EFFECTS OF BIOCHAR ADDITION ON SOIL NITROGEN RETENTION AND VEGETABLE UPTAKE IN INTENSIVE PRODUCTION SYSTEMS, CHINA

by

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ABSTRACT

China has a limited area of cultivated land per capita and an increasing population. Maintaining a high crop yield is essential to meet the large food demand and to assure grain self-sufficiency. With the pace of economic development, the demand for vegetables keeps growing. In Southern China, many of the fields used to grow vegetables were previously under paddy production. Compared to the paddy production system, the vegetable production system is intensive with excessive use of nitrogen fertilizer. Excessive nitrogen fertilizer application has changed soil chemical properties and nutrient dynamics, and thus created a negative impact on sustainable agricultural development.

A preliminary study was conducted in the absence of nitrogen fertilizer to determine the effect of field utilization conversion on soil nitrogen uptake by pakchoi. It was found that soil pH values and organic matter content decreased with intensive vegetable planting and nitrogen leaching loss was higher from vegetable soils compared to that from paddy soils. Although the soil mineral nitrogen content in vegetable soils was higher than that in paddy soils, nitrogen uptake by plants from vegetable soils was lower than that from paddy soils, and decreased quickly in the later growing seasons. The lower plant nitrogen uptake was attributed to the high nitrogen leaching loss and soil acidity caused by the excessive application of nitrogen fertilizer in vegetable production systems. Therefore, it is imperative to find suitable approaches to mitigate nitrogen leaching loss and soil acidity in vegetable production systems and promote nitrogen retention and vegetable nitrogen uptake for sustainable productivity.

Biochar is a fine-grained and porous substance produced through pyrolysis processes, under oxygen-free conditions, from a wide range of biomass. In recent years, biochar has received more attention with regard to its capacity to increase crop yields by ameliorating the soil environment and regulating nutrient processes. According to previous studies, biochar is an option for mitigating soil acidity and nitrogen leaching problems in vegetable soils due to its alkalinity and adsorption properties. However, studies of biochar addition to vegetable production systems have not been well documented. The effect of biochar addition on leachate volume is still lacking. Whether the mineral nitrogen retained by biochar can be re-used by plants is still unknown. Few studies have investigated the effect of biochar addition on nitrogen processes and soil acidity under continuous growing conditions.

Therefore, with the aim of determining the effect of biochar on soil nitrogen retention and vegetable nitrogen uptake, pakchoi was planted in a pot experiment during four continuous

growing seasons with three biochar addition rates (0, 1% w/w and 5% w/w). In the 1st, 2nd and 3rd seasons, pakchoi was applied with ^{15}N-labelled urea and in the 4th season no nitrogen fertilizer was provided.

The results of this study were presented in four parts (soil nitrogen retention, soil acidity, vegetable nitrogen uptake and a distinction between two nitrogen sources in vegetable nitrogen uptake i.e. nitrogen left in the soil and nitrogen loss). The main conclusions are as follows:

- Biochar addition significantly increased the soil mineral nitrogen content by enhancing nitrogen retention in soils and soil nitrogen mineralization. Part of the mineral nitrogen retained by biochar was still bioavailable for plant uptake in the soil. Biochar significantly reduced nitrogen leaching loss by decreasing leachate volumes and nitrate concentrations in the leachate.
- Biochar addition significantly ameliorated or retarded soil acidity by promoting soil pH buffering capacity, reducing soil acidification rates and maintaining soil bases contents induced by biochar. The mitigation of soil acidity was not only as a result of biochar's natural alkalinity but can also be attributed to the altered nitrogen processes (promotion of plant nitrate uptake, reduction of nitrification and nitrate leaching and maintaining soil bases contents) with the addition of biochar. Biochar's mitigation of soil acidity was partly dependent on its effect on soil properties (such as bases contents) and processes (such as nitrification, nitrate leaching and plant nitrate uptake) rather than its natural alkalinity.
- Biochar maintained pakchoi yields and nitrogen uptake during four growing seasons. The fertilizer nitrogen recovery efficency was improved with an increase in the recovery of fertilizer nitrogen in the soil and the decrease in the recovery of fertilizer nitrogen in leachate.
- Fertilizer nitrogen was the major source for pakchoi nitrogen uptake, soil residual nitrogen and nitrogen leaching loss, while nitrogen from soil mineralization was the major nitrogen source for biochar retention. When nitrogen fertilizer was absent in the 4th season, the nitrogen fertilizer left in the soil from the 1st to 3rd seasons decreased sharply and fertilizer nitrogen retained by biochar was simultaneously released.

The conclusion was that biochar addition could promote soil nitrogen retention and maintain high nitrogen uptake by vegetables in continuous growing seasons. However, the comprehensive effect of biochar on nitrogen loss still needs to be assesssed before recommending extended utilization of biochar in vegetable production systems in China.

PREFACE

The research contained in this thesis was completed by the candidate while based in the Discipline of Crop Science, School of Agricultural, Earth and Environmental Sciences, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Pietermaritzburg, South Africa. The research was financially supported by L. Z. Yang through the Special Fund for Agro-scientific Research in the Public Interest, (201503106), L.H. Xue through the National Key Program of Research and Development (2016YFD0801101) and Y.L. Yu through the National Science Foundation for Distinguished Young Scholars of China (41501320).

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

As the candidate's supervisors, we have approved this thesis for submission.

Dr. Alfred Odindo (Supervisor)

Prof. Balakrishna Pillay (Co-Supervisor) Prof. Linzhang Yang(Co-Supervisor)

Date:

DECLARATION 1: PLAGIARISM

I, Yingliang Yu, declare that:

(i) this research reported in this thesis, except where otherwise indicated or acknowledged, is my original work;

(ii) this thesis has not been submitted in full or in part for any degree or examination to any other university;

(iii) this thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons;

(iv) this thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

a) their words have been re-written but the general information attributed to them has been referenced;

b) where their exact words have been used, their writing has been placed inside quotation marks, and referenced;

(v) this dissertation does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the dissertation and in the References sections.

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Signed: Yingliang Yu

Date:

DECLARATION 2: PUBLICATIONS, PATENT AND CONFERENCES

My role in each paper and presentation is indicated. The * indicates corresponding author

Publication 1:	Y.L. Yu, L. H. Xue , L. Z. Yang, S.Y. He, Y. F. Feng and P.F. Hou (2015). Effects of biochar application on pakchoi (Brassica chinensis L.) utilizing nitrogen in acid soil. *Acta Pedologica Sinica*, 52(4), 759-767.
Publication 2:	Y.L. Yu, L. H. Xue , Y. Yang, J.D. Wang, J.J. Duan, S.Y. He and L. Z. Yang, (2015). Influences of biochar addition on soil nitrogen leaching and buffering capacity for vegetable soil. *Research of Environmental Sciences*, 28(12), 1947-1955.
Publication 3:	Y.L. Yu, L. Z. Yang, A.O. Odindo, L.H. Xue, S.Y. He and J. J. Duan (2017). Influences of calcium carbonate and biochar additions on soil nitrogen retention in acidified vegetable soil. *Environmental Science* (Accepted)
Publication 4:	Y.L. Yu, L. Z. Yang, A.O. Odindo, S.Y. He, J. J. Duan and L.H. Xue (2017). Alkaline biochar can improve nitrogen use efficiency by increasing nitrogen retention and pH buffering capacity in vegetable soil. *PloS one* (Submitted)
Patent:	Y.L. Yu, L.H. Xue, S.Y. He, L. Z. Yang and J. J. Duan (2016). A method of soil mineral nitrogen regulation with the interaction of biochar and chemical fertilizer (Applied, No. 201610035232.X)
Conference Presentations:	Y.L. Yu, A.O. Odindo, L. H. Xue and L. Z. Yang (2016). Biochar improved vegetable yield, soil nitrogen utilization and transformation. *IOP Conf. Series: Earth and Environmental Science*, 42, 1.

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THESIS INTRODUCTION

Background

China is the largest producer of vegetables in the world due to its temperate climate and economic development (Zhang and Liu, 2006). Vegetable crops such as cabbage (*Brassica spp)*, tomato (*Lycopersicum solanum)* and bean *(Phaseolus spp)* are commonly grown and form an integral component of the Chinese diet. The total area under vegetable production in China is currently 20 million ha (NBS, 2015) and this is expected to increase due to increasing consumer demands and higher profits for the producers (Verburg and Chen, 2000; Xu *et al.*, 2006).

Nitrogen is an indispensable mineral element needed for vegetable growth and yield performance because of its importance during photosynthesis. The amount of available nitrogen depends on mineralization processes that transform nitrogen from an organic form in the natural soil (Stanford and Smith, 1972). Natural mineralization processes are not able to replenish enough mineral nitrogen to meet the productivity demand in the intensive vegetable production system. It is critical to add nitrogen fertilizer to vegetable production system in order to address the gap between vegetable nitrogen demand and the amount of mineral nitrogen supplied by soil fertility.

The application of fertilizer used to supply nitrogen to the vegetable production system in China is very hi*g*h. Despite the high demand for nitrogen by different types of vegetables, an increasing nitrogen fertilizer application does not consistently result in a yield increase (Zhang *et al.*, 2008; Zhao *et al.*, 2010). Reportedly there is a decreasing trend in vegetable yields in response to the application of excessive nitrogen fertilizer (Min and Shi, 2009). Less than 40% of total nitrogen input by fertilizer can be taken up by vegetables in any season (Huang *et al.*, 2009; Ning-Ning *et al.*, 2010) . The rest of nitrogen gets lost from soil systems causing serious environmental problems and contributing to unhealthy soil condition. Excessive nitrogen fertilizer application is very common and extensive in intensive vegetable production systems in China (Sun et al., 2006; Ju et al., 2009; Min and Shi, 2009; Shi et al., 2009), which is far from the ‘sustainable agriculture’ goal being promoted by the Chinese government. At present, there is an urgent need to find suitable ways of regulating nitrogen for higher nitrogen uptake efficiency and less nitrogen loss in vegetable production systems.

Research problem statement

What are the problems of vegetable production systems in China?

There are a number of challenges that affect vegetable production in China. Firstly, vegetable fields are widely distributed with most of them concentrated in Eastern and Southern China. Individual farmers' fields for vegetable production are small (often less than 0.05 ha) which can supply the needs of their family and surpluses for sale in the village market. In comparison, large agribusinesses companies can rent relatively large fields for production. Secondly, the decision as to which vegetables individual farmers planting is mostly influenced by their dietary habits, while the vegetables chosen by large agribusiness companies depend on vegetable market prices. Thirdly, production is very intensive. It is common to have 3-5 growing seasons in a vegetable field per year and harvesting is done every 2-4 months. The intensive cultivation of vegetables results in a high rate of removal and large amounts of nutrients being removed from the soil. The problem is made worse because frequent vegetable planting means that the fields are occupied for more than 9 months per year and merely 2-3 months are left to allow the soil to recover. Fourth, farmers without scientific advice hold the old opinion 'high fertilizer input, high yield gain', and because the market price of urea was relatively low, they fertilized as much as possible.

Many problems are caused by excessive application of nitrogen fertilizer. Investigations show only 10%-40 % of the nitrogen input from fertilizer can be taken up by vegetables (Huang *et al.*, 2006; Ju *et al.*, 2009). With respect to low nitrogen uptake efficiency, most nitrogen from fertilizer is temporarily left in the soil profile (Ju *et al.*, 2004; Shi *et al.*, 2009) or lost into the atmospheric and hydrological systems(Moll *et al.*, 1982). Generally more than half the total nitrogen fertilizer is lost from vegetable production systems China (Li *et al.*, 2003; Zhu *et al.*, 2005; Hongmei *et al.*, 2007; Min *et al.*, 2011a). Among all the nitrogen processes, leaching is the primary nitrogen loss pathway in vegetable production systems, accounting for over 70%

of total nitrogen loss (Ju *et al.*, 2004; Min *et al.*, 2011a) and is one of the most important contributors to Chinese river eutrophication (Mkhabela *et al.*, 2008; Ding *et al.*, 2010; Yang *et al.*, 2013). Data from China's Yili river catchment shows nitrogen loss from vegetable production systems account for 18.8% of the total aquatic nitrogen load to agricultural non-point pollution with only 8.7% of total planting area (Luo *et al.*, 2015). In addition, soil acidification is another environmental problem caused by excessive nitrogen application. A great number of hydrogen ions, produced in the nitrification process, is left in the soil resulting in an accumulation of hydrogen ions (Malhi *et al.*, 1998) and when leaching occurs, nitrate nitrogen is lost together with bases such as K, Na, Ca, Mg, resulting in increased soil acidity (Barak *et al.*, 1997). After several years of planting vegetables, the decrease of soil pH value is significant (Liu, 2006; Sun *et al.*, 2006).

It is difficult to maintain vegetable yields in soil with high nitrogen leaching loss and soil acidification. It was reported that yields may quickly decline if farmers reduce the application of nitrogen fertilizer to correspond to the amount taken up by the vegetables (Min and Shi, 2009; Xue *et al.*, 2011). Compared to the increasing price of vegetable, the expense of chemical fertilizer is relatively low. Vegetable farmers will prefer to keep applying excessive fertilizer to maintain yields thus ensuring their profits, which have created a vicious cycle contributing to soil degradation.

Why cannot crop yields be maintained by reducing chemical nitrogen fertilizer application rates or replacing with organic manure in the long term?

Excessive application of chemical nitrogen fertilizer is the reason for problems of increased leaching and soil acidity. A number of studies have focused on the issues of reducing chemical nitrogen fertilizer application rates (Tilman *et al.*, 2002; Zhao *et al.*, 2006; Ju *et al.*, 2009) and replacing chemical fertilizer with organic manure (Tester, 1990; Wei *et al.*, 2012). Reducing chemical nitrogen fertilizer application can effectively minimize nitrogen leaching losses and soil acidity in the short term. However, this is unlikely to maintain crop yields in the long term without adding sufficient quantities of nitrogen to supplement the residual nitrogen content in the soil (Ju *et al.*, 2009; Xue *et al.*, 2014) to meet nitrogen crop requirements.

On the other hand, applying organic manure will improve the soils physical structure (Tester, 1990), microbial activity (Xue *et al.*, 2010) and address the problem of acidity (Wei *et al.*, 2012). The benefit of organic manure to soil fertility improvement is accepted by many farmers, as this is evident in the history of crop cultivation in China. However, the lower nitrogen content of organic manure compared with chemical nitrogen fertilizer forces farmers to choose the latter to achieve high vegetable yields. It is estimated that the application rates of organic manure is over 10 times higher than those of chemical nitrogen fertilizer (urea) in order to supply the same amount of nitrogen. Similarly, the problems of soil acidity cannot be completely avoided replacing nitrogen chemical fertilizers with organic manure. This is because both organic and urea-form nitrogen undergo nitrification processes which leads to the production of hydrogen ions contributing to acidic conditions in soils. The soils acidic trend is inevitable as long as the hydrogen ion accumulated due to the nitrogen fertilizer application.

It is clearly evident that reducing chemical nitrogen fertilizer application or replacing with organic manure cannot comprehensively address the existing problems (high nitrogen leaching losses and increased soil acidity) in China's vegetable production system. There is therefore a need to think of new and innovative approaches such as the use of biochar as a soil amendment to maintain vegetable productivity, by reducing nitrogen leaching loss and mitigating soil acidity.

Why could biochar be chosen as soil amendment to ameliorate the problems in vegetable production systems?

Biochar is produced by biomass pyrolysis under low oxygen conditions, resulting in a porous, low density carbon rich material. It has been widely studied as a soil amendment fueled by its potential to change soil conditions (DeLuca *et al.*, 2015) and improve crop yields (Van Zwieten *et al.*, 2010; Spokas *et al.*, 2012; Nguyen *et al.*, 2016). Yin *et al.* (2012) observed that the results of vegetable or crop yields varied considerably after the application of biochar and this was attributed to changes in soil nutrition supply, and microbial activity due to both biochar's characteristics and the soil conditions. However, positive effects on yield generally occurred with a high nitrogen uptake efficiency when biochar addition could meanwhile mitigate or amend some soil problems such as soil acidification, soil sealing and soil organic contamination (Jeffery *et al.*, 2011; Alburquerque *et al.*, 2013; Schulz *et al.*, 2013). Most biochar produced from biomass slow-pyrolysis are adsorptive and alkaline (Lehmann *et al.*, 2007). Meta-analysis shows alkaline biochar can reduce the concentration of iron and aluminum in the soil by liming agents and thus are effective at increasing biomass (Biederman and Harpole, 2013). Several literature reports found the effects of biochar addition on soil fertility could be correlated with improved nutrient retention. This could possibly be explained by biochar's cation adsorption capacity (Liang *et al.*, 2006) or a promotion of nitrogen transformation due to pH increase in acid soils through biochar's acid neutralizing capacity (Van Zwieten *et al.*, 2010). It is reasonable to expect that biochar could be a good option as an amendment that could regulate soil nitrogen retention while at the same time mitigating soil problems for vegetable production systems (converted from conventional crops system mentioned above).

Lack of concern for biochar's impact on nitrogen processes in vegetable production systems

Data on biochar addition has not been well documented when it comes to vegetable production systems (Jia *et al.*, 2012). It is unknown whether the nitrogen adsorbed on biochar still remains available and recovers in latter growing seasons. In addition, few studies have examined the effects of biochar on nitrogen leaching losses and soil acidity when vegetables are growing at the same time. Data referring to the effects of biochar on vegetable yield and nitrogen uptake in several continual growing seasons is lacking. Furthermore, the mineral nitrogen in vegetable soils is from two main sources: transferred by soil nitrogen mineralization and fertilizer application. It is not well understood, whether biochar is likely to interact with residual nitrogen as a result of soil mineralization processes or there would be preference for nitrogen provided by chemical commercial fertilizer sources.

Studies investigating biochar's preference for nitrogen sources should be based on the ^{15}N tracer technique over several continual growing seasons (Bai *et al.*, 2015) with the aim of verifying and explaining the effects of biochar addition on nitrogen retention and uptake by vegetables in intensive vegetable production systems in China.

Aim and objectives of research

Aim

The aim is to study whether using biochar as an amendment can have an effect on improving soil nitrogen retention and uptake by vegetable crops, and reducing acidity in vegetable soils in China.

Objectives

1. To determine the differences of soil chemical properties and nitrogen dynamics between vegetable soils and paddy soils.
2. To determine the effect of biochar addition on soil nitrogen retention in soils used for vegetable production in China.
3. To determine the effect of biochar addition on soil acidity in soils used for vegetable production in China.
4. To determine the effect of biochar addition on nitrogen uptake by vegetable (pakchoi) and yields.
5. To examine the ratios of nitrogen fertilizer to total nitrogen (fertilizer nitrogen + soil mineralized nitrogen) and the recovery of nitrogen fertilizer in plants, soil and leachate with different biochar addition rates.

Preconditions

The current study was based on the following testing preconditions:

1. Vegetable yield is associated with soil nitrogen supply when available phosphorus and potassium are sufficient in soil.

2. Pakchoi (*Brassica chinensis L.*), the most common vegetable, has a similar growing nitrogen demand as other leaf vegetables in the Tailake region, of China.
3. Soil mineral nitrogen content in the vegetable production system is determined by soil nitrogen mineralization and nitrogen fertilizer application.
4. The property of biochar is a resistant amendment. The effects of biochar on nitrogen contents and processes are constant.

Outline

This thesis consisted of six chapters, which are outlined below. The referencing system used in this thesis is based on the referencing style of the Journal of Agricultural Ecosystem Environment. The thesis is in the form of progressive research chapters. The thesis is in the form of discrete research chapters and each chapter follows the format of a stand-alone research paper (whether or not the data in the chapter has already been published). This is the dominant thesis format adopted by the University of KwaZulu-Natal. Thus, there is some unavoidable repetition of references and introductory information between chapters. The outcome of Chapter 2 has been published in *Acta Pedologica Sinica* (Volume 52, No. 4, 2015). Part of data in Chapter 3 and Chapter 4 has been published in *IOP Conf. Series: Earth and Environmental Science* (Volume 42, 2016) and *Research of Environmental Sciences* (Volume 28, 2015). The data in Chapter 4 has been accepted by *Environmental Science* (2017). Application for a Chinese patent (No.201610035232.X) has been made for the research outcomes in Chapter 3.

The structure of this thesis is outlined below:

Chapter	Title
-	Thesis Introduction
1.	Review of literature
2.	Comparison of soil chemical properties and nitrogen dynamics

	between vegetable soils and paddy soils
3.	Effects of biochar addition on nitrogen retention in soils used for vegetable (pakchoi) production
4.	Effects of biochar addition on soil acidity in soil used for vegetable production
5.	Effects of biochar addition on vegetable (pakchoi) nitrogen uptake and recovery efficiency in vegetable production systems
6	General conclusions

Reference

Alburquerque, J.A., Salazar, P., Barrón, V., Torrent, J., del Campillo, M.d.C., Gallardo, A., Villar, R., 2013. Enhanced wheat yield by biochar addition under different mineral fertilization levels. Agronomy for Sustainable Development 33, 475-484.

Bai, S.H., Xu, C.Y., Xu, Z., Blumfield, T.J., Zhao, H., Wallace, H., Reverchon, F., Van Zwieten, L., 2015. Soil and foliar nutrient and nitrogen isotope composition (δ15N) at 5 years after poultry litter and green waste biochar amendment in a macadamia orchard. Environmental Science and Pollution Research 22, 3803-3809.

Barak, P., Jobe, B.O., Krueger, A.R., Peterson, L.A., Laird, D.A., 1997. Effects of long-term soil acidification due to nitrogen fertilizer inputs in Wisconsin. Plant and Soil 197, 61-69.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta‐analysis. GCB Bioenergy 5, 202-214.

DeLuca, T.H., Gundale, M.J., MacKenzie, M.D., Jones, D.L., 2015. Biochar effects on soil nutrient transformations. Biochar for environmental management: science, technology and implementation 2, 421-454.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, & Soil Pollution 213, 47-55.

Hongmei, Y., Zizhong, L., Yuanshi, G., 2007. Comparison of nitrogen loss and use efficiency of vegetable in vegetable field under traditional and improved water and N-fertilizer management. Transactions of the Chinese Society of Agricultural Engineering 2007.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Huang, L.H., Shen, G., Gu, H.R., Qian, X.Y., Shi, X.R., Gullino, M., 2009. Simulation of some impacts of fertilization and water management on nitrous oxide emissions from vegetable field. Journal of Agro-Environment Science 28, 1319-1324.

Jeffery, S., Verheijen, F.G., Van Der Velde, M., Bastos, A.C., 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agriculture, Ecosystems & Environment 144, 175-187.

Jia, J., Li, B., Chen, Z., Xie, Z., Xiong, Z., 2012. Effects of biochar application on vegetable production and emissions of N2O and CH4. Soil Science and Plant Nutrition 58, 503-509.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X., Liu, X., Zhang, F., Roelcke, M., 2004. Nitrogen fertilization, soil nitrate accumulation, and policy recommendations in several agricultural regions of China. AMBIO: a Journal of the Human Environment 33, 300-305.

Lehmann, J., Kern, D.C., Glaser, B., Woods, W.I., 2007. Amazonian dark earths: origin properties management. Springer Science & Business Media.

Li, J.l., Chen, X.p., Li, X.l., 2003. Effect of N fertilization on yield, nitrate content and N apparent losses of Chinese cabbage. Acta Pedologica Sinica 40, 266-272.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F., Petersen, J., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Liu, F.C., 2006. Spatial and temporal variability of soil acidity in typical areas of Taihu Lake region in the last 20 years. Resources and Environment in the Yangtze Basin 15, 744.

