Influences of biochar addition on vegetable soil nitrogen balance and pH buffering capacity

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Abstract. Leaching is a major path for chemical nitrogen fertilizer loss from in vegetable soil, which would destroy soil pH buffering capacity soil and result in acidification. It has been a common phenomenon in Tai Lake Region, China. However, few study focused on the change soil pH buffering capacity, especially the effect of soil amendment on pH buffering capacity. In this study, a pot experiment was conducted to research the effects of biochar addition to a vegetable soil on nitrogen leaching and pH buffering capacity with pakchoi (B.chinensis L.) growth as the experimental crop. The results showed that biochar could significantly increase the pakchoi nitrogen utilization efficiency, decrease 48%-65% nitrogen loss from leaching under the urea continuous applied condition. Biochar also could effectively maintain the content of soil organic matter and base cations. Therefore, it rose up soil pH buffering capacity by 9.4%-36.8% and significantly slowed down acidification rate. It was suggested that 1%-2% addition ratio was recommended from this study when used as similar soil condition.

1. Introduction
Nitrogen leaching and soil acidification have been the most important threatens for vegetable system [1-2]. According to previous studies, utilization efficiency of present nitrogen fertilizer was only 33 % in northern China and 18 % in southern China [3-4], and the rest of them left in soil, released [H⁺] in the process of nitrification and lost from leaching [5]. Additionally, base cations were inclined to loss with leachate contributed to further acidification happening [6]. Regulation nitrogen in vegetable soil will be the key to decrease leaching and mitigate soil acidification.

Biochar, a form of activated carbon, has been used experimentally to solve numerous soil problems in recent years. But studies have indicated that biochar will increase the risk of NO₃⁻-N leaching and [H⁺] concentration by improving soil nitrification [7]. On the other hand, the liming effect of biochar may induce a neutral trend[8] and the adsorption may decrease available nitrogen in soil[9-10], which could change nitrogen transformation and utilization efficiency. The effects of biochar addition on soil leaching and pH buffering capacity would be determined by multi factors. The differences of biochar addition ratios, soil types, fertilizer rates all make the results complicate and various [11] when referring to soil leaching and pH buffering capacity.

We conducted the experiment with soil collected from vegetable field in Taihu Lake region. The field in that region had grown paddy for hundreds of years but some of them was used for vegetable growing in recent 10 year, which brought serious leaching loss and soil acidification due to increasing...
fertilizer input. It was set eight treatments with two nitrogen fertilizer rates and four biochar addition ratios to find the responds of nitrogen leaching on biochar addition, determine the effect of soil pH buffering capacity and nitrogen distributions in different treatments based on biochar recovery method. The results could be used as guide for vegetable soil amendment with biochar in Taihu Lake region.

2. Materials and methods

2.1. Soil, plant and biochar descriptions

Soil was collected from the top 0-20 cm in a vegetable field (31°17’N, 119°54’E) after harvest in Yixing County, Taihu lake region, Jiangsu Province, South-eastern China. This region has a subtropical monsoon climate with an average annual rainfall of 1,177 mm. The field was converted from a paddy field and had a 7-year vegetable plantation history, with 3-4 seasons of leafy vegetables per year. Urea and compound fertilizer were commonly applied at a total rate of 800 kg N/ha per year. The soil is paddy soil, with a pH (H2O) 5.65; an organic matter content 17.9 g/kg; total nitrogen concentrations of 1.87 g/kg, respectively; and mineral nitrogen, phosphorus and potassium concentrations 78.8, 61.0 and 70.1 mg/kg, respectively.

Experiment was carried out with pakchoi (Brassica chinensis L.) as vegetable plant. Biochar (BC) was produced from rice straw using a biogas-energy slow pyrolysis system under oxygen-limited conditions. The temperature was increased to 450 °C then maintained for over 5 hours. The properties in this study are as follows: total nitrogen and carbon concentrations were 12.5 and 503.1 g/kg, respectively; pH 8.9; and BET 7.4 m²/g.

2.2. Experiment design

Experiment was conducted with each pot (28 cm height, 15 cm width and 10cm depth) filled with 2 kg of air-dried soil. Eight treatments were included two nitrogen rates (110 kg N/kg and 0 kg N/kg) and four biochar addition ratios (0% w/w, 1% w/w, 2% w/w and 5% w/w) with six replicates. Chemical N fertilizer (110 mg N/kg) was added to pots in the U and U+BC treatments (P0+U, P0+U+BC, P+U and P+U+BC) at the 14th day following seed germination. P₂O₅ (85 mg /kg) and K₂O (60 mg /kg) were applied as base fertilizers to each pot at the beginning of each growing season.

