tree trimming) char (from 900°C), and one coconut shell char (from pyrolysis temperature 550°C). Before using, the biochar materials were dried at 105°C to eliminate adsorbed water and ground to pass through 2 mm sieve. The amount of 0.50 g material was weighed in 45-mL plastic centrifuge vials. About 22 mL of deionized water was added to the vial. A combination of total 2.5 mL of various amounts of water plus either 1:1 HCl (4-360 uL) or 5N NaOH (6-100 uL) solution was added to the biochar suspension to achieve a pH range of 2-11. Then 2.5 mL of 1000 mg L^{-1} NH_4^+-N solution (prepared from NH_4Cl in deionized water) was added to the vials for an initial target solution concentration of 100 mg L^{-1} NH_4^+-N. Another set of vials for each biochar product without adding NH_4^+ solution was prepared and served as blanks. The biochar suspension was shaken for about 24 hours and then filtered through 0.45 µm Millipore™ filter membrane. The filtrate was analyzed for NH_4^+, which represents the concentration in the liquid phase at adsorption equilibrium. The filter membrane holding the biochar was placed back to the 45 mL vial and shaken with 25 mL 2M KCl for 1 h to extract the adsorbed NH_4^+ directly from biochar. This direct measurement for adsorbed NH_4^+ is more accurate than using the differences between the amount in the solution phase and the total amount added because there was potential NH_3 volatilization loss to the gaseous phase especially at high pH. The suspension was filtered through the MF-Millipore™ filter membrane. The residual biochar was extracted two more times with 2M KCl to recover as much as possible of adsorbed NH_4^+. Carry-over solution NH_4^+-N from previous extraction was corrected in each extraction step. The sum of NH_4^+ from all three 2M KCl filtrates represents the total amount of adsorbed on the biochar.

2. Laboratory Experiment 2 – Effects of biochar on N fertilizer (urea) transformation in soil

Laboratory incubation experiments were conducted to evaluate the effects of biochar and associated variables on N transformation following urea [$CO(NH_2)_2$] addition to soil. Variables studied included soil water content (5%, 10%, and 30%); three biochar products from different feedstocks of almond shells (AS), softwood (SW), and green waste (GW) that were produced at pyrolysis temperature 550 °C, 540 °C, and > 900 °C, respectively; soil type (sand, sandy loam, and loam), manure (diary manure compost, DM; green manure compost, GM), and combination of the manure with SW Biochar. Selected properties of the biochar or manure products for this experiment are provided in Table 2 and for soil in Table 3. Urea was used to observe treatment effects on ammonification (urea hydrolysis) and nitrification processes.

A total of 18 treatments were investigated as listed below. The 18 treatments were divided into four groups as listed below and tested in two sets of experiments due to the large number of soil samples, in which the control was repeated in both sets. Incubation for the first two groups of treatment were conducted from early January and completed in February 2020 and incubation for the soil type and organic amendments began in the middle of March and completed in early May 2020. Each treatment was tested in triplicate.

Treatments for incubation experiments on urea transformation:

Biochar type (Hanford sandy loam, 10% w/w, water content):

1) No char
2) Softwood (SW) char, 1% (w/w)
3) Almond shell (AS) char, 1% (w/w)

4) Green waste (GW) char, 1% (w/w)

Soil water content levels (Hanford sandy loam):
5) No char, 5% (w/w) soil water content
6) SW char at 1% (w/w), 5% (w/w) soil water content
7) No char, 30% (w/w) soil water content
8) SW char at 1% (w/w), 30% (w/w) soil water content

Soil types:
9) Delhi sand, 5% (w/w) water content), no char
10) Delhi sand, 5% (w/w) water content), SW char (1%, w/w)
11) Madera loam, 15% (w/w) water content, no char
12) Madera loam, 15% (w/w) water content, SW char (1%, w/w)

Organic Amendments (Hanford sandy loam, 10% w/w, water content)**:**
13) No char, no manure
14) SW char (1%, w/w), no manure
15) No char, dairy manure compost (1%, w/w)
16) SW char (1%, w/w), dairy manure (1%, w/w)
17) No char, green manure compost (1%)
18) SW char (1%, w/w), green manure compost (1%, w/w)

The incubation experiments were carried out following the procedures described in Cai et al. (2016). Briefly, the amount of air-dry soil that was equivalent to 3 kg oven-dry soil was placed into a large plastic container. The amount of organic materials (biochar or manure) required for treatments was mixed with the soil first. A urea stock solution (15.0 g urea-N L^{-1}) was made by dissolving 32.16 g to a sufficient amount of deionized water to make 1 L of final solution. Twenty mL of the stock solution was added to the amount of DI water that was required to reach the target water content for each treatment and then the solution was sprayed onto the soil with continuous mixing. The final N concentration in each container was 100 mg N kg^{-1}. The well mixed soil was then transferred to a 4 L high density polyethylene container (12.1 cm H x 22.2 cm D x 22.4 cm W). The containers were covered with plastic lids with approximate 7 mm diameter opening in the center for gas exchange and moved to a constant temperature room (25±1 ^{o}C).

Three different textured soils were used in this study: Sand, sandy loam, and loam. The sandy soil was Delhi sand (Mixed, thermic Typic Xeropsamments), collected from Ballico, CA. The sandy loam was Hanford sandy loam, collected from USDA ARS San Joaquin Valley Agricultural Sciences Center at Parlier, CA. The loam soil was Madera loam (fine, smectite, thermic Abruptic Durixeralfs), collected from Bright's Nursery in Le Grand, CA. Except for the soil type, all other treatments were investigated on the Hanford sandy loam. Selected properties of the soils are provided in Table 2.

During the incubation, soil samples were collected daily for the first week, twice for the second week, and weekly thereafter for a total of 50 days. At each sampling time two soil samples (20 g each) were collected from each container. One was for determination of soil pH and the other was for N species analysis. When extraction or analyses cannot be done on time the sample will be stored in -20 °C freezer until processing.

Table 2. Chemical properties of biochar and manure composts used in incubation experiments on effects of biochar on N transformation. The available N values were analyzed right before use.

Organic material[1]	pH	Org-C	Total N	Total P	Total K	NH_4^+-N	NO_3^--N
		(%)	(%)	(mg kg^{-1})	(g kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
Almond shell char (550 °C)	9.8	56.6	0.9	1,146	24.3	2.8	2.0
AG Softwood char (540 °C)	10.3	62.0	0.64	4,208	27.7	2.8	33.4
Green waste char (>900 °C)	7.3	56.8	2.19	576	5.8	-	0.5
Dairy manure	9.3	19.2	2.2	7,466	28.2	191.5	396.3
Green manure	8.6	15.9	1.34	2,445	12.1	106.4	456.3

[1] Almond shell char was prepared by Cool Terra (Camarillo, CA). The softwood char was from AG Biochar, LLC (Modesto, CA). The green waste (wood/tree trimmings) char was from CA Greenest (San Jose, CA). The dairy manure and green manure (yard trimming) composts were obtained from New Era Farm Service (Tulare, CA). The available N species for the batch of material used for this experiment were analyzed right before use.

Table 3. Selected properties for soil used in incubation experiments

Soil	pH	SOM	Total N	CEC	NH_4^+-N	NO_3^--N	Olsen P	Exchangeable-K	Water at 0.33 atm	Water at SP
		(%)	(%)	(meq 100 g^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(%, w/w)	(%, w/w)
Delhi sand	7.2	0.8	0.04	5.4	1.6	15.0	13.3	40	3.0	6
Hanford sandy loam	6.9	1.8	0.09	9.9	3.0	58.1	53.4	187.5	11.2	26
Madera loam	6.9	2.4	0.12	20.5	7.2	34.8	31.3	254.0	20.8	38

Chemical analysis:

Chemical analyses done in our lab included mineral N species [nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+)], soil pH, and total organic C and N. For mineral N species, soil samples were extracted with 2M KCl at 1:2.5 (w/v) ratio. The analysis was done using a colorimetric method (Mulvaney, 1996) on a Lachat QuikChem Flow Injection Analysis System (Lachat Instrument, Loveland, CO, USA). The soil pH was determined in 1:1 soil/water suspension using a pH meter with a combined glass electrode (Orion Research Inc., Boston, MA, USA). Total soil and plant C and N will be determined using combustion methods with a LECO TruMac® CN Macro Analyzer (LECO Corporation, St. Joseph, Michigan).

3. **Field Experiment 1** – Investigation on N dynamics affected by biochar and irrigation level. (See Appendix 1)

4. **Field Experiment 2 –** Effects of biochar, manure, and combination on the fate of N (plant uptake, ammonia volatilization, leaching loss) (See Appendix 2)

F. Data/Results:

1. Laboratory Experiment 1 – Adsorption of N on Biochar

Biochar properties

The seven biochar products vary significantly in moisture, ash content, pH, surface area, and nutrients (Table 1) as well as particle size distribution (Figure 2). These differences were due to the different feedstocks and pyrolysis temperature. The two softwood chars have similar particle size distributions. Almond shell char from 900 °C pyrolysis temperature has higher proportion of finer materials than that from 550 °C. The wood/tree trimming material has ~90% particles larger than 2 mm and >1mm for bamboo and coconut shell chars. High pyrolysis temperature for almond shells resulted in lower C content but the highest nutrients especially K and P among all products and the P and K values are ten times of that from Almond shell at pyrolysis temperature at 550 °C. We do not have the information about biochar production efficiency, but the data suggest that the higher temperature produce more fertilizer like material rather than C-rich material desired for biochar. The two softwood biochar products (CB Biochar and AG Biochar) from different companies at similar pyrolysis temperature (540-550 °C) had similar properties such as pH, EC, nutrient levels (total NPK) and others. The coconut shell biochar went through specific post treatments that neutralize the pH and others. Thus, the product is more expensive than those without the treatments. In field experiments, we selected the almond shell (550 °C) and the softwood biochars for detailed investigations because they represent products that have higher potential for adoption compared to other products.

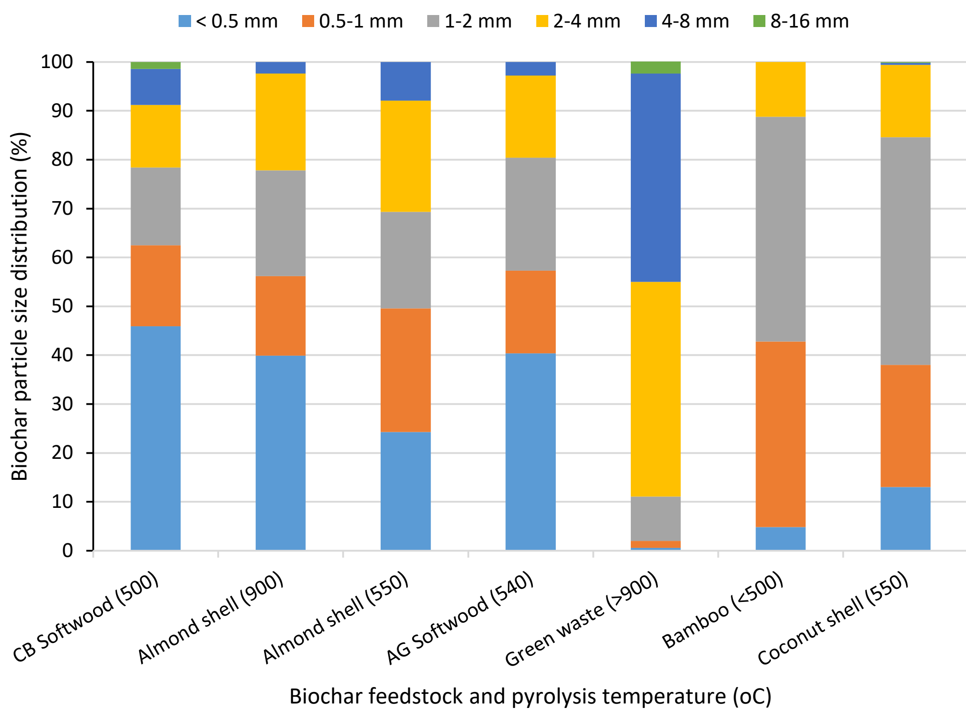

Figure 2. Particle size distribution in biochar products from different feedstocks.

Adsorption of ammonium on biochar

Adsorption isotherms (correlations between the adsorbed NH_4^+ and liquid phase concentration at equilibrium) are shown in Figure 3. For most of the biochar products, the adsorbed ammonium followed a nonlinear increase as the NH_4^+ concentration increased in solution phase. Freundlich model fits the adsorption isotherms for all biochar products. The adsorption constant (Kf) are listed in Table 4 Almond shell char at 500°C and the coconut shell char had the highest adsorption strength and almond shell char at 900°C showed the lowest based on the K_f values. However, Figure 3 shows bamboo char has much lower adsorption amount as concentration increased in solution compared to those softwood chars but its K_f value was much higher than for both softwood chars. This indicates the limitations on the physical meaning of K_f value. Estimated adsorption for NH_4^+ at equilibrium solution concentration of 150 mg L^{-1} did show that the almond shell char 900°C and the bamboo char had lowest adsorption, almond shell char at 550°C had the highest, and all others were between (1,745-2,000 mg kg^{-1}) (Table 4).

The constant 1/n is less than 1 for all biochar products (Table 4). Foo and Hammed (2010) described well that Freundlich model can be applied to multilayer adsorption sites over the heterogeneous surface, demonstrating that the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations. The amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process. Adsorption of ammonium on all biochar products were described well by the model may indicate this is the case. Although there have been no clear mechanisms on ammonium adsorption on biochar, the multiple function groups on the organic rich materials may have involved multiple sites on its adsorption and variation in adsorption energy or strength.

Table 4. Freundlich adsorption constants for ammonium adsorption on biochar

Biochar Type	K_f	1/n	Estimated adsorption of NH_4^+ at Ce=150 mg L^{-1}
Almond shell, 550°C	247.23	0.46	2478.0
Almond shell, 900°C	5.56	0.91	531.3
AG softwood, 540°C	20.19	0.89	1745.2
Bamboo	140.02	0.43	1207.6
CB softwood, 500°C	35.40	0.79	1854.0
CoolTerra coconut, <550°C	269.59	0.40	2000.5
Greenwaste, >900°C	111.81	0.56	1849.7

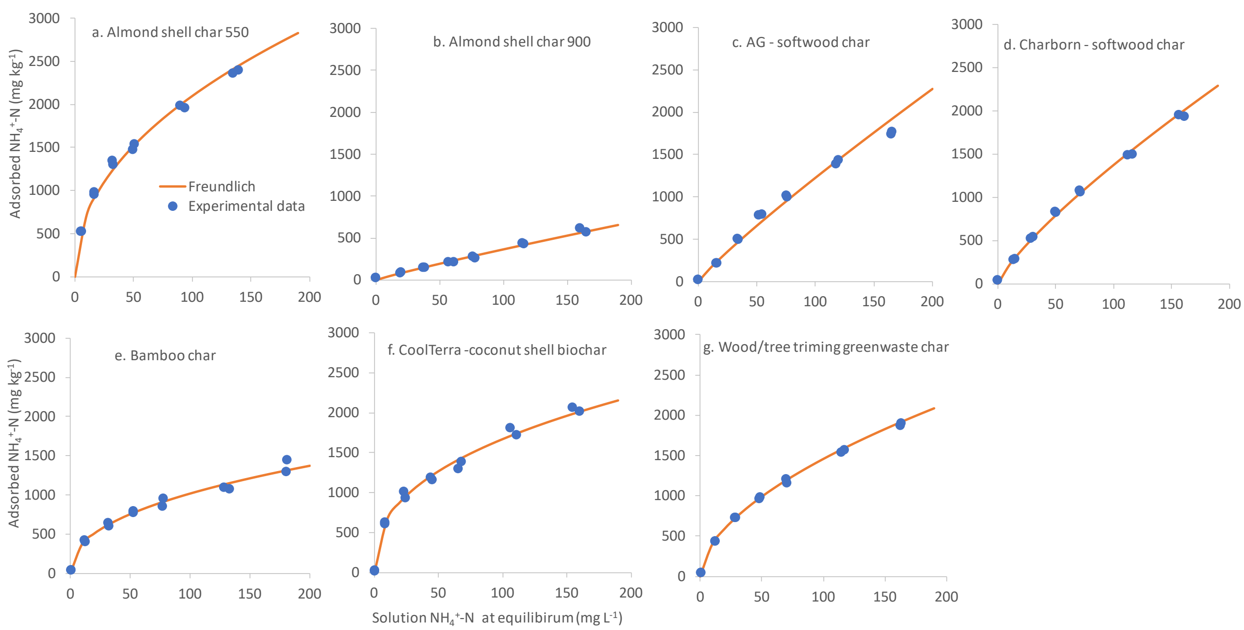

Figure 3. Adsorption isotherm of ammonium on biochar. The solid line is fitted Freundlich equation.

Pearson's pair-wise correlations resulted in no significant finding for any of the biochar variables correlated to adsorption constant (Kf), but a three-step pair-wise correlation using Kendall's resulted in a model with carbonates, Org-C and H_2O, R-Square = 0.99 correlated to Kf. The water content should not have any effects because all biochar materials used for the experiment was oven-dried prior to use. Thus, the results may represent certain properties (e.g., org-C content) that related to the increase or decrease of water contents affected NH_4^+ adsorption. Because there are correlations among the explanatory variables, we cannot say that these three variables are the most important in explaining the differences in Kf. The result means that these three variables (ranks) explain 99% of the variability in ranks Kf, but there can be other sets of variables that do just as well as shown. The analysis can be limited by the number of samples. It is convincing that both carbonate and org-C significantly contributed to the adsorption because carbonate is correlated to pyrolysis temperature or pH and org-C is correlated with more reactive functional sites.

Adsorption envelope of ammonium on biochar

The effects of pH on NH_4^+ adsorption are shown in Figure 4. The adsorption for all biochar products was very low at low pH, increased as pH increased, and reached the maximum at pH range 8-9, but then decreased as pH raised further. The data indicate that the ability of biochar to retain NH_4^+ is highly influenced by type of biochar and pH. Notice three biochar materials (Figure 1abc) with pyrolysis temperature of 500-550^oC had the peak about 1000 mg N kg^{-1} adsorption maximum. Using this number and assuming 30 ton/ha amendment rate, NH_4^+-N adsorption would be about 30 kg N ha^{-1} (27 lbs per acre) which would not be a significant amount of N in soil. If pH below 8 as in most neutral soils, the adsorption capacity could drop to about half. Further, in most agricultural field except paddies under submerged conditions, NH_4^+ is not stable and can be quickly oxidized to NO_3^- through nitrification process. This can be clearly demonstrated in the Lab Experiment 2 (below). All the information suggests that biochar incorporation into soil will not have a significant role to retain N.

Adsorption of NO_3^- on biochar

Nitrate adsorption on most biochar products were very low compared to that for NH_4^+ (Figure 5). Only the almond shell char with pyrolysis temperature at 900 ^oC showed 30% adsorption at low concentration (5 mg L^{-1} initial NO_3^--N concentration) but the high pyrolysis temperature will consume high energy to produce less amount of biochar, thus would not be feasible as an agronomic practice. For most biochar products, the ability to retain NO_3^- is very limited with <5% adsorbed at low concentration and none at the high concentration (50 mg L^{-1} initial NO_3^--N concentration).

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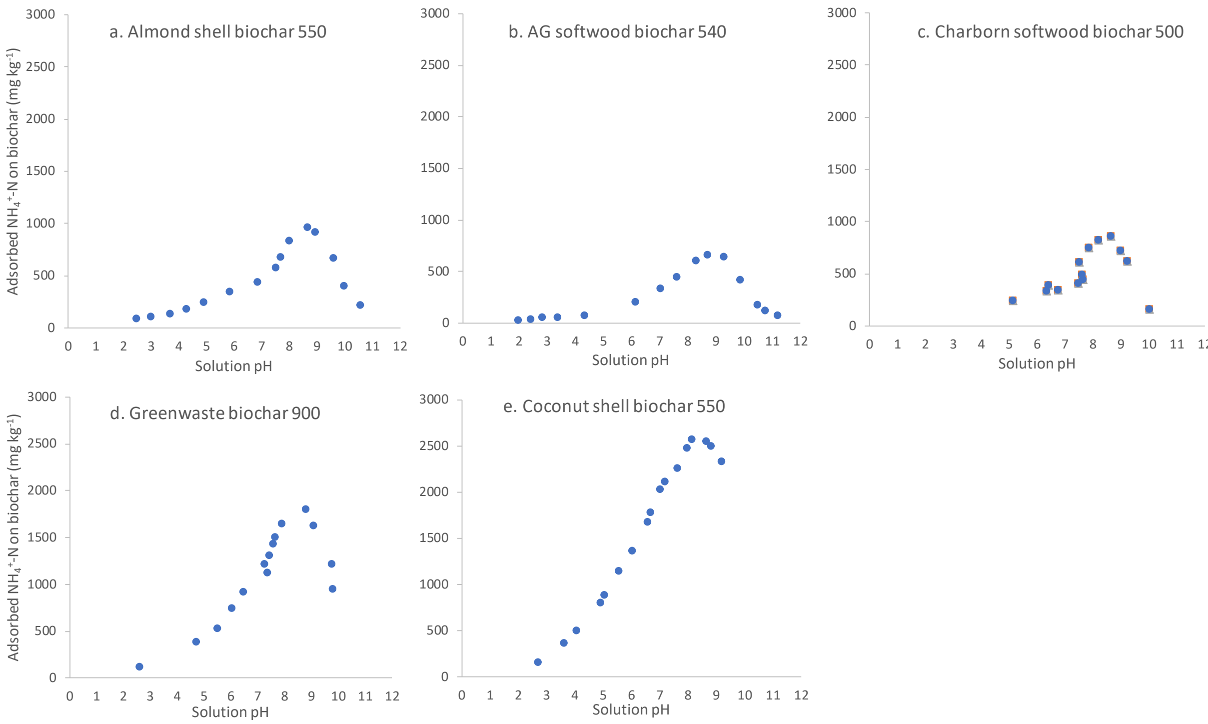

Figure 4. Adsorption envelopes of NH_4^+ on biochar products when initial solution concentration was 100 mg NH_4^+-N L^{-1} at a 5:1 (v/w) solution to biochar ratio.