Luo, Y.X., Gao, B., Yan, X.Y., Jiang, X.S., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Ma, W., Mao, D., Zhang, F., 2000. Nutrients accumulation within vegetable awning (green house) in Shandong province. Phosphate & Compound Fertilizer 3, 028.

Malhi, S., Nyborg, M., Harapiak, J., 1998. Effects of long-term N fertilizer-induced acidification and liming on micronutrients in soil and in bromegrass hay. Soil and Tillage Research 48, 91-101.

Masclaux-Daubresse, C., Daniel-Vedele, F., Dechorgnat, J., Chardon, F., Gaufichon, L., Suzuki, A., 2010. Nitrogen uptake, assimilation and remobilization in plants: challenges for sustainable and productive agriculture. Annals of Botany 105, 1141-1157.

Min, J., Shi, W.M., 2009. Effects of different N rates on the yield, N use efficiency andfruit quality of vegetables cultivated in plastic greenhouse in Taihu lake region. Plant Nutrition and Fertilizer Science 15, 151-157.

Min, J., Shi, W., Xing, G., Zhang, H., Zhu, Z., 2011a. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems.

Nutrient Cycling in Agroecosystems 91, 31.
Min, J., Zhao, X., Shi, W.M., Xing, G.X., Zhu, Z.L., 2011b. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.
Mkhabela, M., Madani, A., Gordon, R., Burton, D., Cudmore, D., Elmi, A., Hart, W., 2008. Gaseous and leaching nitrogen losses from no-tillage and conventional tillage systems following surface application of cattle manure. Soil and Tillage Research 98, 187-199.
Moll, R., Kamprath, E., Jackson, W., 1982. Analysis and interpretation of factors which contribute to efficiency of nitrogen utilization. Agronomy Journal 74, 562-564.
NBS, 2015. China Statistical Yearbook. . China Statistic Press, Beijing., National Bureau of Statistics of China,.
Nguyen, D.H., Scheer, C., Rowlings, D.W., Grace, P.R., 2016. Rice husk biochar and crop residue amendment in subtropical cropping soils: effect on biomass production, nitrogen use efficiency and greenhouse gas emissions. Biology and Fertility of Soils 52, 261-270.
Ning-Ning, M., Tian-Lai, L., Chun-Cheng, W., En-Ping, Z., 2010. Effects of long-term fertilization on soil enzyme activities and soil physicochemical properties of facility vegetable field. Yingyong Shengtai Xuebao 21.
Schulz, H., Dunst, G., Glaser, B., 2013. Positive effects of composted biochar on plant growth and soil fertility. Agronomy for Sustainable Development 33, 817-827.
Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.
Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of Environmental Quality 41, 973-989.
Stanford, G., Smith, S., 1972. Nitrogen mineralization potentials of soils. Soil Science Society of America Journal 36, 465-472.
Sun, R., Wang, D., Lin, J., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.
Tester, C.F., 1990. Organic amendment effects on physical and chemical properties of a sandy soil. Soil Science Society of America Journal 54, 827-831.
Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S., 2002. Agricultural sustainability and intensive production practices. Nature 418, 671.

Van Zwieten, L., Kimber, S., Morris, S., Chan, K., Downie, A., Rust, J., Joseph, S., Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 327, 235-246.

Verburg, P.H., Chen, Y., 2000. Spatial explorations of land use change and grain production in China. Agriculture, Ecosystems & Environment 82, 333-354.

Wei, H.q., Lv, J.l., Xu, M.g., Cai, Z.j., Wang, B.r., 2012. Alkalinity of organic manure and its mechanism for mitigating soil acidification. Plant Nutrition and Fertilizer Science 18, 1159-1167.

Xu, M., Wang, X.K., Jiang, J.X., Sheng, Q.R., 2006. Changes in cultivated land utilization pattern and countermeasures in south Jiangsu Soils 38, 825-829.

Xue, F., Yan, T.m., Yang, L.z., Qiao, J., 2010. Influences of organic fertilizer application on soil biological properties. Chinese Journal of Eco-Agriculture 18, 1372-1377.

Xue, L.h., Yu, Y.l., Yang, L.z., 2011. Nitrogen balance and environmental impact of paddy field under different N management methods in Taihu Lake region. Environmental Science 32, 1133-1138.

Xue, L., Yu, Y., Yang, L., 2014. Maintaining yields and reducing nitrogen loss in rice–wheat rotation system in Taihu Lake region with proper fertilizer management. Environmental Research Letters 9, 115010.

Yang, L.z., Shi, W.m., Xue, L.h., Song, X.f., Wang, S.q., Chang, Z.z., 2013. Reduce-Retain-Reuse-Restore technology for the controlling the agricultural nno-point source pollution in countryside in China: general countermeasures and technologies. Journal of Agro-Environment Science 32, 1-8.

Yin, D.W., Meng, J., Zheng, G.P., Zhong, X.M., Yu, L., Gao, J.P., Chen, W.F., 2012. Effects of biochar on acid black soil nutrient, soybean root and yield. Advanced Materials Research. Trans Tech Publ, pp. 2278-2289.

Zhang, H.z., Liu, S., 2006. The comparison of Chinese vegetable prodution under internantionalization. China Vegetables 3, 1-5.

Zhang, L., Peng, H., Qin, X., 2008. Effect of chemical fertilization application on Chinese crop yield at different stages--based on data from 30 provinces during 1952-2006 period. Agricultural Technical Economy, 85-94.

Zhao, B.q., Li, X.y., Li, X.p., Shi, X.j., Huang, S.m., Wang, B.r., Zhu, P., Yang, X.y., Liu, H., Chen, Y., 2010. Long-term fertilizer experiment network in China: crop yields and soil nutrient trends. Agronomy Journal 102, 216-230.

Zhao, R.F., Chen, X.P., Zhang, F.S., Zhang, H., Schroder, J., Römheld, V., 2006. Fertilization and nitrogen balance in a wheat–maize rotation system in North China. Agronomy Journal 98, 938-945.

Zhu, J., Li, X., Christie, P., Li, J., 2005. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (Capsicum frutescens L.) cropping systems. Agriculture, Ecosystems & Environment 111, 70-80.

Zhu, Z., Norse, D., Sun, B., 2006. Policy for reducing non-point pollution from crop production in China. China Environmental Science Press, Beijing, 135-161.

CHAPTER 1: REVIEW OF LITERATURE

Abstract

China has a limited area of cultivated land per capita and an increasing population, therefore maintaining a high crop yield is of great significance in order to meet the large food demand and to assure grain self-sufficiency. Therefore a primary goal of most farmers is to produce a high crop yield, and without adequate scientific advice they have always applied large amounts of nitrogen fertilizer to ensure sufficient mineral nitrogen in the soil for crop growth. Intensive cultivation is common in China, especially for the vegetable production system. The soil conditions under intensive cultivation was deteriorating even occurred degradation contributing to a reduction of farmland area. Therefore, the findings of nitrogen processes in vegetable soil from the existing studies needed to be reviewed and summarized for addressing the soil problems that restraining nitrogen retention in the vegetable production system.

After summing up the main nitrogen processes of the vegetable production system, it was found that the nitrogen fertilizer applied during this process was usually 4-8 times higher than that of plant demand. Excessive nitrogen fertilizer application caused serious nitrogen leaching loss and soil acidity, which hampered sustainable production within this system. Nitrogen uptake by plants in the vegetable soil with these constraints was always 20%-40% of the nitrogen applied and the yield might be reduced easily by decreased the amount of nitrogen fertilizer. It is necessary to find an approach to mitigate nitrogen leaching loss and soil acidity in vegetable production systems and also promote nitrogen retention and vegetable nitrogen uptake for sustainable productivity.

Biochar is a carbon-rich product derived from pyrolysis of organic material. It has been studied for its potential capacity to affect soil nitrogen content and soil nitrogen transformation processes such as mineralization and nitrification in the agricultural system. Biochar may be an option for mitigating soil acidity and nitrogen leaching problems in vegetable soil due to its alkalinity and adsorption properties.

There is sufficient agricultural residue which can serve as raw material for biochar production in China. Biochar production industries of different sizes are increasing by necessity in Chinese rural areas and biochar-based products (such as biochar-based fertilizer, biochar-based amendments) are chosen as a priority in comparison to returning biochar to the fields directly. Large-scale addition of biochar is possible in China, which will assist in the agricultural residue returning to the field.

However, studies in vegetable production systems are still lacking. Whether the positive effect found in short term experiments or incubation can be consistent or last long is unknown. It is necessary to carry out a study with continual growing seasons to verify and assess the effects of biochar addition on nitrogen retention and uptake by vegetables in intensive production systems in China.

Key words:

Vegetable production system, nitrogen fertilizer application, biochar addition, soil nitrogen content and transformation, vegetable uptake

1.1 Introduction

National food security is a serious issue in China because of its large population and limited area of per capita cultivated land (Chen, 2007; Chen *et al.*, 2013). High yields are expected from the limited cultivated fields to supply enough food for the large population. However, most Chinese farmers hold the traditional opinion 'high fertilizer input, high yield gain', resulting in a large nutrient flux in Chinese agricultural systems. Compared to conventional crops systems (such as paddy, wheat and maize), the vegetable production system is more intensive with a higher fertilizer input and more growing seasons in one year (Ju *et al.*, 2009; Huang *et al.*, 2006; Zhu *et al.*, 2006). Excessive nitrogen fertilizer application is common in the vegetable production system, along with low nitrogen uptake efficiency (Huang *et al.*, 2006; Ju *et al.*, 2011; Zhu *et al.*, 2005). Without fertilizer applied, soil mineral nitrogen is difficult to maintain and vegetable yield is likely to reduce by decreased nitrogen fertilizer application. In order to ensure sufficient mineral nitrogen in vegetable soil, farmers keep increasing fertilizer application, making soil conditions deteriorate. Cultivation of the fields may become unsuitable if soil degradation occurs (Shi *et al.*, 2009; Zhang *et al.*, 2005) and the Chinese government is trying to avoid a reduction in the availability of farmland (Chen, 2007).

Therefore, it is critical to review the existing studies on soil nitrogen processes in vegetable soil in order to determine the major constraints of nitrogen retention in the soil and to find a feasible approach to address these problems in the vegetable production system.

1.2 Conversion of field utilization patterns in China

Utilization patterns of the fields are determined by food demand in the market.

1.2.1 Food demand increases pressure on cultivated land

Cultivated land is an irreplaceable and non-renewable resource that humans rely on to ensure a sufficient food supply and for survival. The Chinese population makes up 22% of the world's total population with less than 9% of the world's cultivated land (Chen, 2007; Chen *et* *al.*, 2013). A review of international literature shows that a decrease of cultivated land area is not only occurring in China, but also happening in other developing countries (Ramankutty *et al.*, 2002). Countries in North America and Europe have a similar experience in terms of the loss of cultivated land during periods of economic development (Caradec *et al.*, 1999; Ramankutty *et al.*, 2002). Data from a Chinese investigation show that the reduced rate of cultivated land area in China is increasing rapidly. Since the economic structural changes in the late 1980s, urbanization and industrialization began to accelerate and large areas of cultivated land have been converted to non-agricultural usages such as industrialized or residential buildings (Chen, 2007). There were 0.2 million hectares of cultivated land converted to non-agricultural usage annually during the period 1986-2000, and more than 1.5 million hectares annually after 2000 (Deng *et al.*, 2006). However, food demand is still increasing with the large population, imposing a heavy burden on agricultural production. More gain is expected to be harvested per unit field. High yields and maintaining these high yields has become critical for ensuring national food security.

1.2.2 Conventional crops field converts to vegetable field

As people's standard of living has improved, the concern about food shortage has gradually changed into a demand for reasonable diets with an emphasis on vegetables and meat served with cereals. Vegetables have become a daily necessity as a dietary component and the price of vegetables have risen since the year 2000. Although the government has instituted policy measures to slow down the increasing costs, the price of vegetables continues to escalate due to market drivers (CCICED, 2004). Cultivation of vegetables can earn more than 8,000 USD/ ha per year in the east of China, while conventional crop farming earns approximately 3,000 USD/ ha per year (conventional crops here mean those such as paddy, wheat and maize treated as staple food in the Chinese diet) (He *et al.*, 2007). The field area used for vegetable planting was 20.4 million hectare in 2015, accounting for 12.5% of the Chinese total cultivated land area in that year compared to that in 2000, when the field area of vegetables increased by 33.6% and the planting rate increased by 27.8% (NBS, 2015) (Fig.1.1). The conversion of conventional crop fields to vegetable fields in the Tailake region of China is more significant with an increase from 1% in 1981 to 18% in 2005 (Wang *et al.*, 2008). This conversion will continue for several years because the demand for vegetables keeps growing with the pace of economic development in China.

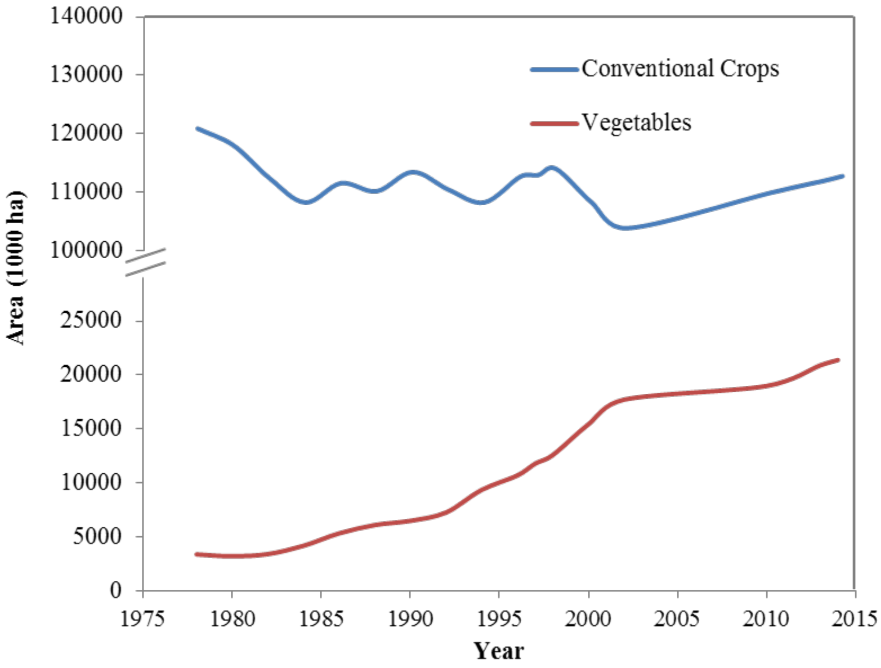


Fig. 1.1 Variation of cultivated land areas for conventional crops production and vegetable production from 1978 to 2015(NBS, 2015).

Despite the conversion of field utilization patterns bringing more profit to Chinese farmers, many problems like acidification, salinization and degradation of the soil has arisen due to different nutrient demands (Yin *et al.*, 2004; Zhang *et al.*, 2005; Sun *et al.*, 2006; Shi *et al.*, 2009). Compared to soil used for planting conventional crops, the nutrient content of soil for vegetable farming is significantly increased by the intensive cultivation practices (more fertilizer applied, more irrigation times and shorter growing seasons) (Jin *et al.*, 2005b). Large amounts of nitrogen left in the soil and high nitrogen loss from leaching (Song *et al.*, 2009; Min *et al.*, 2011b; Luo *et al.*, 2015) and ammonia volatilization (Fayun, 2005; Xi *et al.*, 2010) are always features of a vegetable production system. Vegetable yields are difficult to maintain with the same nitrogen input every year, indicating that soil nitrogen supply declines with vegetable planting. If the application of nitrogen is not managed correctly, the soil will degrade over a number of years and will therefore not be suitable for cultivation.

1.3 Nitrogen processes in the vegetable production system

Agricultural systems are affected by human activities. Farmers apply different materials and management methods to the planting of different crops, which changes the nitrogen processes after field utilization patterns conversion. Soil nitrogen processes affect both nitrogen uptake by the plant and nitrogen loss in the agricultural system. As Figure 1.2 shows, nitrogen in agricultural soil includes the processes of nitrogen input and output. Nitrogen fertilizer, deposition and mineralization processes are regarded as nitrogen input supplying mineral nitrogen for plant growing. Nitrogen output is consisted with nitrogen uptake by plant (crop harvest) and nitrogen loss. The major loss pathways in agricultural systems are leaching, ammonia volatilization and denitrification.

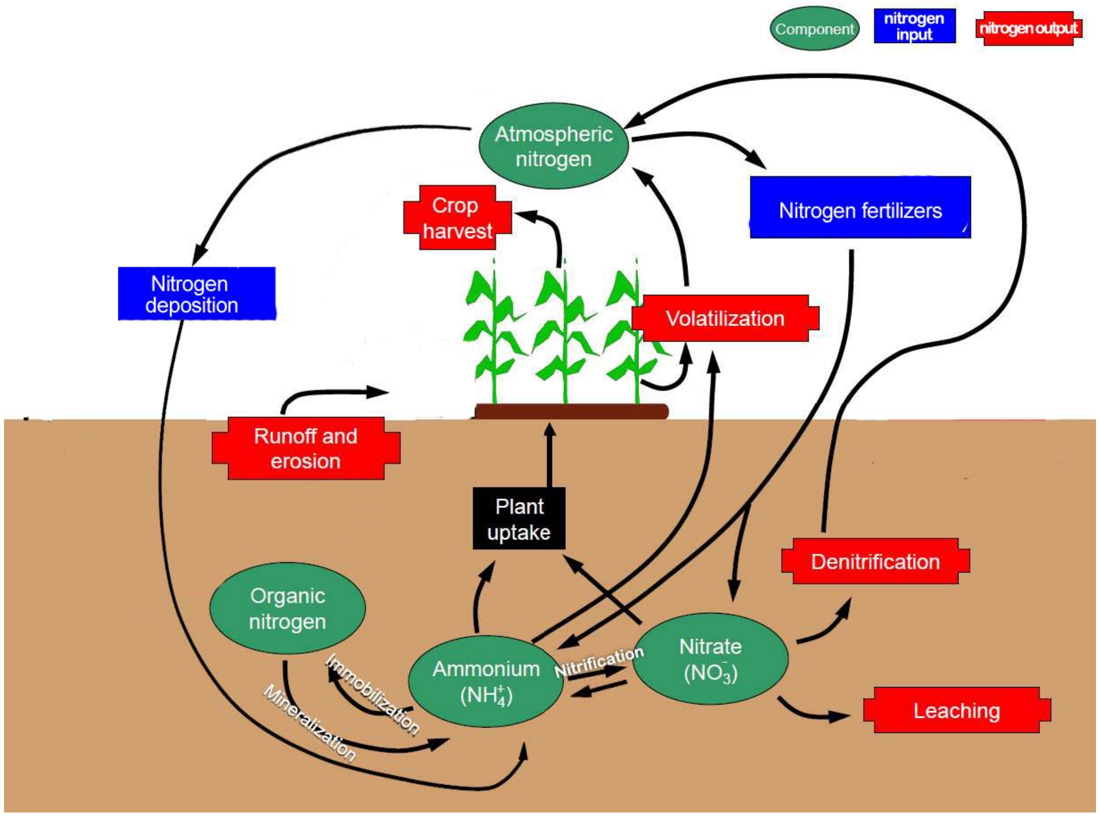


Fig. 1.2 Nitrogen processes in agricultural system

1.3.1 Comparison of nitrogen input in a vegetable production system to that in a conventional crop system

Nitrogen mineralization, fertilizer application and deposition are regarded as nitrogen inputs supplying mineral nitrogen for plant growing.

1.3.1.1 Soil nitrogen mineralization and nitrification

Nitrogen in the soil is mostly organic nitrogen; only a small part of the soil nitrogen pool is mineral nitrogen. Almost all crops depend on mineral nitrogen supplementation; in other word, mineral nitrogen is the available form for crop uptake. Soil nitrogen mineralization is the most important nitrogen process, decomposing organic nitrogen into mineral forms that may be plant-available. Thus, soil nitrogen mineralization is regarded as the predominant nitrogen input process for the agricultural system.

Essentially how much mineral nitrogen the soil can support for crop growth is determined by the nitrogen mineralization rate during the growing period. It is difficult to compare the real nitrogen mineralization rates *in situ* between vegetable production systems and conventional crops systems. Soil from vegetable fields seems to have a higher mineralization rate than that from conventional crops fields because fertilizer utilization efficiency in vegetable production system is lower than that in conventional crops systems (Zhu *et al.*, 2005; Min *et al.*, 2011b). As a result, nitrogen mineralization processes in a vegetable production system have to meet the vegetable nitrogen demand (Li *et al.*, 2003).

Soil properties can have an effect on the nitrogen mineralization rate. Firstly, the ratio of soil total carbon to total nitrogen (TC/TN) has a negative correlation with nitrogen mineralization rate (Sun *et al.*, 2002). Most soil from vegetable fields has lower TC/TN than soil from conventional crop fields due to its high nitrogen inputs, inducing higher soil nitrogen mineralization rates. Secondly, although soil nitrogen mineralization is regarded as being insensitive to acidity, enhancement of nitrogen mineralization is commonly reported after liming of acid soils (Jin *et al.*, 2005a). Acidification is one of the common soil problems occurring in vegetable soil. It implies that soil nitrogen mineralization rates in vegetable production system may be reduced when soil becomes more acidic. Thirdly, soil nitrogen mineralization rate is also affected by soil moisture content. Soil nitrogen mineralization rate increases with soil moisture content increase till the 100% WFPS (Water-Filled Pore Space) in aerobic conditions (Jin *et al.*, 2005a). However, anaerobic conditions will weaken and even restrain the soil nitrogen mineralization process. Negative nitrogen mineralization has even been found in paddy systems due to their flooded environment.

The nitrification process alternately regulates mineral nitrogen forms from ammonium to nitrate and nitrite (trace amounts). Indeed, a high nitrification rate has often been considered as an index of soil fertility, because most crops (except paddy) are inclined to use nitrate as an accessible nitrogen source from soil (Haynes, 2012). Both soil chemical and physical properties have significant effects on the nitrification process when there is enough ammonium existing as substrate. It has been observed that nitrification has a positive relationship with soil pH, and stops when soil pH is less than 4.5 (Fan and Zhu, 2002). The soil moisture content is favorable for nitrification at 50 % - 60 % of WFPS (Water-Filled Pore Space) (Pihlatie *et al.*, 2004; Bateman and Baggs, 2005).

1.3.1.2 Nitrogen fertilizer application

Fertilizer is the main source of nitrogen in the vegetable production system. Compared to the conventional crop system, 2-3 times greater amount of nitrogen fertilizers is applied as a nitrogen resource in order to ensure high yields in the vegetable production system in China and the amount of nitrogen application has been 4-8 times higher than that of plant demand (He *et al.*, 2007). An investigation conducted in the north plains of China found that the average amount of nitrogen fertilizer is 1100-1500 kg N/ha in vegetable fields per year, whereas less than 500 kg N/ha was used in maize-wheat fields (Ma *et al.*, 2000; Ju *et al.*, 2009). Data from the Tailake region of China revealed that vegetable fields receive 900-1300 kg N /ha from nitrogen fertilizer, whereas paddy-wheat fields receive 400-600 kg N /ha (Huang *et al.*, 2006; Zhu *et al.*, 2006; Min *et al.*, 2011b). Furthermore, organic manures are often applied randomly and most farmers do not consider organic manure as part of nitrogen fertilizer in vegetable fields (Huang *et al.*, 2006; Ju *et al.*, 2006). Nitrogen input from fertilizer in the vegetable production system is 3-4 times higher than that in conventional crop systems (He *et al.*, 2007). Despite the rate of nitrogen fertilizer application being varied due to different vegetable types and multiple cropping indices, excessive nitrogen fertilizer application is very common in intensive vegetable production systems in China. The amount of nitrogen fertilizers applied is usually much higher than the recommended amount in vegetable production systems (Zhu *et al.*, 2006).