Biochar was taken turn to wash with 0.5 mol/L HCl, 0.1mol/L NaOH solution and deionized water, and then dried to content weight at 80°C. Some of biochar divided and packed into nylon mesh bags (0.15 mm, 1 g/bag biochar) that allowed water, nutrients and microbes but not soil or biochar particles to pass through. Three biochar packages were buried into the soil in each pot and the rest was mixed with soil till the biochar weight was enough to the ratio of the treatments 15 days before planting starting. One gram of biochar was added to each pot at the end of each growing season to compensate the sampling loss.

Experiment lasted three growing seasons, from Sep. 2014- Apr. 2015 in greenhouse of Jiangsu Academy of Agricultural Sciences. Pak choi was sowed into soil. The day pakchoi germinating was set as the 1st day in each growing season. The quality of seedling was controlled at 30 per pot by thinning at the 7th day after germination. And it was harvest at the 35th day after germination.

2.3. Sampling and measurements

After pakchoi was harvested, the plant biomass was determined by weighing, samples were oven-dried at 70°C until a constant weight was achieved and then filtered through a 0.149-mm sieve the total N (TN) analysis (Flash EA 1112 series; Thermo Finnigan, Elk Grove Village, IL). Plant N accumulation (mg N per pot) = dry biomass of whole plant (g) × total N content (g/g).

One soil composite sample was collected from each pot by mixed five cores sampling. Mineral nitrogen concentrations (NH₄⁺-N, NO₃⁻-N) , soil organic matter, exchangeable K, Na, Ca, Mg and Al were determined by methods from Soil Agricultural Chemical Analysis Method.

The pH buffer capacities were determined by titrating 50 g of each soil sample in sealable polyethylene bags with H₂SO₄ and CaCO₃ at rates of 0, 1×10⁻³, 2×10⁻³, 4×10⁻³, 6×10⁻³ and 8×10⁻³
mol/L mol (H⁺ or 1/2CO₃²⁻)/L/kg. The rates of CaCO₃ were added to the soils as a suspension in distilled water [12]. After amendments were added, they were mixed with the soil. Distilled water was added to each soil/amendment mixture to reach approximately field capacity. The bags were sealed and stored at room temperature for 1 month. The soils were then air-dried and ground for determination of pH (1:2.5, soil:water). Regression analysis was used to determine the buffer capacities within the linear range of the titration curve: \( \text{pH}_{BC} = 1/a \times 10 \), where, \( \text{pH}_{BC} \) = pH buffer capacity of the soil at the end of experimental period (10⁻³ mol H⁺/kg/pH), 1 = one unit pH range used in calculation, a = slope of linear.

The acidification rate is defined as the rate of acid addition that needs to be neutralized in order to maintain a constant pH: \( \text{AR} = \Delta \text{pH} \times \text{pH}_{BC} \times \text{BD} \times \text{Vol} \times 10^6 \), where, AR = acidification rate (10⁻³ mol H⁺/ha), \( \Delta \text{pH} \) = change in pH over the experimental period (pH unit), \( \text{pH}_{BC} \) = pH buffer capacity of the soil at the end of experimental period (10⁻³ mol H⁺ kg⁻¹ pH⁻¹), BD = bulk density of the soil (kg/m³), Vol = volume of soil per unit area (m³/ha), BD × Vol = 2.4 × 10⁶ kg/ha in the soil type.

2.4. Leaching

Over irrigation was utilized to simulate rainfall and to collect leachate, as well as to continuously record the volume. It was set to happen four times each growing season: before sowing, 10th, 20th, and 30th days after germination. The field capacity was 46%, and therefore irrigation water requirement was set as the differences between 50% w/w soil weight and current soil moisture content. Water was irrigated by several times to avoid flooding. Samples were collect six hours after irrigation, and nitrogen concentration and volume were measured for nitrogen leaching loss calculation.

2.5. Statistical analysis

Nitrogen distribution and leaching were showed by means from six replicates in three growing seasons, calculated in pots. However, data related to soil buffering capacity and base cations was acquired from samples collected at the end of experiment. Relative significance of different treatments was accomplished by multivariable analysis. Significant differences among means were determined by Duncan’s multiple range tests at the 5% level. Figures were accomplished by Microsoft Excel 2010.