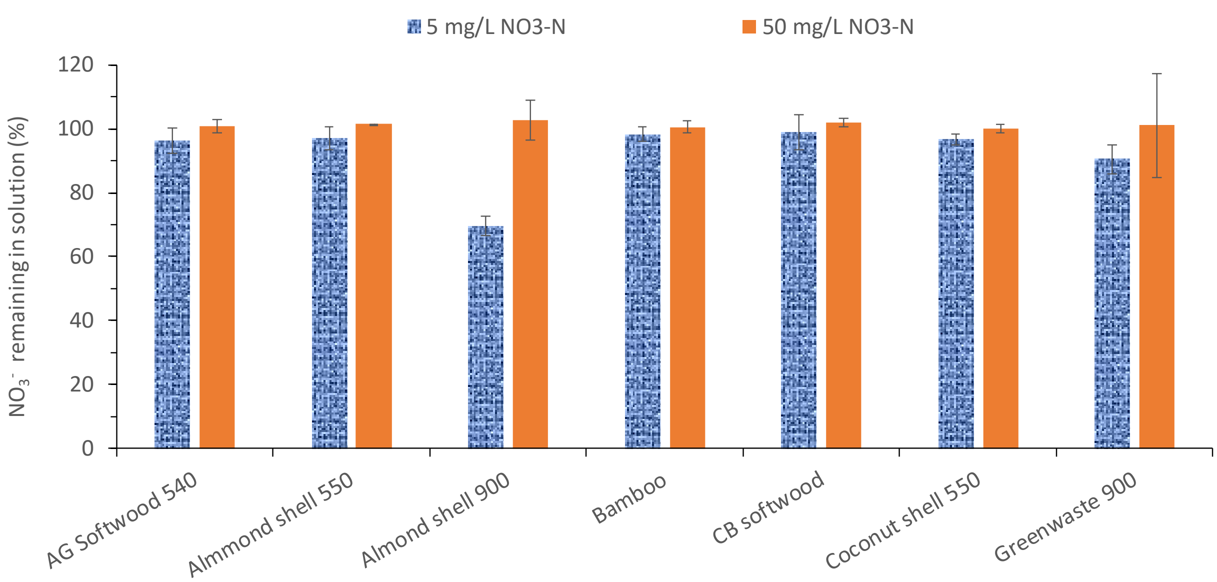

Figure 5. Solution NO_3^--N concentration at equilibrium after 5 or 50 mg L^{-1} were added to biochar suspension. Error bars are standard deviation of duplicates.

2. Laboratory Experiment 2 – Effects of biochar on N fertilizer (urea) transformation in soil

In this experiment, influence of treatments on N transformation (hydrolysis and nitrification) from urea was examined. The reactions are described below according to Barak et al. (1991), and Bolan and Hedley (2003):

$CO(NH_2)_2 + 3H_2O = 2NH_4^+ + 2OH^- + CO_2$ (hydrolysis) [1]

$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$ (nitrification) [2]

The nitrification is a two-step process (Wrage et al., 2001)

$2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O$ (ammonium oxidation) [3]

$2NO_2^- + O_2 = 2NO_3^-$ (nitrite oxidation) [4]

Effects of biochar type and soil moisture

Changes in soil pH, NH_4^+ concentration, and oxidized NO_2^- + NO_2^- concentration for the first set of incubation experiment are shown in Figure 6. The pH change indicates the N transformation processes because urea hydrolysis (ammonification) consumes protons that causes pH increase and nitrification produces protons that causes pH decrease as shown in Eq. [1] and Eq. [2]. The most changes in soil pH occurred during the first two weeks. For most treatments, the pH increased quickly within the first couple of days, which suggests urea hydrolysis. The pH reached a peak by day 3 or 4 and then decreased quickly due to nitrification. The decrease occurred in most treatments except at the highest water content (30%). At the high or saturated soil water content, oxygen diffusion was limited that lead to anaerobic conditions that prevents nitrification. For most treatments, a relatively stable pH was achieved in two weeks suggesting urea transformation completed. An exception was from the dry (5% soil water content) without biochar due to restricted microbial activity.

There were significant differences in the final pH observed among the treatments that was determined by the completion of urea transformation and biochar type (Table 1). A stable pH from a treatment indicates that urea transformation from urea through hydrolysis and nitrification to nitrate was completed. Without biochar, the soil had a final pH that was more than 1 unit lower than original soil (Figure 6), which illustrates the impact on soil acidification from urea or ammonium fertilizer applications, a severe problem in soil degradation in many parts of the world with acidic soils (Tian and Niu, 2015). Biochar has been shown to be effective in mitigating soil acidification (Shi et al., 2019). The lab data from our experiments show that the AS and SW chars, but not GW char, were able to prevent the pH drop, due to its high pH or alkalinity (Table 1).

Nitrogen transformations resulted in the concentration changes of NH_4^+, and the oxidized species (NO_3^- + NO_2^-) (Figures 6b, c). Urea hydrolysis (Eq. [1]) resulted in the increased NH_4^+ concentration, which occurred within the first few days of urea application (peaked on Days 3-4. After the peak, the NH_4^+ concentration began to decrease, which varied significantly among the treatments. For the moisture experiment, NH_4^+ concentration decreased the slowest at 30% soil water content with or without biochar and similarly in the dry soil (5% water content) (Fig. 7a). Soil from all other treatments at 10% water content resulted in disappearance of NH_4^+ in two weeks regardless with or without biochar or the type of biochar incorporated. The data suggest that soil moisture dominates N transformation rather than biochar under the studied conditions.

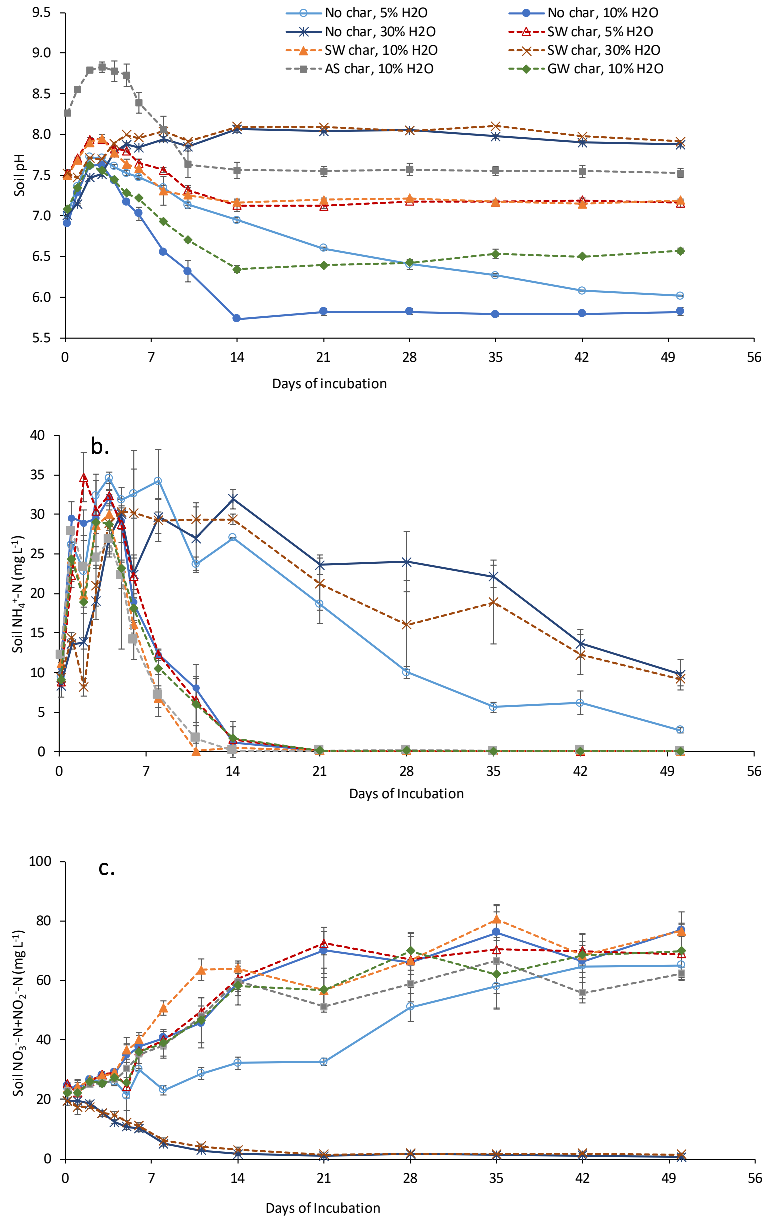

Figure 6. Changes of a) pH, b) NH_4^+ concentration, and b) NO_3^- + NO_2^- concentrations from laboratory incubation experiments with amendment of different biochar type and soil water content. Error bars are standard deviation of the mean (n=3).

The decrease in NH_4^+ concentration was accompanied by an increase in NO_2^- and NO_3^- concentration (Figures 6c) implying nitrification process occurring (Eq. [2]). The data support conclusion drawn based on the NH_4^+ concentration data that very dry or wet soils prohibited oxidation of NH_4^+ (nitrification process) and biochar showed little effects on the process. A stable pH or in NO_2^- and NO_3^- concentration from each treatment were achieved in two weeks suggesting completion of N transformation with an exception in the very dry soil (5% water content) where nitrification was slow but continues throughout the incubation period.

Effects of biochar and mixed with composts on N transformation in different soil types

Figure 7 shows the changes in soil pH, NH_4^+ concentration, NO_2^-, and NO_3^- + NO_2^- concentration for the second set of incubation experiment with biochar treatment in different soil types or biochar mixed with dairy or green manure composts in the sandy loam. The NO_2^- data signals ammonia oxidation, the first step of nitrification [Eq. 3].

Soil types showed significant differences in N transformation. The sandy soil showed similar increase in pH, i.e., no differences in urea hydrolysis from other soils, but much slower pH decrease from nitrification process without biochar and biochar addition resulted in faster stabilization although higher pH (Figure 7a). This is also supported by the higher NH_4^+ concentration (Figure 7b), and much higher NO_2^- (Figure 7c) in the sandy soil without biochar. Biochar apparently accelerated ammonium oxidation as shown by the sudden drop in both NH_4^+ and NO_2^- concentrations by Day 14. The slow process was further supported by the slowly increase in NO_3^- concentration throughout the incubation period (Figure 7d). Ammonium oxidation was fast in other two soils or treatments. The slower nitrification in sandy soil was most likely due to lower microbial population or activities. The data imply that nitrification in sandy soils generally takes longer time than other types of soil and biochar can accelerate the process.

For the fine textured loam soil, faster hydrolysis or nitrification occurred that caused earlier increase and then drop in NH_4^+ concentration (Figure 7b). There appeared some accumulation in NO_2^-, but considered not much different from the soil, sandy loam due to large variability (Figure 7c). A stabilized pH was achieved within two weeks indicating completion of urea transformation.

Among the organic material treatments tested in the sandy loam soil, there were small difference in urea transformation. Biochar addition appeared to stabilize pH earlier at least for several days which was also supported by earlier peak NO_3^- + NO_2^- concentrations, suggesting biochar can accelerate urea hydrolysis and nitrification in all soils and this is probably due to its ability to increase water retention, higher pH that benefit both processes. Biochar mixed with either dairy manure or green manure showed similar trend according to soil pH changes (Figure 7a) although the difference can be barely observed in the concentration changes of NH_4^+ and NO_3^- + NO_2^-. The differences in the final soil pH among treatments were also caused by the treatment materials that had different pH values (Table 1).

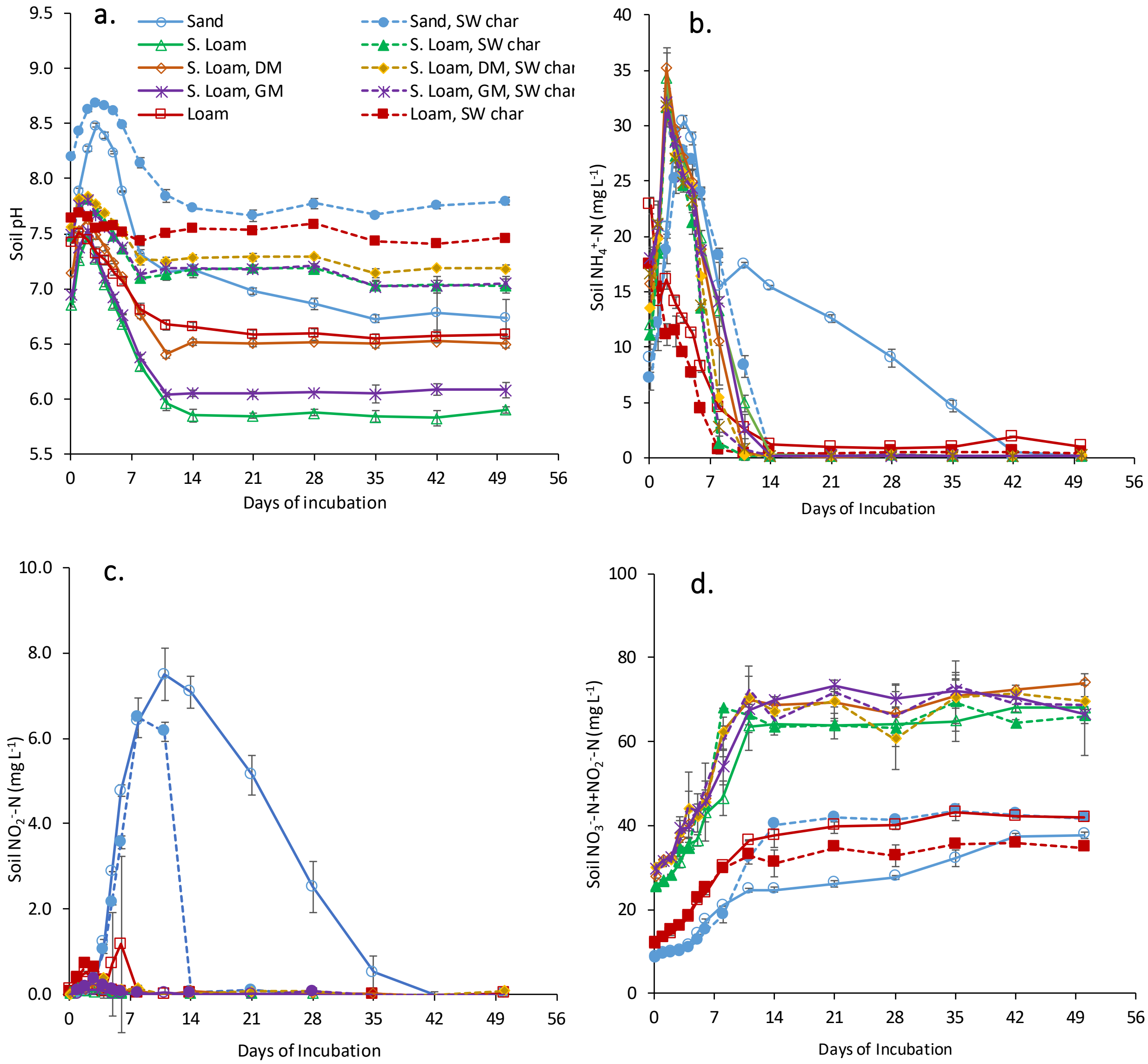

Figure 7. Changes of a) pH, b) NH_4^+ concentration, c) NO_2^-, and d) NO_3^- + NO_2^- concentrations from laboratory incubation experiments with different soil types or mixed biochar with manure composts. Error bars are standard deviation of the mean (n=3).

G. Discussion and Conclusions:

Biochar did not show direct link to crop yield or benefits in N management

Based on the lab experimental data it was not surprising that biochar did not show direct benefit to improve crop yield, biomass production, or N uptake. The main reason may be that the soil was a relatively fertile sandy loam with no physical or chemical constraints for growing plants except nutrients. Biochar treatment up to 58 t ha^{-1} (Field Experiment 1) did not show yield or N uptake differences except irrigation level showed more impact. At the same irrigation level, although biochar did increase soil water content (Gao et al., 2020, **Appendix 1**), the increased retention was not enough to show impact on crop growth. Positive effects of biochar on crop production were observed more when biochar significantly improved some of the soil limiting factors for crop growth such as improved soil physical and chemical properties or increased water retention in coarse textured soil (Basso et al., 2013; Yu et al., 2013) or neutralized pH in acidic soils (Major et al., 2010; Cornelissen et al., 2018; Mensah and Frimpong, 2018).

Field data also showed that there were no overall biochar effects in reducing either ammonia volatilization or leaching loss (Table 3) although temporary pH effect from manure or biochar was observed on NH_3 volatilization from the first year (Field Experiment 2). These can be fully explained by the laboratory experimental results because biochar generally does not possess significant capacity to adsorb N. Biochar products showed some capacity to adsorb NH_4^+ with the maximum 1000 mg N kg^{-1} observed at pH 8-9, and at neutral pH the adsorption was reduced by about half. At 40 t ha^{-1} biochar rate, this can translate to about 20 kg N ha^{-1} (less than 10% total N applied) that may be adsorbed. Furthermore, NH_4^+ is not stable in most oxygenated environment and tends to be oxidized to NO_3^-, which adsorption to biochar is extremely low. These facts can explain why biochar could not significantly retain N or effectively reduce leaching from this study and others.

Biochar should be promoted as an effective strategy to sequester C

Although biochar did not show significant effects in improving yield, increasing NUE, and reducing N losses, there have been undeniable benefits from adding biochar amendment to soil. Both field experiments showed that biochar increased SOC, increased soil water retention, and improved soil health (Gao et al., 2020; Dangi et al., 2019). Many studies also reported these undeniable benefits (Jeffery et al., 2011; Purakayastha et al., 2019; Kannan et al., 2020). Agricultural land uses have resulted in the loss of 133 Pg C from the soil and the hotspots are often associated with major cropping regions and degraded grazing lands (Sanderman et al., 2017). Depletion of SOC leads to many detrimental effects on and threatens sustainability of cropping systems. It has shown that prehistorically modified soils rich in C are the basis for sustainable agriculture (Glaser, 2007). Biochar can persist in soils on a centennial scale (Wang et al., 2016). Thus, biochar plays an important role in sustainable crop production and such practices can be or should be exercised for suitable conditions. Agricultural burning can be easily replaced by partial burning to produce biochar) as biochar can last in soil for many thousand years (Glaser, 2007). Biochar is a significant source of P or K (Table 1; data from Field Experimental 2). Depending on production conditions, biochar at 20 t ha^{-1} can provide 340 kg K ha^{-1} and then inorganic fertilizer can be substantially reduced.

Commercial biochar products by far are still too expensive as a feasible practice for growers. A more economical way to produce biochar in situ should be sought to significantly reduce production and operation costs. There are various low costs methods to produce biochar (https://biochar-us.org/biochar-production). Growers have tremendous capacity to invent methods to make biochar if no other options such as burning are allowed. Further, various programs have been encouraging conservation practices including returning biomass to soil or producing biochar. Policies for offering C credit can be very useful to promote such practice.

Conclusions

Based on both lab and field studies, soil amendments with biochar did not show direct link to improving yield, increasing N uptake or use efficiency, or reducing environmental loss such as ammonia volatilization or nitrate leaching. Biochar does significantly increased SOC and improve other properties such as increased water retention as well as supply nutrients especially K. Biochar should be promoted as a conservation practice to replace agricultural burning to sequester C to sustain soil productivity. This practice should be promoted to preserve organic C as much as possible. Current commercial products are too expensive for growers, but many in-situ low cost methods can be explored. Policies that promote such practice by offering C credit can be very helpful to encourage adoption of conservation practices in large scale.

H. Challenges and modification of original research plan

1. Collection of leaching water was originally planned using piezometers but there were difficulties to obtain water samples because of mostly unsaturated soil conditions. We then adopted a direct method to collect leaching N using resins that proved working efficiently.

2. The most significant challenge we ran into is the reduced laboratory activities since early 2020 because of the Covid-19 Pandemic. Following both federal and state guidelines for staying at home and social distancing, the number of people working together in the lab was limited, which resulted in some delay in sample processing and analyses. Laboratory Experiment 2 was the last experiment to be completed during the project. We did our best to make timely progress and completed all sampling and analyses for preparing this report except one parameter: nitrite (NO_2^-) that was partially completed by the time this final report is due. This was caused by a technician who had to go under quarantine for over three weeks. Missing the partial NO_2^- data, however, does not affect the conclusions of the report because the data only affect the two steps of nitrification process (Eqs. [3] and [4]). All samples will be analyzed, and the data will be used for scientific publications.

3. The originally planned laboratory experiment 3 was replaced by expanding Laboratory Experiment 2. This was because the data will not add more understanding on the impact of biochar on crops and N movement when applied in the field and we have the information collected from two field experiments. Instead, we investigated the effects of manure and mixed with biochar on N transformation. There are more unknowns in this regard that are worthwhile to study because many growers apply manure in their fields.

4. It should be noted that study on temperature effect in Lab Experiment 2 was originally planned but could not executed because of the addition of other more important treatments as described above. We expect that temperature would mostly affect reaction rates. Fertilizers are applied during crop growing season when temperature is relatively high. Thus, all incubation experiments done at room temperature should provide the information needed to achieve the project objectives.

I. Project Impact

1. The project answered several questions about how biochar interacts with N in soil and why there are no positive effects to increase N retention in soil because adsorption of N is limited to ammonium-N, but the most stable N form is nitrate that shows little adsorption. The results explain very well why field observations showed little effects of biochar to increase crop yield, improve N uptake, or reduce N losses via volatilization or leaching. However, there are undeniable benefits of biochar to sequester C and improve soil properties. Positive effects of biochar to improve crop yield may be observed for soils with severe constrains for plant growth that can be significantly improved by biochar.

2. This research validated that biochar is still a valuable practice to adopt in agriculture. Loss of C in agricultural soils continues contributing to soil and environmental degradation and threatens sustainability of crop production. Organic C rich soils are the basis for sustainable agriculture. Biochar is one of the effective strategies to increase or preserve soil organic C as shown in both field experiments.

3. The project identified situations when biochar can be used and feasible as an effective strategy to increase soil organic C to replace the harmful agricultural burning that is detrimental to air quality and causes 100% loss of C. Current commercial biochar products are too expensive for growers but in-situ production can significantly reduce costs.

4. Policies (e.g., C credit) that promote biochar production and use can encourage adoption of the practice. Because no direct benefits to increase crop yield or N uptake can be guaranteed when using biochar, growers hesitate adoption of such practice. However, increasing soil organic C is proven one of the long-term solutions to sustain crop production and biochar is one of the strategies and should be adopted whenever suitable.

J. Outreach Activities Summary:

2017**.** One presentation was given at 2017 California Plant and Soil Conference and several field presentations were given during 2017 to different groups who were visiting USDA-ARS San Joaquin Valley Agricultural Sciences Center. Participants included specialty crop advisors, teachers from high schools, and K-12 students as well as a number of international visitors, which included people from China, Japan, and Uzbekistan.

2018. The project findings were presented on a field day “Whole Orchard Recycling and Other Orchard Waste Amendments” on October 30, 2018, held at California State University, Fresno. Over 50 attendees including growers, extension advisors, consultants, commodity organization representatives, and state policy makers were present. Dr. Gao gave a classroom presentation entitled “Potential of Biochar Amendment on Water and Nutrient Management” and field demonstrations on data collection for N movement. Another presentation was scheduled at the ASA-CSSA-SSSA meeting on January 6-9, 2019 in San Diego but was cancelled due to the Federal government shutdown.

2019: Dr. Gao gave a presentation entitled “Soil Biochar Amendment to Improve Nitrogen and Water Management” at the 2019 Nutrient Management Conference sponsored by FREP and WPHA on Oct 28-30 at DoubleTree by Hilton Fresno Convention Center, Fresno, CA. (Gao and Wang, 2019)

Dr. Gao gave a presentation on organic amendments to improve soil productivity research at USDA Future Scientists Program for high school teachers on May 13, 2019 at USDA-ARS, Parlier, CA and also at the 11th STEM Conference in Reedley College to Jr. high and high school students on April 27th, 2019.