When excessive nitrogen is applied in the vegetable production system, hydrogen ions, produced from the nitrogen nitrification process, gather in the soil profile and thereby increase soil acidity. The decline (0.7-1.96 unit) of soil pH values has been reported after the soil used to plant conventional crops was converted for planting vegetables (Yin *et al.*, 2004; Zhang *et al.*, 2005; Sun *et al.*, 2006). If farmers are not given scientific advice they may apply more nitrogen fertilizer to maintain the yields in the following year, making soil acidity worse.

1.3.1.3 Other input

Irrigation water, wet deposition and seeds are also nitrogen inputs for the agricultural system. Nitrogen from wet deposition and seeds are very little in most condition of both vegetable production system and conventional crops system. However, contributions of irrigation water to nitrogen input are dependent. Compared to crops planted in dry fields, vegetables need a considerable amount of water for growing. Irrigation times and amounts of irrigated water used are more than for conventional crops planted in dry fields. An investigation conducted in the China north plain found that nitrogen from irrigation water input to the vegetable production system is 84 times higher than the input to the maize-wheat system; the nitrogen contribution from irrigation water represents over 10% of the nitrogen input in the vegetable production system, whereas the nitrogen contribution from irrigation water is less than 1% of the total nitrogen input in maize-wheat system (Ju *et al.*, 2006). However, when compared to paddy planting in flooded conditions, results are very different. Studies in China's Tailake region found that the nitrogen contributions of irrigation water are less than 1% and 3-6% of the nitrogen input in the vegetable production system and paddy-wheat system, respectively (Min *et al.*, 2011b; Xue *et al.*, 2011). Not only the volume but also the nitrogen concentration of the irrigation water determines the nitrogen contribution by irrigating. A nitrogen balance study carried out in Japan showed 30%-43% nitrogen contribution from irrigation water due to the high nitrogen content (4-12 mg/L) in underground water (Kyaw *et al.*, 2005). Shallow groundwater used as an irrigation source in China's north plain also has high nitrate concentrations resulting in a high nitrogen supply. Less nitrogen is taken into vegetable production system via irrigation in China's Tailake region because river water is used instead of shallow groundwater.

1.3.2 Comparison of nitrogen output in vegetable production systems with that in conventional crops system

The process of nitrogen outputs can be used to determine the balance of nitrogen in the agricultural system and estimate whether the nitrogen input is adequate. There are three major aspects of nitrogen output in vegetable production system: nitrogen uptake by plants, nitrogen left in soil and nitrogen loss.

1.3.2.1 Nitrogen uptake by plant

The nitrogen uptake by the plant is considered as an effective part, calculated as uptake efficiency. Studies show that nitrogen unused by crops accounted for 41%-49% in the paddy-wheat system (Zhao *et al.*, 2009) and 45% in the maize-wheat system (Ju *et al.*, 2006). The vegetable production system has a lower uptake efficiency than the conventional crop systems (Zhu *et al.*, 2005) due to excessive fertilization (Li *et al.*, 2003). Data in China's Tailake region shows vegetables can take up 20%-40 % of the total nitrogen applied from fertilizer (Huang *et al.*, 2006) and it falls to less than 10% in China's north plain (Ju *et al.*, 2011).

1.3.2.2 Nitrogen left in soil

Numerous studies have shown that yields do not increase significantly when the nitrogen fertilizer application rate exceeds a certain value, but the part of nitrogen left in soil increases sharply (Raun and Johnson, 1995; Bhogal *et al.*, 2000). High nitrogen inputs and low plant uptake in the vegetable production system results in 4.5-5.2 times higher soil residual nitrogen than that in conventional crop soil (Wang *et al.*, 2002). Cao *et al.* (2008) evaluates that there is more than half of the nitrogen input from fertilizer temporarily left in the vegetable soil profile. Soil ammonia nitrogen content increased 21 times and nitrate nitrogen content increased 22 times after soil planting patterns changed from paddy to vegetable (Yin *et al.*, 2004). Nitrate nitrogen is the predominant residual nitrogen in soil, which is 5.9-6.2 times higher than ammonia nitrogen in vegetable soil (Wang *et al.*, 2002). Most nitrate nitrogen is concentrated in the upper soil layer than in the rest of the profiles because of the nitrification of ammonium nitrogen and mineralization of organic matter occurring in the aerobic upper soil layer (Byrnes, 1990). Remarked residual nitrate nitrogen occurred with content reaching 936 mg/kg in the top 0.1 m of soil, and then the catch crop significantly reduces the average soil nitrate nitrogen to 195 mg/kg during the fallow period (Shi *et al.*, 2009). In addition, nitrate nitrogen in soil easily moves continuously downwards with the free flow of water in the soil profile as opposed to ammonium nitrogen. Ju *et al.* (2006) found the amount of residual nitrate nitrogen in the 0-90 cm soil layer was 270-5038 kg N/ha in vegetable soil and 172-1452 kg N/ha in maize-wheat soil. The corresponding range of values in the 90-180 cm soil layer are 224-3273 kg N/ha in vegetable soil and 96-1993 kg N/ha in maize-wheat soil. The large amounts of residual nitrate nitrogen in the 90-180 cm soil layer indicates a substantial leaching potential of nitrate in the vegetable production system.

1.3.2.3 Nitrogen loss

Nitrogen loss is closely correlated with amounts of nitrogen application in the agricultural system. The rate of nitrogen loss in the vegetable production system can reach 52-75% (Li *et al.*, 2003; Zhu *et al.*, 2005) and the data of conventional crop systems depends on many practical factors. The nitrogen loss paths in two planting patterns are also quite different. Leaching, ammonia volatilization and denitrification are the main nitrogen loss pathways for both paddy and vegetable production systems.

Paddy fields are more likely to have high ammonia volatilization loss induced by their flooded water. Many studies have reported that ammonia volatilization is the main nitrogen loss pathway in paddy fields (Cai, 1997; Wang *et al.*, 2007; Xue *et al.*, 2011; Xu *et al.*, 2012), accounting for up to 40% of the nitrogen input (Zhu and Chen, 2002). Additionally, it is also an important component of nitrogen loss in maize-wheat systems due to alkaline soil (Qian *et al.*, 1997; Wang *et al.*, 2004). A few studies have examined ammonia volatilization in vegetable production systems and found nitrogen loss from ammonia volatilization was relatively low (Liu *et al.*, 2003; Xi *et al.*, 2010; Min *et al.*, 2011b). Soil planted with vegetables is usually more acidic than that planted with paddy. Ammonia volatilization could be remarkably restrained when the soil environment becomes acidified. The acidification trend may be used to explain the low rate of nitrogen loss via ammonia volatilization in vegetable production systems (Haruna Ahmed *et al.*, 2008).

Due to large soil residual nitrogen and frequent irrigation, vegetable production systems have a greater potential for nitrogen leaching compared to conventional crop systems (Thompson *et al.*, 2007). For example, data from China's Yili river catchment revealed that vegetable fields in that region contribute 18.8% of the total aquatic nitrogen load to agricultural non-point pollution with only 8.7% of total planting area (Luo *et al.*, 2015). Previous studies showed that leaching is the primary nitrogen loss pathway in vegetable production system, accounting for over 70% of the total nitrogen loss (Min *et al.*, 2011a). Min *et al.* (2011b) planted three vegetables successively and found the nitrogen loss via leaching was 9-17 kg N/ha, 84-232 kg N/ha and 16-32 kg N/ha in tomato, cucumber and celery growing seasons, respectively. The considerable nitrogen loss via leaching ranging from 43-328 kg N/ha per year was also found in the maize-wheat system (Liu *et al.*, 2003). Additionally, bases such as K^+, Ca^{2+}, Na^+, Mg^{2+} get lost with nitrate nitrogen leaching, accelerating acidification in vegetable soil (Yin *et al.*, 2004; Han *et al.*, 2014).

However, nitrogen loss via leaching in the paddy-wheat system is quite low, estimated at 3-27 kg N/ha per year, accounting for 2% of nitrogen fertilizer application rates (Xing and Zhu, 2000; Zhu *et al.*, 2000; Zhu and Chen, 2002).

Another possible pathway of nitrogen loss from vegetable production systems may be denitrification (He *et al.*, 2007; Mei *et al.*, 2009; Deng *et al.*, 2012). More nitrogen loss may occur via denitrification from vegetable production systems than that lost from conventional crop systems because of a high nitrogen fertilizer application rate, and proper aerobic conditions in vegetable production systems can provide major substrates for nitrous oxide production (Bouwman *et al.*, 2002). Previous studies provide data that the loss rate of nitrous oxide emissions of the nitrogen input ranges from 0.3 to 4.9 % in rice-wheat systems (Zhu and Chen, 2002; Zou *et al.*, 2005; Yao *et al.*, 2009) and from 0.1 % to 11 % in vegetable production systems (Mei *et al.*, 2009; Deng *et al.*, 2012). Sometimes denitrification losses are negligible, and the variety of soil denitrification partly depends on changes in rainfall (Liu *et al.*, 2003).

1.4 Lack of concern for nitrogen processes in vegetable production systems

The lack of concern towards agricultural advice is always mentioned when foreign scholars and professors discuss excessive nitrogen fertilizer application in Chinese vegetable production systems. Indeed, inadequacy of nitrogen management has seriously affected soil health, creating a negative impact on sustainable agricultural development. Plenty of research focusing on soil nitrogen processes has been carried out, supported by government or public funds. However, three realistic problems pose a challenge to nitrogen reform in China.

- Many small vegetable fields are located around individual farmers' homes, making it difficult to institute mechanized production and regional scale management. Field management decisions, such as what to plant, when to till, how much and when to fertilize, are all decided by individual farmers (Fig. 1.3).

(a) Large conventional paddy field managed with agricultural

(b) Small vegetable fields distributed around individual farmers' houses mechanization

Fig. 1.3 Difference in size between conventional crop fields and vegetable production fields

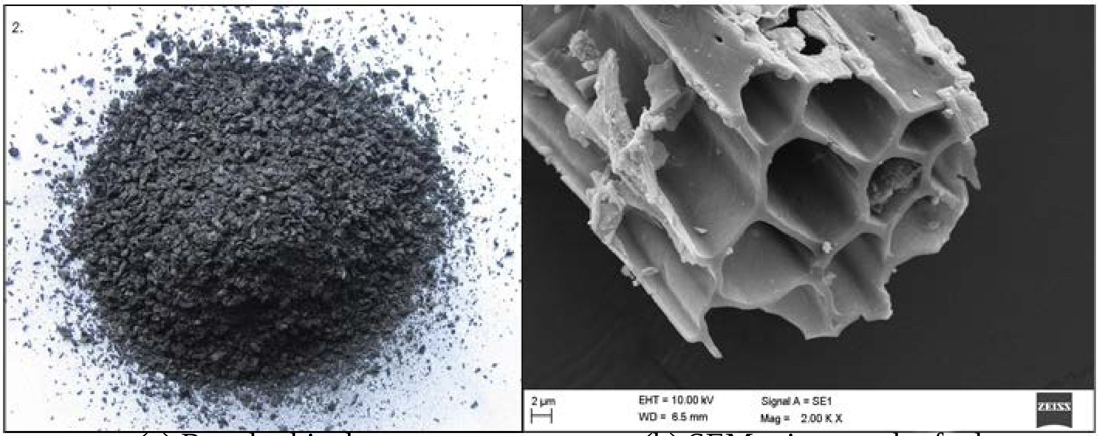
- Economic development has accelerated the urbanization process and, increasingly, young people born in villages move to the cities for a better education and profitable jobs, leaving the elders, who have a limited education, to farm. Most of these elders hold the outdated opinion that applying more fertilizer will reap higher yields. There are no standardized recommendations for fertilizer application in most agricultural areas in China, and individual farmers usually apply large amounts of nitrogen fertilizer in order to ensure high yields.
- On the other hand, vegetable production expands rapidly, resulting in the appearance of large agribusiness companies. Large fields are rented for 3-5 years for vegetable production with the goal of making profits as soon as possible, with no attention being paid to soil health because they will leave and find another field when the soil condition is no longer suitable for planting.

Perhaps some theoretical evidence from scientific research could be used to address the problems mentioned above. However, the best agricultural management will be useless if it is not incorporated into the processes that provide scientific advice to individual farmers and large agribusiness companies. The extension workers should provide advice based on the specific conditions of each field to ensure the suitability of the nitrogen management. Regulation of and policies pertaining to vegetable markets are also needed to avoid the overuse of vegetable fields by large agribusiness companies.

1.5 Biochar addition changes nitrogen processes in cultivated system

Biochar is defined as a carbon(C)-rich product derived from pyrolysis of organic material in the partial or total absence of oxygen at relatively low temperatures (Lehmann, 2009) (Fig.

1.4).The concept of biochar comes from *Terra preta* (black earth) of the Amazon basin, and is a type of dark, fertile anthropogenic soil with a high content of soil organic matter and other nutrients. Biochar contains condensed aromatic structures showing a high degree of chemical and microbial stability in the soil environment (Novak *et al.*, 2009b; Kuzyakov *et al.*, 2014). Thus, biochar could be used as a mechanism to sequester carbon as a tool for offsetting anthropogenic carbon dioxide emissions in the future (Lehmann *et al.*, 2006). Woolf *et al.* (2010) assessed that implementing a sustainable biochar program globally could mitigate up to 12% of current anthropogenic carbon dioxide emissions. Besides biochar’s potential to sequester fixed atmospheric carbon, its agronomic benefits have attracted interest in recent years (Lehmann, 2009; Spokas *et al.*, 2012). The key physical property of most biochars is their highly porous structure, low density and large surface area with charged particles (Downie *et al.*, 2009; Atkinson *et al.*, 2010). This structure can influence the retention of important nutritive cations and anions (nitrogen and phosphorus) (Steiner *et al.*, 2008; Dempster *et al.*, 2012b; Yao *et al.*, 2012). It also can provide a special living space and resource for microbial growth (Lehmann *et al.*, 2007; Kolb *et al.*, 2009). Additionally, alkalinity is another important chemical property of most biochars that will influence the forms and transformations of soil elements (Lehmann *et al.*, 2007). When added to soil, biochar will interact with the physical and biological components of the soil (Glaser *et al.*, 2002; Steiner *et al.*, 2008; Atkinson *et al.*, 2010), and create effects throughout the ecosystem. Although the effects vary depending on different soil types and biochar properties (determined by different raw material and pyrolysis methods), the addition of a new carbon source into the soil is bound to change nitrogen cycling in the soil.



(a) Regular biochar (b) SEM micrograph of wheat

Fig. 1.4 Different magnifications of biochar

1.5.1 Effects of biochar addition on soil nitrogen content and transformations

1.5.1.1 Adsorption

Biochar's porosity and the presence of both polar and nonpolar surface sites suggest it is possible to adsorb nutrients ions (Cao and Harris, 2010; Laird *et al.*, 2010; Hale *et al.*, 2013). In addition, biochar with a high TC/TN ratio has a greater potential for adsorption of nitrogen ions from soil to biochar inducing sustained higher nitrogen fertility in surface soils (Steiner *et al.*, 2007). Many studies using biochar as a soil amendment to control nitrogen leaching loss showed that biochar can improve soil nitrogen retention by adsorbing ammonium, ammonia and nitrate nitrogen (Cao and Harris, 2010; Ding *et al.*, 2010; Laird *et al.*, 2010; Spokas *et al.*, 2012; Yao *et al.*, 2012) and then still maintain bioavailability until subsequently utilized by the plant (Taghizadeh-Toosi *et al.*, 2012). However, direct adsorption of ammonium and nitrate nitrogen biochar has not been extensively studied. Most data referred to here are calculated with the reductions of ammonium and nitrate nitrogen in leachate or solution.

Some studies estimate biochar's maximum adsorptive rate of ammonium nitrogen by kinetic models resulting in 0.85-3.24 mg N/g (Ding *et al.*, 2010; Zhu *et al.*, 2012). The maximum ammonium nitrogen adsorption from slurry at 1400 mg N/L can reach to 44.64 mg/g and 39.8 mg/g for wood and rice husk biochar (Kizito *et al.*, 2015), which was attributed to the adsorptive capacity of biochar's superior BET surface area and presence of dissolved matter in the slurry (Saltalı *et al.*, 2007). These results are much higher than those calculated in leaching experiments. Yao *et al.* (2012) examined biochar produced using different raw materials and pyrolysis temperatures and found biochar could remove ammonium nitrogen from solution with adsorptive rates ranging from 0.05 to 0.19 mg N/g and nitrate nitrogen with adsorptive rate ranging from 0.02 to 0.64 mg N/g. Dempster *et al.* (2012b) found that biochar would adsorb both ammonium nitrogen and nitrate nitrogen when added into an ammonium nitrate solution, with the adsorptive rate of ammonium nitrogen ranging from 0.02 to 0.25 mg N/g and the adsorptive rate of nitrate nitrogen ranging from 0.02 to 0.19 mg N/g. Compared to ammonium adsorption, nitrate adsorption of biochar has been reported to be insignificant in most studies(Lehmann *et al.*, 2003; Jones *et al.*, 2010; Hale *et al.*, 2013).

Adsorptive rates of ammonium nitrogen and nitrate nitrogen vary widely with biochar's characteristics and the nitrogen contents of solutions, but there is a significant relationship that adsorptive rates of both ammonium nitrogen and nitrate nitrogen increase with increased nitrogen content of solution. Biochar produced using a high pyrolysis temperature has the potential for higher nitrate nitrogen absorption, because absorption of nitrate nitrogen is a result of base functional groups on biochar (Kameyama *et al.*, 2012). Different from nitrate nitrogen, the reason generally given for the adsorption of ammonium nitrogen is cation exchange capacity (Cheng *et al.*, 2008) and pore structures (Amonette and Joseph, 2009; Saleh *et al.*, 2012) of biochar.

1.5.1.2 Mineralization, immobilization and nitrification

Nitrogen mineralization and immobilization are transformation processes occurring at the same time and are affected by TC/TN ratios in both the soil and biochar. The result of these two transformation processes determines the mineral nitrogen content in soil. Typically as TC/TN ratio increases, nitrogen immobilization would be enhanced. With respect to the high TC/TN ratio in biochar, it may be speculated that nitrogen immobilization would be enhanced after biochar was added to soil. However, the effects of biochar addition on soil nitrogen are quite complicated. Various results have been reported that biochar addition increased nitrogen mineralization (Castaldi *et al.*, 2011; Bruun *et al.*, 2012), decreased nitrogen mineralization (Dempster *et al.*, 2012a), or had no effect on mineralization (Streubel *et al.*, 2011). Two potential mechanisms presented below may be helpful to explain the effects of biochar on soil nitrogen mineralization. (1)The amount of labile carbon content in biochar may result in microbial-available soil nitrogen becoming immobilized (Bruun *et al.*, 2012) and (2) the addition of biochar will stimulate soil nitrogen mineralization by mineralizing the nitrogen coming from a more recalcitrant fraction (Nelissen *et al.*, 2012).

Nitrification represents the oxidation of organic nitrogen (via heterotrophic organisms) or ammonium nitrogen to nitrate nitrogen by autotrophic bacteria and archaea (Leininger *et al.*, 2006; Jia and Conrad, 2009). Nitrification is the first and rate-limiting step in nitrogen cycling. Biochar addition to forest soils has been found to increase nitrification, whereas the effects in agricultural systems are inconsistent. Biochar was added to forest soils and it was found that promotion of soil nitrification was attributed to the alleviation of factors limiting nitrification by biochar addition instead of a result of limited substrate increasing (DeLuca *et al.*, 2002; Berglund *et al.*, 2004). A short-term increase in nitrification suggests that biochar can adsorb some organic compounds which inhibit nitrification or cause immobilization of ammonium nitrogen (DeLuca *et al.*, 2006). The long-term effect of enhancing nitrification is found due to biochar addition after a forest fire, which has been ascribed to the promotion of soil conditions resulting in an increase in the abundance of ammonia-oxidizing bacteria (Ball *et al.*, 2010).

Different from forest soils, most soil in the agricultural system already contains high nitrate nitrogen and exhibits inherently high rates of nitrification before biochar addition. Some studies suggest that the content of ammonium nitrogen may be reduced by the absorption of biochar and thus the nitrification process may be affected because of limited substrate (Steiner *et al.*, 2007; Spokas *et al.*, 2012). However, in contrast to this result it has been reported that a significant increase in nitrification rates with the addition of biochar and the increase in nitrification is attributed to a greater substrate for autotrophic nitrifying bacteria (Nelissen *et al.*, 2012). Similarly, experiments using coastal alkaline soils show that biochar addition can enhance the abundance of both nitrifiers and alter the composition of ammonia oxidizers by increasing the diversity of ammonia-oxidizing bacteria (Song *et al.*, 2014). Improvement of nitrification may be partly explained by the change in soil chemical properties induced by biochar addition. Ulyett *et al.* (2014) found that biochar addition enhances nitrification with pH increase in the condition with nitrogen fertilizer application.

1.5.2 Effects of biochar addition on plant growth

Maintaining crop yields has a special meaning for China relating to its national stability and security. The possibility of negative impacts on crop yields caused by biochar would block the widespread promotion of biochar addition. However, crop yield is a result of the complex interaction between biochar and soil nutritive properties (Chan *et al.*, 2008). Adding biochar to soils may produce effects on properties such as soil fertility, water retention or microbial activity (Atkinson *et al.*, 2010; Lehmann *et al.*, 2011; Spokas *et al.*, 2012). In recent years, an increasing number of studies has highlighted concerns about the amending function of biochar (Chan *et al.*, 2008; Novak *et al.*, 2009a; Yao *et al.*, 2012; Zhang *et al.*, 2012). Benefits arising from biochar addition to degraded soil have been emphasized, however negative effects on crop yield have also been reported (Thomas *et al.*, 2013). Spokas *et al.* (2012) reviews the inconsistent effects of biochar addition on agronomic yields and suggests that approximately 50% of the compiled studies observed short-term positive yield or growth effects, 30% reported no significant differences and 20% noted negative yield or growth effects. Cranedroesch *et al.* (2013) sumarized the findings from 84 studies that the yield response increased over time since initial application, but characteristics of biochar (such as biochar pH, percentage carbon content, or temperature of pyrolysis) could be used as significant predictors of yield impacts. A meta-analysis of 371 independent studies concluded that biochar addition to soils on average results in increased aboveground productivity, crop yield and total soil nitrogen, compared with control conditions (Biederman and Harpole, 2013). Negative yield impact was reported after biochar addition and attributed to the over-use of biochar in China (Cheng *et al.*, 2016). The same retardation of quinoa growth was also found by Kammann *et al.* (2012) with a high biochar addition rate. It seemed that the short-term use of biochar was more possible to find various effects on yield (Jay *et al.*, 2015) and the reasons inducing negative plant effects have not been fully understood due to the lack of knowledge of biochar. However, it is more important to summarize the existing studies and find the potential reasons for the positive effects induced by biochar addition.

To assess biochar's role in improving nutrient supply in soils, the effect of biochar addition on soil nutrient retention and plant nutrient uptake should be noted especially (Sohi *et al.*, 2010; Spokas *et al.*, 2012).