3. Results and discussion

3.1. Mineral nitrogen distribution under different biochar ratios

As showed in figure 1, 4%-22% mineral nitrogen from fertilizer was absorbed by biochar from soil, and the nitrogen content absorbed increased with the rate of biochar addition. Biochar addition improved pakchoi nitrogen accumulation by 95%, 101%, 71% at 1% biochar addition, 2% biochar addition, 5% biochar addition, respectively. Nitrogen residual rate reached 46% of fertilizer input when without biochar addition. All biochar addition could reduce nitrogen residual, but the decreased residual content was not in proportional to biochar addition rates.

3.2. Effect of biochar addition on soil nitrogen leaching

The biochar addition could reduce leachate volume for its porosity. More biochar addition showed better volume-reduce function. As showed in table 1, the reduction of leachate volume under 5% biochar addition was 35% - 60% in three growing season, the corresponding values were 28%-44% and 28%-44% under 1% biochar addition and 2% biochar addition, respectively.

The nitrogen concentration of leachate was 10-27 mg/L in treatments without chemical nitrogen fertilizer, and it increased to 72-100 mg/L in treatments after nitrogen fertilizer. Averagely, biochar addition decreased the nitrogen concentration of leachate by 33.3%. The reduction of nitrogen concentration of leachate showed no significant differences among different biochar addition ratios. Therefore, nitrogen leaching loss was reduced by 48.3%, 53.7% and 65.0% in 1%, 2% and 5% biochar addition treatments, respectively.
Figure 1. The mineral nitrogen distribution under different biochar ratios. Dotted line presented the nitrogen content (220 mg per pot) from chemical nitrogen fertilizer input.

Table 1. Effect of biochar addition on soil leaching.

| Biochar addition ratios and treatments | Leachate volume (mL/season) | Nitrogen concentration (mg/L) | Nitrogen leaching loss (mg/season) |
|---------------------------------------|-----------------------------|-------------------------------|----------------------------------|
| 0 No nitrogen fertilizer              | 308.26±38.41a               | 16.29±3.05a                  | 5.07±2.62a                      |
| 1% Nitrogen fertilizer                | 229.38±37.27b               | 15.74±2.72a                  | 3.50±0.92a                      |
| 2% No nitrogen fertilizer             | 192.41±37.00bc              | 16.19±3.65a                  | 2.96±0.96a                      |
| 5% Nitrogen fertilizer                | 152.90±29.87c               | 16.46±4.08a                  | 2.12±1.28a                      |
|                                       | 45.30±13.57b                |                               | 6.93±4.11b                      |

3.3. Effect of biochar addition on soil pH buffering capacity

No significance change of pH presented in treatments without nitrogen fertilizer after three growing season compared to original soil (Table 2). It indicated that plant selective adsorption in this study did not contributed to soil acidification significantly. Furthermore, biochar addition did not enhance soil pH in study period. However, chemical nitrogen fertilizer input without biochar reduced both soil pH 0.44 units and buffering capacity. Biochar addition increased soil pH buffering capacity in treatments without nitrogen fertilizer by 21.6%, 24.3% and 36.8% at 1%, 2% and 5% addition ratios, respectively. The corresponding ratios with nitrogen fertilizer were 9.4%, 20.2% and 27.2%, respectively. Moreover, soil acidification rate was affected by nitrogen fertilizer in the absence of biochar addition. Biochar addition decreased soil acidification rate by 37.1%, 80.4% and 17.0% at 1%, 2% and 5% addition ratios when compared to treatment without biochar addition.
Table 2. Changes of soil pH, buffer capacities and acidification rates under different treatments.

| Biochar addition ratios and treatments | pH    | pHBC (10^{-3} mol/kg) | AR (10^3 mol/hm^2) |
|--------------------------------------|-------|-----------------------|---------------------|
| 0                                    | No nitrogen fertilizer | 5.78±0.12 a | 8.56±0.24bc | -2.64±2.46c |
|                                        | Nitrogen fertilizer | 5.21±0.10 c | 7.45±0.58d  | 7.80±1.43 a  |
|                                        | No nitrogen fertilizer | 5.64±0.14 a | 10.42±0.87a | 0.24±3.50bc |
| 1%                                   | No nitrogen fertilizer | 5.40±0.16bc | 8.15±0.33cd | 4.91±3.34ab |
|                                        | Nitrogen fertilizer | 5.82±0.09a  | 10.65±0.18a | -4.23±2.26c |
| 2%                                   | No nitrogen fertilizer | 5.57±0.12ab | 8.95±1.09bc | 1.53±2.58abc |
|                                        | Nitrogen fertilizer | 5.61±0.11ab | 11.72±0.10a | 1.12±2.95bc |
| 5%                                   | No nitrogen fertilizer | 5.37±0.14bc | 9.48±0.33b  | 6.47±3.18ab |
|                                        | Nitrogen fertilizer | 5.65±0.05a  | 9.01±0.39bc |