2020. Scheduled meeting presentations or other outreach activities were cancelled in due to Covid-19.

A peer-reviewed article was published based on research for this project: Gao, S., D. Wang, S. Dangi, Y. Duan, T. Pflaum, and T. Turini. 2020. Nitrogen dynamics affected by biochar and irrigation level in an onion field. Sci Total Environ. 714, 136432. (**Appendix 1**)

A manuscript entitled “Influence of biochar and manure on nitrogen dynamics and uptake by processing tomato and garlic plants“ has been prepared for submission to the Journal of Plant Nutrition and Soil Science based on the two-year (2018-2019) field experiment 2. (**Appendix 2**)

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L. Appendix:

Appendix 1 – Field Experiment 1: Investigation on N dynamics affected by biochar and irrigation (Manuscript accepted for publication by Sci. Total Environ.**)**

Nitrogen dynamics affected by biochar and irrigation level in an onion field

Suduan Gao[a]*, Dong Wang[a], Sadikshya R. Dangi[a], Yinghua Duan[b], Tom Pflaum[a], Jim Gartung[a], Ruijun Qin[c] and Thomas Turini[d]

[a] USDA-ARS, San Joaquin Valley Agricultural Sciences Center, 9611 South Riverbend Ave., Parlier, CA 93648.
[b] Chinese Academy of Agricultural Sciences, Institute of Agricultural Resources and Regional Planning, Beijing, 100081, China.
[c] Oregon State University, Hermiston Agricultural Research & Extension Center, Hermiston, OR 97838
[d] UCNAR, University of California Cooperative Extension, Fresno County, CA 93710.

* Corresponding author. Tel: (559) 596-2870; Fax: (559) 596-2851; e-mail: suduan.gao@ars.usda.gov

ABSTRACT

Soil amended with biochar has many potential environmental benefits, but its influence on the fate of nitrogen (N) under irrigated conditions is unclear. The objective of this research was to determine the effects of biochar and interactions with irrigation on N movement in soil, gas emissions, and leaching. A three-year study was conducted in an onion field with three main irrigation treatments (50, 75, and 100% of a reference that provided sufficient water for plant growth) and three biochar amendment rates (0 or control, low char - applied first year at 29 Mg ha^{-1}, and high char - added both first and second year for a total 58 Mg ha^{-1}) as sub-treatments in a split-plot design. Nitrogen fertilizer was applied three times during first year growing season, but weekly the second year. Ammonia (NH_3) volatilization, nitrous oxide (N_2O) emission, and nitrate (NO_3^-) in soil pore water were monitored during growing season, and annual N (total and NO_3^-) changes in soil profile were determined for first two years. Nitrate leaching was measured in the third year. Ammonia volatilization was affected by fertilization frequency with higher loss (5-8% of total applied) when fertilizer was applied in large doses during the first year compared to the second year (4-5%). Nitrous oxide emissions were ≤ 0.1% of applied N for both years and not affected by any treatments or fertilization frequency. Nitrate concentration in soil profile increased significantly as irrigation level dropped, but most of the NO_3^- was leached by winter rain. There was no significant biochar effect on total N gas emissions or soil NO_3^- accumulation, but significant irrigation effect and interaction with biochar were determined on soil NO_3^- accumulation. High leaching was associated with biochar amendment and higher irrigation level. Irrigation strategies are the key to improving N management and developing the best practices associated with biochar.

Keywords: ammonia volatilization, nitrous oxide emission, soil porewater N, nitrate leaching, drip irrigation.

1. Introduction

Most crop production has been relying on large input of nitrogen (N) fertilizer for decades resulting in a steady increase in mineral (synthetic) fertilizer use over time, but N use efficiency has decreased in the majority of regions in the USA (Swaney et al., 2018). Nitrogen loss to the environment has many inevitable consequences, such as groundwater contamination, air pollution, and greenhouse gas emissions. In California, N fertilizers from agricultural fields was the major source for the statewide nitrate (NO_3^-) pollution in groundwater (Harter et al., 2012). Subsequent regulatory decisions have been or are in the process of being made that require monitoring and reporting of N in production fields. Agriculture is also the major source of the greenhouse gas nitrous oxide (N_2O), which has a global warming potential ~300× that of an equivalent amount of carbon dioxide (CO_2). Ammonia (NH_3) in the air has detrimental effects on human health and the largest sources are from dairy and N fertilizers (USEPA, 2016). Effective N management targets increasing N retention in soil, reducing losses to the environment, and the development of practices that relies on a better understanding of major pathways and dynamics of N in production systems.

Ammonia volatilization and NO_3^- leaching from fertilization are difficult, if not impossible, to avoid. Ammonia volatilization is largely affected by fertilizer type, application method, and soil pH (Terman, 1979; Cameron et al., 2013). Nitrate leaching is caused by its high solubility/mobility and NO_3^- is the dominant form of N in most soils. Between the two major mineral N species (NH_4^+ and NO_3^-), NH_4^+ (dominant under anaerobic conditions) can be more strongly retained by fixation to soil particles or incorporation in organic materials. Minimizing N losses will depend on practices that can increase N retention in soil for plant uptake. Most studies have not focused on the complete N cycle, but systematic and integrated approaches are needed to identify solutions to the complex problems and sustain production systems.

Even with a number of benefits, biochar amendment has not been widely adopted in agricultural fields mainly due to high costs and the lack of conclusive data under field conditions. Biochar, which is produced from heating organic materials under limited oxygen, has the benefits of carbon sequestration, mitigating contamination problems, and improving soil physical, chemical and biological properties (Glaser et al., 2002; Ahmad et al., 2014; Lehmann and Joseph, 2009). Biochar is also shown to increase soil water holding capacity, especially in coarse textured soils (Basso et al., 2013; Yu et al., 2013) that would increase water use efficiency and reduce leaching, but improvement of infiltration rate in some soils could also increase leaching (Barnes et al., 2014; Li et al., 2018). Irrigation may or may not result in leaching that depends on several factors and information in this regard has not been clear. Some studies showed that biochar in soil reduced N leaching (Singh et al., 2010; Xu et al., 2016; Borchard, et al., 2019), NH_3 volatilization (Thangarajan et al., 2018; Mandal et al., 2019; Sun et al., 2019), and N_2O emissions (Singh et al., 2010; Fidel et al., 2019; Liu et al., 2019). Others show that the biochar increased NH_3 (He et al., 2018; Sha et al., 2019; Wei et al., 2020) and N_2O (He et al., 2018; Yoo et al., 2018; Senbayram et al., 2019) losses. Biochar amendment to soil can either increase or decrease N leaching depending on application methods (Li et al., 2018) and soil type (Liu et al., 2017). Many studies were done in laboratory conditions that cannot be extrapolated to field scale (Fidel et al., 2019). Meta-analyses have shown significant variation in biochar effects on greenhouse gas emissions (Liu et al., 2019), N in soil and leaching (Gao et al., 2019), and microbial community structures and activities (Zhang et al., 2018). Knowledge of N dynamics affected by biochar amendment and interaction with irrigation level is very limited for irrigated agroecosystems. The objective of this research was to determine the effect of biochar and interaction with irrigation level on N movement in soil, gas emissions, and leaching loss in a field experiment for processing bulb onion production. This study would show if biochar amendment practice in irrigated agriculture can provide significant soil and environmental benefits.

2. Materials and Methods

2.1. Field experiment, treatments, and operation

A field experiment was conducted at the USDA-ARS, San Joaquin Valley Agricultural Sciences Center, Parlier, CA. The soil is Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents). The experiment was established in late fall of 2015 and processing bulb onions were grown for three years to test the incorporation of biochar with different irrigation levels on onion growth, and the fate of N applied by examining the N movement in soil and losses to the environment. A split-plot design was used with irrigation (surface drip) levels as the main treatment and biochar rates as the sub-plots in three replications. The three irrigation levels were 50%, 75%, and 100% of a reference level. The 100% irrigation level was maintained by keeping soil water potential at approximately -25 kPa or volumetric water content at 22%. Biochar treatment included control (no biochar), one-time application of biochar at the beginning of the experiment, and two biochar applications (adding biochar again in the second year).

A vineyard was pulled out in 2013 and the field was planted with oats as a cover crop during winter season and fallowed at other times. The field was cultivated before applying the biochar treatment in 2015. Biochar from softwood feedstock was provided by Charborn, LLC (Oakland, CA, USA). The biochar was produced at a pyrolysis temperature ~500 ^oC, and had organic C >56%, pH 9.5, and surface area 229 m^2 g^{-1}. Total N, NH_4^+-N, and NO_3^--N were 0.5%, 25.9 mg kg^{-1}, and 24.5 mg kg^{-1} (dry wt), respectively. The biochar was stored uncovered outdoors, was rained on, and had at the time of use a water content near 50%. The amount of wet biochar was weighed, spread on soil surface using a manure spreader, and then incorporated into the soil at about 15-20 cm depth before forming planting beds. The final biochar application rate was 29 dry Mg ha^{-1}. Each treatment plot was 2 m wide and 20 m long covering two beds with a center to center distance of 0.94 m. The beds were formed using a field bed shaper and onion seeds (variety: H850 dehydrator from Olam Spices & Vegetables, Hanford, CA, USA) were sown. The beds were destroyed after first harvest in 2016. Soil was re-cultivated and the biochar treated plots were split in the middle. Half of the plot was amended with another biochar application (~29 Mg ha^{-1}) using the same technique used the year before. The first-year biochar application only will be referred to as the low-char treatment (29 Mg ha^{-1}) and two years of biochar applications (total 58 Mg ha^{-1}) as the high-char treatment. Beginning in the second year, the following nine treatments are investigated:

1. 50% irrigation, Control (no biochar amendment)
2. 50% irrigation, Low char (biochar applied in 2015 only at 29 Mg ha^{-1})
3. 50% irrigation, High char (biochar applied in both 2015 and 2016 at total 58 Mg ha^{-1})
4. 75% irrigation, Control
5. 75% irrigation, Low char
6. 75% irrigation, High char
7. 100% irrigation, Control
8. 100% irrigation, Low char
9. 100% irrigation, High char

Information about the field operation is summarized in Table 1. For all treatments, the same fertilization regime was used. Urea was applied via surface broadcast before forming beds. During the growing season, urea and ammonia nitrate containing 32% N with half from urea and half from ammonium nitrate (UAN32) was applied with irrigation water four times in 2016, but weekly (thirteen times) in 2017. Irrigation was stopped about one month before harvest.

2.2. Sampling and measurements

During the first two years (2016 and 2017), NH_3 volatilization, N_2O emission, and N concentration changes in soil pore water were measured. In 2016, NH_3 and N_2O emissions were sampled up to four times a week following each fertilization event and sampling frequency was reduced with time as emission rates decreased. In 2017, NH_3 and N_2O emissions were sampled two or three times each week. Weekly soil pore water and seasonal (early spring and after harvest) soil samples in profile were collected to monitor N concentration changes during the first two years. In the third year, direct N leaching was collected using resin collectors. Different combinations of treatments were selected for monitoring gas emissions each year. In 2016, two irrigation levels (100% and 75%) with or without biochar treatments were selected. All three irrigation levels and two biochar amendment rates plus the control were selected for NH_3 in 2017 and N leaching in 2018. For N_2O emissions, two irrigation levels (50% and 100%) for all three biochar treatments were monitored.

2.2.1. NH_3 volatilization

Ammonia volatilization was measured using the original design and later a modified version of semi-static (open) chamber described in Jantalia et al. (2012). For the first year, the chambers were made of 2 L polyethylene terephthalate (PET) soda bottles following the procedures of Jantalia et al. (2012). Since the PET chambers were easily deformed, they were replaced with chambers constructed from polyvinyl chloride (PVC). The PVC chamber was made from PVC pipe (~15 cm id x 30 cm h). A PVC pipe cap was modified for each chamber with a 6 cm long and 1.3 cm i.d. tube installed through the center of the cap. Inside the chamber is a central wire support with an attachment hook at the top, a foam support hook, and a horizontal loop at the bottom end to hold a 60-mL plastic jar containing an acidic trapping solution that was described in Jantalia et al. (2012). The acidic trapping solution was 1 M sulfuric acid (H_2SO_4) plus 4% glycerol ($C_3H_8O_3$) in deionized water. The acidic trapping solution was prepared by adding 55.5 mL of 18 M H_2SO_4 (certified ACS plus), and 40 mL $C_3H_8O_3$ (USP/FCC) (both chemicals from Fisher Scientific, Pittsburgh, PA, USA) to 600 mL deionized water before diluting to 1000 mL with deionized water. A strip (25 cm × 2.5 cm × 3 mm) of polyfoam (Foam Factory, Macomb, MI, USA) had one end soaked in the acidic trapping solution and the other end was pulled up and fastened to the foam support hook. The large surface area of the foam strip is to increase exposure to and trapping NH_3 by dissolving into the acid solution on the foam to form NH_4^+. The trapping was done for 24 hours. The foam was rinsed three times with 50 mL of the acidic trapping solution, rinses and original solution were combined, diluted to 250 mL, and analyzed for NH_4^+ using an Astoria 2 Analyzer (Astoria-Pacific Inc., Clackamas, OR, USA) with the colorimetric method described by Mulvaney (1996). Average NH_3 volatilization rate during a sampling (f_{NH3}, g m^{-2} h^{-1}) was calculated by

$$f_{NH3} = \frac{M_{NH3}}{\Delta t\ A} \tag{1}$$

where M_{NH3} was the total amount of NH_3 (g) trapped in the acid solution, Δt was the sampling time (h), and A was the surface area (m^2) covered by the chamber. Cumulative or total NH_3 volatilization during the growing season (T_{NH3}, g ha^{-1}) was estimated by

$$T_{NH3} = \sum_{i=1}^{n} f_{NH3^i} \times \Delta T_i$$

where i and n represent the first and the last of sampling during growing season. The percentage of volatilization referring to fertilization was calculated by the cumulative NH_3 loss divided by total N applied. Ammonia trapping efficiency of the PVC chamber was 77% of that by the PET chamber based in lab tests. Both flux and cumulative emissions for the second-year measurements were calculated using the correction factor so the data between the two years are comparable.

2.2.2. N_2O emissions

Nitrous oxide emissions were measured using passive chamber with an auto-sampler method (Gao et al., 2017). During sampling, the chamber was placed on a metal base that was inserted into soil for approximate 5 cm depth. Upon closure of the chamber (i.e., by sealing the chamber top to the base) 20 mL of gas inside the chamber were collected using gas-tight syringes every 30 min for up to 1.5 hours. A linear increase of N_2O concentration inside the chamber was observed. Each gas sample was preserved by injecting into a 10-mL glass vial that was previously flushed with ultra-zero grade air to reduce background N_2O level. The sample was analyzed for N_2O concentration using a gas chromatograph (Agilent Technologies 6890N Network GC System) equipped with a gas autoinjector (Agilent Technologies G1888 Headspace Sampler) , a HP-PLOT Q column, and a micro electron capture detector (all from Agilent Technologies, Santa Clara, CA, USA). Emission flux (μg m^{-2} h^{-1}) was calculated by:

$$f = \frac{VdC}{Adt} \tag{3}$$

or

$$f = b\frac{V}{A} \tag{4}$$

where b is the slope of a linear regression for N_2O concentration (μg N_2O-N m^{-3}) increase within the chamber with time (h), *V* is the chamber volume (m^3), *A* is the surface area (m^2) covered by the chamber. Cumulative emission loss was calculated similarly as NH_3 volatilization (Eq. 2). Sampling for both NH_3 and N_2O emission began prior to pre-plant fertilizer application (in November 2015) to obtain a baseline, winter rain season (no irrigation), and after irrigation (growing season) until irrigation was terminated for harvest.

2.2.3. Soil pore water and soil sampling

Soil pore water samples were collected using porous ceramic cups that were installed at two soil depths (25 and 50 cm) following the method described in Curley et al. (2011). Difficulties in sampling pore water increased with time, it was especially difficult from 50% and 75% irrigation treatments to obtain enough volume for analysis. Towards the end of the growing season very little pore water could be obtained in most locations due to clogging or drying out of the sampling suction cup. Only enough data were obtained for reporting from March to May 2016. The pore water pH and electrical conductivity (EC_{25c}) were determined for samples with sufficient volume using an Oakton pH 700 meter (Oakton Instruments, Vernon Hills, IL, USA) and an Orion Model 150 conductivity meter (Thermo Fisher Scientific, Waltham, WA, USA). Soil samples in 1-m soil profile at 20 cm increment were sampled before and after each growing season. Samples were analyzed for total soil organic C (SOC) and N (SON) using LECO Trumac CN Analyzer (LECO Co., St. Joseph, Michigan, USA). The samples were also extracted with 2M potassium chloride (KCl, certified ACS, Fisher Scientific, Pittsburgh, PA, USA) (Knepel, 2003). Water samples or the extractants were analyzed for mineral N species (NH_4^+ and NO_3^-) using colorimetric methods (Mulvaney, 1996) on the Astoria 2 Analyzer (Astoria-Pacific Inc., Clackamas, OR, USA). Most of the later samples were analyzed only for NO_3^- because NH_4^+ was found to be <1% in pore water samples or <5% in soil extracts.

2.2.4. NO_3^- leaching

In the third year of the field experiment, it was decided to measure direct N leaching or that likely moved out of the root zone. The resin collector method was adopted based on the information on “how to make resin bags” from Roots Lab at Penn State University (2017). After testing several ion exchange resins on trapping efficiency for NO_3^-, AMBERLITE™ PWA5 Ion Exchange Resin (drinking water grade, DuPont™, 2019) was selected to construct the collectors. The resin is a NO_3^- selective, macroreticular, and strong base anion exchange material that is used for removing NO_3^- from potable water. Preparation of the collectors followed the procedure described by Penn State University (2017). Since most of the onion roots were in the top 30 cm of soil during fertilization period (UGA, 2017), the collectors were buried at 25 cm depth by assuming that N moved to this depth would likely be leached out. Four replicated collectors were installed in each treatment plot. Using a backhoe, a 100 cm-wide trench was excavated to a depth of 40-55 cm on the side of the soil bed. At 25 cm below the surface of the soil, a lateral tunnel (50 cm wide, 30 cm deep towards the bed center, and 10 cm high) was dug by hand that allowed for the placement of four collectors side by side below the surface drip irrigation line. The collectors were placed at 25 cm depth and packed tightly with soil from below. The trench was backfilled with soil. The collectors were buried on 5 January 2018 and retrieved after harvesting on 7 September 2018. About 136 mm precipitation (88% of the 2017-2018 total season precipitation 155 mm) was received after the collectors were buried and before irrigation began. Nitrogen collected on the resin included soil N leached by rain before (Fig. 1) and by irrigation during the growing season. After retrieval, all of the resin from each collector was homogenized and a fraction was extracted with 2M KCl for three times to ensure >90% recovery based on lab tests. The potential leaching loss during the collection period was estimated.

2.3. Statistical analysis

A MIXED procedure was used for tests of the gas (NH_3 and N_2O) emissions and leaching data using SAS® version 9.4 (SAS, 2013). Irrigation level, biochar treatment, and their interaction are the fixed effects and the replications (reps) and irrigation or biochar by reps are random effects. For soil profile N data analysis, a MIXED procedure was used to fit a repeated measure, mixed model. The fixed effects are irrigation level, biochar treatment, soil depth, and their interactions. The random effects are replications (rep), and all interactions (irrigation × rep, biochar × rep, and irrigation × biochar × rep). The three-way interaction (irrigation × biochar × rep) was used to define the experimental units for incorporating a first order, and autoregressive covariance structure among the repeated measures in depth. Focus was on the significant irrigation type × biochar interaction for which the least square means and their 95% confidence intervals were obtained. For N leaching data, because no significant fixed effects were observed, differences from the control was performed using Dunnett’s adjustment for multiplicity.

3. Results

3.1. NH_3 and N_2O emissions

Ammonia volatilization and N_2O emission measurements during the growing seasons (early spring fertilization to harvest) in 2016 and 2017 are shown in Fig. 2 and 3, respectively. Data from beginning of the field experiment to the first spring fertilization/irrigation when all plots received rain only showed that both NH_3 and N_2O emission rates were low with no significant differences between control and biochar treatments. From November 2015 to March 2016, NH_3 volatilization and N_2O emission rates for the control and biochar treatment were 17.3 and 16.6 μg N m^{-2} h^{-1}, and 4.8 and 4.6 μg N m^{-2} h^{-1}, respectively. These values were substantially lower than those measured during growing season, especially after each fertilization event (Fig. 2a, 2c).

Before first fertilization in early spring 2016, NH_3 volatilization was as low as 0.1–0.2 mg m^{-2} h^{-1}. Immediately following fertilization on 28 March, a peak of NH_3 volatilization was observed (Fig. 2a), which dropped quickly. The peak volatilization was repeated following the second fertilization (25 April) when temperature increased. Following the third fertilization (16 May), the peak was much smaller, possibly due to higher plant uptake and plant shading. A similar pattern was observed for N_2O with a peak observed following fertilization (Fig. 2c), but with higher variability than that of NH_3. In 2017 due to weekly fertilization, fluctuation in NH_3 and N_2O emission rates were observed weekly (Fig. 3a, 3c). Higher peaks in the early growing season appeared from 100% irrigation level for NH_3 in 2016 and both gas emissions in 2017.

Total NH_3 volatilization loss during the irrigation growing season ranged from 11.4–18.2 kg N ha^{-1} in 2016, higher than those found in 2017 (9.4–10.5 kg N ha^{-1}) (Fig. 2b, 3b). Estimates of total N_2O emissions were similar between the years ranging from 0.13–0.22 kg N ha^{-1} (0.06–0.1% of total N applied) in 2016 and 0.18–0.23 kg N ha^{-1} (0.08–0.1% of the N applied) in 2017 (Fig. 2d, 3d). Total NH_3 volatilization losses were higher, accounting for 5.1–8.1% in 2016 and 3.9–4.5% in 2017 of the total N applied. The data show higher NH_3 loss in 2016 when fertilizer was applied a few times in a large quantity compared to the weekly application in smaller amounts in 2017, but there were no apparent differences in N_2O emissions.

There were no significant biochar or irrigation (between 75% and 100% levels) treatment effects on total NH_3 or N_2O emission loss, but significant irrigation × biochar interaction was identified in 2016 (Table 2). In 2017, no significant differences were observed among any of the treatment effects for total NH_3 loss, but significant biochar and irrigation interaction on N_2O was identified (Table 3).

3.2. Soil pore water N

Available data on soil pore water N during the first onion growing season are shown in Fig. 4. Reported is NO_3^- concentration because NH_4^+ accounted for only 0.3–0.5% of the total mineral N species. Due to many missing data points, the figure only shows the trend of how pore water N concentration changed with time at the two soil depths (25 and 50 cm). The N concentration was initially high but continued declining throughout the growing season at a faster rate at 25 cm depth than that at 50 cm. Towards the end of the growing season, N concentration at 25 cm depth from 100% irrigation was substantially lower than that from 75% irrigation. Figure 5 shows impact of biochar incorporation on soil pore water pH and electrical conductivity (EC_{25c}). Biochar treatments at 75% irrigation resulted in the highest pH, higher than the control all season long at 25 cm depth. Biochar treatment at 100% irrigation level had similar pH values as the control possibly due to dilution factor (Fig. 5a). The average pH of the biochar treatment increased by 0.4 unit at 75% irrigation and 0.2 unit at 100% irrigation, compared to the respective control. Lower irrigation level show higher EC_{25C} values at 25 cm depth (Fig. 5b), but higher values are shown from 100% irrigation level at 50 cm depth (Fig. 5d) due to the leaching influence.