- Improvement of soil cation exchange capacity properties following biochar addition has been reported to have a close relationship to the reduction of nutrients leaching loss (Cheng *et al.*, 2006; Novak *et al.*, 2009a; Singh *et al.*, 2010). Additionally, biochar can improve nutrition retention by increasing soil water-holding capacity (Lehmann *et al.*, 2003; Laird *et al.*, 2010) allowing more time for crop uptake.
- Nutrient content in soil can be affected by biochar via two pathways: direct introduction, immobilization or adsorption and indirect regulation on transformation processes.
- Direct introduction (bringing from the various raw material of the biochar production) (Hass *et al.*, 2012), nitrogen immobilization (due to the high TC/TN ratios of biochar) (Rondon *et al.*, 2007) and direct adsorption of soil nutrients (Steiner *et al.*, 2008; Laird *et al.*, 2010) mentioned in 1.3.1.1 changes the nutrient content in the soil. However, the nutrient content in the soil directly affected by biochar addition is slight and short-lived.
- Indirect regulation through complex physiochemical reactions with soil particles play a dominant role in soil nutrient contents (Spokas *et al.*, 2012). Analysis also demonstrates that biochar-induced changes of soil pH significantly affect crop productivity/ yield, and alkaline biochar seems to have a more pronounced and positive effect on crop productivity/ yield than acidic biochar (Biederman and Harpole, 2013). The improvement of soil mineral nutrient content induced by an increase in pH could be considered as one of the major reasons for this positive effect (Rondon *et al.*, 2007; Steiner *et al.*, 2008).

Another way biochar may affect crop yield is through reducing the mobility of toxic elements. Liming of biochar decreases soil H^+ content, changes the chemical valences of some heavy metals (such as Al and Cd) and immobilizes organic contaminants in the soil, creating a more favorable soil environment for crop growth (Novak *et al.*, 2009a; Hass *et al.*, 2012). Delays in biochar-induced yield improvements have been reported, with a negative or no significant effect in the initial year followed by a yield increase in subsequent years (Gaskin *et al.*, 2010; Major *et al.*, 2010). Aging of the biochar is considered as an explanation to the alteration of biochar's chemical property which changes the effects of biochar on yields (Cheng *et al.*, 2006; Singh *et al.*, 2010).

1.5.3 Effects of biochar addition on nitrogen loss

1.5.3.1 Nitrogen leaching

Although biochar's direct contribution to soil nitrogen content is small (Hass *et al.*, 2012), a consensus that biochar addition can reduce nitrogen leaching loss when added with nitrogen fertilizer has almost been reached (Lehmann *et al.*, 2003; Steiner *et al.*, 2008; Ding *et al.*, 2010; Major *et al.*, 2010; Dempster *et al.*, 2012b; Yao *et al.*, 2012).

However, the effects of biochar on nitrogen leaching loss is a result of the combination of physical, chemical, and biological processes (Laird *et al.*, 2010), which leads to considerable variety in the reducing processes and the potential mechanisms due to different soil types.

- Ammonium nitrogen

A significant reduction of ammonium nitrogen leaching due to biochar addition has been confirmed by most studies (Lehmann *et al.*, 2003; Ding *et al.*, 2010; Singh *et al.*, 2010; Kizito *et al.*, 2015). The biochar-induced increase in cation exchange capacity (Liang *et al.*, 2006; Cheng *et al.*, 2008) could be partly responsible for the reduction of ammonium nitrogen leaching loss (Singh *et al.*, 2010). Increasing the retention of water can also decrease nutrient movement and leaching (Major *et al.*, 2010). Dempster *et al.* (2012b) found a significant decrease in ammonium nitrogen leaching by 20% following clay and biochar addition and this indicated an improved water-holding capacity resulting from the biochar addition playing a comparatively greater role in decreasing ammonium nitrogen leaching than ammonium nitrogen adsorption. Ding *et al.* (2010) found a similar result that a 0.5% biochar addition to the surface soil layer retards the vertical movement of ammonium nitrogen into the deeper layers and thereby reduces ammonium nitrogen leaching loss by 15.2% to a depth of 20 cm.

- Nitrate nitrogen

There is no consensus about the effects of biochar addition on nitrate nitrogen leaching loss. Lehmann *et al.* (2003) and Kameyama *et al.* (2012) found no nitrate is adsorbed by biochar. Laird *et al.* (2010) found an increase of nitrate nitrogen leaching loss after incubation of 45 weeks and attributed this promotion to enhanced mineralization of organic nitrogen stimulated by the high rate of biochar addition. However, other studies found significant decreases in nitrate nitrogen leaching loss following biochar addition (Dempster *et al.*, 2012b; Yao *et al.*, 2012) ascribed to both sorption processes and an increased water-holding capacity. The high anion retention is likely to be due to the positive charge of biochar (Cheng *et al.*, 2008). Alternatively, it may be due to the decrease in nitrification (Dempster *et al.*, 2012a). It seems that the changes of nitrogen mineralization and nitrification by biochar addition will determine the trend of nitrate leaching loss.

- Dissolved organic nitrogen

Few studies have examined the effect of biochar on dissolved organic-nitrogen (DON) leaching. Dempster *et al.* (2012b) found that biochar had no effect on levels and argued that the dissolved organic nitrogen in leachate carrying a negative charge had a competitive relation to nitrate nitrogen for biochar adsorption.

1.5.3.2 Nitrous oxide emissions

Many studies have shown that biochar addition can mitigate nitrous oxide emissions from soil (Yanai *et al.*, 2007; Steiner *et al.*, 2010; Zhang *et al.*, 2010), while a few studies find no difference (Scheer *et al.*, 2011) or an increase (Clough *et al.*, 2010) in nitrous oxide emissions due to biochar addition. The possible mechanisms influencing nitrous oxide emission or denitrification are proposed as follows:

- Soil moisture can affect denitrification by regulating soil aeration (Case *et al.*, 2012; Kammann *et al.*, 2012) and a higher oxygen content induces denitrification inhibition. However, changes induced by biochar addition in soil moisture depend on both the type of soil and biochar application rate (Van Zwieten *et al.*, 2010a).

- Biochar addition alters the amounts of mineral nitrogen content as a substrate for denitrification. A reduction in the soil mineral nitrogen content due to biochar's adsorption and retention of ammonium nitrogen is always correlated with reduced nitrous oxide emissions (Singh *et al.*, 2010; Steiner *et al.*, 2010). Crop planting (assimilating nitrogen from soil) also creates competition with microbes for nitrogen utilization in the soil (Saarnio *et al.*, 2013). On the contrary, promotion of nitrous oxide emissions is found when biochar increases mineral nitrogen content in soil (Clough *et al.*, 2010).
- Alkaline biochar increases soil pH and thus enhances nitrous oxide reductase activity (Yanai *et al.*, 2007) that drives denitrification through to N_2, resulting in the conversion of nitrite and nitrate to nitrous oxide (Van Zwieten *et al.*, 2010b).

However, most effects of biochar on nitrous oxide emissions are a result of short-term field studies and lab incubations. Results may be not persistent in the longer term with *in situ* experiments (Jones *et al.*, 2012) due to the age of biochar (Liang *et al.*, 2006) or other changes in soil nitrogen cycling. Because the effects on the physical properties of soil and microbes are lacking, it is difficult to assess and identify which mechanisms play more significant roles in nitrous oxide emissions. Therefore, long-term *in situ* experiments are needed to determine biochar's role in mitigating N_2O fluxes and its potential mechanisms.

1.5.3.3 Ammonia volatilization

Ammonia volatilization from agricultural soil was significantly related to the ammonium nitrogen content and the pH of the soil (Huijsmans *et al.*, 2003; Xi *et al.*, 2010). Since most biochar produced by pyrolysis is alkaline, soil pH will be affected following biochar addition (Yuan *et al.*, 2011; Wu *et al.*, 2012). Furthermore, the adsorption of biochar will decrease the ammonium nitrogen content in soil (mentioned in 1.3.1.1) (Ding *et al.*, 2010; Kizito *et al.*, 2015) and a direct adsorption of ammonia on biochar is also shown after exposure to ammonia gas resulting in an average 6.7 mg/g increase in the total nitrogen content of biochar (Taghizadeh-Toosi *et al.*, 2012). These interactional processes can influence the pH value and the ammonium/ammonia content in surface soil and thereby the final ammonia volatilization losses.

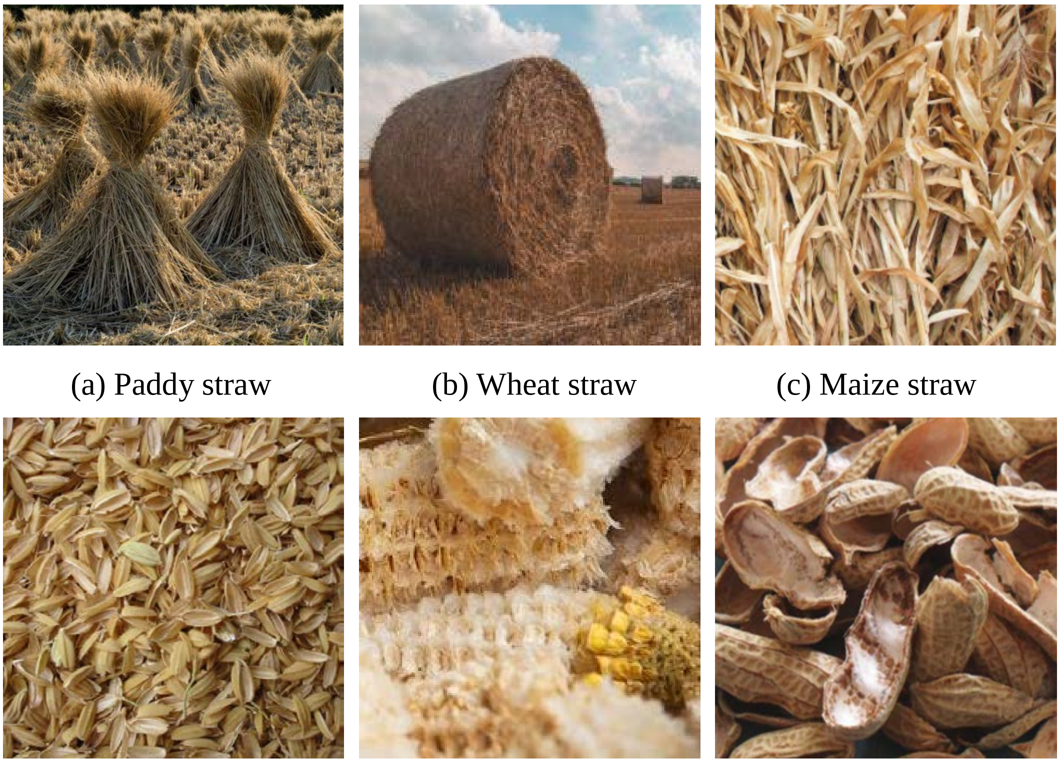
The rates of biochar addition also depend on the degree of the effect on ammonia volatilization induced by biochar. Feng *et al.* (2017) examined ammonia volatilization loss from paddy field with two additional rates of biochar and found that 3% biochar additions increased ammonia volatilization, and biochar added with 0.5% rate did not significantly increase the ammonia volatilization. A similar result was reported by Sun *et al.* (2017) who found no significant differences in ammonia volatilization loss when biochar was added at the rate of 0.5% and 1% to paddy soil, while a remarkable increase was detected when biochar was added at the rate of 2% and 4%. The increased ammonia volatilization is attributed to increased pH of the soil and reduced nitrification processes induced by biochar application.

However, the effects of biochar application on the ammonia volatilization in vegetable production systems have been neglected. Further studies on ammonia volatilization are still needed as data to assess the proper rate of biochar addition combined with consideration of the benefit of promoting yields and reducing nitrogen leaching (Zhang *et al.*, 2012; Zhao *et al.*, 2014; Sun *et al.*, 2017).

1.6 Biochar in China: Status quo of research and trend of development

1.6.1 Raw material

Biochar has been very popular in research areas, but its effect on natural substance cycling is questionable for several reasons. One of the most important reasons is which raw materials should be used for biochar production. It is possible that forest may be demanded if hardwood is used as mainly raw material. This is the inevitable consideration in the process of marketization of biochar production. However, the answer to this question is clear in China, as agricultural residue (Fig. 1.5) will supply enough raw material for biochar production.



(a) Paddy straw (b) Wheat straw (c) Maize straw

(d) Rice hull (e) Corn cob (f) Peanut shell

Fig. 1.5 Common agricultural residue can serve as raw material for biochar production in China

For example, the straw production in China accounts for 20%-30% of the worldwide straw production (Wang *et al.*, 2010). Chinese use straw as fodder for feeding livestock or as a building material from the ancient era. However, with the advance of agricultural modernization, most fodder and building material have been replaced by industrial production and therefore plenty of straw is left in the field. Data shows the annual straw produced from conventional crops (like maize, paddy and wheat) has reached up to 650 million tons in China, while less than 20% of straw is returned to field and the rest exceeding 50% is largely wasted (Li *et al.*, 1998; Shi, 2011). The abandonment of straw brings serious non-point organic matter emissions and nutrient losses. If part of the wasted straw is used for producing biochar, carbon and nutrients can be returned into the agricultural system with biochar addition into soil. The pyrolysis process of biochar creates a link between agricultural residue and renewable resources, through the efficient utilization of agricultural residue.

Furthermore, Chen *et al.* (2013) holds the view that not all of the agricultural residue should be used for biochar production in China. Some of agricultural residue has been effectively used for returning fields or compost. Only the agricultural residue that used to be treated as waste should be transferred to biochar for reuse. However, Meng *et al.* (2011) estimate that more than 30 million tons of biochar can be produced by using 20% of the straw in China. This amount of biochar (30 million tons) can be used as a carbon basis for processing fertilizer or other soil amendments, and then can be applied to the cultivated land with an area of up to 70 million ha.

1.6.2 How to use

1.6.2.1 Suitable fields

Beneficial effects of biochar in terms of increased crop yield and improved soil quality have been widely reported (Glaser *et al.*, 2002; Chan *et al.*, 2008; Novak *et al.*, 2009a; Yao *et al.*, 2012; Zhang *et al.*, 2012) and thus agricultural biochar production is rapidly developing in China (Meng and Chen, 2013). However, it is impossible that biochar can be applied to all cultivated fields. It means that farmers should be encouraged to add biochar to some special fields, where they can get more benefits from biochar addition. Fields with intensive production and fields with low fertility should be prioritized for biochar addition (Chen *et al.*, 2013).

Fields with intensive production always correspond with the soil having relatively high fertility. Vast crop biomass is harvested from intensive production systems every year. Massive amounts of nutrients are applied to ensure the nutrients supplying to crops growth. Plenty of nutrients, not utilized timely, are left in soil and then get lost. Soil nutrient retention reduces gradually and even soil fertility degrades with such large fluxes. Crop production from intensive fields plays a primary role in supplying food to meet the demand from the large Chinese population. It is critical to maintain sustainable development by recovering soil fertility of intensive fields. Biochar addition is helpful to improve nutrient retention in intensive planting and thereby creates benefits to stabilize yield and reduce loss.

On the other hand, China uses 9% of the worlds cultivated fields to feed 22% of the world population (Chen *et al.*, 2013). The requirement of crop yields is high due to the low per capita cultivated area. However, the area of fields with low fertility accounts for 70% of total cultivated land in China (NBS, 2015), which has brought tremendous pressure on food supply. The main reasons for low fertility of Chinese agricultural soil are:

- Poor soil physical condition. It is very difficult to preserve soil water when there is a high sand content and nutrients are inclined to be lost via leaching. Biochar addition can improve the hydraulic condition of sandy desert soil and increase crop yield by 22 Mg/ha (Laghari *et al.*, 2015). However, Jeffery *et al.* (2015) reports a significant finding that the hydrophobicity of biochar can prevent water entering its internal pore structure resulting in no effect on sandy soil water retention. Jeffery *et al.* (2015) also points out that the hydrophobicity of biochar can be altered by improving the biochar production process.
- Soil salinization is the accumulation of water-soluble salt in soil, usually along with intensive greenhouse agriculture, causing a deterioration or loss of soil function. Studies clearly show that biochar addition can mitigate negative effects of salt on plant growth by its strong adsorption (Thomas *et al.*, 2013).
- Soil pH value. Soil acidification is a common trend in Chinese intensive agricultural fields, while biochar is mostly neutral to basic. Thus, biochar is widely accepted as improving soil pH value or decreasing acidity. Meta-analysis results reveal that biochar addition can on average increase the soil pH value from 5.3 to 6.2 (Verheijen *et al.*, 2010).
- Soil heavy metal and organic pollution. Biochar has the potential to control contamination *in situ*. (Cao and Harris, 2010). It can be used as an additive for reducing the bioavailability and mobility of toxic trace metals (Beesley and Marmiroli, 2011; Uchimiya *et al.*, 2011b), or used as a contaminant mitigation agent to control different soil organic pollutants (Beesley *et al.*, 2010) in water and soil. The short-term effects of biochar on soil heavy metal mobility organic pollution are controlled by intraparticle diffusion and soil pH increase (Zhang *et al.*, 2013). A recent study also provides evidence that the surface ligand and other function groups of biochar may make an effort to stabilize heavy metal (Cu, Ni, Cd and Pb) (Uchimiya *et al.*, 2011a) or organic pollution in the long term (Zhang *et al.*,

2013).

In these low fertility soils, biochar is regard as a reliable soil amendment. It will be rewarding if there is an improvement in crop production with the addition of biochar and this can mitigate the negative constraints on soil fertility.

1.6.2.2 Usage

Biochar, with its characteristics of small volume and light weight, is difficult to transport and add directly into soil. It is easy to get lost and produces serious dust (Meng and Chen, 2013) during transport. Additionally, much labor is needed to add biochar to soil because there is no special farm machinery for biochar addition in China. Most of the biochar remaining on the surface of the soil will be blown away by the wind and cause near-surface air pollution. Based on the existing agricultural facilities and measures, some studies recommend that biochar should be added into soil in the form of biochar-base products (Novak and Busscher, 2013). This usage mode avoids the need of special farm machinery and extra labor for biochar addition. For example, when the rate of biochar in biochar-based products accounts for approximately 60% of the total weight, 0.5×10^3 kg/ha biochar is added into the soil with the application rate of biochar-based fertilizer or amendment at 0.8×10^3 kg/ha (Meng *et al.*, 2011). With the increase in biochar addition times, the amount of biochar in soil is accumulating and its effects on soil properties and fertility gradually appears.

The specialized uses of biochar can further improve the economic prospects for biochar utilization (Novak and Busscher, 2013). Biochar can be impregnated with chemical fertilizers to serve as a slow-release fertilizer (Khan *et al.*, 2008) and can also be blended with compost (Steiner *et al.*, 2010), which increases biochar’s nutrient content (Cao and Harris, 2010). The alkalinity of biochar makes it possible to be a remediation tool for acid mine soils and biochar can also be used as a nutrient recovery agent due to its adsorption (Streubel *et al.*, 2011).

1.6.3 Biochar production patterns in China

At present, in the Chinese biochar production industry there are two main patterns: centralized and distributed. Each of them develops according to the local agricultural production pattern (individual farmers or large agribusiness companies) and transportation condition (convenient or not). Centralized biochar production industries are inclined to be built in some agricultural areas having large agribusiness companies which provide sufficient agricultural residues for biochar production. In addition, these areas are always accompanied by relatively complete agricultural production chains, decreasing the cost of labor and raw material transportation and promoting the development of centralized biochar production industries.

However, in the other agricultural areas with individual farmers, it is hard to collect agricultural residue used as raw material for biochar production from small-sized fields. The agricultural residue such as straw decomposes easily due to environmental moisture. A novel production pattern is enabled. The suggestion is that small distributed biochar factories should be built nearby these agricultural fields (Chen *et al.*, 2013). These small factories can offer initial biochar production by primary biochar production technology, which effectively cuts down the transportation cost of biochar production and utilization. Simultaneously, distributed biochar production could provide more work opportunities for local villagers that would further reduce labor costs.

1.7 Conclusion

Conversion of the fields cultivated pattern responses to the changes of dietary structure. More conventional crop fields have already been converted for planting vegetables to meet the increasing population demands, and the trend of land-use change will continue for several years. Compared to the conventional crop system, the vegetable production system is cultivated more intensively with much higher nutrient input, especially nitrogen. The amount of nitrogen fertilizer application is many times more than the amount of nitrogen uptake by vegetables in the Chinese vegetable production system. The excessive nitrogen application is causing high nitrogen leaching loss and also contributes to soil acidity. The yield of vegetables is difficult to maintain after soil degradation induced by excessive nitrogen application. Many studies find that biochar addition can increase or maintain crop biomass/yield by improving the soil environment with promoted soil nitrogen retention and mitigated soil constraints. There are vast agricultural residue resources (like maize straw, wheat straw, paddy straw, corncob, rice hull etc.) that can serve as raw material for biochar production in China, and centralized and distributed biochar production industries are increasing based on practical conditions in some area. Biochar may be the appropriate amendment that can mitigate nitrogen leaching and soil acidity in China's vegetable production system. At the same time, data on biochar's effects on continual growing seasons in vegetable production system is still lacking. Thus, it is critical to conduct an experiment with several growing seasons to determine and evaluate the effects of biochar addition on the nitrogen retention and uptake by vegetables in intensive vegetable production systems in China.

References

Amonette, J., Joseph, S., 2009. Physical properties of biochar. In 'Biochar for environmental management. Science and technology'.(Eds J Lehmann, S Joseph) , 33-53.

Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337, 1-18.

Ball, P., MacKenzie, M., DeLuca, T., Holben, W., 2010. Wildfire and charcoal enhance AOB in forests of the Inland Northwest. Journal of Environmental Quality 39, 1243-1253.

Bateman, E., Baggs, E., 2005. Contributions of nitrification and denitrification to N2O emissions from soils at different water-filled pore space. Biology and Fertility of Soils 41, 379-388.

Beesley, L., Marmiroli, M., 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environmental Pollution 159, 474-480.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution 158, 2282-2287.

Berglund, L., DeLuca, T., Zackrisson, O., 2004. Activated carbon amendments to soil alters nitrification rates in Scots pine forests. Soil Biology and Biochemistry 36, 2067-2073.

Bhogal, A., Murphy, D., Fortune, S., Shepherd, M., Hatch, D., Jarvis, S., Gaunt, J., Goulding, K., 2000. Distribution of nitrogen pools in the soil profile of undisturbed and reseeded grasslands. Biology and Fertility of Soils 30, 356-362.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta‐analysis. GCB Bioenergy 5, 202-214.

Bouwman, A., Boumans, L., Batjes, N., 2002. Emissions of N2O and NO from fertilized fields: Summary of available measurement data. Global Biogeochemical Cycles 16.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biology and Biochemistry 46, 73-79.

Byrnes, B., 1990. Environmental effects of N fertilizer use—an overview. Fertilizer Research 26, 209-215.

Cai, G.X., 1997. Ammonia volatilization. Nitrogen in soils of China. Springer, pp. 193-213.

Cao, B., Xu, Q., He, F., Cai, G., 2008. Nitrogen use efficiency and fate of N fertilizers applied to open field vegetables. Acta Agriculturae Nucleatae Sinica 22, 343-347.

Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresource Technology 101, 5222-5228.

Caradec, Y., Lucas, S., Vidal, C., 1999. Agricultural landscapes: over half of Europe’s territory maintained by farmers. European Commission’s Directorate General for Agriculture and Rural Development, web site.

Case, S.D., McNamara, N.P., Reay, D.S., Whitaker, J., 2012. The effect of biochar addition on N 2 O and CO 2 emissions from a sandy loam soil–the role of soil aeration. Soil Biology and Biochemistry 51, 125-134.

Castaldi, S., Riondino, M., Baronti, S., Esposito, F., Marzaioli, R., Rutigliano, F., Vaccari, F., Miglietta, F., 2011. Impact of biochar application to a Mediterranean wheat crop on soil microbial activity and greenhouse gas fluxes. Chemosphere 85, 1464-1471.