Soil organic matter content reduced 9.4%-18.2% by planting three growing seasons, but biochar addition mitigated the reduction (Table 3). The same trends were also found in contents of base cations. Contents of exchangeable K⁺, Na⁺ and Mg²⁺ decreased 35.8%-69.0%, 61.1%-63.0% and 43.7%-51.6% in treatments without biochar addition. Exchangeable K⁺ was the most affected by nitrogen fertilizer in especial. However, biochar maintained contents exchangeable K⁺, Na⁺ and Mg²⁺, even increased exchangeable K⁺ content 34.7%. Otherwise, contents of exchangeable Ca²⁺ and Al³⁺ seemed no significant responses to nitrogen fertilizer or biochar addition.

It could be demonstrated that the effect of biochar on soil pH buffer capacities was not direct but multipath. And differences between addition ratios were not always significant. However, biochar effectively reduced nitrogen leaching (Table 1) and maintain the content of soil organic matter and base cations (Table 3), which mitigating the acidification caused by the invalidation of first-level buffering system[13] and the increasing of CEC induced by addition of biochar[14].

Table 3. Changes of contents of soil organic matter and base cations under different treatments.

| Biochar addition ratios and treatments | Organic matter (g/kg) | Content of base cations (10^{-3} mol/kg) |
|--------------------------------------|-----------------------|----------------------------------------|
|                                       | K⁺       | Na⁺       | Ca²⁺      | Mg²⁺      | Al³⁺      |
| 0                                    | 14.65±1.44c | 4.02±1.26c | 3.15±0.37b | 52.57±4.11a | 9.97±0.72c | 3.66±0.63a |
|                                        | 16.21±1.69bc | 1.94±0.18d | 3.31±0.34b | 27.79±0.65c | 8.57±0.50c | 3.24±0.19a |
| 1%                                   | 17.42±2.03bc | 5.95±0.76b | 9.03±0.42a | 40.11±2.19ab | 14.71±3.87b | 3.90±0.21a |
|                                        | 18.09±1.99abc | 6.16±0.89b | 7.68±0.63a | 42.24±2.13ab | 19.79±4.08a | 3.56±0.67a |
| 2%                                   | 18.14±1.51abc | 6.87±0.87b | 9.38±0.82a | 45.92±3.15a | 15.02±0.80b | 3.76±0.16a |
|                                        | 21.00±1.80a  | 6.11±0.68b | 8.93±0.99a | 46.25±5.79a | 20.39±2.62a | 3.94±0.58a |
| 5%                                   | 17.57±2.02bc | 8.43±1.00a | 8.47±0.91a | 37.75±3.68b | 17.31±0.62b | 3.54±0.21a |
|                                        | 19.46±2.03ab | 4.87±0.78c | 8.16±0.95a | 40.33±5.34ab | 17.63±3.25b | 3.57±0.33a |
| Original soil:                       | 17.90±1.87a | 6.26±1.04b | 8.51±0.69a | 44.50±4.88ab | 17.70±2.64b | 3.59±0.26a |
4. Conclusion
Biochar addition had significant effects on soil nitrogen distribution balance. Nitrogen utilization efficiency increased from 41% to 81% with 2% biochar addition, and residual nitrogen was decreased from 46% to 8%. Biochar addition reduced soil nitrogen leaching loss 48%-65% at different addition ratios. The reduction mechanism showed different under different biochar addition ratios. Reduction was induced to low nitrogen concentration in leachate at 1% and 2% biochar addition ratios, while contributed to decreased leaching volume at 5% biochar addition ratio. Biochar mitigated soil pH decrease though it decreased 0.44 units by nitrogen fertilizer without biochar. Meanwhile, it increased soil pH buffering capacity by 22%-37%, and reduced acidification rate by 80%-170% by maintaining the contents of soil organic matter and base cations.

Acknowledgements
Funding for this work was supported by a project grant from the National Science Foundation for Distinguished Young Scholars of China (Grant No. 41501320), and the Special Fund for Agro-scientific Research in the Public Interest (Grant No. 201503106).

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