3.3. Soil N

Changes in NO_3^- concentration in soil profile before establishing the field treatments to the end of the two growing seasons are shown in Fig. 6. The field had high residual NO_3^- concentration from the previous crops, especially in the top 50 cm soil. After the winter rain season (24 March 2016), surface soil N concentration decreased to below 1 mg kg^{-1} indicating that most of the residual N had leached out. By the end of first growing season (August 2016, Fig. 6a), NO_3^- distribution in the profile showed significant differences among irrigation treatments: highest in the 50% irrigation and lowest in the 100% irrigation. The concentration was the highest in surface soil at 100% and 75% irrigation levels, but decreased then increased slightly with soil depth increases. At 50% irrigation level, the concentration increased as soil depth increased up to 40 mg N kg^{-1}, significantly higher than those at lower irrigation levels. The accumulated NO_3^--N, was reduced to < 2 mg N kg^{-1} by March 2017 after winter rain (Fig. 6b). After the second (2017) growing season, the N profile showed a similar pattern as that in 2016. The data clearly show that NO_3^- accumulated during growing season that depended highly on irrigation level, but the accumulated mobile N was mostly leached by winter precipitation. Statistical analyses showed that irrigation, soil depth, and irrigation × soil depth interaction had significant impact on the soil N data, but biochar and any interactions with biochar had no significant effects for both 2016 and 2017 (Tables 4 and 5).

3.4. Nitrogen leaching

Figure 7 provides the total N leaching collected using resin collectors buried under the beds from early January to September 2018. Statistical analysis did not show any significant effects of irrigation, biochar, or their interaction due to large variations. When biochar main effects were compared with the control only in statistical analysis, the leaching loss from the low biochar treatment versus that from the control had a p value 0.081. Figure 7 shows that most of the high N leaching was associated with biochar treatments and all controls showed lower leaching.

3.5. Onion bulb yield

Statistical analyses on fresh bulb yield showed that for both 2016 and 2017, biochar treatment had no significant effect but irrigation and interaction with biochar significantly affected the yield (Table 6). The yield data and differences among treatments are provided in Table 7. In 2016, the yield at 50% irrigation level regardless of biochar treatment were significantly lower than those at 75% and 100% irrigation with no significant differences between the 75% and 100% irrigation levels. In 2017, irrigation with biochar treatment showed a similar trend, but the control at 50% irrigation showed a higher yield than biochar treatments. The high-char at 100% irrigation level gave significantly higher yield than some of the treatments at 75% irrigation level.

4. Discussion

4.1. NH_3 volatilization

The two-year field measurement showed a higher NH_3 volatilization during the first year than the second year, but no significant effects of biochar or irrigation treatment were found on cumulative NH_3 volatilization loss. Higher emission flux following fertilization events were observed the first year from biochar treatments (Fig. 2a), which can be explained by the higher soil water pH caused by biochar treatment (Fig. 5a). The biochar used in this study has a higher pH (9.5) that favor NH_3 formation, but the ability of biochar to adsorb NH_4^+ could potentially reduce NH_3 volatilization. Both roles were believed to be at play and resulted in no significant biochar effects. Laboratory test showed that the biochar has an adsorption capacity of < 1.0 mg N kg^{-1} for NH_4^+ (unpublished). The amount of biochar applied to the soil in this study (29–58 Mg ha^{-1}) could retain only 30–60 kg NH_4^+-N ha^{-1}. Ammonium is not stable in most aerobic conditions and can quickly oxidize to NO_3^-. Cai et al. (2016) observed that biochar did not affect urea hydrolysis rate nor the nitrification rate except that the amount of N subjected to nitrification appeared to be reduced, partially due to adsorption. The field data suggest that the role of adsorption in reducing NH_3 volatilization from the drip irrigation/fertigation system is limited. Similar results on increased NH_3 volatilization by biochar were reported (He et al., 2018; Wei et al., 2020). Sha et al., (2019) reviewed literature findings and concluded that the pH of soil and biochar were crucial factors affecting NH_3 volatilization and biochar application to acidic soil could stimulate NH_3 loss.

The two year field data suggest that NH_3 volatilization was more affected by the frequency and quantity of UAN32 applied and larger doses led to higher volatilization loss in 2016 (up to 8% of total applied) compared to that in smaller doses in higher application frequency in 2017 (<5% of N applied). Fertilization frequency and the amount of fertilizer applied each time should be considered to minimize the loss. In this study drip tubing was placed on soil surface, and subsurface fertigation is another strategy as studies have shown that deeply placed fertilizers reduced NH_3 losses (Rochette et al., 2013; Beeman et al., 2018).

4.2. N_2O emissions

Nitrous oxide emission from the two-year field measurements did not show significant biochar or irrigation effect, but significant interactions between biochar and irrigation were identified (Tables 2 and 3) suggesting that biochar has altered soil conditions under different irrigation level that influenced microbial processes. Nitrous oxide is produced through several pathways during nitrification and denitrification that are mediated by microbes (Wrage et al., 2005). Denitrification under higher soil moisture condition has led to much higher N_2O emissions than under low soil moisture that favors nitrification process (Cai et al., 2016). The ability of biochar to retain higher soil moisture in microsites could promote more denitrification especially at high irrigation levels (Fig. 2).

Studies of biochar effect on N_2O emissions vary greatly. Some showed positive emission reduction (Zhang et al., 2012; Thangarajan et al., 2018), but others reported no effects (Suddick and Six 2013; Dicke et al., 2015; Sun et al., 2017) or even increased N_2O emissions (He et al., 2018; Yoo et al. 2018). The inconsistent results are due to the differences in studied conditions including soil and biochar properties. Different hypotheses have been proposed for biochar to reduce N_2O emissions, such as N immobilization, enzymatic activities alteration, and potentially toxic effect on microbial communities (Cayuela et al., 2014). Cai et al. (2016) illustrated that a biochar with a pH of 7.6, which is lower than most biochar products, did not show effects on nitrification rate except that the amount of N subject to nitrification was reduced. The complexity of the biochar-soil N interaction, moisture condition, and temperature all affect N_2O production.

4.3. Effects of irrigation level vs. biochar on NO_3^- mobility in soil

Nitrate was the dominant mineral species and the major source of N leaching in this study. The higher mobility of NO_3^- in the soil was clearly demonstrated by soil pore water samples collected during the growing season with >99% as NO_3^- (Fig. 4). Soil samples collected in the field before biochar treatment showed 99% as NO_3^- in 2M KCl extracts (including both soluble and adsorbed NH_4^+). The concentration was also very high (47–70 mg NO_3^--N kg^{-1}) in the top 50 cm soil (Fig. 6). Analysis of surface (0–50 cm) fresh soil samples in early spring indicated 99% of the N disappeared that can only be attributed to leaching by winter rain. Further examination in early spring 2016 showed that 66% (±17%) and 84% (±14%) of N was NO_3- in 2M KCl extracts at soil depth 0–25 cm and 25–50 cm, respectively. The increased percentage of NH_4^+ in surface soil implies some retention of NH_4^+ by the incorporated biochar.

Nitrate status in the Hanford sandy loam was affected by irrigation level or precipitation and plant uptake. The biochar used in this study showed no adsorption capacity for NO_3^- from solution concentration ranging from 5–50 mg N L^{-1} (unpublished). Higher irrigation level (e.g., 100%) showed lower accumulation of N in the soil profile attributed to both downward movement and plant uptake as the 100% irrigation produced consistently high yield (Table 7). Similarly, the highest accumulation of N in soils at 50% irrigation was due to reduced leaching and lower plant uptake. The same pattern was repeated in two consecutive years. The data suggest that both N fertilization and irrigation could be decreased for onion production to reduce leaching and address the regional groundwater contamination problem.

4.4. N leaching

The leaching shown in Fig. 7 was partially from late rains and irrigation during the growing season, but little is known regarding how much NO_3^- from the previous cropping had been leached by the time the resin collectors were buried because the majority of the annual precipitation fell after the collectors were installed. Figure 6 shows the irrigation effect on N accumulation during growing season and most of N leached out by winter rain. Winters of 2015-2016 and 2016-2017 were considered wet years and that of 2017-2018 was a normal year in the Central Valley of California (Fig. 1). The data suggest that most of the N accumulated in the soil can be easily washed out in the typical sandy loam soil in the studied region and biochar amendment at rate as high as 58 Mg ha^{-1} did not reduce leaching. Most of the high leaching losses appear to be associated with biochar amendment (Fig. 7). The possible mechanisms of biochar to reduce N leaching include 1) increase in cation exchange capacity (CEC) or the ability of biochar to adsorb N species especially NH_4^+, and 2) increase in soil water holding capacity (Glaser et al., 2012). Although some studies reported that biochar can adsorb NO_3^- depending on pyrolysis temperature and post treatment (Zhao et al., 2018; Sanford et al., 2019), the biochar used in this study showed little adsorption for NO_3^-. The biochar can adsorb NH_4^+, which can convert to NO_3^- within days under aerobic conditions (Cai et al., 2016).

Biochar can increase soil water holding capacity that would reduce leaching as demonstrated in some studies (Basso et al., 2013; Xu et al., 2016). Fischer et al. (2019) synthesized literature-derived data and found that biochar increased long-term evapotranspiration rates and therefore plant water availability by increased soil water retention capacity especially in water-limited regions. An increase in water holding capacity by the biochar in the field was observed. At -33 kPa, soil water content was determined to be 12.1%, 13.3%, and 14.3% in surface soils for the control, the low char, and the high char treatments, respectively. The effects of biochar on soil water are two-fold: it can increase water retention to reduce leaching, but it can also either increase or decrease water infiltration rate that affects leaching depending on soil type. Barnes et al. (2014) found that 10% biochar amendment rate decreased the saturated hydraulic conductivity (K_{sat}) by 92% in sandy soil but increased the K_{sat} by 328% in clay-rich soil. Bulk density of a biochar treated sandy loam was up to 9% less than non-treated control (Basso et al., 2013). Li et al. (2018) found there was a balance between NO_3^- leaching and K_{sat} based on biochar amendment rate and application depth. Li et al. (2018) found that low amendment rate reduced leaching and decreased K_{sat}, but high amendment rate increased leaching because of increased K_{sat}. In this study, bulk density measured about five months after biochar incorporation were 1.40 and 1.59 g cm^{-3} at 15 cm and 30 cm depth, respectively, for the control that dropped to 1.26 and 1.51 g cm^{-3}, respectively, for the low biochar treatment. The increased pore volume could have increased K_{sat} or leaching.

The Hanford sandy loam has a low SOC, low EC_{25C}, high bulk density, and slow infiltration rate due to a surface seal formation and gypsum or other amendment is often needed to improve water penetration (Oster et al., 1984; Ajwa and Trout, 2006). The biochar incorporation reduced bulk density, increased pore volume, and likely enhanced water infiltration rate to increase leaching. The low water infiltration rate soil may also involve unstable preferential flow during redistribution (Wang et al., 2003). The low char treatment shows NH_4^+ retention, while the high char treated soil shows infiltration rate increase. Similar scenarios on N leaching and infiltration rate affected by biochar amendment rate were explained well by Li et al. (2018).

More soil column studies (e.g., Knowles et al., 2011; Xu et al., 2016; Li et al., 2018) and few field studies (Güereña et al., 2013; Haider et al., 2017) illustrated that biochar significantly reduced N leaching. The reduction was apparent in a sandy soil amended with biochar at 15–30 Mg ha^{-1} (0–15 cm depth) by greater NO_3^- stocks in the top soil and reduced stock in subsoil (Haider et al., 2017). Biochar incorporation increased N retention and reduced leaching in a manufactured or waster-derived soil by increasing retention and immobilization of N (Schofield et al., 2019). Similarly adding biochar to subsurface flow constructed wetlands improved NH_4^+ removal (50-64%) and total N removal (82-86%) by altering microbial community (Deng et al., 2019). The effects of biochar to reduce contaminant movement is apparent but changes in environmental or soil physical conditions determines the outcome.

4.5. Evaluation of biochar as an agronomic practice and research gaps

The important roles of biochar are C sequestration by increasing C storage in soil and improvement of soil productivity for more biomass production. Biochar treatments in the current study did not show significant increase in SON (data not shown), but increased SOC significantly by 0.4–0.9% in surface soil after 1-2 years of application at 29 Mg ha^{-1} each year (Fig. 8). These numbers translate to SOC increase about 400–900 kg ha^{-1}, which is only a fraction (2-3%) of biochar applied. This indicates that most of the biochar applied had not been broken down to the SOC fraction. Many studies also showed improvement on SOC by biochar (Zhang et al., 2012; Suddick and Six, 2013) because biochar can suppress the long-term turn-over of SOM and promote C sequestration (Schofield et al., 2019). Although biochar increases SOC, reduces gas emissions, decreases leaching, and improves yield, these attributes have not overcome the unwillingness by growers to adopt the use of biochar. Meta-analysis showed whether biochar addition increase NH_3 volatilization is highly dependent on effects on soil pH and as most biochar have high pH, acidic biochar can benefit for reducing the volatilization (Sha et al., 2019). Biochar application in soil reduced N_2O emissions more strongly in paddy or sandy soils but the effect was not long-term and was negligible after one year (Borchard et al, 2019). Soil NO_3^- concentrations are generally unaffected by biochar amendment; leaching can be reduced only when significant increase in total N retention from biochar prevails (Borchard et al., 2019; Deng et al., 2019; Schofield et al., 2019). Biochar can either improve (e.g., Zhang et al., 2012) or have no effects (e.g., Haider et al., 2017; Gao et al., 2019) on crop yield. Adding biochar to acidic soil increased yield by raising soil pH (Jin et al., 2019). Crane-Droesc et al. (2013) summarized that soil CEC and OC were strong predictors of yield improvement with soils in poor conditions associated with positive response. These can explain the large variations, including from this field study, on the various response of field parameters to biochar amendment. This study suggests that biochar's influence on crop production and N dynamics is strongly affected by irrigation management. The strong impact by irrigation may lead to an underestimation of biochar effects. Future examination on biochar effects must specify irrigation or moisture conditions.

As a C sequestration strategy, biochar amendment involves significant costs. Timmons et al. (2016) estimated net carbon sequestration cost by biochar ranged from \$82–119 ton per of CO_2 with a mean of \$102 per ton CO_2 assuming biochar increased crop yield by 10%. With no yield increase, the costs would be higher. Unless carbon credit can be traded in, the cost barrier will continue hindering adoption of biochar as a feasible practice in agricultural field. Significantly reducing biochar production costs, such as using soil pit kiln suggested by Schmidt (2014) or other on-site methods, would promote the development of a sustainable agricultural practice. Cost-benefit analysis is necessary in promoting biochar amendment practice such as by Pandit et al. (2018) who determined that optimal biochar application dose was 15 t ha^{-1} after considering all C price scenarios for soils with poor water and nutrient retention in Nepal. Other innovative ideas such as using biochar bound urea (Shi et al., 2020) to improve plant growth and nutrient management should be explored.

There has been little research to evaluate the pros and cons on producing biochar or direct return of biomass (crop residues or woodchips) to soils. The latter will have much lower costs and possible long-term impact on soil health. Producing biochar resulted in immediate release of CO_2 (usually >50%) from pyrolysis; the char may persist a long time in soil, which remains unknown. Biomass in soil will be subject to decomposition that releases CO_2 gradually but the energy source for soil microbes provides the key to maintaining the overall soil health. More research efforts to answer these questions can assist long-term decision making on how biochar should be used to provide essential benefits in agricultural fields.

5. Conclusions

Based on the data collected from an onion field, the benefits of biochar for reducing N loss including emissions and leaching or improving yield were not observed in the irrigated production system although biochar significantly increased SOC. No effect on NH_3 volatilization could be due to competing effects 1) the increased pH causes a shift in the NH_4^+ / NH_3 equilibrium (Eq. 5) to produce more NH_3 but 2) the biochar is much more effective in adsorbing NH_3 leading to a decrease in NH_3 volatilization.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (5)$$

No effects on N_2O emissions in the field is more complicated by biochar affecting microbial communities, C turnover, and other microbial processes. Biochar showed a tendency to increase N leaching because of its inability to adsorb NO_3^-. Biochar showed limited ability to retain NH_4^+, but likely increased water infiltration rate by decreasing soil bulk density that resulted in increased leaching. For the soil with a low SOC and high bulk density, irrigation showed a profound impact on yield, N accumulation, and N leaching. Biochar benefits for soil improvement and crop production might be overshadowed by the irrigation treatment. Future research to evaluate biochar benefits must consider irrigation level and their interaction under specific conditions.

The high costs of biochar production are major hurdles for adoption as a common agronomic practice. Efforts should be directed more to low-cost methods in production and application in agricultural fields, and some innovative approaches should be explored to use biochar that can directly improve nutrient use efficiency and reduce loss to the environment as well as promote long-term soil improvement. Low-cost biochar versus direct biomass return to soil should be evaluated for their differences in C sequestration, soil health, and ecosystem performance.

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Table 1. Onion-biochar experiment field operations during 2016 and 2017.

Growing season	2016	2017
Biochar treatment, pre-plant fertilizer; bed formation	November–December 5, 2015	November–December 1, 2016
Planting date	9 December 2015	5 December 2016
Onion variety	Dehydrator H850 from Olam West Coast Inc.	Dehydrator H850 from Olam West Coast Inc.
Fertilizer application	Pre-plant fertilizer N (34 kg urea-N ha^{-1}) and P; four times N (N-pHuric† and UAN 32‡) from 29 January to 16 May 2016; 45 kg N ha^{-1} (N-pHuric) on 29 January 67 kg ha^{-1} on 28 March; 56 kg ha^{-1} on 25 April; and 22 kg ha^{-1} on 16 May 2016. Total N applied: 224 kg ha^{-1}	Pre-plant fertilizer N (24 kg urea-N ha^{-1}) and P; Weekly N (UAN 32) application from 4 April through 26 June 2017: 34 kg ha^{-1} on 4 April; 11 kg ha^{-1} weekly application from 12 April - 8 May; and 17 kg ha^{-1} weekly application from 15 May through 26 June 2017. Total N applied: 232 kg ha^{-1}
Harvest Dates	10 August for 50% irrigation, 24 August for 75% irrigation, and 7 September for 100% irrigation treatment	15 August for 50% irrigation, and 6 September for 75% and 100% irrigation treatments.

† N-pHuric, urea sulfuric acid (urea sulfate) 5/49 (15-0-0-16S, 49% sulfuric acid);

‡ UAN32, urea and ammonia nitrate containing 32% N with half from urea and half from ammonium nitrate).

Table 2. ANOVA Mixed Procedure tests of the fixed effects on NH_3 and N_2O cumulative emission losses during 2016 growing season.

	Type 3 tests of fixed effects			
Effect	Num of DF	Den DF	F Value	Pr>F
		NH_3		
Irrigation†	1	5.24	1.81	0.2333
Biochar treatment‡	1	5.24	0.15	0.7134
Irrigation × biochar	1	5.24	6.89	0.0447
		N_2O		
Irrigation†	1	2	1.81	0.3106
Biochar treatment‡	1	4	1.56	0.2800
Irrigation × biochar	1	4	8.35	0.0445

† Irrigation treatment: 75%, 100%

‡ Biochar treatment: control (no biochar), and biochar (applied in 2015)

Table 3. Mixed procedure for tests of the fixed effects on NH_3 and N_2O cumulative emission losses during 2017 growing season

	Type 3 tests of fixed effects			
Effect	Num of DF	Den DF	F Value	Pr>F
		NH_3		
Irrigation†	2	5.8	0.90	0.4578
Biochar treatment‡	2	11.2	0.86	0.4487
Irrigation × biochar	4	11.2	0.41	0.8002
		N_2O		
Irrigation†	1	4	0.13	0.7379
Biochar treatment‡	2	8	4.29	0.0541
Irrigation × biochar	2	8	15.64	0.0017

† Irrigation level: 50%, 75%, and 100% for NH_3; 50% and 100% for N_2O.

‡ Biochar treatment: control (no biochar), and low-biochar (applied in 2015 only), and high-biochar (applied in both 2015 and 2016)

Table 4. Mixed procedure for tests of the fixed effects on soil nitrate-N concentrations at the end of 2016 growing season

	Type 3 tests of fixed effects			
Effect	Num of DF	Den DF	F Value	Pr>F
Irrigation†	2	26	14.03	<0.0001
Biochar treatment‡	3	26	1.83	0.1664
Biochar trt × irrig	6	26	0.77	0.5971
Soil depth§	4	93.4	13.81	<0.0001
Biochar trt × soil depth	12	93.9	0.91	0.5449
Irrig × soil depth	8	94	7.71	<0.0001
Biochar trt × irrig × soil depth	24	92.3	1.08	0.3862

† Irrigation level: 50%, 75%, and 100%
‡ Biochar treatment (Trt): control (no biochar), and low-biochar (applied in 2015 only), and high-biochar (applied in both 2015 and 2016)
§ Soil depth: 0–100 cm at 20 cm increment

Table 5. Mixed procedure for tests of the fixed effects on soil nitrate-N concentrations at the end of 2017 growing season

	Type 3 tests of fixed effects			
Effect	Num of DF	Den DF	F Value	Pr>F
Irrigation†	2	28.8	15.85	<0.0001
Biochar treatment‡	4	28.8	0.99	0.4227
Biochar trt × irrig	8	28.8	0.65	0.7280
Soil depth§	4	96.6	38.60	<0.0001
Biochar trt × soil depth	16	105	1.29	0.2161
Irrig × soil depth	8	103	2.25	<0.0001
Biochar trt × irrig × soil depth	32	101	1.14	0.2999

† Irrigation level: 50%, 75%, and 100% of a reference level
‡ Biochar treatment (Trt): control (no biochar), low biochar (applied in 2015 only), and high biochar (applied in both 2015 and 2016)
§ Soil depth: 0–100 cm at 20 cm increment

Table 6. Mixed procedure for tests of the fixed effects on yield in 2016 and 2017

	Type 3 tests of fixed effects			
Effect	Num of DF	Den DF	F Value	Pr>F
		2016		
Irrigation†	2	6.04	44.65	0.0002
Biochar treatment	3	17.2	1.68	0.2090
Irrigation × biochar	6	17.2	3.99	0.0111
		2017		
Irrigation†	2	28	31.53	<0.0001
Biochar treatment	4	28	0.91	0.4740
Irrigation × biochar	8	28	0.0138	0.0138

† Irrigation level: 50%, 75%, and 100% of a reference level
‡ Biochar treatment: control (no biochar), low biochar (applied in 2015 only), and high biochar (applied in both 2015 and 2016)

Table 7. Fresh onion bulb yield for the first two growing seasons.

Treatment	Fresh bulb yield (kg ha^{-1}) †	
	2016	2017
50% irrigation, control	40,453 (a)	39,239 (a)
50% irrigation, low char	37,030 (a)	27,358 (b)
50% irrigation, high char	-	29,917 (b)
75% irrigation, control	48,465 (b)	36,767 (ac)
75% irrigation, low char	55,312 (b)	42,017 (ad)
75% irrigation, high char	-	36,767 (ac)
100% irrigation, control	53,358 (b)	42,353 (ad)
100% irrigation, low char	55,236 (b)	40,984 (acd)
100% irrigation, high char	-	44,694 (de)

† Means following by different letters in the same column indicate significant differences (p<0.05).