CCICED, 2004. China's Agricultural and Rural Development in the New Era. In: Development, C.C.f.I.C.o.E.a. (Ed.), Challenges, Opportunities and Policy Options-Policy Recommendations and Executive Summary, Beijing, p. 23.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2008. Agronomic values of greenwaste biochar as a soil amendment. Soil Research 45, 629-634.

Chen, J., 2007. Rapid urbanization in China: a real challenge to soil protection and food security. Catena 69, 1-15.

Chen, W.F., Zhang, W.m., Meng, J., 2013. Advances and Prospects in Research of Biochar Utilization in Agriculture. Scientia Agricultura Sinica 46, 3324-3333.

Cheng, C.H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72, 1598-1610.

Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37, 1477-1488.

Cheng, X.Y., Zhang. W.M., Meng, J., Yang, X.， Zhao, Q.W., 2016. Effect of Biochar on Maize Dry Matter Accumulation and Yield. Journal of Maize Sciences,.

Clough, T.J., Bertram, J.E., Ray, J., Condron, L.M., O'Callaghan, M., Sherlock, R.R., Wells, N., 2010. Unweathered wood biochar impact on nitrous oxide emissions from a bovine-urine-amended pasture soil. Soil Science Society of America Journal 74, 852-860.

Cranedroesch, A., Abiven, S., Jeffery, S., Torn, M.S., 2013. Heterogeneous global crop yield response to biochar: a meta-regression analysis. Environmental Research Letters 8, 925-

932.
DeLuca, T., MacKenzie, M., Gundale, M., Holben, W., 2006. Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests. Soil Science Society of America Journal 70, 448-453.
DeLuca, T., Nilsson, M.C., Zackrisson, O., 2002. Nitrogen mineralization and phenol accumulation along a fire chronosequence in northern Sweden. Oecologia 133, 206-214.
Dempster, D., Gleeson, D., Solaiman, Z.i., Jones, D., Murphy, D., 2012a. Decreased soil microbial biomass and nitrogen mineralisation with Eucalyptus biochar addition to a coarse textured soil. Plant and Soil 354, 311-324.
Dempster, D.N., Jones, D.L., Murphy, D.V., 2012b. Clay and biochar amendments decreased inorganic but not dissolved organic nitrogen leaching in soil. Soil Research 50, 216-221.
Deng, J., Zhou, Z., Zheng, X., Liu, C., Yao, Z., Xie, B., Cui, F., Han, S., Zhu, J., 2012. Annual emissions of nitrous oxide and nitric oxide from rice-wheat rotation and vegetable fields: a case study in the Tai-Lake region, China. Plant and Soil 360, 37-53.
Deng, X., Huang, J., Rozelle, S., Uchida, E., 2006. Cultivated land conversion and potential agricultural productivity in China. Land Use Policy 23, 372-384.
Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, & Soil Pollution 213, 47-55.
Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. Biochar for environmental management: Science and Technology, 13-32.
Fan, X.h., Zhu, Z.l., 2002. Potential of Nitrification in the Three Soil Profiles of China. Chinese Journal of Soil Science 33, 124-125.
Fa, H.,. Yin Bin ,Jin X.X., Cao Bing, Cai Guixin. 2005 Ammonia volatilization from urea applied to two vegetable fields in nanjing suburbs. Acta Pedologica Sinica 2.
Feng, Y., Sun, H., Xue, L., Liu, Y., Gao, Q., Lu, K., Yang, L., 2017. Biochar applied at an appropriate rate can avoid increasing NH3 volatilization dramatically in rice paddy soil. Chemosphere 168, 1277-1284.
Gaskin, J.W., Speir, R.A., Harris, K., Das, K., Lee, R.D., Morris, L.A., Fisher, D.S., 2010. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agronomy Journal 102, 623-633.
Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal-a review. Biology and Fertility of Soils

35, 219-230.

Hale, S., Alling, V., Martinsen, V., Mulder, J., Breedveld, G., Cornelissen, G., 2013. The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere 91, 1612-1619.

Han, J., Luo, Y., Yang, L., Liu, X., Wu, L., Xu, J., 2014. Acidification and salinization of soils with different initial pH under greenhouse vegetable cultivation. Journal of Soils and Sediments 14, 1683-1692.

Haruna Ahmed, O., Husin, A., Husni Mohd Hanif, A., 2008. Ammonia volatilization and ammonium accumulation from urea mixed with zeolite and triple superphosphate. Acta Agriculturae Scandinavica Section B-Soil and Plant Science 58, 182-186.

Hass, A., Gonzalez, J.M., Lima, I.M., Godwin, H.W., Halvorson, J.J., Boyer, D.G., 2012. Chicken manure biochar as liming and nutrient source for acid Appalachian soil. Journal of Environmental Quality 41, 1096-1106.

Haynes, R., 2012. Mineral nitrogen in the plant-soil system. Elsevier.

He, F., Chen, Q., Jiang, R., Chen, X., Zhang, F., 2007. Yield and nitrogen balance of greenhouse tomato (Lycopersicum esculentum Mill.) with conventional and site-specific nitrogen management in Northern China. Nutrient Cycling in Agroecosystems 77, 1-14.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Huijsmans, J., Hol, J., Vermeulen, G., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. Atmospheric Environment 37, 3669-3680.

Jay, C.N., Fitzgerald, J.D., Hipps, N.A., Atkinson, C.J., 2015. Why short - term biochar application has no yield benefits: evidence from three field - grown crops. Soil Use & Management 31, 241-250.

Jeffery, S., Meinders, M.B., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F., Mommer, L., van Groenigen, J.W., 2015. Biochar application does not improve the soil hydrological function of a sandy soil. Geoderma 251, 47-54.

Jia, Z., Conrad, R., 2009. Bacteria rather than Archaea dominate microbial ammonia oxidation in an agricultural soil. Environmental Microbiology 11, 1658-1671.

Jin, X., Fan, X., Cai, G., 2005a. Nitrogen transformation and losses in soils grown with vegetables. Soils 37, 492-499.

Jin, X., Fan, X., Cai, G., 2005b. Nitrogen transformation and losses in soils grown with vegetables. SoilS 37, 492-499.

Jones, B.E., Haynes, R., Phillips, I., 2010. Effect of amendment of bauxite processing sand with organic materials on its chemical, physical and microbial properties. Journal of Environmental Management 91, 2281-2288.

Jones, D., Rousk, J., Edwards-Jones, G., DeLuca, T., Murphy, D., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. Soil Biology and Biochemistry 45, 113-124.

Ju, M., Xu, Z., W.M., S., Guang-Xi, X., Z.L., Z., 2011. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X., Kou, C., Zhang, F., Christie, P., 2006. Nitrogen balance and groundwater nitrate contamination: comparison among three intensive cropping systems on the North China Plain. Environmental Pollution 143, 117-125.

Kameyama, K., Miyamoto, T., Shiono, T., Shinogi, Y., 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. Journal of Environmental Quality 41, 1131-1137.

Kammann, C., Ratering, S., Eckhard, C., Müller, C., 2012. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from soils. Journal of Environmental Quality 41, 1052-1066.

Khan, M.A., Kim, K.W., Mingzhi, W., Lim, B.K., Lee, W.H., Lee, J.Y., 2008. Nutrient-impregnated charcoal: an environmentally friendly slow-release fertilizer. The Environmentalist 28, 231-235.

Kizito, S., Wu, S., Kirui, W.K., Lei, M., Lu, Q., Bah, H., Dong, R., 2015. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. Science of The Total Environment 505, 102-112.

Kolb, S.E., Fermanich, K.J., Dornbush, M.E., 2009. Effect of charcoal quantity on microbial biomass and activity in temperate soils. Soil Science Society of America Journal 73, 1173-

1181.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14 C analysis. Soil Biology and Biochemistry 70, 229-236.

Kyaw, K.M., Toyota, K., Okazaki, M., Motobayashi, T., Tanaka, H., 2005. Nitrogen balance in a paddy field planted with whole crop rice (Oryza sativa cv. Kusahonami) during two rice-growing seasons. Biology and Fertility of Soils 42, 72-82.

Laghari, M., Mirjat, M.S., Hu, Z., Fazal, S., Xiao, B., Hu, M., Chen, Z., Guo, D., 2015. Effects of biochar application rate on sandy desert soil properties and sorghum growth. Catena 135, 313-320.

Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D., 2010. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158, 436-442.

Lehmann, J., 2009. Biochar for environmental management: An introduction. In 'Biochar for environmental management: Science and technology'.(Eds J Lehmann, S Joseph) pp. 1–12. International Biochar Initiative: Westerville, OH, USA.

Lehmann, J., da Silva, J.P., Steiner, C., Nehls, T., Zech, W., Glaser, B., 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant and Soil 249, 343-357.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems–a review. Mitigation and Adaptation Strategies for Global Change 11, 395-419.

Lehmann, J., Kern, D.C., Glaser, B., Woods, W.I., 2007. Amazonian dark earths: origin properties management. Springer Science & Business Media.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota–a review. Soil biology and biochemistry 43, 1812-1836.

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G., Prosser, J., Schuster, S., Schleper, C., 2006. Archaea predominate among ammonia-oxidizing prokaryotes in soils. Nature 442, 806.

Li, J.J., Bai, J.M., Overend, R., 1998. Evaluation of Chinese biomass resources availiability. China Environmental Science Press, Beijing.

Li, J.L., Chen, X.P., Li, X.L., 2003. Effect of N fertilization on yield, nitrate content and N apparent losses of Chinese cabbage. Acta Pedologica Sinica 40, 266-272.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F., Petersen, J., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Liu, X., Ju, X., Zhang, F., Pan, J., Christie, P., 2003. Nitrogen dynamics and budgets in a winter wheat–maize cropping system in the North China Plain. Field Crops Research 83, 111-124.

Luo, Y.X., Gao, B., Yan, X.Y., Jiang, X.S., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Ma, W., Mao, D., Zhang, F., 2000. Nutrients accumulation within vegetable awning (green house) in Shandong province. Phosphate & Compound Fertilizer 3, 028.

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant and Soil 333, 117-128.

Mei, B., Zheng, X., Xie, B., Dong, H., Zhou, Z., Wang, R., Deng, J., Cui, F., Tong, H., Zhu, J., 2009. Nitric oxide emissions from conventional vegetable fields in southeastern China. Atmospheric Environment 43, 2762-2769.

Meng, J., Chen, W.f., 2013. Biochar in China: Status Quo of Research and Trend of Industrial. Journal of Shenyang Agricultural University 15, 1-5.

Meng, J., Zhang, W.m., Wang, S.B., Xu, Z.J., Chen, W.F., 2011. Development and prospect of carbonization and returning technology of agro-forestry residue. Journal of Shenyang Agricultural University 42, 387-392.

Min, J., Shi, W., Xing, G., Zhang, H., Zhu, Z., 2011a. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems. Nutrient Cycling in Agroecosystems 91, 31.

Min, J., Zhao, X., Shi, W.M., Xing, G.X., Zhu, Z.L., 2011b. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.

NBS, 2015. China Statistical Yearbook. . China Statistic Press, Beijing., National Bureau of Statistics of China,.

Nelissen, V., Rütting, T., Huygens, D., Staelens, J., Ruysschaert, G., Boeckx, P., 2012. Maize biochars accelerate short-term soil nitrogen dynamics in a loamy sand soil. Soil Biology and Biochemistry 55, 20-27.

Novak, J., Busscher, W., 2013. Selection and use of designer biochars to improve characteristics of southeastern USA Coastal Plain degraded soils. Advanced biofuels and bioproducts. Springer, pp. 69-96.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A., 2009a. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil science 174, 105-112.

Novak, J.M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., 2009b. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Annals of Environmental Science 3, 195-206.

Pihlatie, M., Syväsalo, E., Simojoki, A., Esala, M., Regina, K., 2004. Contribution of nitrification and denitrification to N 2 O production in peat, clay and loamy sand soils under different soil moisture conditions. Nutrient Cycling in Agroecosystems 70, 135-141.

Qian, J.H., Doran, J.W., Weier, K.L., Mosier, A.R., Peterson, T.A., Power, J.F., 1997. Soil denitrification and nitrous oxide losses under corn irrigated with high-nitrate groundwater. Journal of Environmental Quality 26, 348-360.

Ramankutty, N., Foley, J.A., Olejniczak, N.J., 2002. People on the land: Changes in global population and croplands during the 20th century. AMBIO: A Journal of the Human Environment 31, 251-257.

Raun, W.R., Johnson, G.V., 1995. Soil-plant buffering of inorganic nitrogen in continuous winter wheat. Agronomy Journal 87, 827-834.

Rondon, M.A., Lehmann, J., Ramírez, J., Hurtado, M., 2007. Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. Biology and Fertility of Soils 43, 699-708.

Saarnio, S., Heimonen, K., Kettunen, R., 2013. Biochar addition indirectly affects N 2 O emissions via soil moisture and plant N uptake. Soil Biology and Biochemistry 58, 99-106.

Saleh, M.E., Mahmoud, A.H., Rashad, M., 2012. Peanut biochar as a stable adsorbent for removing NH4-N from wastewater: a preliminary study. Advances in Environmental Biology, 2170-2177.

Saltalı, K., Sarı, A., Aydın, M., 2007. Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality. Journal of Hazardous Materials 141, 258-263.

Scheer, C., Grace, P.R., Rowlings, D.W., Kimber, S., Van Zwieten, L., 2011. Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia. Plant and Soil 345, 47-58.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.

Shi, Y.c., 2011. China's resources of biomass feedstock. Chinese Engineering Science 13, 16-23.

Singh, B., Singh, B.P., Cowie, A.L., 2010. Characterisation and evaluation of biochars for their application as a soil amendment. Soil Research 48, 516-525.

Sohi, S., Krull, E., Lopez-Capel, E., Bol, R., 2010. A review of biochar and its use and function in soil. Advances in Agronomy 105, 47-82.

Song, K., Xu, A., Zhang, W., 2009. Study on nitrogen leaching in farmlands with different crops in riverine plain area of Taihu Lake. Journal of Nanjing Agricultural University.

Song, Y., Zhang, X., Ma, B., Chang, S.X., Gong, J., 2014. Biochar addition affected the dynamics of ammonia oxidizers and nitrification in microcosms of a coastal alkaline soil. Biology and Fertility of Soils 50, 321-332.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of Environmental Quality 41, 973-989.

Steiner, C., Das, K., Melear, N., Lakly, D., 2010. Reducing nitrogen loss during poultry litter composting using biochar. Journal of Environmental Quality 39, 1236-1242.

Steiner, C., Glaser, B., Geraldes Teixeira, W., Lehmann, J., Blum, W.E., Zech, W., 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. Journal of Plant Nutrition and Soil Science 171, 893-899.

Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macêdo, J.L.V., Blum, W.E., Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant and Soil 291, 275-290.

Streubel, J., Collins, H., Garcia-Perez, M., Tarara, J., Granatstein, D., Kruger, C., 2011. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Science Society of America Journal 75, 1402-1413.

Sun, H., Lu, H., Chu, L., Shao, H., Shi, W., 2017. Biochar applied with appropriate rates can reduce N leaching, keep N retention and not increase NH 3 volatilization in a coastal saline

soil. Science of Total Environment 575, 820-825.
Sun, H., Tang, Y., Zhao, Q., 2002. Nitrogen mineralization of prunings of six N2-fixing hedgerow species in a dry valley of the Jinsha river. Pedosphere 12, 25-31.
Sun, R.J., Wang, D.j., Lin, J.H., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.
Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M., 2012. Biochar adsorbed ammonia is bioavailable. Plant and Soil 350, 57-69.
Thomas, S.C., Frye, S., Gale, N., Garmon, M., Launchbury, R., Machado, N., Melamed, S., Murray, J., Petroff, A., Winsborough, C., 2013. Biochar mitigates negative effects of salt additions on two herbaceous plant species. Journal of Environmental Management 129, 62-68.
Thompson, R., Martínez-Gaitan, C., Gallardo, M., Giménez, C., Fernández, M., 2007. Identification of irrigation and N management practices that contribute to nitrate leaching loss from an intensive vegetable production system by use of a comprehensive survey. Agricultural Water Management 89, 261-274.
Uchimiya, M., Chang, S., Klasson, K.T., 2011a. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. Journal of Hazardous Materials 190, 432-441.
Uchimiya, M., Klasson, K.T., Wartelle, L.H., Lima, I.M., 2011b. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. Chemosphere 82, 1431-1437.
Ulyett, J., Sakrabani, R., Kibblewhite, M., Hann, M., 2014. Impact of biochar addition on water retention, nitrification and carbon dioxide evolution from two sandy loam soils. European Journal of Soil Science 65, 96-104.
Van Zwieten, L., Kimber, S., Morris, S., Chan, K., Downie, A., Rust, J., Joseph, S., Cowie, A., 2010a. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 327, 235-246.
Van Zwieten, L., Kimber, S., Morris, S., Downie, A., Berger, E., Rust, J., Scheer, C., 2010b. Influence of biochars on flux of N2O and CO2 from Ferrosol. Soil Research 48, 555-568.
Verheijen, F., Jeffery, S., Bastos, A., Van der Velde, M., Diafas, I., 2010. Biochar application to soils. A critical scientific review of effects on soil properties, processes, and functions. EUR 24099, 68-69.
Wang, H., Dong, Y.h., Li, D.C., Velde, B., An, Q., Guo, Z.X., Zuo, Q.D., 2008. Evolution of soil chemical properties in the past 50 years in the Tai Lake Region, China. Soil and

Tillage Research 100, 54-59.

Wang, X.Z., Zhu, J.G., Gao, R., Yasukazu,H., Feng, K., 2007. Nitrogen Cycling and Losses Under Rice-Wheat Rotations with Coated Urea and Urea in the Taihu Lake Region. Pedosphere 17, 62-69.

Wang, Z.H., Liu, X.J., Ju, X.T., Zhang, F.S., Malhi, S., 2004. Ammonia volatilization loss from surface-broadcast urea: comparison of vented-and closed-chamber methods and loss in winter wheat–summer maize rotation in North China Plain. Communications in Soil Science and Plant Analysis 35, 2917-2939.

Wang, Z., Zong, Z., Li, S., 2002. Difference of several major nutrients accumulation in vegetable and cereal crop soils. The Journal of Applied Ecology 13, 1091-1094.

Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., 2010. Sustainable biochar to mitigate global climate change. Nature Communications 1, 1.

Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., Chen, Y., 2012. Chemical characterization of rice straw-derived biochar for soil amendment. Biomass and Bioenergy 47, 268-276.

Xi, B., Zhang, J., Zuo, Q., Zou, G., Zhai, L., Liu, H., 2010. Study on the loss of ammonia volatilization and its influencing factors on the soil of protected vegetable fields. Plant Nutrition and Fertilizer Science 16, 327-333.

Xing, G., Zhu, Z., 2000. An assessment of N loss from agricultural fields to the environment in China. Nutrient Cycling in Agroecosystems 57, 67-73.

Xu, J., Peng, S., Yang, S., Wang, W., 2012. Ammonia volatilization losses from a rice paddy with different irrigation and nitrogen managements. Agricultural Water Management 104, 184-192.

Xue, L., Yu, Y., Yang, L., 2011. Nitrogen balance and environmental impact of paddy field under different N management methods in Taihu Lake region. Huan Jing Ke Xue 32, 1133-1138.

Yanai, Y., Toyota, K., Okazaki, M., 2007. Effects of charcoal addition on N2O emissions from soil resulting from rewetting air‐dried soil in short‐term laboratory experiments. Soil Science & Plant Nutrition 53, 181-188.

Yao, Y., Gao, B., Zhang, M., Inyang, M., Zimmerman, A.R., 2012. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere 89, 1467-1471.

Yao, Z., Zheng, X., Xie, B., Mei, B., Wang, R., Butterbach-Bahl, K., Zhu, J., Yin, R., 2009.

Tillage and crop residue management significantly affects N-trace gas emissions during the non-rice season of a subtropical rice-wheat rotation. Soil Biology and Biochemistry 41, 2131-2140.

Yin, R., Zhang, H.y., Huang, J.f., Lin, X.g., Wang, J.h., Cao, Z.h., 2004. Comparsion of microbiological properties between soils of rice-wheat rotation and vegetable cultivation. Plant Nutrition and Fertilizing Science 10, 57-62.

Yuan, J.H., Xu, R.K., Wang, N., Li, J.Y., 2011. Amendment of Acid Soils with Crop Residues and Biochars. Pedosphere 21, 302-308.

Zhang, A., Bian, R., Pan, G., Cui, L., Hussain, Q., Li, L., Zheng, J., Zheng, J., Zhang, X., Han, X., 2012. Effects of biochar amendment on soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: a field study of two consecutive rice growing cycles. Field Crops Research 127, 153-160.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D., 2010. Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. Agriculture, Ecosystems & Environment 139, 469-475.

Zhang, H.y., Yin, R., Huang, J.f., 2005. Changes in soil biochemical properties caused by cropping sys tem alteration from rice wheat rotation to vegetable cultivation. Soils 37, 182-186.

Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Bolan, N.S., Pei, J., Huang, H., 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environmental Science and Pollution Research 20, 8472-8483.

Zhao, X., Wang, S., Xing, G., 2014. Nitrification, acidification, and nitrogen leaching from subtropical cropland soils as affected by rice straw-based biochar: laboratory incubation and column leaching studies. Journal of Soils and Sediments 14, 471-482.

Zhao, X., Xie, Y.x., Xiong, Z.q., Yan, X.y., Xing, G.x., Zhu, Z.l., 2009. Nitrogen fate and environmental consequence in paddy soil under rice-wheat rotation in the Taihu lake region, China. Plant and Soil 319, 225-234.

Zhu, J., Han, Y., Liu, G., Zhang, Y., Shao, X., 2000. Nitrogen in percolation water in paddy fields with a rice/wheat rotation. Nutrient Cycling in Agroecosystems 57, 75-82.

Zhu, J., Li, X., Christie, P., Li, J., 2005. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (Capsicum frutescens L.) cropping systems. Agriculture, Ecosystems & Environment 111, 70-80.

Zhu, K., Fu, H., Zhang, J., Lv, X., Tang, J., Xu, X., 2012. Studies on removal of NH 4+-N from aqueous solution by using the activated carbons derived from rice husk. Biomass and Bioenergy 43, 18-25.

Zhu, Z., Chen, D., 2002. Nitrogen fertilizer use in China–Contributions to food production, impacts on the environment and best management strategies. Nutrient Cycling in Agroecosystems 63, 117-127.

Zhu, Z., Norse, D., Sun, B., 2006. Policy for reducing non-point pollution from crop production in China. China Environmental Science Press, Beijing, 135-161.

Zou, J., Huang, Y., Jiang, J., Zheng, X., Sass, R.L., 2005. A 3 - year field measurement of methane and nitrous oxide emissions from rice paddies in China: Effects of water regime, crop residue, and fertilizer application. Global Biogeochemical Cycles 19.

CHAPTER 2: COMPARISON OF SOIL CHEMICAL PROPERTIES AND NITROGEN DYNAMICS BETWEEN VEGETABLE SOILS AND PADDY SOILS

Abstract

The increasing demand for vegetables in China has led to intensive vegetable production and excessive use of inorganic nitrogen fertilizers. This has caused changes in soil chemical properties and a decline of soil fertility. In Southern China, many of the fields used to grow vegetables were previously under paddy production. The conversion of paddy fields to vegetable soils could have an effect on soil chemical properties and nutrient dynamics in relation to nitrogen availability. The objective of this study was to investigate changes in soil chemical properties and nutrient dynamics in vegetable fields after conversion from paddy fields.

Topsoil (0-20cm) from typical vegetable fields (converted from paddy soil several years ago) and paddy soils from experimental sites were collected from China's Tailake region. The soil samples were characterized to determine differences in the chemical properties between soils from the paddy fields and those previously used for paddy production and subsequently converted to vegetable production. An experiment was conducted in the absence of nitrogen fertilizer to determine the effect of field utilization conversion on soil nitrogen uptake by pakchoi and leaching loss.