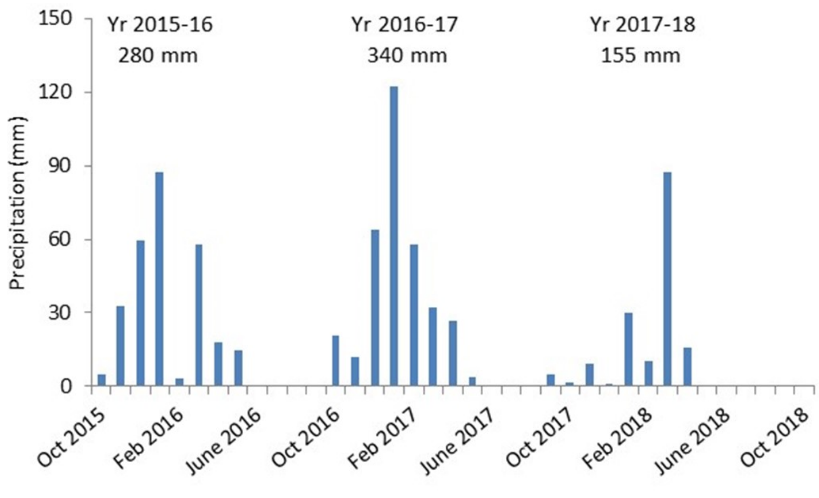

Fig. 1. Daily precipitation received during the onion field experiment investigating effects of biochar and irrigation on N dynamics.

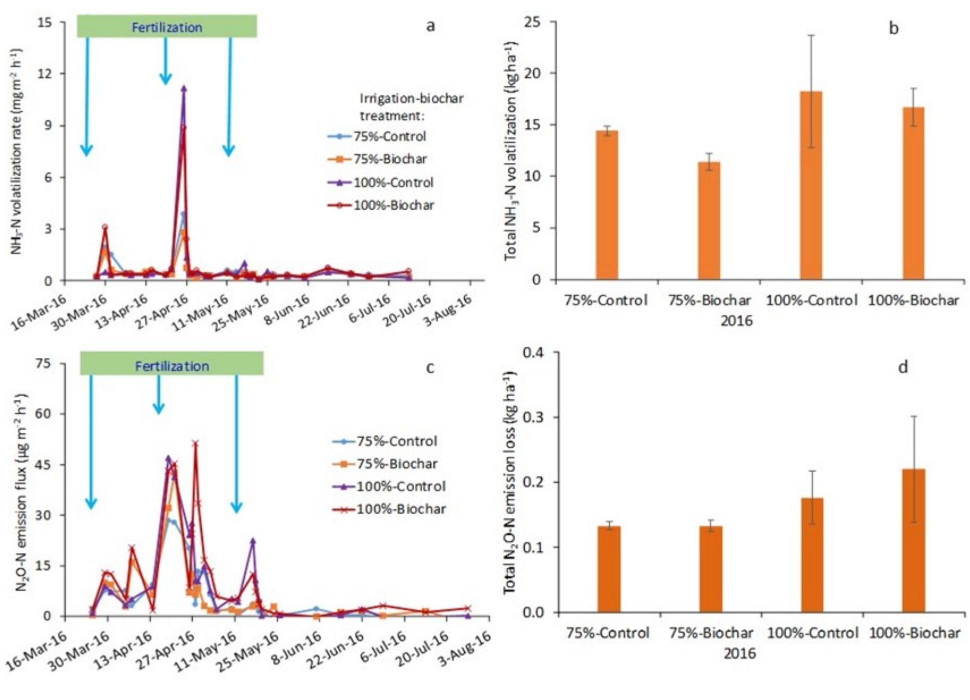

Fig. 2. Emission rates and total loss of ammonia (NH_3) and nitrous oxide (N_2O) measured during 2016 onion growing season. Error bars for rate and flux are omitted for improved readability. Error bars for total loss are standard deviation of three estimated values.

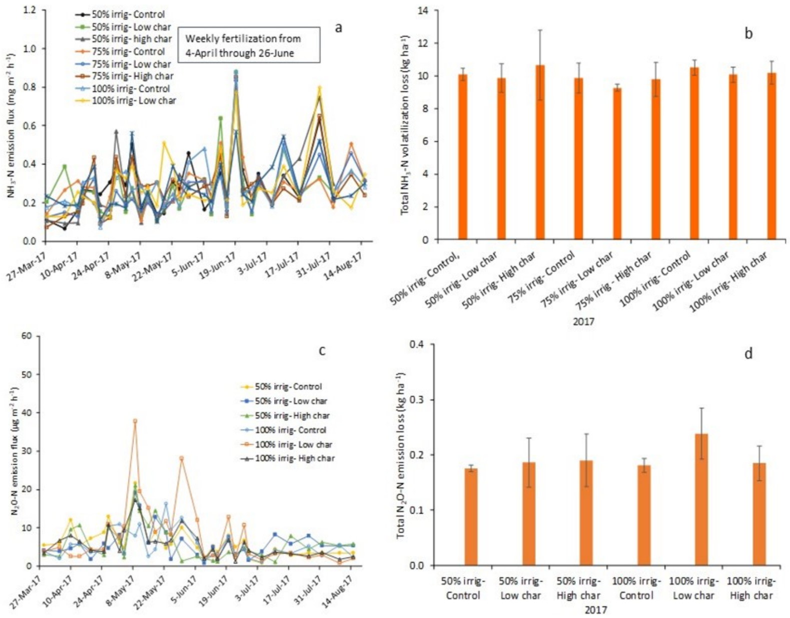

Fig. 3. Emission rates and total loss of ammonia (NH_3) and nitrous oxide (N_2O) measured during 2017 onion growing season. Error bars for rate and flux are omitted for improved readability. Error bars for total loss are standard deviation of three estimated values.

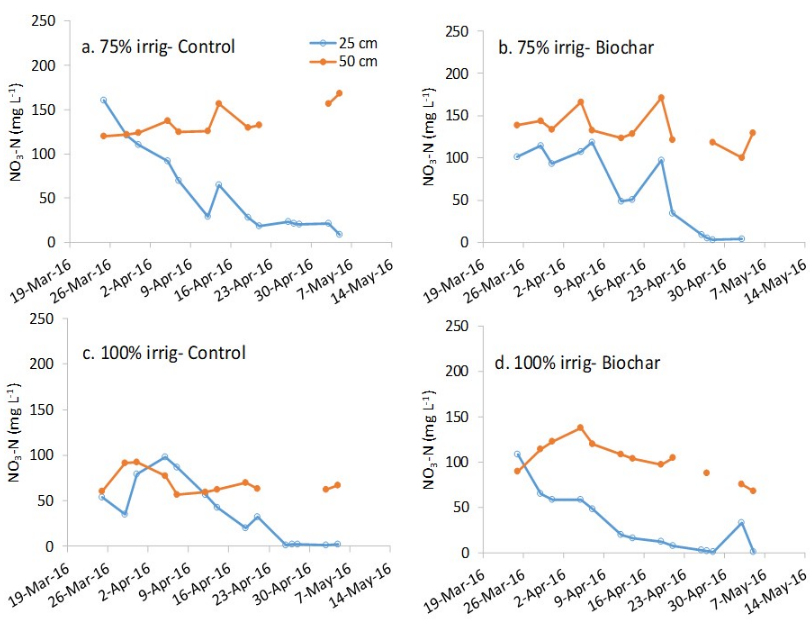

Fig. 4. Nitrate concentration in soil pore water collected from two soil depths during onion growing season in 2016. Error bars are omitted due to either overlapping between treatments or unavailable replicated measurements due to difficulties in obtaining enough sample volume.

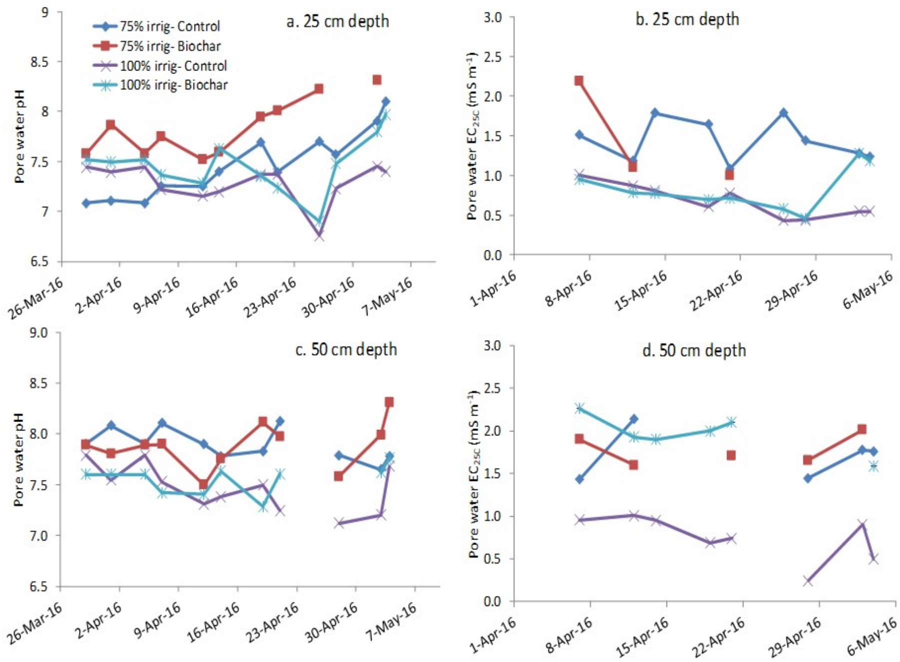

Fig. 5. Soil pore water pH and EC25C from biochar plots in comparison with control plots from 75% and 100% irrigation levels during onion growing season in 2016. Error bars are omitted due to overlapping between treatments or lack of replicated measurements due to difficulties in obtaining enough sample volume.

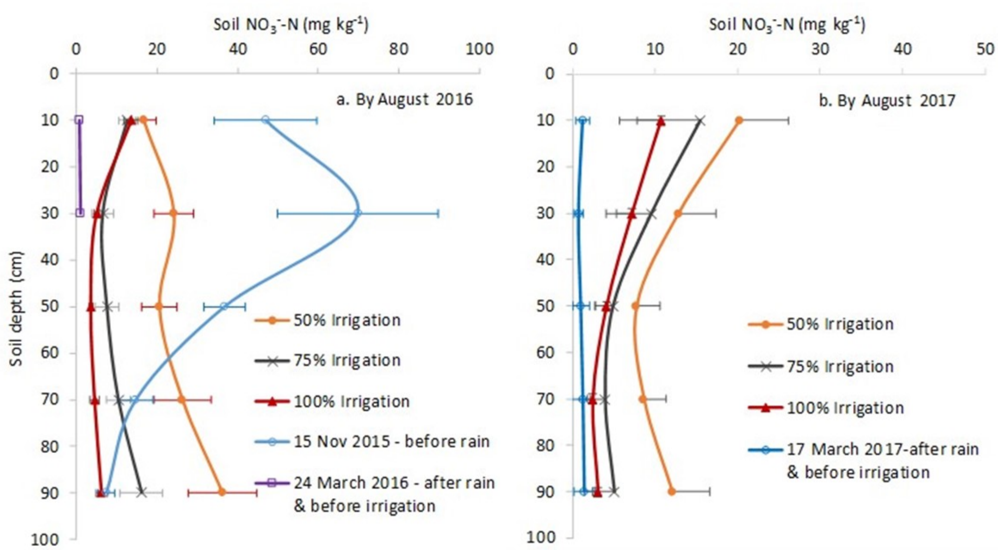

Fig. 6. Nitrate concentration in soil profile from three irrigation levels before and at the end of (a) 2016 and (b) 2017 onion growing seasons (August). Error bars are standard deviation of the mean (n=3).

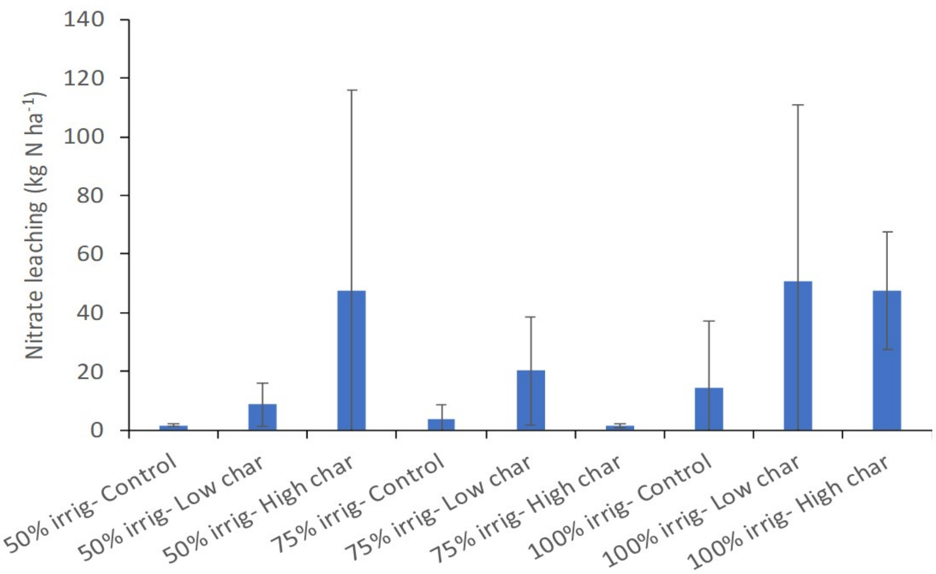

Fig. 7. Nitrate leachate captured from the onion field from different irrigation levels and biochar treatments. The collection period was from 5 January–7 September 2018. The field received 136 mm precipitation January–April followed by irrigation until harvest. Error bars are standard deviation of the mean (n=3).

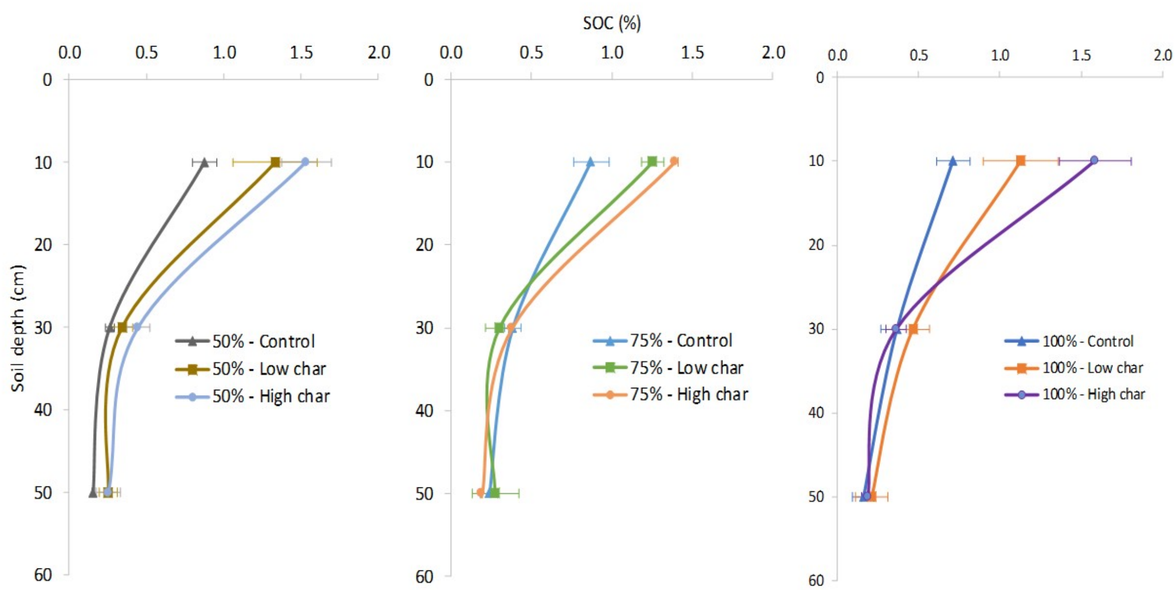

Fig. 8. Soil organic carbon (SOC) concentration in soil profile in August 2018 from three irrigation levels and biochar treatments. Error bars are standard deviation of the mean (n=3).

Appendix 2 – Field Experiment 2: Investigation of biochar and manure on N

A manuscript prepared for submission to J. Plant Nutr & Soil Sci.

Influence of biochar and manure on nitrogen dynamics and uptake by processing tomato and garlic plants

Suduan Gao [1*], Yinghua Duan[1,2], Dong Wang[1], Thomas Turini[3]

[1] USDA-ARS, Water Management Research Unit, San Joaquin Valley Agricultural Sciences Center, 9611 South Riverbend Ave., Parlier, CA 93648-9757, United States of America.

[2] Chinese Academy of Agricultural Sciences, Institute of Agricultural Resources and Regional Planning, Beijing 100081, China

[3] UCNAR, University of California Cooperative Extension, Fresno County, CA 93710, United States of America

Abstract

Background: Organic amendments improve soil healthy but its role in improving N management has not been well quantified.

Aim: This research evaluated the influence of biochar and manure incorporation in soil on crop yield, N uptake, changes in soil and environmental losses, and use the information to assess N requirement by crops and project fertilization needs.

Methods**:** A two-year field experiment was conducted by growing processing tomato (Lycopersicon esculentum Mill.) followed by a dehydrator garlic (*Allium sativum*). Treatments included two biochar products with feedstock of almond shell or softwood at 20 or 40 tonne (t) ha^{-1}, dairy manure compost at 20 t ha^{-1}, combinations of the manure and the biochar (each at 20 t ha^{-1}), and a control. All treatments received the same amount of available N, P, and K.

Results: There were no significant treatment effects on crop yield, biomass, and N uptake as well as ammonia volatilization and leaching loss. The N requirement to produce fresh tomato fruits and garlic bulbs ranged from 3.2–3.8 kg N Mg^{-1} and 9.9–10.0 kg N Mg^{-1}, respectively. However, about half of the N for tomato and 93% for garlic plants would be removed from soil by harvesting. Fertilization needs for N to produce the regional average yield at 110 Mg ha^{-1} for tomatoes and 19.5 Mg ha^{-1} for garlic were 263 kg N ha^{-1} or 247 kg N ha^{-1} at 70% NUE, respectively. The rates would change according to target yield, soil storage, and NUE.

Conclusions: Soil amendments with biochar or manure did not show direct link to crop yield and NUE. The N sequestered per unit biomass production and removed proportion from field at harvest are relatively stable parameters that can be used to project fertilization needs.

Keywords: Ammonia volatilization • Nitrogen distribution in plant • N requirement • Nitrate leaching • Soil organic carbon • Soil total N

1 Introduction

Nitrogen (N) continues to be one of the most important and challenging nutrients to manage for crop production. Large chemical fertilizer input has led to increased yield, but substantial amount ends up being lost to the environment that has resulted in undesirable consequences including surface water enrichment from run off, groundwater pollution from nitrate (NO_3^-), air quality degradation from reactive N volatilization such as ammonia (NH_3), and contribution to global warming by producing a potent greenhouse gas nitrous oxide (N_2O) (*USEPA*, 2019). Nitrogen fertilization has also led to severely degraded soil quality (*Sainju* et al., 2019; *Raza* et al., 2020). Nitrate pollution in groundwater is linked to major source from agricultural fields (*Harter and Lund*, 2012; *Hansen* et al., 2017). Nitrogen use efficiency (NUE) has been declining over the past decades (*Swaney* et al., 2018). These problems require diligent efforts to develop sustainable practices.

The benefits of improving soils and N management with organic amendments have been demonstrated in many studies. Biochar, a carbon-rich material produced from organic feedstocks through pyrolysis, has been promoted as a soil amendment to sequester carbon and improve soil health by increasing soil organic C (SOC), and improving soil biophysicochemical properties (*Glaser* et al., 2002; *Ahmad* et al., 2014; *Lehmann and Joseph*, 2009). Biochar was shown as an effective N management strategy for improved soil water retention especially in coarse textured soils (*Singh* et al., 2010; *Xu* et al., 2016; Borchard et al., 2019) and reduced leaching (*Singh* et al., 2010; Xu et al., 2016; *Borchard* et al., 2019). Some studies also showed reduced NH_3 volatilization (*Thangarajan* et al., 2018; *Mandal* et al., 2019; *Sun* et al., 2019). However, studies vary widely with no positive effects on leaching (*Li* et al., 2018; *Gao* et al., 2020), or even increased NH_3 (*He* et al., 2018; *Sha* et al., 2019; *Wei* et al., 2020) suggesting that the effects of biochar on N dynamics is dependent on soil and environmental conditions. To develop biochar as a beneficial agronomic practice there is a need to evaluate its influence on N dynamics during crop production cycle.

In addition to improving soil properties, composted animal manure is a valuable N source with some tied into organic compounds. The organic N serves as a storage and only becomes available for plants from mineralization. In contrast, N from synthetic (inorganic) fertilizer is readily available to plants. Most of the N (urea or ammonium) can be quickly converted to highly mobile NO_3^- in most soils that is subject to not only plant uptake but also leaching. Some investigations looked into combining organic N source with inorganic fertilizer in conventional farming. Long-term combination of manure with chemical fertilizer at a 7:3 ratio resulted in higher crop yield, NUE, soil organic carbon (SOC), and nutrient (N, P) accumulation in soil (Duan et al., 2014) that also demonstrated the potential to reduce N loss to the environment (Duan et al., 2016; Huang et al., 2017). Although many studies investigated the contribution of manure to soil available N, more work is needed on the combinations of the N sources that not only increase yield but also minimize environmental loss.

Pyrolysis results in biochar that is considered inert and N-poor, but manure is rich in N, other nutrients, and microbes. Research has also shown benefits of mixing manure with biochar on soil, nutrients, and plants. Biochar increased N retention by reducing NH_3 volatilization in composting of poultry litter likely due to adsorption or incorporation of ammonium (NH_4^+) in organic compounds during microbial utilization of dissolved organic C **(**Agyarko-Mintah et al., 2017; Janczak et al., 2017**).** Manure combined with biochar in field increased soil nutrient content and positively influenced cotton roots physiology (Zhang et al., 2020). Combined biochar with chicken or horse manure increased tomato yield (Antonious, 2018) although no positive synergic effect was found in a soil poor in nutrients (Trupiano et al., 2017). However, the benefits of biochar are inconclusive due to many factors involved (Gao et al., 2019, Liu et al., 2019). Better understanding of the interactions between the different C or N sources are still largely needed for N management.

The Central Valley of California is one of the most productive regions in the world by producing many vegetable crops at high yield with 100% irrigated agriculture under a Mediterranean climate. Crop production faces several challenges including water shortage, widely spread groundwater NO_3^- pollution, and climate change (Joyce et al., 2011; Harter and Lund, 2012; Ullrich et al., 2018). Sustainable practices are needed to address these challenges. Current practices for meeting N or fertilization needs are based on the positive correlation between fertilizer application rate and crop yield and/or quality. This approach requires consideration of other factors such as soils where fields with low fertility would require higher fertilization rates to increase N uptake and yield, but over-application could occur if not managed carefully. Few studies have been conducted to evaluate all facets associated with N dynamics including the N input, output, and changes in soil. More accurate estimates for crop N requirement are necessary to guide N fertilization management. The objective of this research was to evaluate the influence of biochar and manure incorporation on crop yield, N uptake, N and C changes in soil and losses to environment, and use the information to assess N requirement by crops and project fertilization needs.