Results showed that soil pH values and organic matter content were lower in the vegetable soils compared with the paddy soils. Leaching loss was higher in three growing seasons from vegetable soils compared to that from paddy soils. Pakchoi uptake from vegetable soils was decreased during three growing seasons and lower than that from paddy soils in the 3rd season. The higher soil mineral nitrogen content might contribute more to the higher leaching loss. The lower nitrogen uptake from vegetable soils was attributed to lower soil pH value, lower soil organic matter and higher leaching loss. The potential of soil degradation in vegetable soils after conversion from paddy soils should be given more attention in further work.

Key words:

Conversion from paddy to vegetable cultivation, intensive vegetable production systems, paired experiment, Nitrogen uptake by plant, Nitrogen leaching loss

2.1 Introduction

Intensive vegetable production systems are very common in China (Ju et al., 2009; Liang et al., 2013). Maintaining a high vegetable crop yield per unit area is critical to meet the demand for vegetables from the large population. This is crucial because the land area available for vegetable cultivation is limited (Chen, 2007). Farmers often apply excessive chemical nitrogen fertilizer to maximize crop yields (Huang *et al.*, 2006; Zhu *et al.*, 2006; Ju *et al.*, 2009; Min *et al.*, 2011b). The large quantities of chemical nitrogen fertilizer applied can promote the amount of available nitrogen for immediate crop growth; however, it also causes remarkable changes in the soil nitrogen processes, resulting in decreased efficiency of nitrogen uptake (Li *et al.*, 2003; Zhu *et al.*, 2005; Min *et al.*, 2011a) and many negative environment effects, such as soil acidification (Ju *et al.*, 2007; Shi *et al.*, 2009; Guo *et al.*, 2010; Liang *et al.*, 2013; Han *et al.*, 2014), nutrient leaching loss (Song *et al.*, 2009; Min *et al.*, 2011a), and soil microbial community shifts (Zhang *et al.*, 2008; Shen *et al.*, 2010; Tian *et al.*, 2011). After long-term application of chemical fertilizer, the changed soil processes lead to lower soil fertility and threaten future sustainable agriculture (Tilman *et al.*, 2002; Chen, 2007; Ju *et al.*, 2009; Shi *et al.*, 2009).

Many fields used for conventional crop (paddy, wheat and maize) production have been converted to vegetable production (pakchoi, cabbage, bean, kale, etc.) in recent years (Deng *et al.*, 2006; Darilek *et al.*, 2009; NBS, 2015). This trend is likely to continue for several years to meet the increasing demand of vegetable consumption. Compared with conventional crop production (such as paddy, wheat and maize), vegetable production often requires larger inputs of nutrients (especially nitrogen) and irrigation with more growing seasons (vegetable is grown three or five times in the same field per year). For example, paddy-wheat planting was always applied 500-600 kg/ha N in the Tailake region of China, while more than 800 kg/ha N was applied for vegetable planting (Jin *et al.*, 2005; Huang *et al.*, 2006; Shi *et al.*, 2009). The soil properties (Zhang *et al.*, 2005; She and Zhang, 2008; Han *et al.*, 2014; Wang *et al.*, 2014), soil microbial community (Lin *et al.*, 2004; Shen *et al.*, 2010) and of course soil nitrogen processes (Cao *et al.*, 2004; Yin *et al.*, 2004) are changed with the conversion of paddy fields to vegetable production and excessive nitrogen fertilizer application. These investigations found that (1) soil ammonia nitrogen content increased 21 times and nitrate nitrogen content increased 22 times; (2) soil pH value declined 0.7-1.96 unit (Yin *et al.*, 2004; Zhang *et al.*, 2005; Sun *et al.*, 2006). The increased soil mineral nitrogen content and soil acidity in the vegetable fields could pose challenges with respect to nitrogen losses occurring as a result of leaching (Cao *et al.*, 2004; Min *et al.*, 2011a) and contaminate surface and ground water bodies, thus causing more serious agricultural non-point pollution (Luo *et al.*, 2015). The changes of soil nitrogen process in vegetable fields after conversion from paddy fields induced the negative effects mentioned above.

Therefore, it is critical to understand the differences in soil nitrogen processes between paddy soils and vegetable soils (converted from paddy production fields) and find the best approach to improving vegetable soil fertility. Not many studies have focused on the comparison of nitrogen processes in fields used for vegetable production and those previously used for paddy production and recently converted to vegetable production. Furthermore, most studies on soil nitrogen processes of different agricultural soils were more concerned about various nitrogen application rates. In fact, the study conducted in the absence of fertilizer application can be more pronounced to represent the basic condition of soil nitrogen processes, but relative studies were relative scarce.

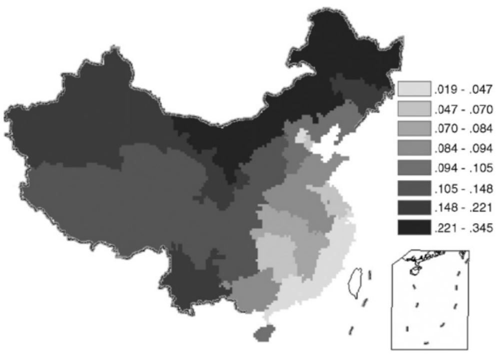
Soil nitrogen processes include both nitrogen input and output processes. Nitrogen fertilization is the major ways in which the element is added into soil, except for biological nitrogen fixation and mineralization processes. Plant nitrogen uptake and nitrogen loss are the main methods of nitrogen output (Wen *et al.*, 2017). Plant nitrogen uptake is also an important indicator of soil fertility. Several studies in the literature have reported that soil nitrogen losses through leaching contribute to more than half of nitrogen loss in vegetable soils (Min *et al.*, 2011a). Thus, plant nitrogen uptake and nitrogen losses through leaching can be used as indicators in the absence of nitrogen fertilizer application to describe the differences in soil nitrogen processes between paddy and vegetable soils.

Considering that vegetable systems had no settled plant species and vegetable fields applied with different amounts of nitrogen fertilizer, it is difficult to directly compare soil fertility by the data collected from different fields in different time. Therefore, in this study we conducted a laboratory experiment (paddy field and vegetable field were adjacent) with pakchoi planting on both paddy and vegetable soils, and paddy and vegetable soils were collected from adjacent fields. The comparison of the data from these soils described the varieties of (1) chemical properties in paddy and vegetable soils, and the differences in (2) nutrient dynamics including plant nitrogen uptake and nitrogen leaching loss in the absence of nitrogen fertilizer. Through this analysis, we wanted to determine the difference in soil chemical properties and nitrogen dynamics between vegetable soils and paddy soils.

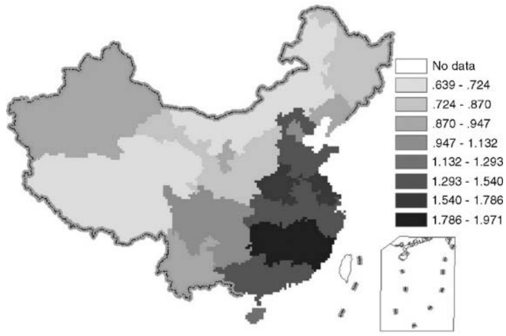
2.2 Sampling site background information

Paddy and vegetable soils were collected from the Tailake region in Jiangsu Province, China. The Tailake region is located in China's major ancient agricultural regions due to its temperate climate and soil fertility. Paddy is the main conventional crop that has been cultivated for hundreds of years (Zheng, 2000) in this region. The Tailake region was famous for high paddy yields and surplus production from this region was transported to other areas of China in ancient times (Zhou, 2000).

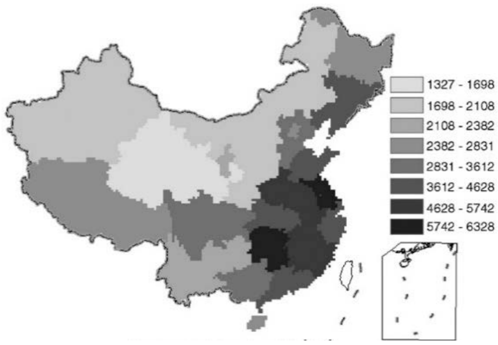
However, agricultural production has changed with economic development. A major proportion of the land area in the Tailake region is found in Jiangsu province, which is one of the most economically developed regions in China. Millions of young people from other provinces have been flocking into Jiangsu province and large areas of cultivated fields have been transformed into factory buildings and property construction, resulting in a reduction of available land for cultivation (Fig. 2.1 a) and greater pressure on agricultural production. To ensure the food supply, farmers in the Tailake region have increased the growing seasons and fertilizer application to produce a high crop grain yield per hectare per year. It has become one of the most intensive agricultural production regions in China, because both the multiple cropping indexes and the yield per hectare gain in this region have been placed at the highest level in China (Fig. 2.1 b and c).



(a) Cultivated field per capita (ha)



(b) Multiple cropping index



(c) Gain yield per hectare (kg)

Fig. 2.1 Variation of area per capita, utilization intensity and productivity of cultivated field (NBS, 2015)

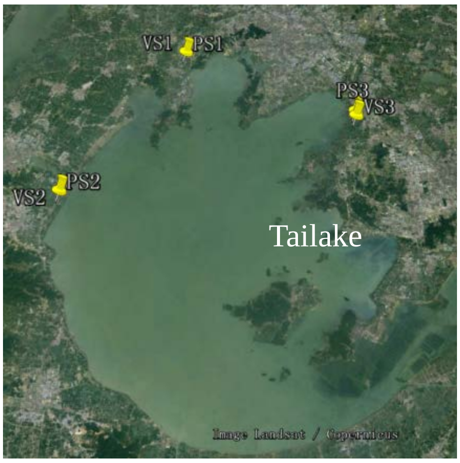
Economic development has also changed the cultivated pattern in the Tailake region. Vegetables play an increasingly important role in Chinese people's diet. Farmers are converting fields used for paddy production to vegetable cultivation to meet consumer demand. Vegetable cultivation has become the main agricultural activity due to its high profit. The area used for vegetable cultivation in the Tailake region has rapidly increased from 1% of the total cultivated field in 1981 to 18% in 2005 (Wang *et al.*, 2008).

The change in land use from growing conventional crops such as maize, wheat and rice to vegetable production is also occurring in Northern China, where farmers are planting vegetables in the fields previously used to plant maize and wheat. However, the main difference between paddy production and maize/wheat cultivation is that paddys are planted under flooded anaerobic soil conditions, while maize /wheat are planted in dry land or irrigation environments, with aerobic soil conditions, similar to conditions for vegetable production. The effects on soil nitrogen processes are likely to be considerable when fields previously used for paddy production are converted into vegetable fields in the Tailake region rather than the conversion from maize /wheat field to vegetable production in Northern China. Furthermore, the average annual precipitation is more than 1,000 mm in the Tailake region, which is much higher than that in Northern China which is about 600 mm(He *et al.*, 2007a), and the risk of nitrogen loss via leaching is much higher in the Tailake region. Therefore, soil collected from the Tailake region is more representative when comparing the differences of soil nitrogen processes between vegetable soils and conventional crop soils.

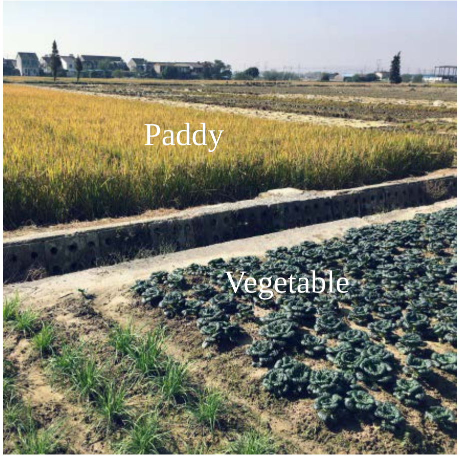
2.3 MATERIALS AND METHODS

2.3.1 Experimental site selection and description

Three pairs of paddy-vegetable soils were collected (PS1-VS1, PS2-VS2 and PS3-VS3) from different cities in the Tailake region in Jiangsu Province (Fig 2.2 a). All soils are evolved from same pathway and classified as the same soil type. The vegetable fields where soil was sampled are alongside paddy fields (Fig 2.2 b) and were used for paddy cultivation for hundreds of years but have been converted to vegetable cultivation in the past 10 years. An investigation was carried out before sampling to study information from the crops planted in each field. The details are presented in Table 2.1.



(a) Sampling pairs in satellite photos



(b) Picture of sampling place for pair 2

Fig. 2.2 Locations of the three pairs (paddy soil & vegetable soil) of soil samples collected. VS means the place for sampling the vegetable soil. PS means the place for sampling the paddy soil. The number after VS and PS references the pair the soils belonged to.

Table 2.1 Descriptions of the sampling at the experimental sites

		Pair 1		Pair 2		Pair 3	
		PS1	VS1	PS2	VS2	PS3	VS3
longitude and latitude		31°31'35"N 120°06'35"E		31°17'18"N 119°54'13"E		31°24'28"N 120°25'05"E	
Village		Hudai town, Wuxi city		Dingshu Town, Yixing city		Wangting town, Suzhou city	
Climate		Sub-tropical monsoon climate. Annual mean air temperatures are 15.5 ℃ in Hudai, 15.7 ℃ in Dingshu and 16.6 ℃ in Wangting. Annual mean rainfalls are 1068 mm in Hudai, 1177 mm in Dingshu and 1038 mm in Wangting.					
Soil type		Gleyed paddy soil Evolved from lacustrine deposits Classified as Hydragric Anthrosols Surface soil layer : 0-20 cm					
Cultivated pattern (recent years)		Fields of PS1 and PS2 are planted with the rotation of summer paddy (June-October) and winter wheat (November- following May). Fields of PS3 are planted with the rotation of summer paddy (June-October) and rape (November- following May). Fields used for vegetable production of VS1, VS2 and VS3 are all planted with different vegetables rotations. The last year before soil was sampled, tomato, celery and lettuce were successively planted in VS1 field; pakchoi cabbage，tomato, cucumber and celery were successively planted in VS2 field; chilli, tomato and spinach were successively planted in VS3 field。					
Annual fertilizer application (kg/ha)	N	500	1500	500	1000	500	900
	P	120	360	120	360	160	300
	K	150	450	90	450	90	400
Duration		>100 years	5 years	>100 years	10 years	>100 years	8 years

2.3.2 Soil sampling

Soil was sampled from the 3 experiment sites between June and July 2015. Each soil sample (20 kg) was collected from the top 0–20 cm by a combination of 10 pores for each field.

After thorough mixing, the soil was divided into two portions. One portion of the sample weight was used for testing the soil's chemical properties. The other portion was air-dried and pulverized for the pot experiment.

2.3.3 Pot experiment and plant sampling

A pot experiment was carried out in the greenhouse at Jiangsu Agricultural Academy of Science (32°2'14''N, 118°51'58''N), Jiangsu, China. The greenhouse was maintained at a temperature between 15℃-30℃. Six soils from three paddy-vegetable pair fields were used for pakchoi (*Brassica chinensis L.*) planting. One pot was considered as an individual unit and each soil was used for planting with three replicates (in three respective pots). Each pot, measuring 28 cm in height, 15 cm in width and 10 cm in depth, was filled with 2 kg air-dried soil. Before the seed was sown, 85 mg P/kg and 120 mg K/kg chemical fertilizers were applied as base fertilizers to each pot at the beginning of each growing season. The seeds weighed 0.2 g (about 50-60 seeds) and were sown into the soil of each pot. The germination time was calculated from planting date until more than 35 seeds had germinated (3-5 days after sowing). The water- holding capacities of six soil samples were examined before the pot experiment, and soil moisture in each pot was maintained at 60% water-holding capacity of each soil sample by irrigating twice a week during the whole period of experiment. The water added to each pot was determined by its soil moisture, tested by a soil moisture content analyser (Spectrum, USA). Pakchoi was harvested 35 days after germination time. After that, the soil in the pot was turned over and air-dried for 14 days. Then a new growing season began with the same process mentioned above. The experiment was conducted over three growing seasons without any nitrogen fertilizer application from the beginning of September 2015 until January 2016. The planting and management schedule is presented in Table 2.2.

Table 2.2 Dates of cultivation and management for the pot experiment

Growing seasons	Activity	Date
1st season	Sowing and basal P,K fertilization	11 September, 2015
	Germination	14 September, 2015
	Four times over irrigation for simulating leaching	20 September, 2015 27 September, 2015 4 October, 2015 11 October, 2015
	Harvest and air drying soil	18 October, 2015
2nd season	Sowing and basal P,K fertilization	27 October, 2015
	Germination	30 October, 2015
	Four times over irrigation for simulating leaching	6 November, 2015 13 November, 2015 20 November, 2015 27 November, 2015
	Harvest and air drying soil	4 December, 2015
3rd season	Sowing and basal P,K fertilization	17 December, 2015
	Germination	21 December, 2015
	Four times over irrigation for simulating leaching	28 December, 2015 4 January, 2016 11 January, 2016 18 January, 2016
	Harvest and air drying soil	25 January, 2016

2.3.4 Simulation of leaching and leachate sampling

The collection of leachates from the six soils was done by placing a tray under each pot to collect all the leachate flowing out from the three pores at the bottom of pots (Fig.2.3). Leachate from the six soils was collected via a tray placed under each pot, gathering the liquid flowing out of the three pores at the base of the pot.

Increased irrigation was implemented four times (at the 7th, 14th, 21st and 28th days) in every growing season to simulate natural rainfall conditions in the glasshouse. The amount of deionized water was 1.05 L for every excessive irrigation (4.2 L every season) for each pot (equivalent to 25 mm precipitation per time and 100 mm precipitation in one growing season). Deionized water was added several times and in small quantities to avoid water flowing down along the inner wall. The process of irrigation continued over a period of two hours and all leachate was collected from the trays 6 hours later.

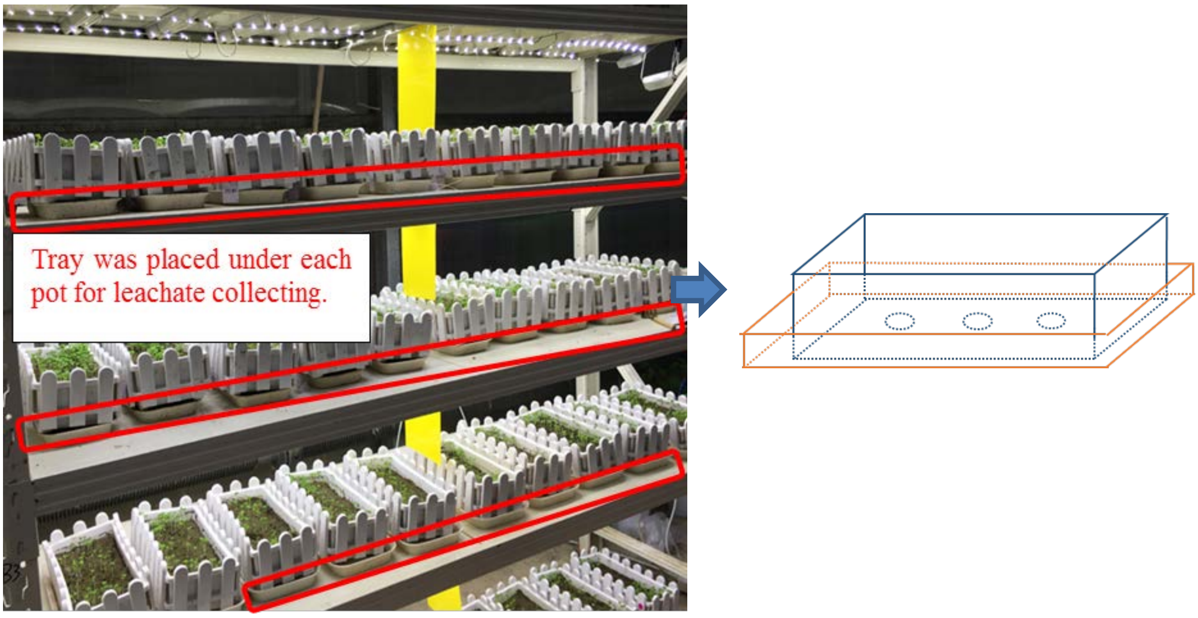


Fig. 2.3 Pot experiments leachate collecting

2.4 Sample analysis

2.4.1 Soil

Soil samples collected from the three pairs were characterized by their chemical properties using the methods described below:

Soil pH value was determined by using a sample of air-dried soil mixed with deionized water in a ratio of 1:2.5 (soil: water) and the pH value of the clear supernatant was measured using a pH electrode (Hach Corp., Italy). The determination of soil organic matter content (SOM) was calculated by multiplying the data of total organic carbon by 1.724. Total Organic Content (TOC) was measured using a TOC analyzer (Thermo Finnigan, Elk Grove Village, IL). Soil mineral nitrogen content (Mineral N) was calculated from the sum of ammonium and nitrate nitrogen. A fresh soil sample was extracted with 2 M KCl (soil: solution ratio was 1:10) for 1 h. The ammonium and nitrate concentrations of the extract were determined using a continuous-flow analyzer (Skalar Corp., Netherlands).

Soil available P: The air-dried soil sample was extracted with 0.5 M sodium bicarbonate (pH 8.5) and phosphate concentration of the extract was determined according to the method of Olsen (Olsen, 1954).

Soil available K: The air-dried soil sample was extracted with 1 M ammonium acetate (soil:solution ratio was 1:10) for 1 h and K concentration of the extract was determined by flame-photometry.

Soil total nitrogen content (Total N): The air-dried soil sample was used to determine Total N by the Kjeldahl method.

Soil total phosphorus content (Total P): The air-dried soil sample was digested with potassium persulphate and 30% v/v sulphuric acid and phosphate concentration of the extract was measured using the acidic molybdate –ascorbic acid method (Zhou *et al.*, 2001).

Soil cation exchange capacity (CEC): The air-dried soil sample was used to determine the CEC using the ammonium acetate method (Sumner and Miller, 1996).

2.4.2 Plant

The pakchoi cabbage above ground was harvested on the 35th day of each growing season and sampled. Fresh pakchoi cabbage from each pot was respectively weighed and recorded as the yield. It was harvested and oven-dried at 70°C until it became a constant mass and then recorded as plant dry biomass. The dry biomass was then ground and filtered through a 0.149-mm sieve for tissue nitrogen content analysis using an elemental analyzer (Thermo Finnigan, Elk Grove Village, IL). Plant nitrogen uptake by the plant was calculated using the following Equation 2.1:

$$m_{(plant\ uptake)} = m_{(plant)} \times w_{(tissue\ nitogen)} \quad \text{(Equation2.1)}$$

Where, $m_{(plant\ uptake)}$= Nitrogen uptake by pakchoi in one season (mg/pot), $m_{(plant)}$= the weight of plant dry biomass (g/pot) and $w_{(tissue\ nitogen)}$= tissue nitrogen content (mg/g)

2.4.3 Leaching

Leachate volumes were measured and recorded immediately after sampling from each pot. Each sample was filtered through a 0.45 lm membrane and the ammonium and nitrate concentrations determined using a continuous-flow analyzer (Skalar Corp., Netherlands). The amount of nitrogen loss via leaching was calculated with the Equation 2.2 and 2.3:

$$m_{n\ (leaching\ loss)} = \rho_{n\ (leachate\ nitrogen)} \times V_{n\ (leachate)} \quad \text{(Equation 2.2)}$$

Where, $m_{n\ (leaching\ loss)}$= amount of nitrogen loss via leaching in *n* time (mg/pot), $\rho_{(leachate\ nitrogen)}$ =mineral nitrogen concentrations (ammonium concentration and nitrate concentration) of leachate in *n* time (mg/L), $V_{(leachate)}$ = volume of leachate in *n* time (L/pot) and n=1,2,3,4 means the data from 1st, 2nd, 3rd and 4th leaching in one growing season.

$$m_{(leaching\ loss)} = \sum_{n=1}^{4} m_{n\ (leaching\ loss)} \quad \text{(Equation 2.3)}$$

Where, $m_{(leaching\ loss)}$ = amount of nitrogen loss via leaching in one growing season (mg/pot).

2.4.4 Nitrogen output

Nitrogen output in this study was estimated by the sum of nitrogen uptake by pakchoi and nitrogen leaching loss with the Equation 2.4:

$$m_{(output)} = m_{(plant\ uptake)} + m_{(leaching\ loss)} \quad \text{(Equation 2.4)}$$

Where, $m_{(output)}$ = Nitrogen output from one pot in one season (mg/pot).

Yield scale nitrogen leaching loss was used to describe how much nitrogen will be lost via leaching for getting one gram yield of pakchoi growth. It was calculated with the ratio of nitrogen leaching loss to yield the Equation 2.5:

$$Ratio_{(L/Y)} = m_{(leaching\ loss)} / Yield_{(plant)} \quad \text{(Equation 2.5)}$$

Where, $Ratio_{(L/Y)}$ = the ratio of nitrogen leaching loss to yield (mg/g), $Yield_{(plant)}$ = the pakchoi yield in one season (g/pot)

2.4.5 Statistical analyses

The mean and standard differences (presented in figures) of three replications were used to ascertain yield, nitrogen uptake by the plant, volumes of leachate, amount of nitrogen lost via leaching and total nitrogen output. A paired-T test was conducted to determine the significant difference between each pair of soils at the 5% level. Duncan multiple-range test was used to accomplish the significant differences in the value (of yield, nitrogen uptake, leaching loss and total output) among three growing seasons at the 5% level (SPSS ver. 16.0 for Windows, SPSS Inc., USA).

2.5 Results

2.5.1 Chemical properties of soils

The soil pH, CEC, contents of organic matter (SOM), mineral nitrogen, available P, available K, total N and total P are the chemical properties offering good information of the soil fertility status, so these indicators were used to evaluate the soil environmental problems in this study. The main chemical properties of paddy and vegetable soils were measured immediately after sampling (Table 2.3). Average soil pH values were 6.61 and 5.81 for paddy and vegetable soils, respectively. Soil pH values of vegetable soils were significantly lower than paddy soils (P=0.013). Soil organic matter of paddy soils was on average 27.84 g/kg, which was significantly higher than 22.37 g/kg of vegetable soils (P=0.030). Soil mineral N of vegetable soils were significantly higher than paddy soils (P=0.036) with average soil mineral N of vegetable soils (94.57mg/kg) over 2 times higher than that in paddy soils (43.90mg/kg). Soil CEC of vegetable soils were marginally significantly lower than paddy soils (P=0.076). The other properties such as available P, available K, total N and total P did not differ significantly between paired paddy-vegetable soils (P>0.05). The corresponding average values for paddy and vegetable were 35.77 mg/kg and 94.87 mg/kg, 139.67 mg/kg and 140.63 mg/kg, 1.85 g/kg and 1.35 g/kg 0.59 g/kg and 0.62 g/kg, respectively.

Table 2.3 Main chemical properties of the paddy soils and the vegetable soils

	PS1	PS2	PS3	Mean$_{(PS)}$	VS1	VS2	VS3	Mean$_{(VS)}$
pH	6.99	6.20	6.65	6.61	6.09*	5.58*	5.76*	5.81 *
SOM (g/kg)	31.90	24.80	26.80	27.83	28.30	17.90*	20.90*	22.37 *
Mineral N (mg/kg)	37.40	53.20	41.10	43.90	87.20*	78.80*	117.70*	94.57 *
Ammonium N (mg/kg)	2.10	7.60	3.70	4.47	4.10	6.30	8.00	6.03
Nitrate N (mg/kg)	35.30	55.60	37.40	42.77	83.10	72.50	109.70	88.43*
Available P (mg/kg)	37.90	48.90	20.50	35.77	187.00*	64.10	33.50	94.87
Available K (mg/kg)	108.80	142.10	169.00	139.67	147.00	182.20	92.70*	140.63
Total N (g/kg)	1.88	1.79	1.89	1.85	1.06	1.14	1.85	1.35
Total P (g/kg)	0.61	0.62	0.55	0.59	0.56	0.60	0.69	0.62
CEC(cmol/kg)	13.40	15.50	17.80	15.57	11.30	10.90*	11.20*	11.13

Note: Data with the same color shading present the soils from the same pair. '*' represents the significant differences of mean value between paddy and vegetable soils determined by paired-T test (P<0.05).

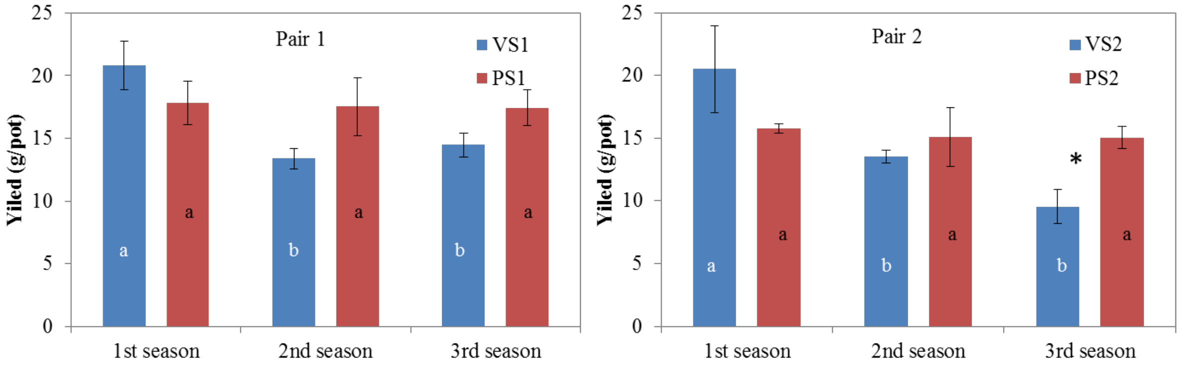
2.5.2 Yield and nitrogen uptake by the vegetable plant

Data was collected on pakchoi yields at the end of each growing season. The results showed a decreasing trend with respect to yield in the treatment without fertilizer application over the three continuous growing seasons (Fig. 2.4). The average yield of pakchoi was 20.39 g/pot, 13.64 g/pot and 11.47 g/pot for the 1st, 2nd and 3rd growing season in vegetable soils, respectively (Fig. 2.4 d). The decrease of average pakchoi yield was significantly different between that in the 1st growing season and that in the2nd & 3rd growing seasons in vegetable soils. However, the yield of pakchoi in paddy soils remained unchanged over the three growing seasons with corresponding values of 16.31 g/pot, 16.66 g/pot and 16.13 g/pot.

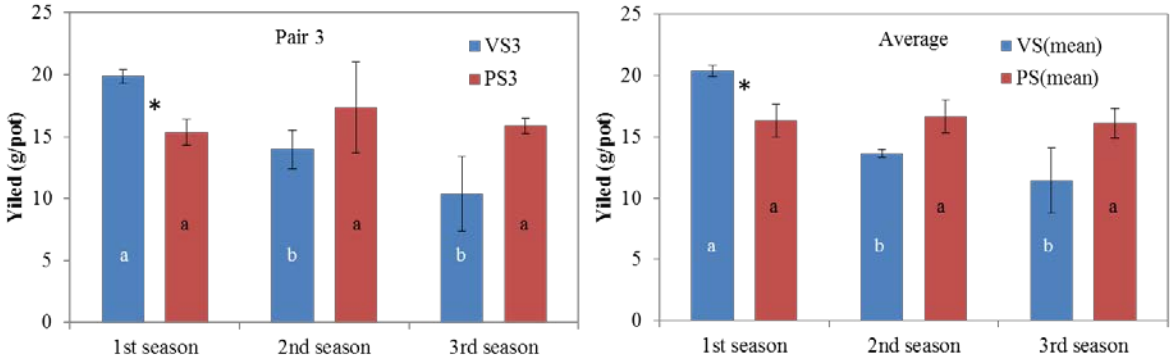
The yields of pakchoi between paddy and vegetable soils merely showed a significant difference in the 1st of pair-three soils (P=0.025, Fig. 2.4c) and 3rd seasons of pair-two soils (P=0.043, Fig. 2.4b). For the other growing seasons in different pairs, the yield of pakchoi between paddy and vegetable soils showed no significant difference (P >0.05).

The results on the nitrogen uptake from vegetable soils showed significant decreasing trends in the three continuous growing seasons (Fig. 2.5). Average nitrogen uptake was 68.80 g/pot, 41.77g/pot, 23.23g/pot for the 1st, 2nd and 3rd growing seasons, respectively (Fig. 2.5 d).

The trend of nitrogen uptake by pakchoi in paddy soils showed a difference between the 1st and 3rd seasons between different pairs. In pair 2, nitrogen uptake by pakchoi in paddy soils showed a decreasing trend, but in the other two pairs significant changes only occurred in the 3rd growing season (Fig. 2.5 b).

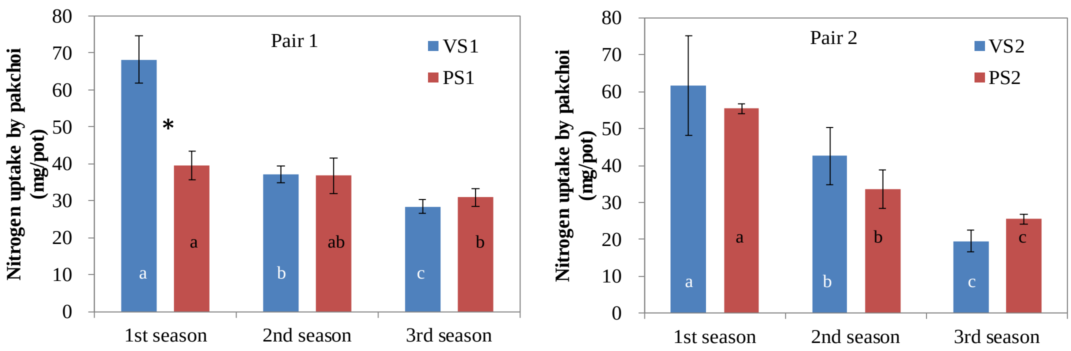


(a) Pakchoi yield in pair-one soils (b) Pakchoi yield in pair-two soils

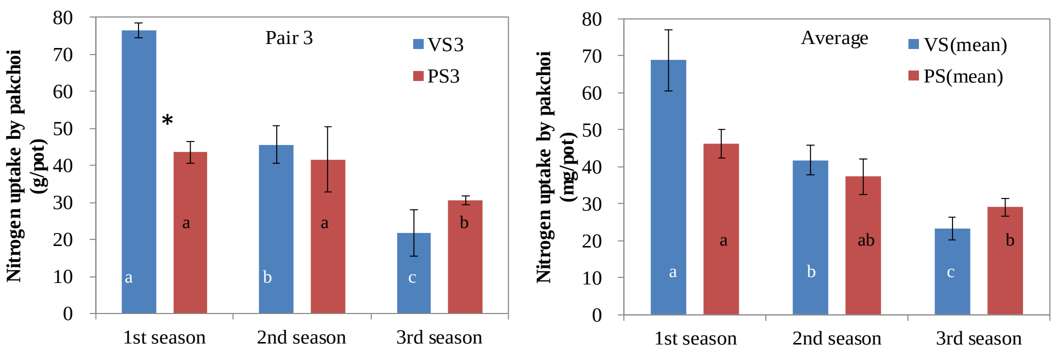


(c) Pakchoi yield in pair-three soils (d) Average pakchoi yield

Fig. 2.4 Pakchoi yields in three seasons. VS1= vegetable soil in pair 1; PS1= paddy soil in pair 1; VS2= vegetable soil in pair 2; PS2= paddy soil in pair 2; VS3= vegetable soil in pair 3; PS3= paddy soil in pair 3. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain season determined by paired T test (P<0.05). SD in the same color with the same letters are not significantly different, determined by Duncan 's multiple-range test (P<0.05).



(a) Nitrogen uptake by pakchoi in pair 1 (b) Nitrogen uptake by pakchoi in pair 2



(c) Nitrogen uptake by pakchoi in pair 3 (d) Average nitrogen uptake by pakchoi

Fig. 2.5 Nitrogen uptake by pakchoi plant in three seasons. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain season determined by paired T test (P<0.05). SD in the same color with the same letters are not significantly different, determined by Duncan 's multiple-range test (P<0.05).

The difference with regard to nitrogen uptake was significant between vegetable and paddy soils in the 1st growing season (P=0.031 in pair 1 and P=0.006 in pair 3) apart from the result for pair 2. In comparison to paddy soils, vegetable soils promoted nitrogen uptake by pakchoi by 72%-75% in pair 1 and pair 3. However, nitrogen uptake by pakchoi from vegetable soil was lower than that from paddy soil in the 3rd growing season although not significant (P>0.05). In the other growing seasons, the difference of nitrogen uptake by pakchoi between vegetable and paddy soils was not significant (P>0.05).

2.5.3 Nitrogen leaching loss

The excessive irrigation for stimulating leaching was precisely controlled at 4.2 L/pot every growing season. The leachate volumes in one season ranged between 0.83 and 1.41 L/pot from each pot, contributing 19.76%-33.57% of the total amount of water from over-irrigation (Fig. 2.6). The leachate volumes did not change much over the three growing seasons for both vegetable and paddy soils (Fig. 2.7). However, leachate volumes in vegetable soils were higher than in paddy soils, and differed significantly in the 1st season (P=0.02). Total leachate volume over the three seasons from vegetable soil averaged 19.80 % -21.00% and was higher than that from paddy soil (P=0.001 in pair 2 and P=0.033 in pair 3) in pair 2 and 3 (Fig. 2.6).

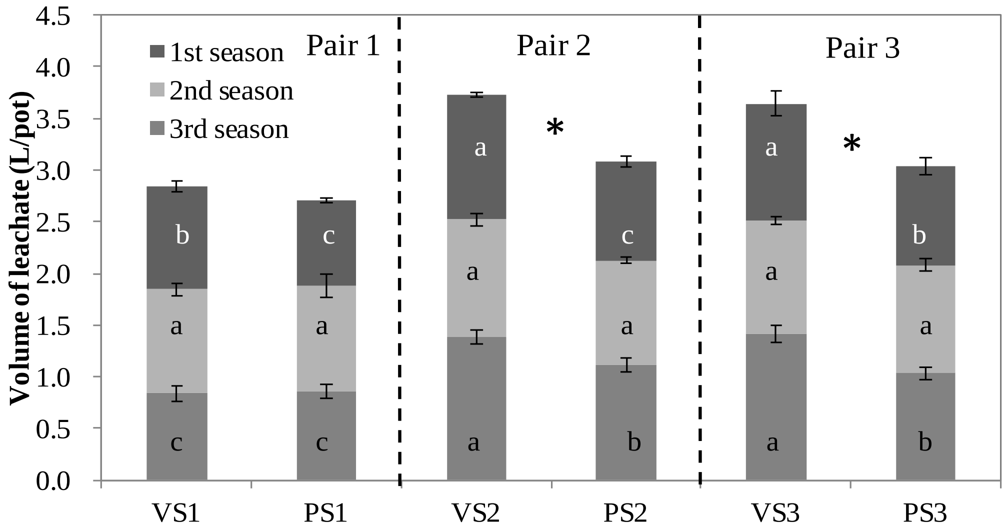


Fig. 2.6 Volumes of leachate in three seasons. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain pair determined by paired T- test (*P*<0.05). SD in the same color with the same letters are not significantly different, determined by Duncan's multiple-range test (*P* <0.05).

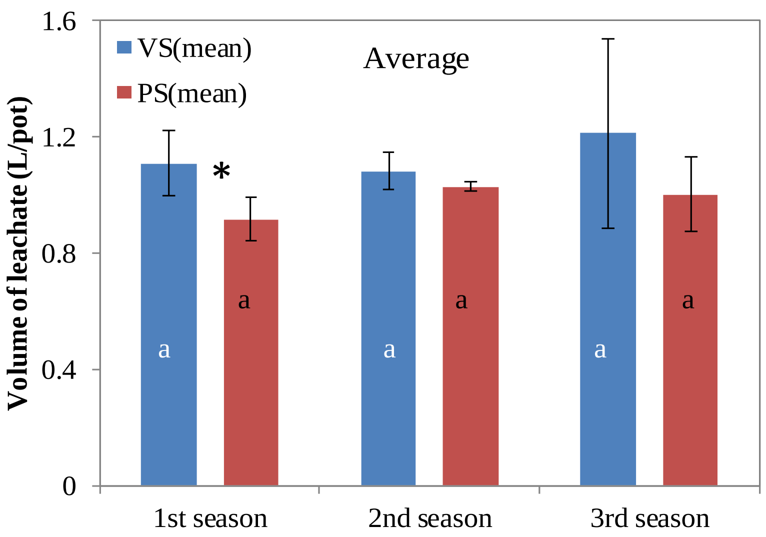
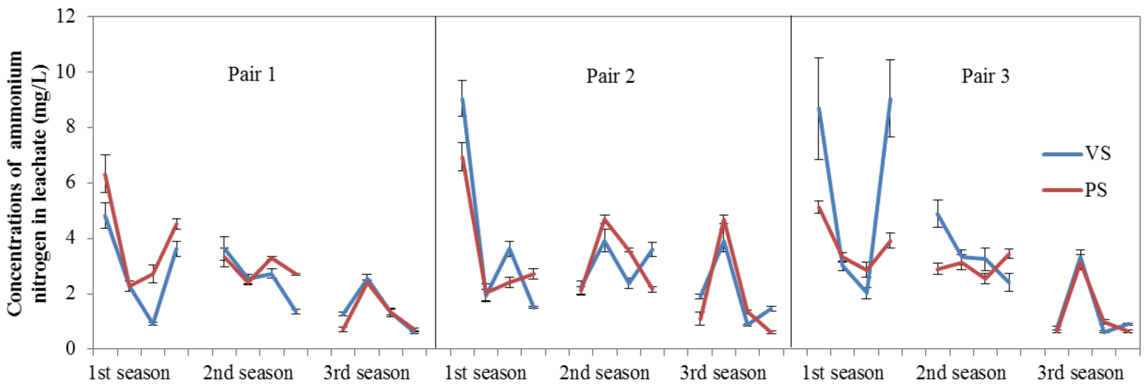


Fig. 2.7 Average volumes of leachate in vegetable and paddy soils. VS= vegetable soils; PS= paddy soils. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain season determined by paired T test (*P*<0.05). SD in the same color with the same letters are not significantly different, determined by Duncan 's multiple-range test (*P*<0.05).

The volumes of leachate among three vegetable soils and three paddy soils were different. Generally, the volumes of leachate from pair 2 and pair 3 were higher than those from pair 1 for both soils (Fig. 2.5).

Mineral nitrogen concentrations in leachate were measured weekly at the same interval over the three growing seasons. The ammonium and nitrate nitrogen concentrations in the leachate ranged between 0.60-9.03 mg/L and 1.25-39.64 mg/L, respectively (Fig. 2.8). Nitrate nitrogen was the dominant form in the leachate, accounting for 55.24%-91.85% of the total mineral nitrogen concentration. Generally, the trends of both ammonium and nitrate nitrogen concentrations between vegetable and paddy soil were similar during the three seasons. The peak of both ammonium and nitrate nitrogen concentrations showed in 1st leachate measurement (1st week of 1st growing season). There were no significant differences ($P < 0.05$) between the vegetable and paddy fields with respect to ammonium nitrogen concentration in leachate. However, the nitrate nitrogen concentration in leachate from vegetable soils was much higher than that from paddy soils.

The mineral nitrogen loss via leaching showed significant differences between vegetable and paddy soils. For all three pairs, leaching nitrogen loss from vegetable soil averaged 82.31% and was higher than that from paddy soil (Fig. 2.9). The differences of nitrogen loss between vegetable and paddy soil continued to dwindle from 15.25 mg/pot 1st growing season to 1.98 mg/pot 3rd growing season.



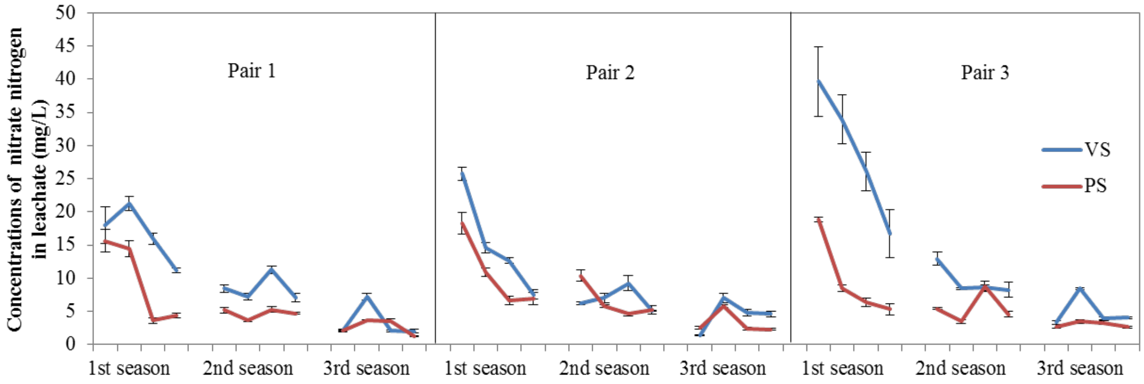


Fig. 2.8 Mineral nitrogen concentrations in leachate. VS= vegetable soils; PS= paddy soils. There are four data in each season with interval every 7 days. Vertical lines represent the SD of the means (n = 3).

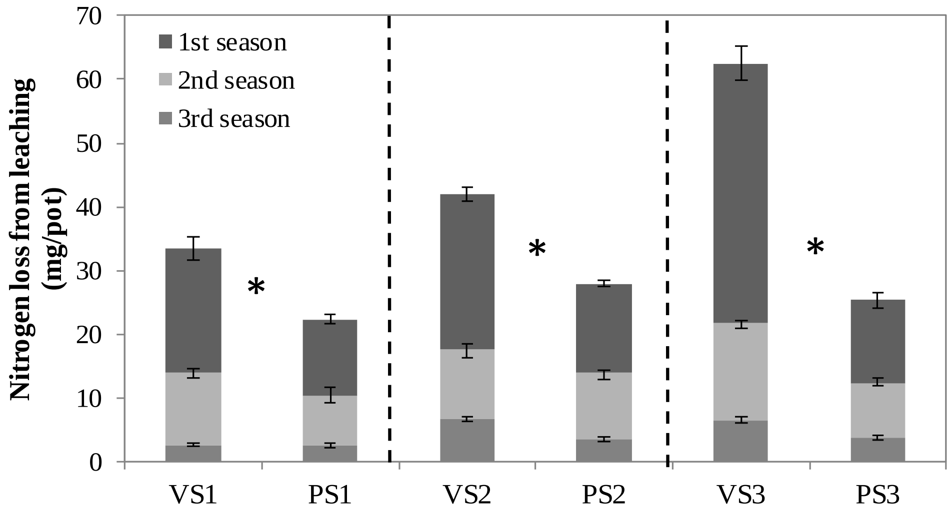


Fig. 2.9 Mineral nitrogen loss from leaching. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain pair determined by paired T test (P<0.05).