2 Materials and Methods

2.1 Field experiment and treatment

A two-year field experiment was conducted in 2018 and 2019 with processing tomato (Lycopersicon esculentum Mill.) for the first year and garlic (*Allium sativum*) for the second year at the USDA Agricultural Research Service, San Joaquin Valley Agricultural Sciences Center (latitude, 36^{o} 35’ 36.74” N; longitude, 119^{o} 30’ 48.71” W), Parlier, California, USA. The two crops were selected because the study location is in Fresno County, the top county to produce both crops (USDA-NASS 2019). California produces roughly 95% of the processed tomatoes and over 90% commercial garlic in the United States (USDA-ERS 2017). The soil was Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents). The soil had a pH of 7.2, CEC of 9.1 cmol(+) kg^{-1}, and distribution of particles as sand, silt and clay in 58%, 33%, and 9%, respectively.

Eight treatments in three replications were tested in the study using combinations of two biochar products derived from feedstocks of either almond shells (AS) or soft woods (SW), two application rates at 20 or 40 t (tonne, dry weight basis) ha^{-1}, and a manure compost at 20 t ha^{-1}:

1. No biochar, no manure (Control)
2. AS char at 20 t ha^{-1} (AS char 20)
3. AS char at 40 t ha^{-1} (AS char 40)
4. SW char at 20 t ha^{-1} (SW char 20)
5. SW char at 40 t ha^{-1} (SW char 40)
6. Manure compost at 20 t ha^{-1} (Manure 20)
7. Manure at 20 t ha^{-1}, AS char at 20 t ha^{-1} (Manure+AS char)
8. Manure at 20 t ha^{-1}, SW char at 20 t ha^{-1} (Manure+SW char)

Almond shell char was produced at pyrolysis temperature of 550 ^oC by Cool Terra (Camarillo, CA). The SW char was produced at similar pyrolysis temperature (540 ^oC) by AG Biochar, LLC (Modesto, CA). The manure was a dairy manure compost from New Era Farm Service (Tulare, CA). The nutrient levels for these materials are provided in Table 1.

All treatments were designed to receive the same amount available NPK during the growing season. The total seasonal available N in soil for processing tomatoes was targeted at 350 kg ha^{-1} that included the soil N and available N from biochar or manure. For manure N, 10% total organic N in the manure was assumed to be mineralized. For example, a lab incubation study found that 14–19% organic N was mineralized from fecal components after 168 days (Cusick et al., 2006). As a result, actual inorganic N fertilizer applied ranging from 187 kg ha^{-1} in manure treatments to 238 kg ha^{-1} in the control. These values are within the range of recommendation in the region (140–280 kg N ha^{-1}, Hartz et al., 1996). Phosphorous and K fertilizer applications were adjusted in all treatments to the highest amount of available P (173 kg ha^{-1}) and K (780 kg ha^{-1}) in the combined biochar and manure treatments by applying various amounts of single superphosphate [$Ca(H_2PO_4)_2$] and potassium sulfate (K_2SO_4). This led to two times or higher of the recommended P and K values (up to 69 kg P ha^{-1} or 185 kg K ha^{-1}, Hartz et al., 1996) applied for the first growing season, thus no P and K were applied for the second crop (garlic) when only inorganic N fertilizer was applied. For garlic, N fertilization rates varied significantly in the region (100–400 lbs per ac, or 112–448 kg ha^{-1}) within which yield increased significantly as the N rate increased and the maximum yield was achieved at 336 kg N ha^{-1} (Voss et al., 2000). As N rate increased further to 448 kg N ha^{-1} the percentage of dry mass was reduced regardless irrigation levels (Cantwell et al., 2000, CDFA report).

The available N from biochar and manure was counted in the base fertilizer application for tomatoes. To achieve the same amount of available N in all plots (~65 kg ha^{-1}) at the beginning, urea N was applied from 0 in the manure (7.9 kg ha^{-1} mineral N) and biochar (0.8-2.4 kg ha^{-1}) combined treatment to 9.2 kg ha^{-1} in the control. The inorganic N fertilizer was applied three more times (1 May, 22 May, and 11 June in 2018) during the growing season as UAN 32 at equal amount (~76.4 kg N ha^{-1}) each time. Drip irrigation was used for both crops. The N input as well as P and K from biochar, manure, and inorganic fertilizer for the various treatments for tomato growing season are shown in Figure 1. For garlic, no base fertilizer was applied at planting because of projected slow growth and potential leaching loss during winter rain season. During garlic growing season UAN32 was applied on 18 March, 8 April, and 28 April in 2019 in equal amounts each time (76.4 kg N ha^{-1}; total 230 kg N ha^{-1}).

The field experiment was conducted in microplots following a randomized complete block design. The microplots were constructed using concrete irrigation pipes with a 50-cm inner diameter and inserted into soil to about 1.5 m deep. There were at least 1.2 m distance between any of the two plots. The microplots were filled with surrounding soil until reaching the soil depth at 50 cm. The top 50 cm depth was filled with surface soil from a previously planted vineyard. All biochar, manure or base fertilizers were mixed with the top 15 cm soil using a concrete mixer before filling. The soil was settled for four days before transplanting.

Seedlings of an early ripening local variety of processing tomato were obtained from a local nursery. Three seedlings were transplanted to each plot on 30 March 2018. Transplanting density of processing tomatoes in the region typically ranged 17,300 to 22,200 per ha (Hartz et al., 1996) where raised beds, that are approximately 1.5 m wide with plant spacing of 50 cm, are often used in large field production (Mitchell et al., 2012). The density in the microplot appeared much higher (~100,000 per ha) than that in field production, but plants access more space than the actual plot area. To compare with field production, data collected from the microplots were normalized by the number of plants or dry matter production per unit area.

Tomato harvest was done on 26 July 2018. After harvesting, the plots were fallowed for about three months. Then the top 15 cm soil was manually cultivated prior to planting garlic. A dehydrator garlic variety (LE4050) was obtained from Olam Spices & Vegetables, Hanford, CA, USA. Fifteen cloves were planted in each plot on 16 October 2018 and garlic was harvested on 27 June 2019. The density was about 514,000 per ha in the microplots, which was similar to commercial field for garlic dehydrator planting density at 518,700 per ha (Larry Hanson, Olam Spices & Vegetables, personal communication).

2.2 Field sampling, measurement, and analysis

As a major pathway for N loss during crop growing season, NH_3 volatilization was measured daily following each N application during the first week, then reduced to 2–3 times a week or weekly until next fertilizer application. Ammonia volatilization was measured using a semi-static (open) chamber method, which was originally designed by Jantalia et al. (2012) and modified by Gao et al. (2020). Because of the small size of the plot, the chamber was constructed using a PVC pipe (10 cm id x 30 cm h) and a PVC cap connected to a 6 cm long and 1.3 cm id PVC tube at the cap center for venting. The chamber was placed in the center of each plot for about 24 hours for each measurement. The NH_3 volatilization rate was calculated by the total amount trapped within the chamber and divided by the sampling time and surface area of the chamber.

Seasonal NH_3 loss was estimated by integrating the products of the volatilization rates and time.

Potential N leaching was measured using resin collectors described in Gao et al. (2020). The collectors were installed at 50 cm depth before planting and retrieved after harvest. Three collectors were installed in each plot. A subsample of the resin materials in each collector was extracted three times with 2M KCl at >90% recovery and analyzed for NO_3^-. Total N collected was calculated as an indicator for potential leaching, i.e., it does not present total loss especially for tomatoes because some roots can go deeper. Therefore, soil samples at 0–25, 25–50, and 50–75 cm depths were collected at the beginning and end of the experiment, and determined for NO_3^-, total organic C and N.

At harvest, the plants were cut at the ground level. Fresh tomato fruit or garlic bulb yield and all above-ground biomass were measured for each plot. Subsamples of fresh tomato fruits (separated to red and green) or garlic cloves and leaves or the stems were collected. For garlic, after fresh yield was measured, peeled cloves (flesh), skins of the cloves, and the leaves were separated, weighed, and sampled separately. All samples were dried at ≤65 ^{o}C for water content, ground using a plant material grinder, and analyzed for total C and N.

Total C and N analysis for soil and plant samples were determined using a LECO TruMac® CN Macro Analyzer (LECO Corporation, St. Joseph, Michigan, USA). For soil NO_3^- analyses, soil samples were extracted with 2M KCl at 1:2.5 (w/v) ratio. Ammonium and NO_3^- in solution were analyzed using a colorimetric method (Mulvaney, 1996) on a Lachat QuikChem Flow Injection Analysis System (Lachat Instrument, Loveland, CO).

2.3 Data processing and statistical analysis

Data on yield or biomass, N concentration, total N uptake, cumulative NH_3 emissions, potential N leaching at 50 cm soil depth from resin collectors, and soil organic C or total N were analyzed by performing One-way analysis of variance (ANOVA) using SAS 9.4 (SAS Institute, 2013).

Nitrogen partitioning in plant parts was estimated by the amount of biomass multiplying its N concentration and the sum was the total N uptake during the growing season. The amounts of N sequestered into tomato fruits or garlic bulbs were considered being removed at harvest as other biomass (leaves, stems etc.) would be left in the field in practice. The amount of removed was used to project N replenishment or fertilization needs assuming the same crop to be planted next season. This assumption allows us to estimate N application rate at a target NUE. Such approach was to minimize excessive application of fertilizers and seek effective management practices for sustainable crop production and ecosystem health.

The yield, biomass or N uptake data were processed at plot and plant level. To evaluate N requirement, the amounts of N sequestered to produce the average or maximum yield were estimated. The information was used to evaluate N or fertilization management strategies and to compare with that in the literature.

3 Results

3.1 Yield and biomass

There were no significant differences in the marketable yield for tomato fruits and garlic bulbs among all treatments (Figure 2). Fresh tomato production ranged from 2.9–3.5 kg per plant and that for garlic bulbs ranged from 92–98 g per plant (bulb). Variations in tomato yield were larger than that for garlic. The data suggest that treatment effects may be larger following treatment, but the effects diminish over time.

3.2 Nitrogen distribution in plants, total uptake, and removable amount by harvesting

Nitrogen concentrations in tomato and garlic plant tissues are provided in Figure 3. There were no significant differences between the treatments for any parts of the plants, however the differences were significant between different plant parts. For tomato, N concentration followed the order of red fruits (2.43–3.50%, dry weight basis) > green fruits (1.85–2.48%) ≥ leaves and stems (1.99–2.42%) (Figure 3a). Fresh tomato fruits (the parts that would be removed upon harvest) contained an average of 94.6% water. As a result, N concentration was in the range of 0.15–0.20% (or an average of 0.17%) in fresh tomato fruits. For garlic plants, the highest N concentration was found in flesh of cloves (2.52–2.88%, dry weight basis), which was about 5 times or higher than that in the leaves or the skins of cloves (Figure 3b). Garlic bulbs contained 62.4% water content. The N concentration in fresh bulb (parts will be removed upon harvest) was in the range of 1.36-1.51%. All data suggest a relocation of N to edible parts of the plants by harvest. This phenomenon is more profound in garlic than in the tomato plants.

The dry biomass and total N uptake in two different portions are shown in Figure 4. Nitrogen sequestered in the edible portions would be removed from the field, but that in leaves or stems would remain in the field or return to soil. For tomatoes, biomass of leaves and stems was higher although N concentration was lower than those in fruits. As a result, the total N uptake in tomato fruits ranged (6.5–8.5 g per plant), which was 40–48% (ave. 47% or about half) of total plant N uptake and would be removed from the field by harvesting. For garlic plants, however, the mass of the skin and clove flesh accounted for 17% and 83% of the bulb, respectively. They contributed to a total N uptake in bulbs ranging from 0.8 to 0.9 g per plant, accounted for 92–94% (ave. 93%) of total N uptake that would be removed at harvest.

3.3 Nitrogen sequestered by plant per unit yield.

The N uptake per unit dry or fresh tomato fruit or garlic bulb are given in Table 2. Again, there were no significant treatment effects on the N sequestered for both plants. The much higher water content in fresh tomatoes than fresh garlic bulbs resulted in the difference in the sequestered amount of N per unit dry mass versus fresh mass as well as between the two plants. The values ranged from 3.2–3.8 kg N Mg^{-1} for fresh tomatoes and 8.8–10.0 kg N Mg^{-1} for fresh garlic bulbs. These values provide the basis for N requirement to produce a target yield and are used to project fertilization needs in the discussion.

3.4 Ammonia volatilization

Ammonia volatilization was highly affected by fertilization event during both crop growing seasons. Figure 5 shows the volatilization rates during tomato growing season (data for garlic growing season are not shown). The rate peaked following each of the three N fertilizer applications during the growing season with much higher peaks in May compared to that in June. Much lower peaks were also observed following the fertilizer application at transplanting when no or very small amount of urea was applied. Following fertilization on 1 May, most biochar treatments resulted in higher NH_3 volatilization rate than the control with the highest from the AS char at 40 t/ha (Figure 5a) which continued being the highest following fertilization on May 22. Manure incorporation, especially when combined with biochar, also led to higher NH_3 volatilization rates (Figure 5b) in May. However, after the last fertilizer application in June the volatilization was significantly reduced from all treatments. This was likely due to increased shading and/or plant uptake. The differences in emission peak among treatments were much smaller in 2019 implying that amendment of biochar and manure increased NH_3 volatilization loss temporarily following treatment, but the effects diminished over time.

Estimated total NH_3 volatilization loss during each growing season ranged from 17–39 kg N ha^{-1} in 2018 and 9–11 kg N ha^{-1} with no significant differences among the treatments for both years (Table 2). The loss was roughly about 7–17% in 2018 and 4–5% in 2019 of total N applied. The cooler temperature and early harvesting date for garlic likely contributed to the lower volatilization compared to that in 2018 tomato growing season.

3.5 Nitrate concentration changes in soil profile and leaching collected at 0.5 m depth

Soil NO_3^- concentrations at the beginning or end of garlic growing season are shown in Figure 6. Initial nitrate concentration was similar, higher in top 50 cm soil, and lower in soil below. After two years of growing seasons, the concentration in surface layer was significantly reduced suggesting plant uptake and/or downward movement. At the end of the experiment, the NO_3^- concentrations in soil profiles were generally lower than initial conditions. There were no differences in NO_3^- concentrations in the profiles among treatments.

Nitrate downward movement captured at 50 cm soil depth using the resin collectors during tomato and garlic growing season are provided in Table 3. The results showed no significant differences among the treatments in the total N captured. The data only illustrate that N mobility was not affected by the organic amendments. Total available N (soil storage, treatment input) in the soil was 350 kg ha^{-1} during tomato growing season and 230 kg ha^{-1} for garlic. All the data suggest that the amount of N applied did not result in accumulation in soil or was not considered excessive.

3.6 Changes in soil total C and N

Soil total C and N after two years of treatments with biochar or manure treatments are shown in Figure 7. There were significant differences in both C and N among the treatments, but only in surface soil where treatments were applied. High biochar rate (40 t ha^{-1}) and manure incorporated treatments showed significantly higher soil C and N compared to the control or low rate of biochar. There were little changes in soil C or N below 25 cm soil depth. The highest SOC was from biochar at 40 t ha^{-1} and the highest soil N was from manure combined with the biochar.

4 Discussion

4.1 Why no influence observed from biochar or manure incorporation on crop growth and the fate of N

It was not surprising that this study did not show direct benefit from soil amendments with either manure or biochar to improve crop yield, biomass production, and N uptake (Figures 2-4). There were no synergetic effects either when the two materials combined. The main reason may be that the soil was a relatively fertile sandy loam with no physical or chemical constraints for growing plants except nutrients. Biochar treatment at a much higher rate (58 t ha^{-1}) in a large field study on the same soil used in this study illustrated similar findings except where irrigation level showed more impact (Gao et al., 2020). Irrigation level was the same among all treatments in current study. Positive effect of biochar on crop production were observed when biochar significantly improved some of the soil limiting factors for crop growth such as improved soil physical and chemical properties or increased water retention in coarse textured soil (Basso et al., 2013; Yu et al., 2013) or neutralized pH in acidic soils (Major et al., 2010; Mensah and Frimpong, 2018; Cornelissen et al., 2018). Further, the positive effect of biochar on crop yield and soil acidity in an Ultisol was observed fading during five growing seasons (Cornelissen et al., 2018).

There were also no biochar effects in reducing either ammonia volatilization or leaching loss (Table 3) although temporary pH effect from manure or biochar was observed on NH_3 volatilization from the first year (Figure 5). Evaluation of biochar products from the AS and SW feedstocks showed some capacity to adsorb NH_4^+ with a maximum of 1,000 mg N kg^{-1} at pH 8-9, and at neutral pH the adsorption was reduced by 40% (Gao and Wang, 2019). At 40 t ha^{-1} biochar rate, this can translate to about 20 kg N ha^{-1} (less than 10% total N applied) may be adsorbed. Furthermore, NH_4^+ is not stable in most oxygenated environment and tends to be oxidized to NO_3^-, where adsorption to biochar was extremely low. These facts can explain why biochar could not significantly retain N or effectively reduce leaching from this study and others (e.g., Gao et al., 2020).

The leaching loss was different between the two crop growing seasons. The N captured at 50 cm soil depth were 15–21% of total available N (350 kg ha^{-1}) during tomato growing season and 19–29% of the total N (580 kg ha^{-1}) for the two growing seasons. No accurate assessment on leaching loss for the garlic season could be made because of no accurate measurement in soil available N after winter rain season where losses was inevitable due to leaching. The values for the two season's loss suggest that the leaching loss during garlic growing season was higher than that from the tomato season. This was because garlic plants went through the winter raining season and also had much shallower roots. Tomato roots can extend > 90 cm deep in soil profile although most of the roots are found in the top half m of soil (Hartz, 2017).   Garlic roots are expected to be much shallower although no information about garlic root distribution can be found in the literature. The information suggests that the leaching loss might be overestimated for tomato growing season as some N in soil below 50 cm depth could be taken by the plants. Previous field data proved that most soil NO_3^- was leached out of rooting zone by winter rain (Gao et al., 2020). Thus, reducing N leaching during winter season presents a great challenge as it contributes to significantly higher leaching and the organic amendments do not appear offering a solution. While growing winter cover crop may offer some help to reduce leaching, minimizing the presence of available N in soil before rain season should be one of the foci to address the problem.

4.2 Fertilization needs based on N requirement by plants

Only a few references can be found in the literature that determined the amount of N required per unit yield production and our results agree with available data for processing tomatoes. Geisseler (2016) conducted a comprehensive literature review and summarized N concentrations in harvested plant parts. The average N concentration in harvested processing tomatoes were 2.61–2.73 lbs per ton of fresh fruits, equivalent to 1.31–1.37 g N kg^{-1} or 0.131–0.137% N for fresh mature tomatoes. The values were equivalent to 2.6% based on dry weight that was in the lower end of our measurements (2.7–3.5%, Figure 2). Geissler acknowledged possible reasons for the calculated amount of N removed based on survey that might underestimate the actual amount removed. A most recent study by Geisseler et al. (2020) showed that N concentration in the fruits averaged 1.5 g N kg^{-1} (0.15%). Our measurement of N in the fresh tomatoes was very close (0.15–0.20%, ave. 0.17%) to their findings. These numbers suggest that the amount of N sequestered by tomato plants was very similar between studies, thus can be used to project N needs for production based on target yield across regions.

One of the largest variables to predict N needs for processing tomatoes is the target yield. Processing tomato yield has been continuously increasing (USDA NASS, 2019; 2020). Average yield in the region has increased from 80.4 to 111.6 Mg ha^{-1} from 2006 to 2019. A study conducted in the Central Valley of California between 2017–2018 under surface drip irrigation indicated even higher yield ranging from 130-140 Mg ha^{-1} (Geisseler et al., 2020). To project N requirement by the crop, we used the 2019 average yield, i.e., 110 Mg ha^{-1} for processing tomatoes (USDA NASS 2020). The total N requirement to produce the yield, the removal from the field by harvesting fresh fruits, and the N replenishment for producing next crop (if the same crop to be planted) are estimated in Table 2. Similar approach was used for garlic plants.

Information on garlic yield and N requirement is very limited. We used the average yield of 19.5 Mg ha^{-1} in 2019 (USDA NASS, 2020). The value was much closer to that (8.42 ton per acre or 18.3 Mg ha^{-1}) reported by Tyler et al. (1988). Our results showed that the

N uptake for fresh bulbs ranged from 8.8-10.0 kg N per fresh ton of bulbs. Little information can be found on N uptake or removal by garlic plants. An international study in India by Thangasamy and Chavan (2017) reported N partitioning to garlic plants was 8.4 kg N Mg^{-1} fresh bulb but their yield was extremely low (6.7 t ha^{-1}). The data suggest agreement in N sequestered per unit garlic yield under two very different production environment that indicate again the N sequestered by plants per unit yield or biomass appears to be a good parameter to project nutrient requirement. Large number of studies ((e.g., Tyler et al., 1988; Cantwell et al., 2000; Shashidhar et al., 2005) determining fertilization needs by seeking correlations between N fertilization rates and yield is insufficient because poor soils would require higher fertilization rates to achieve a target yield. Thus, this study is valuable and helps to fill part of the gap by determining N uptake and removal, and project fertilization needs for a target yield.

At harvest, the N removal for the tomatoes from our experiment was ave. 47% of total N uptake by all above-ground biomass. This percentage of removal was lower than that by Geissler et al (2020) who determined that the N removal accounted for 64% of the total N in the aboveground biomass. The discrepancy of near 20% difference may be further assessed especially under field production conditions. For garlic, the removal by harvest was much higher than garlic at 93% of total N sequestered in above-ground biomass. The removed amounts would be the N needed to replenish in the soil assuming the same crop to be planted next season. These would be via fertilization or organic amendments shown in the last two columns of Table 2.

Using the N partitioning in plants and % of removal, projected N requirement was 181 kg ha^{-1} for tomatoes and 173 kg ha^{-1} for garlic for the average yield (110 Mg ha-1 for tomato and 19.5 Mg ha-1 for garlic) in the studied region. The two crops required similar amount of N and the reason was that N partitioning in garlic plants was higher in concentration and also with much higher removal from the field at harvest. Fertilization needs can vary significantly depending on a target NUE. Our projection at a 70% NUE resulted in fertilization needs of 243–283 (ave. 263) kg N ha^{-1} for tomatoes or 230–260 (ave. 247) kg N ha^{-1} for garlic. Geissler et al. (2020)'s projection on N needs were 208–250 kg ha^{-1} at nearly 20% higher yield, but much higher NUE (90%). These data are in general agreement but with different assumptions.

4.3 Nutrient budgeting with organic amendments

Results from this study suggest that organic amendments improved soil physical, chemical, and biological properties as well as supply substantial amounts of nutrients for plants (Figure 1). Although biochar or manure did not show significant effects in improving yield, increasing NUE, and reducing N losses, they show undeniable benefits to significantly increase SOC and improve water retention and ecological health (Suddick and Six, 2013; Dangi et al., 2019; Gao et al., 2020). Thus, biochar plays an important role in C sequestration by increasing C storage and improving soil productivity, which can be important considering that SOC in many regions around the world including California continues to decline for various reasons but largely due to dependency on synthetic fertilizers. Manure or biochar at rate as high as 40 t ha^{-1} provided more P and K for plant needs (Figure 1). Thus, when organic amendments are used, nutrient budgeting needs to be made so that effective use of all nutrients, especially P and K from the amendments can be factored in. This study suggests that at 20 t ha^{-1} rate, manure can provide available nutrients for P and K at 160 kg P ha^{-1}, and 400 kg K ha^{-1}. These values suggest that inorganic fertilizer for P or K should be substantially reduced or not needed when adequate amount of manure or biochar are incorporated into soil.

5 Conclusions

Based on the field study, soil amendments with biochar and manure or both did not improve yield, increase N uptake, or reduce environmental loss such as ammonia volatilization or nitrate leaching. However, it is evident that these organic amendments provided two direct major benefits: 1) improved soil physicochemical properties, and 2) supplied other essential nutrients for plant growth. For the latter, biochar or manure at a sufficient rate can provide the full P and K needs by plants. For meeting plant nutrient requirement, the amendment application rate should be set to a certain limit depending on the source. None of the organic amendments altered N sequestration by either the processing tomato or garlic plants so that the amount of N sequestered and removed at harvest is a reliable parameter to guide fertilization applications. The biomass or N mass removed from the field vary tremendously between plants. In this study, 47% of total N uptake by tomato plants or 93% for garlic are subjected to be removed that would require replenishment for next crop. Fertilization needs should also consider nutrients in soil, irrigation water, and any other inputs as well as potential losses to maximize NUE and minimize unintended losses that are detrimental to the environment.

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Table 1: Nutrients in soil and organic materials used for field experiment†

Biochar feedstock (pyrolysis T ºC)	Total Org-C (%)	Total N (%)	Total P (mg kg^{-1})	Total K (g kg^{-1})	Ammonium (NH_4^+-N) (mg kg^{-1})	Nitrate (NO_3^--N) (mg kg^{-1})	Extract. P (mg kg^{-1})	Extract. K (g kg^{-1})
Soil	0.72	0.07	-	-	2.5	22.1	53.5	0.2
Almond shell char (550)	56.6	0.62	1,146	24.3	2.8	60.0	305	16.1
Softwood (540)	62.0	0.58	4,208	27.7	2.8	33.4	310	18.4
Manure compost	19.2	2.16	-	-	225	170	8,355	20.8

† All nutrients were based on dry mass by determining water content at 105ºC for soil or ≤65 ºC for organic materials. Ammonium and nitrate were from 2M KCl extract. Extractable P and K were from 2% acetic acid extracts.

Table 2: Nitrogen uptake by processing tomato and garlic plants and estimates of fertilization rate for average yield in production field

Treatment	N uptake (kg t fresh dry-bulbs)	N uptake (kg t^{-1} fresh-bulbs)	Total N uptake (kg ha^{-1})†	N to be removed at harvest (kg ha^{-1})‡	N fertilizer needed at 70% NUE (kg ha^{-1})
Tomato plants:					
Control	57.8 (12.4)	3.6 (0.4)	399.8	187.3	258.6
AS char 20	59.6 (17.4)	3.2 (1.1)	356.0	166.8	247.6
AS char 40	53.9 (17.7)	3.2 (0.9)	353.0	165.4	250.0
SW char 20	60.8 (4.9)	3.8 (0.7)	422.0	197.7	273.0
SW char 40	51.3 (3.0)	3.6 (0.5)	394.6	184.8	271.1
Manure 20	57.4 (16.7)	3.6 (1.6)	399.7	187.3	282.5
Manure+AS char	53.1 (9.9)	3.2 (0.7)	356.8	167.1	257.5
Manure+SW char	53.1 (12.8)	3.5 (0.9)	401.7	188.2	263.6
Ave.	**55.9**	**3.5**	**385.4**	**180.6**	**263.0**
Garlic plants:					
Control	26.4 (1.0)	10.0 (0.0)	194.0	181.6	259.5
AS char 20	25.8 (1.7)	9.8 (0.4)	190.1	177.9	254.2
AS char 40	24.3 (4.4)	9.3 (1.2)	180.6	169.1	241.6
SW char 20	26.3 (1.5)	9.7 (0.2)	189.7	177.6	253.7
SW char 40	24.8 (0.5)	9.5 (0.1)	184.0	172.3	246.1
Manure 20	24.1 (2.4)	9.0 (0.7)	175.4	164.2	234.6
Manure+AS char	23.7 (2.3)	8.8 (1.0)	171.4	160.5	229.2
Manure+SW char	26.8 (2.0)	9.9 (0.9)	192.7	180.4	257.7
Ave.	**25.3** (**2.0**)	**9.5 (0.6**)	**184.7**	**173.0**	**247.1**

† The high yield in the region was 110 Mg ha^{-1} or 19.5 Mg ha^{-1} for garlic ((USDA NASS, 2019).

‡ Total N uptake by plants removed was 47% for tomato and 93% for garlic plants. These values were the N uptake in fresh fruits or bulbs that were harvested.

Table 3: Measured total NH_3 volatilization loss and nitrate leaching with resin collectors installed at 50 cm soil depth from biochar and manure treatments during tomato (29 March – 24 July 2018) and garlic (16 October 2018–6 June 2019) growing season.

	NH_3-N volatilization (kg ha^{-1})				Nitrate-N collected at 50 cm soil depth (kg ha^{-1})			
	Tomato (2018)		Garlic (2019)		Tomato (2018)		Garlic (2019)	
Control	23.0	(10.1)	10.5	(0.9)	60.5	(11.4)	54.3	(9.7)
AS char 20	21.8	(5.0)	9.4	(1.2)	62.5	(14.0)	68.4	(2.9)
AS char 40	39.4	(18.3)	10.3	(1.4)	69.6	(33.8)	100.1	(41.6)
SW char 20	32.1	(19.6)	10.1	(0.5)	73.6	(13.4)	57.5	(1.1)
SW char 40	22.3	(3.0)	11.3	(0.8)	69.4	(18.7)	48.4	(25.7)
Manure 20	16.6	(4.1)	11.1	(0.6)	52.4	(21.7)	88.7	(45.6)
Manure + AS char	21.8	(12.1)	9.9	(0.9)	51.6	(23.7)	68.4	(9.2)
Manure + SW char	25.7	(3.7)	9.9	(0.6)	55.0	(5.7)	54.3	(28.6)

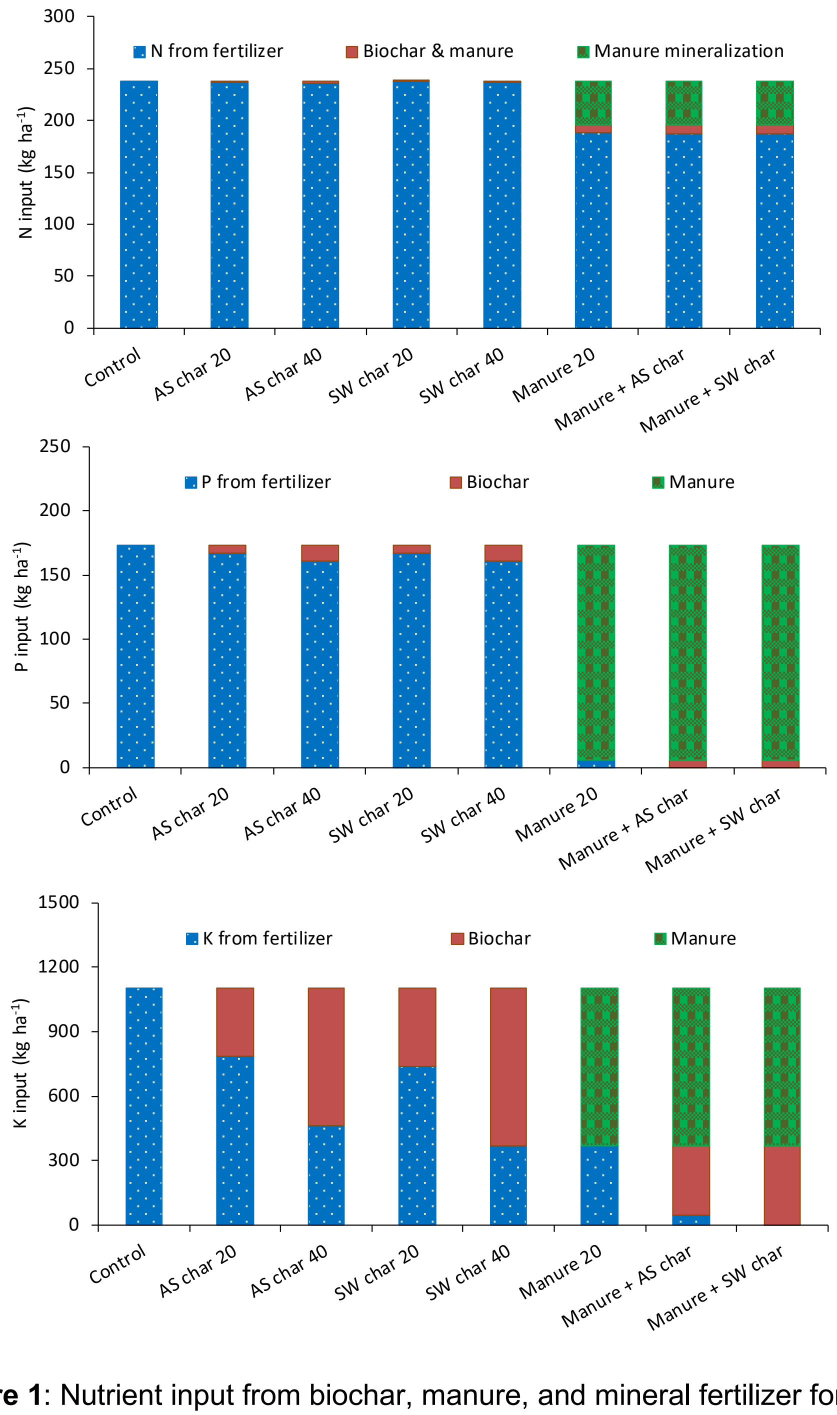


Figure 1: Nutrient input from biochar, manure, and mineral fertilizer for various treatments during the first year of the field experiment. Manure mineralization was estimated at 10% of organic-N. P and K from biochar and manure were estimated based on extractable values only. Note that manure was a major source for both P and K and biochar supplied similar amount of K as manure.

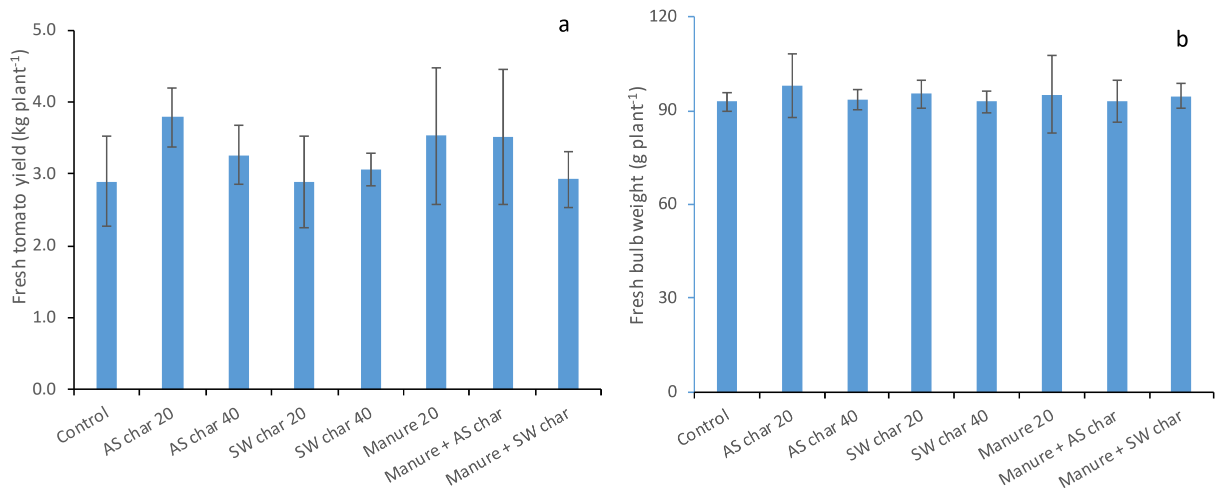


Figure 2: Fresh tomato (a, 2018) and garlic (b, 2019) yield from biochar and manure treated soils. Error bars are standard deviation of three replicates.

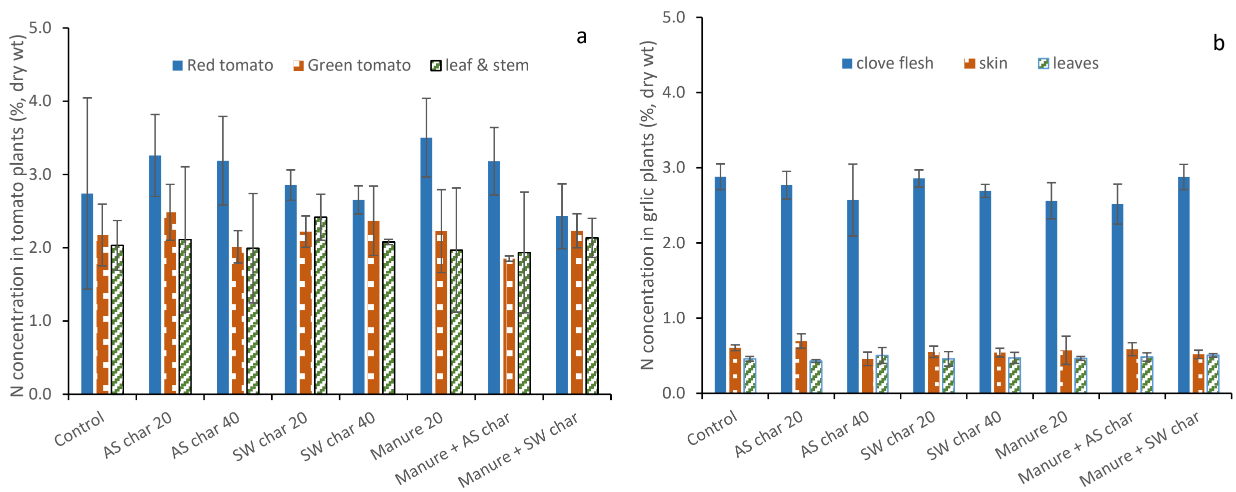


Figure 3: Nitrogen concentration in different parts of tomato (a) and garlic (b) plants from biochar and manure treated soils. Error bars are standard deviation of three replicates.

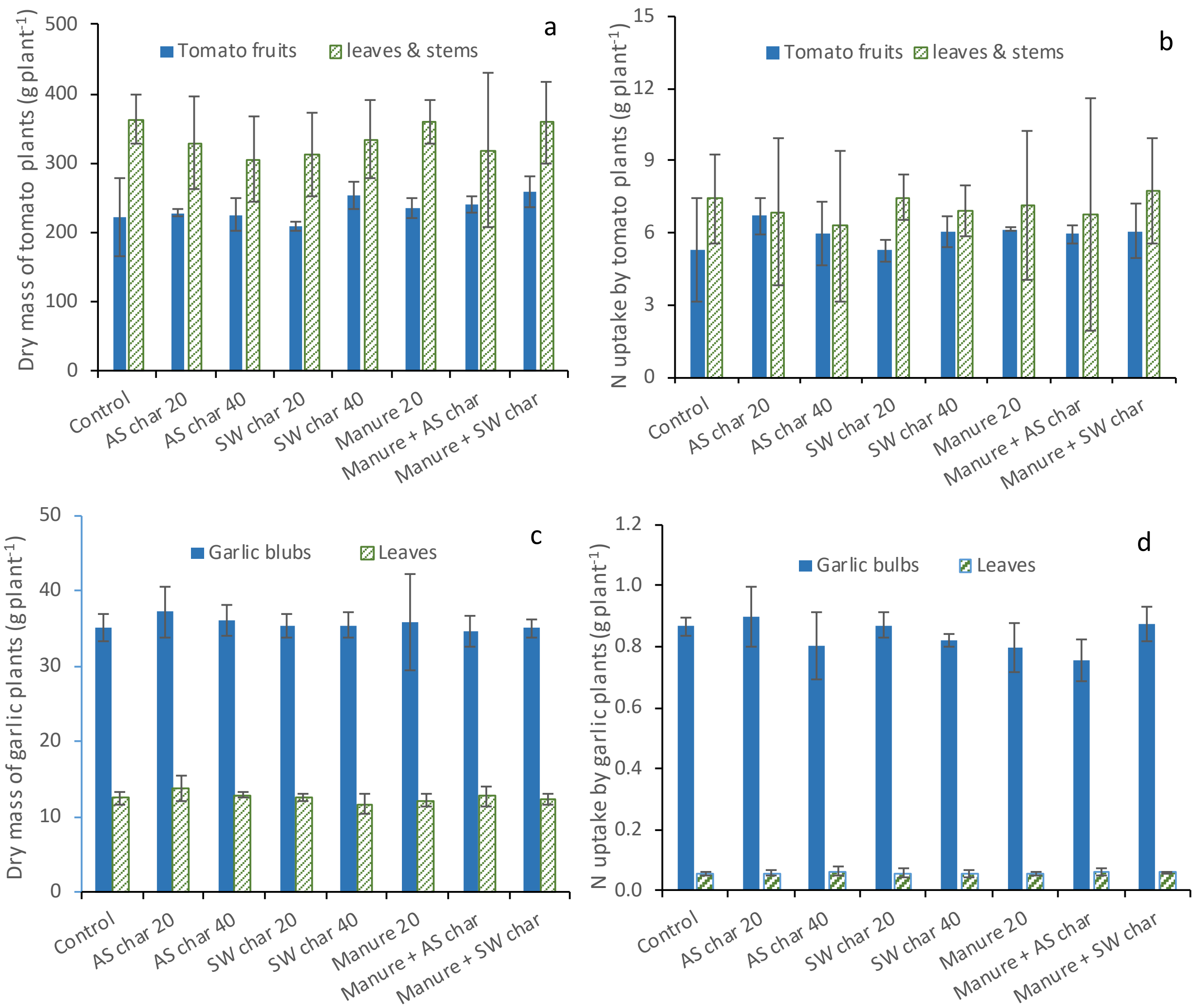
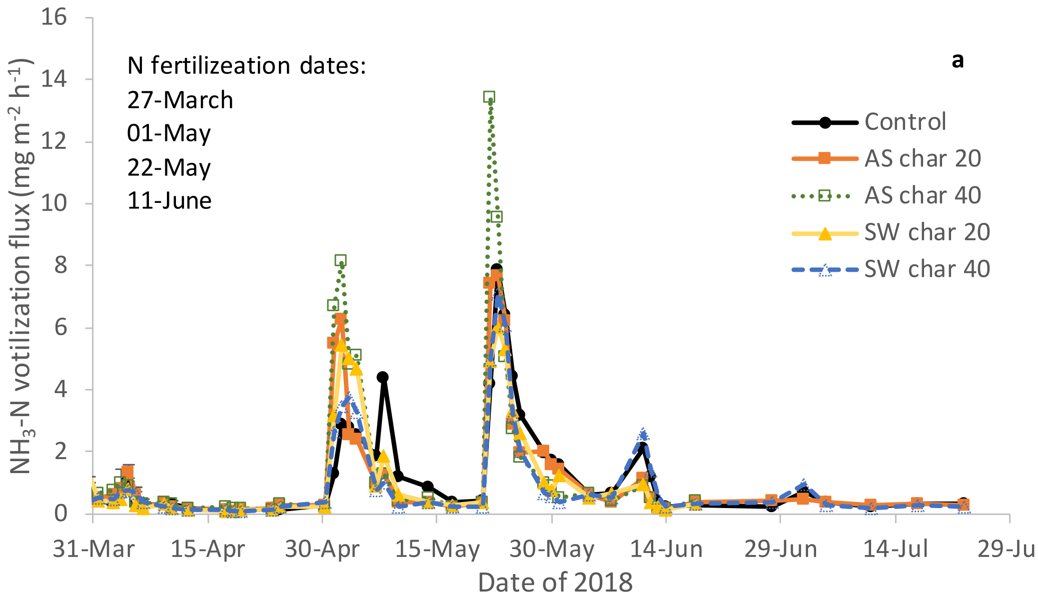


Figure 4: Tomato (a) biomass and (b) N uptake and those (c, d) for garlic plants from biochar and manure treated soils. The amount of N sequestered in fruits or bulbs would be subject to removal at harvest. Error bars are standard deviation of three replicates.



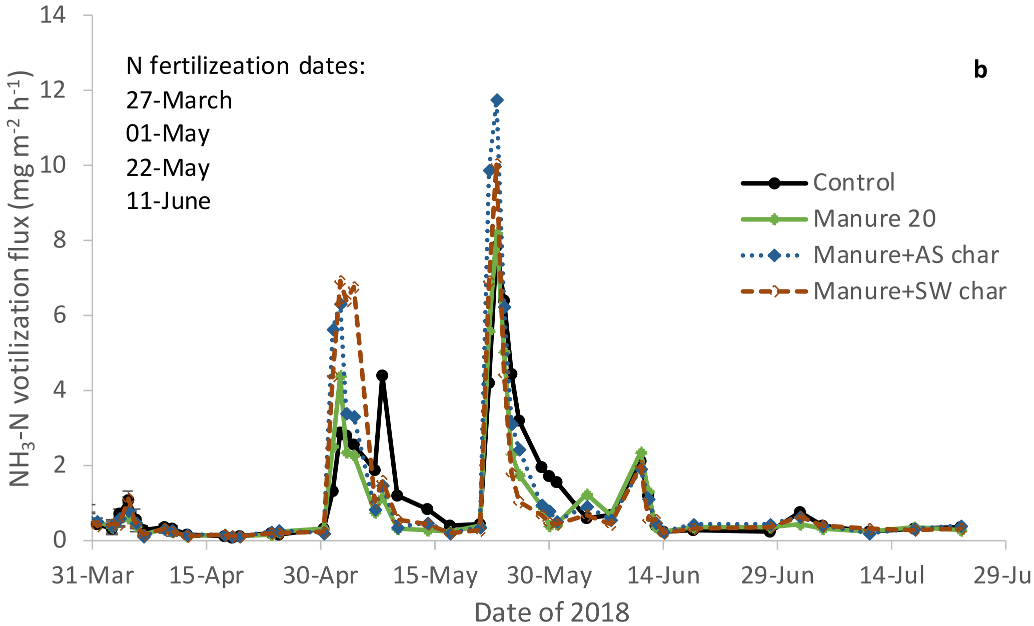


Figure 5: Ammonia volatilization rates measured during tomato (left) and garlic (right) growing season from a) biochar amendment rate and b) manure and combination with biochar amendment. Error bars are omitted for better legibility.

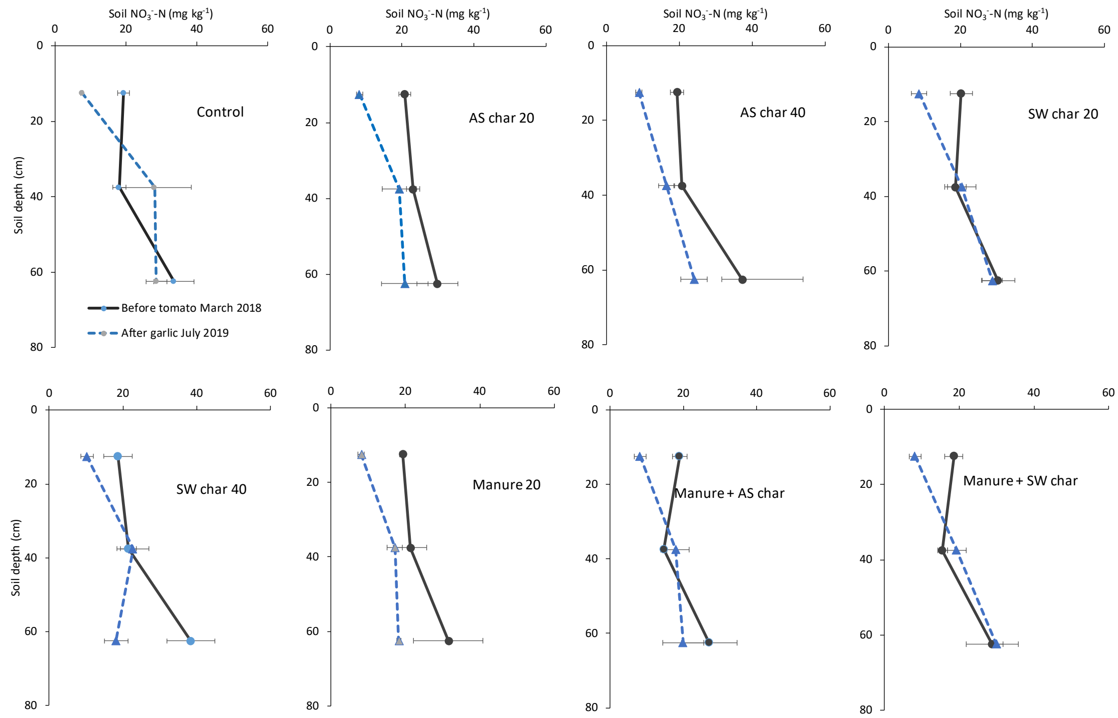


Figure 6: Nitrate concentration in soil profile at the beginning of tomato (March 2018) and after garlic (July 2019) growing season. Error bars are standard deviation of three replicates.

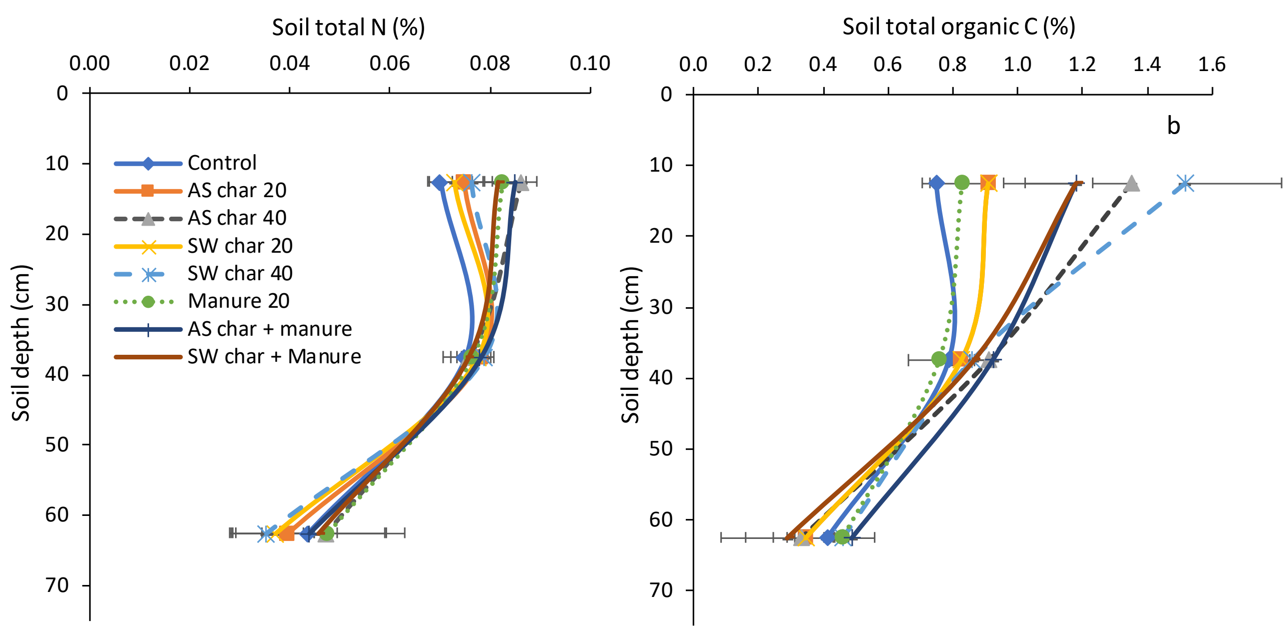


Figure 7: Total organic C and N in soil profile after two years of biochar and manure treatments. Error bars are standard deviation of three replicates.

M. Factsheet/Database

1. **Project Title:** Soil biochar amendment to improve nitrogen and water management

2. **Grant Agreement Number:** 16-0597-SA

3. **Project Leaders:**

Suduan Gao, Research Soil Scientist
USDA-ARS, San Joaquin Valley Agricultural Sciences Center (SJVASC)
9611 S. Riverbend Ave.
Parlier, CA, USA 93648
Tel: (559) 596-2870
e-mail: suduan.gao@usda.gov

Dong Wang, Research Soil Scientist
USDA-ARS, SJVASC
9611 S. Riverbend Ave.
Parlier, CA, USA 93648
Tel: (559) 596-2852
e-mail: dong.wang@usda.gov

4. **Start Year/End Year:** January 2017–December 2020

5. **Location:** 9611 S. Riverbend Ave., Parlier, CA 93611

6. **County:** Fresno

7. **Highlights:**

- Biochar significantly increased soil organic carbon and increased soil water retention but showed no change in crop yield.
- Biochar did not increase N uptake or reduce N losses such as ammonia volatilization, nitrous oxide emissions, and nitrate leaching.
- All biochar products have some capacity to adsorb ammonium, but have little adsorption for nitrate, which is the dominant N form in most soils.
- As a soil amendment, biochar should be promoted for long-term benefits to sustain soil productivity and crop production.

8. **Introduction**

Use of inorganic (synthetic) fertilizers continues to increase over time in crop production, but overuse or improper management has resulted in low use efficiency and detrimental environmental consequences. Effective N management strategies are needed to increase N uptake and minimize environmental loses. Biochar, which is a carbon rich material produced by heating organic materials at high temperature under no or limited oxygen, has the potential to improve soil properties, increase N retention, and reduce N losses but studies reported inconsistent results. This project was designed to examine the mechanisms of biochar interaction with N in lab, evaluate the effects on plant growth, and investigate the fate of N fertilizers in the field for vegetable crop production.

9. Methods/Management

Two laboratory experiments and two field experiments were conducted. The lab experiments were carried out to characterize seven biochar products from different feed stocks, determine the adsorption capacity for major mineral N species, and evaluate the N transformation from urea application as affected by biochar. The first field experiment investigated the effects of biochar and its interaction with irrigation level on N dynamics in an onion field for three years. The second field experiment investigated the effects of biochar in combination with manure on N dynamics for two years with processing tomato followed by garlic using microplots. Crop yield, N uptake, C and N status change in soil profile, ammonia volatilization, and N leaching were determined in both field experiments.

10. Findings

Laboratory data showed that biochar has some capacity to adsorb NH_4^+, but is highly pH dependent. The maximum adsorption (~1000 mg N kg^{-1}) occurred at pH 8-9, but the adsorption was reduced by half at pH 7. Further NH_4^+ is not stable in most soils unless under saturated conditions it is quickly oxidized to nitrate, which showed little adsorption on biochar. Thus, the ability of biochar to retain N is very limited.

The first field experiment demonstrated the dominant irrigation effect on crop production and interaction with biochar on soil nitrate accumulation or movement in soil. Biochar increased soil water retention but was not significant enough to reduce leaching. The second field experiment showed similar findings that soil amended with biochar did not affect crop yield, biomass production, N uptake, and N losses. However, both field data showed that biochar significantly increases SOC and supplies substantial amounts of nutrients, especially potassium, to improve soil productivity.

Although biochar did not show significant effects in improving yield, increasing N uptake, and reducing N losses, biochar as a soil amendment should be promoted because of its undeniable benefits to sequester C that sustains soil productivity**.** The loss of C in agricultural soils will continue contributing to soil and environmental degradation that threatens the sustainability of crop production. There are many proofs that C-rich soils are the basis for sustainable agriculture. Thus, any strategy including biochar that returns organic C to soil should be encouraged to replace practices that do otherwise such as agricultural burning, which is detrimental to air quality and results in 100% loss of C. Current commercial biochar products are too expensive for growers, but in-situ production can significantly reduce costs. Policies (e.g., C credit) that promote the practice can encourage adoption of biochar as one of the strategies to sustain agricultural production.

N. Copy of the Product/Results:

1. Presentation Abstract at 2017 California Plant and Soil Conference, January 31 - February 1, 2017, Fresno, CA.

PROFESSIONAL (NON-STUDENT) POSTERS

Effects of Biochar Amendment and Fertilizer Sources on Serrano Chili Pepper Yield, Uptake, and Nitrogen Fate

Julio Perez*, Suduan Gao, Robert Shenk, and Aileen Hendratna, *Presenter
Contact Name: Julio Perez, USDA Agricultural Research Service
9611 S Riverbend Ave, Parlier, CA 93648; (559) 596-2999, Fax (559) 596-2851,
Julio.Perez@ars.usda.gov

Efficient nitrogen (N) management strategies are a key approach in addressing the increase of food demand and environmental protection. Failing to achieve adequate nitrogen use efficiency (NUE) in agricultural systems can cause damaging outcomes including degradative water quality, increase in greenhouse gas emissions and economic loss. Understanding balanced and appropriate uses of inorganic and organic nitrogen fertilizers can improve NUE, increase overall crop yield and preserve environmental quality. The objective of this research is to determine the effectiveness of biochar amendment and nitrogen fertilizer sources on NUE improvement in serrano pepper production. A field pot experiment was conducted with treatments of biochar amendments and various combinations of inorganic and organic N fertilizers. Although the first year data did not show significant differences in pepper yield, biochar amendment and incorporation of organic N at lower ratio appeared to increase total plant N uptake. During the growing season, NH_3 volatilization increased after fertilization events, but with lower or delayed peaks from organic N. Nitrous oxide production was reduced in soil profile from both biochar amendment and organic N source. We continue this study to determine the long term benefits of N source and soil amendment for crop production.

2. 2019. Presentation at 27th CDFA-FREP Conference, October 28-30, Fresno, CA

Soil Biochar Amendment to Improve Nitrogen and Water Management

Project Investigators

Suduan Gao, Research Soil Scientist
USDA-ARS, San Joaquin Valley Agricultural Sciences Center (SJVASC)
9611 S. Riverbend Ave., Parlier, CA 93648
suduan.gao@ars.usda.gov

Dong Wang, Research Soil Scientist
USDA-ARS, SJVASC
9611 S. Riverbend Ave., Parlier, CA 93648
dong.wang@ars.usda.gov

Cooperators

Tom Turini, Farm Advisor
Cooperative Extension Fresno County, Fresno, CA 93710. taturini@ucanr.edu

Kurt Hembree, Weed Management Farm Advisor, Cooperative Extension Fresno County, Fresno, CA 93710
kjhembree@ucanr.edu

Niles Brinton, CEO
Charborn, LLC, Oakland, CA 94612
info@charborn.com

INTRODUCTION

Nitrogen (N) is an essential element for crop production. Unused N from fertilizer application is also the source of contamination that impacts environmental quality. Ammonia (NH_3) volatilization from soil has detrimental effects on human health and accounts for the largest mass loss in gaseous form for N. Use of N fertilizer is the major source of atmospheric emissions of nitrous oxide (N_2O, a potent greenhouse gas). Nitrogen leaching from agricultural fields has been identified as the major cause for the statewide groundwater pollution in California (CA). Regulatory decisions have been in place or are in the process of being made that require monitoring and reporting of N use in production fields.

Biochar, which is produced from heating organic materials at high temperature under limited oxygen, has shown the benefits of organic carbon storage (sequestration), improving soil properties, and mitigating environmental contamination problems. Many studies illustrated potential benefits of biochar in increased N retention, reduced N leaching, and decreased gas emissions. However, variabilities in observed biochar effects are large with many showing no or negative effects. There are large gaps in our understanding of what effects biochar products could have on N dynamics especially under field conditions.

OBJECTIVES

The goal of this study is to determine the overall benefits and best practices of using biochar as a soil amendment in N and water management in vegetable crop production systems. Specific objectives are:

1. To determine effects of soil amended with biochars (produced from different feedstocks found in the San Joaquin Valley of California) on adsorption capacity for NH_4^+ and NO_3^- and N transformation (urea hydrolysis and nitrification) rates as well as soil-water retention.
2. To determine effective amendment rate of biochar products and irrigation rates

on crop response and N fate under field conditions.

DESCRIPTION

For objective 1, laboratory studies have been carried out to characterize biochar products (e.g., surface area, chemical composition), and then tested for their adsorption capacity of N species (ammonium NH_4^+ and nitrate NO_3^-) and pH effects. Seven biochar products from different feedstocks were collected including two freshly made from almond shells from California orchards, two from softwood, and one each from wood/tree trimming, bamboo, or coconut shells. They vary in pyrolysis temperature, particle size, composition, etc. All products were tested for their adsorption capacity of N and selected products were tested for pH effects.

For objective 2, a three-year field experiment was conducted to evaluate soil incorporation of biochar and irrigation rates on crop response and N losses to the environment. The field experiment was established at the USDA-ARS, San Joaquin Valley Agricultural Sciences Center, Parlier, CA. Processing bulb onions were grown for three years (2016-2018). The soil is Hanford sandy loam (coarse-loamy, mixed, super active, nonacid, thermic Typic Xerorthents). Treatments included three irrigation levels with or without biochar amendments first year and a high char treatment was added in the second year. Field design was a split-plot with three irrigation levels as main treatments (50, 75, and 100% of a reference that provides sufficient water for plant growth), and three biochar amendment rates as sub-treatments [0, low char (29 t/ha), and high char (58 t/ha)] in three replications. The biochar was produced from softwood by Charborn LLC (Oakland, CA). Fertilizers were applied four times during first growing season but weekly during the second growing season. Soil at the end of the growing season was sampled and analyzed for N. Ammonia and N_2O emissions were measured using chamber methods described in Gao et al. (2017) and Jantalia et al. (2012), respectively. Nitrate leaching was collected during the third year using resin method (Penn State, 2017).

RESULTS AND DISCUSSION

Adsorption of N species on biochar. Preliminary data on adsorption isotherm have shown that all biochar products exhibit some ability to adsorb NH_4^+, but not NO_3^-. The pH effects on NH_4^+ adsorption are shown in Figure 1. The adsorption was minimal at low pH, increased with pH increase, reached the maximum between pH 8-9, and then decreased as pH was raised further. Almond shell char and two softwood chars showed NH_4^+-N adsorption capacity up 1 g kg^{-1}, which translates to 30 kg N adsorption per hectare at biochar application rate of 30 ton ha^{-1}. However, at pH 7 the amount of adsorption can be reduced to half and it is unknown how long before the adsorbed NH_4^+ can be oxidized to NO_3^-, which is most mobile among N species. Overall, the ability of biochar to retain N is expected to be small.

Onion field experiment. Ammonia volatilization rates increased significantly following each N fertilizer application with much higher peaks when fertilizer was applied fewer times during 2016 growing season with a larger amount each time. Total NH_3 loss during the growing season ranged from 11.4-18.2 kg N ha^{-1} in 2016, higher than those in 2017 (7.2-8.1 kg N ha). Nitrous oxide emission followed a similar pattern, but total N_2O emissions were similar between the years ranging from 0.13-0.22 in 2016 and 0.18-0.23 kg N ha^{-1} in 2017. The total NH_3 volatilization loss accounted for 5.1-8.1% in 2016 and 3.0-3.5% in 2017 of the total amount of fertilizer applied, but the total N_2O emissions were much smaller

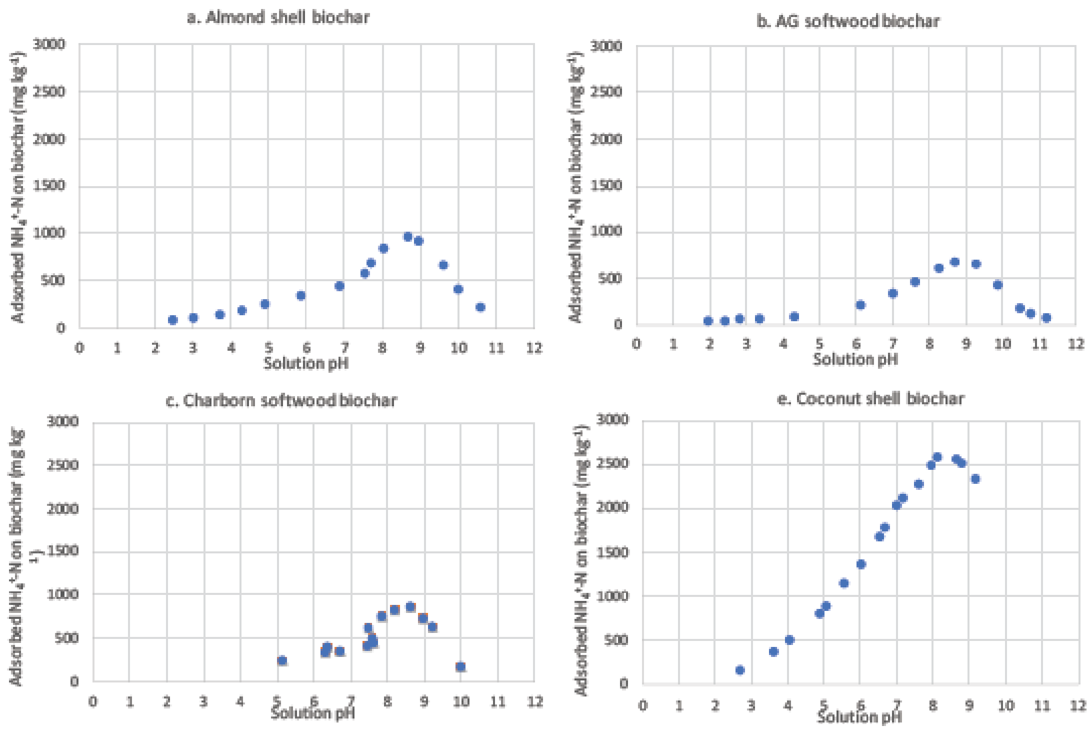


Figure 1. Adsorption envelope of NH_4^+ on biochar products from different biochars when initial solution concentration was 100 mg NH_4^+-N L^{-1} at a 50:1 (v/w) solution:biochar ratio.

(0.06-0.1% for 2016 and 0.08-0.1% for 2017).

Statistical analyses showed that for the first two years, biochar effect was not significant, but irrigation and interaction with biochar significantly affected the yield. The 50% irrigation level regardless with or without biochar had significantly lower yield than those at 75% and 100% irrigation, with no significant difference between the 75% and 100% irrigation levels. In 2017, irrigation with biochar treatment showed a similar trend, but the control at 50% irrigation showed a high yield similar to the higher irrigation levels and significantly higher than biochar treatments at the same irrigation level. For both years, the high-char treatment at 100% irrigation level gave consistently high yield that are significantly higher than some of the treatments at 75% irrigation level. N uptake was positively correlated with yield.

By the end of each growing season, NO_3^- in the profile showed significant differences among irrigation treatments: highest in the 50% irrigation and lowest from the 100% irrigation. The concentration was the highest in surface soil for 100% and 75% irrigation levels, but below 20 cm the concentration increased as soil depth increased for all irrigation levels with the greatest increase for the 50% irrigation treatment. All the accumulated N, however, was leached out by early spring after the winter rain season. Statistical analyses showed irrigation, soil depth, and irrigation × soil depth interaction had significant impact on the soil N data, but no significant effect of biochar and its interaction with other treatments was observed.

Nitrogen leaching data collected in the third year showed large variations among treatments. Statistical analysis did not show any significant effects of irrigation, biochar, or their interactions. However, when biochar main effects were compared with the control only, the low biochar treatment versus the control had a p value of 0.081. Most of high N leaching was observed from biochar treatments and all controls showed low leaching indicating biochar at least did not reduce leaching.

TAKE-HOME MESSAGE

Based on three-year data from an onion field experiment, there was no clear benefit of biochar on N management in terms of reducing N losses, and irrigation levels showed greater impact on N dynamics and crop production. There were no significant effects of biochar on ammonia or nitrous oxide emissions. Biochar showed a tendency to increase N leaching, which may be due to its ability to increase infiltration. Biochar showed some ability to retain NH_4^+, but likely also increased water infiltration rate by decreasing soil bulk density. Irrigation showed a profound impact on yield, N accumulation, N mobility, and N leaching. Lower irrigation levels led to higher accumulation of soil nitrate, but all was subject to leaching from winter rain. The high costs of biochar production are the major hurdles for adoption as a common agronomic practice at this time. Efforts should focus on low-cost methods in biochar production when suitable and incorporation in agricultural fields may provide long-term benefits in organic carbon storage. In addition, low-cost biochar versus direct biomass return should be evaluated.

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ACKNOWLEDGEMENTS

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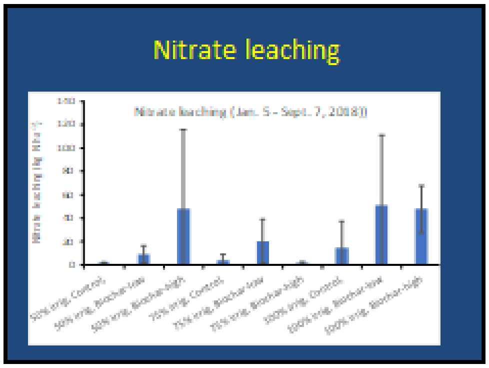
3. Presentation slides on Field Day. October 30, 2018, California State University, Fresno



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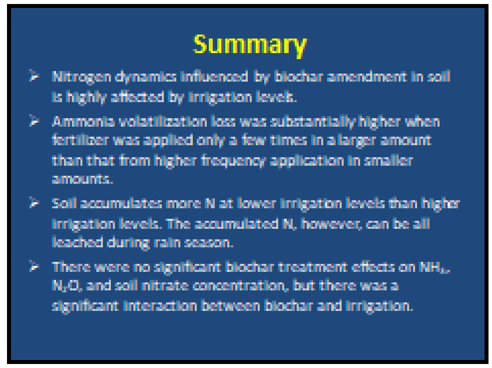

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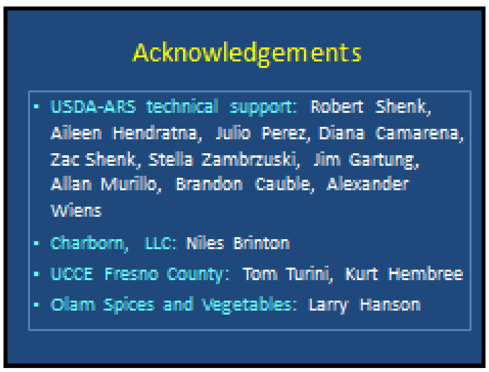

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4. Appendix I is a copy of a published paper under support of this project.

5. Appendix 2 is a copy of a manuscript prepared for submission to Journal of Plant Nutrition and Soil Science.