2.6 Discussion

2.6.1 Changes in soil pH values, organic matter and mineral nitrogen contents between paddy and vegetable soils

Soil pH values, organic matter and mineral nitrogen content were significantly affected by field utilization patterns conversion in this study (Table 2.3).

The increased content of mineral nitrogen in vegetable soils could be attributed to the high amounts of nitrogen fertilizer application before sampling from the vegetable fields. However, the data of mineral nitrogen content in vegetable soils in this study were 1.5-3 times of that in paddy soils, much lower than the data reported in other studies. Collection timing was one possible explanation for the lower mineral nitrogen content in vegetable soils. All vegetable soils used in this study were collected during June to July (rainy season) 2015 and more than two weeks from the previous vegetable growing season. It is well-known that mineral nitrogen in soil is very active and is easily transported with water to the deeper soil layers or is lost via volatilization in the fallow period. Similarly, Shi *et al.* (2009), Deng *et al.* (2006) and Yin *et al.* (2004) found the mineral nitrogen content in soil was more than 900 mg/kg after the vegetable harvest in the Tailake region. Moreover, it was speculated that plenty of mineral nitrogen got lost in the two weeks fallow period, which enhanced the differences between paddy and vegetable soils.

In comparison to paddy soils, the significant decrease of pH value in vegetable soil was found in each pair. Although nitrification is one of the processes causing soil pH to decrease in all agricultural soils, most of the acidifying function of nitrification can be balanced out when the uptake of nitrate by plants could compensate the nitrate released by nitrification (Gijsman, 1990; Shen et al., 2010). A previous study found an increase in soil pH values during the plant growing period due to nitrate uptake and assimilation by plants (Shi et al., 2009). However, nitrogen input from fertilizer was far beyond the demands of vegetable growth in vegetable production systems. It was speculated that the excessive hydrogen ion produced by nitrification would accelerate the process of acidification in the vegetable soil. In addition, the aerobic conditions of vegetable production systems promoted the nitrification process, while the flooded conditions in paddy field retarded it (Carreres et al., 2003; Ni et al., 2007). On the other hand, the part of mineral nitrogen not utilized by the vegetable plant increased the risk of leaching loss. Nitrate would be lost along with bases on the soil colloid, contributing to a relatively rapid decrease in soil pH. Furthermore, Huan *et al.* (2007) reported a high sulfate concentration in the vegetable soil during the mineralization of organic substances.

Nevertheless, in this study it was not possible to specify the contribution of each individual process to the decrease in soil pH. Soil pH value is widely accepted as a crucial factor regulating a range of soil nitrogen processes (Kemmitt et al., 2006; He et al., 2007b; Pietri and Brookes, 2008; Shen et al., 2010) and affects other soil properties (Liang et al., 2006).

It was really unexpected that the organic matter content in vegetable soils showed a significant decrease merely 5-10 years after field utilization was converted from paddy cultivation (Table 2.3), and the negative effect from vegetable cultivation on organic matter content seems to grow stronger over time. The major difference in organic matter content between the vegetable and paddy soils was found in pair 2, with vegetables having the longest cultivation time. It was acknowledged that the decomposing rate of organic matter was closely related to the aeration condition of the soil (Wang et al., 2014). There were more than three months per year that the soil planting paddy was in the anaerobic condition. The flooding inhibited the decomposition of organic matter in paddy soil and contributed to the accumulation of organic matter (Sheng et al., 2013; Wissing et al., 2013). However, the soil for vegetable cultivation was always under aerobic conditions and turned over (after every growing season) several times per year, both factors providing better conditions for organic matter decomposition (West and Post, 2002; Saha et al., 2011). On the other hand, the plant root residue was the direct organic matter added into soil. Compared to paddy, vegetable roots were shorter and fewer with lower root to shoot ratio (Bergqvist et al., 2014; Ju et al., 2015). Sometimes farmers uprooted the vegetable plant for harvesting and some vegetable roots were grown for food. Thus, the vegetable biomass left in the soil was very small. In addition, soil mineral nitrogen was a source for microbes as it was found that the high mineral nitrogen content may simulate microbial activity (Chen et al., 2014; Tian et al., 2015) and promote soil organic matter decomposition.

The decrease in both soil pH value and organic matter content could be considered as an indication of soil fertility decline. Changes in the chemical properties of vegetable soils confirm that the current cultivated pattern within the vegetable production system is a threat to sustainable agricultural development in China.

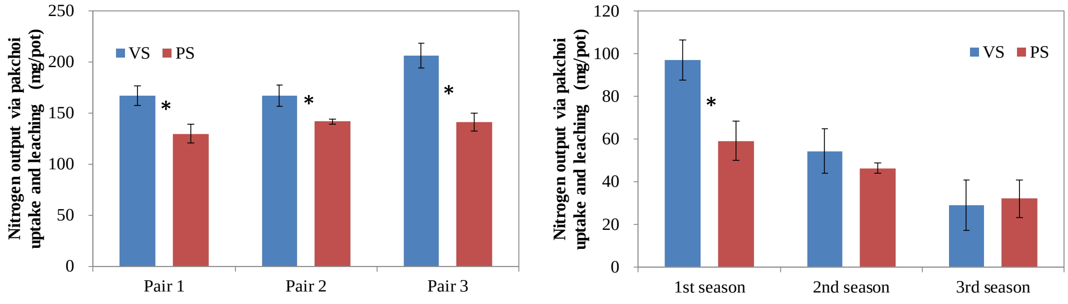
2.6.2 Soil nitrogen output from the two fields

In this study pakchoi uptake and leaching loss were the two chosen domain pathways to represent the nitrogen output. Nitrogen uptake by pakchoi was considered as an effective measure of nitrogen output while nitrogen leaching loss was considered unusable.

With significant changes in pakchoi yield and nitrogen uptake, while no significant change of pakchoi yield was found in paddy soils (Fig. 2.4, Fig. 2.5). It was believed that high yield was contributed to the soil mineral nitrogen supply. Pakchoi assimilated less nitrogen from vegetable soils than from paddy soils in the 3rd season and much more mineral nitrogen was leached out from vegetable soils than from paddy soils during three seasons. It was implied the decreasing mineral nitrogen content caused by leaching could be the reason for lower yield in vegetable soils. It was indicated that although mineral nitrogen contents were higher in vegetable soil (Table 2.3), stable pakchoi yield was still difficult to maintain in the absence of nitrogen fertilizer. It might explain why farmers keep applying large amounts of nitrogen fertilizer every growing season to ensure the yield.

The difference in soil nitrogen leaching loss was mainly determined by the mineral nitrogen content in soils between three soil pairs because no more nitrogen was applied in this experiment. As Table 2.3 shown, the significance of soil mineral content could be attributed to the difference in nitrate nitrogen content. In addition, nitrate nitrogen was the nitrogen form mineral assimilated by plant, the major left in soil profile and also the dominant form that mineral nitrogen loss via leaching (Fig. 2.8). It has been widely reported that an improper soil environment (Table 2.3, discussed in 2.6.1) was one factor weakening the effective nitrogen output from vegetable soils (Zhang *et al.*, 2010; Fan *et al.*, 2011; Shang *et al.*, 2014).

However, the total nitrogen output (the amount of nitrogen uptake by pakchoi and leaching loss) from vegetable soils was significantly higher than that from paddy soils (Fig. 2.10 a). It was demonstrated that the unusable nitrogen output from vegetable soil was higher than that from paddy soil. On the other hand, the significant difference between these two soils was only observed in the 1st season (Fig. 2.10 b), implying that the unusable nitrogen output could be reduced as long as fertilizer application was regulated.

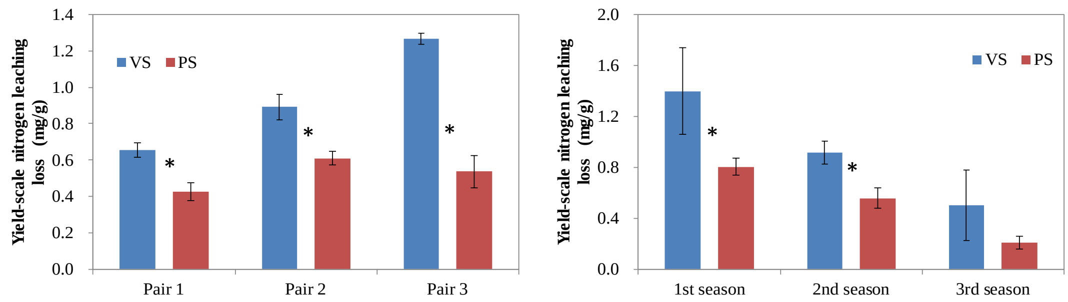


(a) The total nitrogen output of three seasons in each pair

(b) The average nitrogen output in each season

Fig. 2.10 Nitrogen output. Bars represent the SD of the means (n = 3). '*' represents the significant differences between paddy and vegetable soils in certain pair or season determined by paired T test (*P*<0.05).

Analyzing the yield and nitrogen leaching loss, it was interesting to find that more nitrogen was lost for pakchoi growth per gram yield from vegetable soils than from paddy soils (Fig. 2.11). This difference between vegetable and paddy soils was significant in the 1st and 2nd seasons. It suggests that high nitrogen leaching loss reduced the efficiency of nitrogen output in vegetable soils and the negative effect of leaching would weaken if the mineral nitrogen was limited. Therefore, leaching was another critical factor affecting nitrogen availability and uptake by pakchoi in vegetable production systems.



(a) In three pairs

(b) In three seasons

Fig. 2.11 Yield-scale nitrogen leaching loss. Bars represent the SD of the means (n = 3). '*'

represents the significant differences between paddy and vegetable soils in certain pair or season determined by paired T test (*P*<0.05).

2.7 Conclusion

Vegetable production increased soil mineral nitrogen content and concurrently decreased soil pH value and organic matter content. These changes may reduce soil fertility and threaten the sustainable utilization of vegetable fields. The nitrogen output from vegetable soils was higher than that from paddy soils. However, the effective soil output for plant uptake was reduced and the unusable output via leaching loss was increased after the conversion from paddy to vegetable cultivation. Nitrogen output could be regulated by controlling fertilizer use in the short term. However, the low nitrogen efficiency of vegetable soil for supplying pakchoi growth was induced by both the improper soil environment and high nitrogen leaching loss. Consideration of soil chemical property problems and nitrogen processes in the vegetable production system are necessary, therefore a new approach should be a priority.

References

Bergqvist, C., Herbert, R., Persson, I., Greger, M., 2014. Plants influence on arsenic availability and speciation in the rhizosphere, roots and shoots of three different vegetables. Environmental Pollution 184, 540-546.

Cao, Z., Huang, J., Zhang, C., Li, A., 2004. Soil quality evolution after land use change from paddy soil to vegetable land. Environmental Geochemistry and Health 26, 97-103.

Carreres, R., Sendra, J., Ballesteros, R., Valiente, E.F., Quesada, A., Carrasco, D., Leganés, F., de la Cuadra, J.G., 2003. Assessment of slow release fertilizers and nitrification inhibitors in flooded rice. Biology and Fertility of Soils 39, 80-87.

Chen, J., 2007. Rapid urbanization in China: a real challenge to soil protection and food security. Catena 69, 1-15.

Chen, R., Senbayram, M., Blagodatsky, S., Myachina, O., Dittert, K., Lin, X., Blagodatskaya, E., Kuzyakov, Y., 2014. Soil C and N availability determine the priming effect: microbial N mining and stoichiometric decomposition theories. Global Change Biology 20, 2356-2367.

Darilek, J.L., Huang, B., Wang, Z., Qi, Y., Zhao, Y., Sun, W., Gu, Z., Shi, X., 2009. Changes in soil fertility parameters and the environmental effects in a rapidly developing region of China. Agriculture, Ecosystems & Environment 129, 286-292.

Deng, X., Huang, J., Rozelle, S., Uchida, E., 2006. Cultivated land conversion and potential agricultural productivity in China. Land Use Policy 23, 372-384.

Fan, M., Shen, J., Yuan, L., Jiang, R., Chen, X., Davies, W.J., Zhang, F., 2011. Improving crop productivity and resource use efficiency to ensure food security and environmental quality in China. Journal of Experimental Botany 63, 13-24.

Gijsman, A.J., 1990. Rhizosphere pH along different root zones of Douglas-fir (Pseudotsuga menziesii), as affected by source of nitrogen. Plant and Soil 124, 161-167.

Guo, J.H., Liu, X.J., Zhang, Y., Shen, J., Han, W., Zhang, W., Christie, P., Goulding, K., Vitousek, P., Zhang, F., 2010. Significant acidification in major Chinese croplands. Science 327, 1008-1010.

Han, J., Luo, Y., Yang, L., Liu, X., Wu, L., Xu, J., 2014. Acidification and salinization of soils with different initial pH under greenhouse vegetable cultivation. Journal of Soils and Sediments 14, 1683-1692.

He, F., Chen, Q., Jiang, R., Chen, X., Zhang, F., 2007a. Yield and nitrogen balance of greenhouse tomato (Lycopersicum esculentum Mill.) with conventional and site-specific nitrogen management in Northern China. Nutrient Cycling in Agroecosystems 77, 1-14.

He, J.Z., Shen, J.P., Zhang, L.M., Zhu, Y.G., Zheng, Y.M., Xu, M.G., Di, H., 2007b. Quantitative analyses of the abundance and composition of ammonia - oxidizing bacteria and ammonia - oxidizing archaea of a Chinese upland red soil under long - term fertilization practices. Environmental Microbiology 9, 2364-2374.

Huan, H., Zhou, J., Duan, Z., Wang, H., Gao, Y., 2007. Contributions of greenhouse soil nutrients accumulation to the formation of the secondary salinization: a case study of Yixing City, China. Agrochimica 51, 207-221.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Jin, X., Fan, X., Cai, G., 2005. Nitrogen transformation and losses in soils grown with vegetables. Soil 37, 492-499.

Ju, C., Buresh, R.J., Wang, Z., Zhang, H., Liu, L., Yang, J., Zhang, J., 2015. Root and shoot traits for rice varieties with higher grain yield and higher nitrogen use efficiency at lower nitrogen rates application. Field Crops Research 175, 47-55.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X.T., Kou, C.L., Christie, P., Dou, Z., Zhang, F., 2007. Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain. Environmental Pollution 145, 497-506.

Kemmitt, S.J., Wright, D., Goulding, K.W., Jones, D.L., 2006. pH regulation of carbon and nitrogen dynamics in two agricultural soils. Soil Biology and Biochemistry 38, 898-911.

Li, J.l., Chen, X.p., Li, X.l., 2003. Effect of N fertilization on yield, nitrate content and N apparent losses of Chinese cabbage. Acta Pedologica Sinica 40, 266-272.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F., Petersen, J., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Liang, L., Zhao, X., Yi, X., Chen, Z., Dong, X., Chen, R., Shen, R., 2013. Excessive application of nitrogen and phosphorus fertilizers induces soil acidification and phosphorus enrichment during vegetable production in Yangtze River Delta, China. Soil Use and Management 29, 161-168.

Lin, X., Yin, R., Zhang, H., Huang, J., Chen, R., Cao, Z., 2004. Changes of soil microbiological properties caused by land use changing from rice–wheat rotation to vegetable cultivation. Environmental Geochemistry and Health 26, 119-128.

Luo, Y.x., Gao, B., Yan, X.y., Jiang, X.s., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Min, J., Shi, W., Xing, G., Zhang, H., Zhu, Z., 2011a. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems. Nutrient Cycling in Agroecosystems 91, 31.

Min, J., Zhao, X., Shi, W.M., Xing, G.X., Zhu, Z.L., 2011b. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.

NBS, 2015. China Statistical Yearbook. . China Statistic Press, Beijing., National Bureau of Statistics of China,.

Ni, W.Z., Li, J.P., Zhu, Z.L., 2007. Occurrence of nitrification-denitrification and gaseous nitrogen loss process in flooded rice soil. Progress in Natural Science 17, 6-10.

Olsen, S.R., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. United States Department Of Agriculture; Washington.

Pietri, J.A., Brookes, P., 2008. Relationships between soil pH and microbial properties in a UK arable soil. Soil Biology and Biochemistry 40, 1856-1861.

Saha, D., Kukal, S., Sharma, S., 2011. Landuse impacts on SOC fractions and aggregate stability in typic ustochrepts of Northwest India. Plant and Soil 339, 457-470.

Shang, Q., Ling, N., Feng, X., Yang, X., Wu, P., Zou, J., Shen, Q., Guo, S., 2014. Soil fertility and its significance to crop productivity and sustainability in typical agroecosystem: a summary of long-term fertilizer experiments in China. Plant and Soil 381, 13-23.

She, Z., Zhang, Y., 2008. The characteristics and problems in development of agriculture and rural areas for the areas with a rapid economic development. Economic Geography 28, 460-463.

Shen, W., Lin, X., Shi, W., Min, J., Gao, N., Zhang, H., Yin, R., He, X., 2010. Higher rates of nitrogen fertilization decrease soil enzyme activities, microbial functional diversity and nitrification capacity in a Chinese polytunnel greenhouse vegetable land. Plant and Soil 337, 137-150.

Sheng, R., Meng, D., Wu, M., Di, H., Qin, H., Wei, W., 2013. Effect of agricultural land use change on community composition of bacteria and ammonia oxidizers. Journal of Soils and Sediments 13, 1246-1256.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.

Song, K., Xu, A., Zhang, W., 2009. Study on nitrogen leaching in farmlands with different crops in riverine plain area of Taihu Lake. Journal of Nanjing Agricultural University.

Sumner, M., Miller, W., 1996. Cation exchange capacity and exchange coefficients. Methods of Soil Analysis Part 3—Chemical Methods, 1201-1229.

Sun, R.j., wang, D.j., Lin, J.h., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.

Tian, W., Wang, L., Li, Y., Zhuang, K., Li, G., Zhang, J., Xiao, X., Xi, Y., 2015. Responses of microbial activity, abundance, and community in wheat soil after three years of heavy fertilization with manure-based compost and inorganic nitrogen. Agriculture, Ecosystems & Environment 213, 219-227.

Tian, Y., Zhang, X., Liu, J., Gao, L., 2011. Effects of summer cover crop and residue management on cucumber growth in intensive Chinese production systems: soil nutrients, microbial properties and nematodes. Plant and Soil 339, 299-315.

Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S., 2002. Agricultural sustainability and intensive production practices. Nature 418, 671.

Wang, H., Dong, Y.h., Li, D.c., Velde, B., An, Q., Guo, Z.x., Zuo, Q.d., 2008. Evolution of soil chemical properties in the past 50 years in the Tai Lake Region, China. Soil and Tillage Research 100, 54-59.

Wang, H., Guan, D., Zhang, R., Chen, Y., Hu, Y., Xiao, L., 2014. Soil aggregates and organic carbon affected by the land use change from rice paddy to vegetable field. Ecological Engineering 70, 206-211.

Wen, X., Yanpeng, C., Xinan, Y., Yan, H., Li, Z., 2017. Soil nitrogen supply capacity as an indicator of sustainable watershed management in the upper basin of Miyun Reservoir. Ecological Indicators.

West, T.O., Post, W.M., 2002. Soil organic carbon sequestration rates by tillage and crop rotation. Soil Science Society of America Journal 66, 1930-1946.

Wissing, L., Kölbl, A., Häusler, W., Schad, P., Cao, Z.H., Kögel-Knabner, I., 2013.

Management-induced organic carbon accumulation in paddy soils: the role of organo-mineral associations. Soil and Tillage Research 126, 60-71.

Yin, R., Zhang, H.y., Huang, J.f., Lin, X.g., Wang, J.h., Cao, Z.h., 2004. Comparsion of microbiological properties between soils of rice-wheat rotation and vegetable cultivation. Plant Nutrition and Fertilizing Science 10, 57-62.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D., 2010. Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. Agriculture, Ecosystems & Environment 139, 469-475.

Zhang, H.Y., Yin, R., Huang, J.F., 2005. Changes in soil biochemical properties caused by cropping sys tem alteration from rice wheat rotation to vegetable cultivation. Soils 37, 182-186.

Zhang, N., Wan, S., Li, L., Bi, J., Zhao, M., Ma, K., 2008. Impacts of urea N addition on soil microbial community in a semi-arid temperate steppe in northern China. Plant and Soil 311, 19-28.

Zheng, J.G., 2000. Rice-wheat cropping system in China. Soil and Crop Management Practices for Enhnaced Productivity of the Rice-Wheat Cropping System in the Sichuan Province of China'(Eds Hobbs PR and Gupta RKO: 1-10. Rice-Wheat Consortium Paper Series 9 (RWC-CIMMYT, New Delhi, India).

Zhou, L., 2000. Agro-geography of China. Beijing: Science Press.

Zhou, Q., Gibson, C.E., Zhu, Y., 2001. Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK. Chemosphere 42, 221-225.

Zhu, J., Li, X., Christie, P., Li, J., 2005. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (Capsicum frutescens L.) cropping systems. Agriculture, Ecosystems & Environment 111, 70-80.

Zhu, Z., Norse, D., Sun, B., 2006. Policy for reducing non-point pollution from crop production in China. China Environmental Science Press, Beijing, 135-161.

CHAPTER 3: EFFECTS OF BIOCHAR ADDITION ON NITROGEN RETENTION IN SOILS USED FOR VEGETABLE (PAKCHOI) PRODUCTION

Abstract

Low nitrogen retention and high leaching losses are major constraints limiting mineral nitrogen content in soils for uptake and use by vegetable plants during production. Vegetable farmers apply excessive amounts of fertilizer to replace the losses and application rates are very high in regions with heavy rainfall. It was hypothesized that biochar addition to soils used for vegetable production could improve nitrogen retention and reduce losses through leaching, thus making more nitrogen available for vegetable plant uptake.

A pot experiment was conducted with soil collected from a vegetable field in the Tailake region. Three levels of biochar (0, 1% w/w, 5% w/w) were added into the soil in the no nitrogen and nitrogen conditions. The soil ammonium nitrogen content was increased due to biochar addition from 5.64 mg/kg to 12.47 mg/kg and 20.28 mg/kg to 34.54mg/kg in the no nitrogen and nitrogen conditions, respectively. It could be attributed to mineral nitrogen retention of biochar and enhanced soil nitrogen mineralization. Volume and nitrate concentration of leachate was significantly decreased in soils amended with biochar by 17%-58% and 6%-35%, respectively. Biochar addition could increase soil water retention capacity and residence time of nitrate nitrogen for pakchoi uptake. Our results also show that mineral nitrogen retained by biochar could be re-utilized by plants. The data suggest that biochar could be used as a potential soil amendment to improve soil nitrogen retention for vegetable production. Therefore, the nitrogen fertilizer application for maintaining vegetable yield may be reduced by biochar addition. Nonetheless, the correct additional rate of biochar addition needs to be further studied before large-scale application in vegetable production fields.

Key words:

Soil nitrogen retention, vegetable system, biochar addition, leaching, mineralization

3.1 Introduction

Nitrogen is an indispensable nutrient element for crop growth and is found in soils mostly in organic forms. Just a small part of the soil nitrogen pool is in mineral form. Although most crops depend on mineral nitrogen supplementation as it is the available form for crop uptake, it is also active and easily lost from the soil environment by leaching and volatilization, and is removed with sediment.

Compared to the production of conventional crops, maintaining optimum soil nitrogen quantities in vegetable fields is difficult due to the highly intensive and continuous cultivation commonly practiced during vegetable production (Min *et al.*, 2011; Wang *et al.*, 2014). Vegetable fields are usually plowed three to five times in one year after every harvest season (Huan *et al.*, 2007; Shi *et al.*, 2009; Qiu *et al.*, 2010). Frequent cultivation destroys the soil aggregate structure and reduces soil nutrient retention (Qi *et al.*, 2011; Yan *et al.*, 2012; Wang *et al.*, 2014). Nitrogen losses via leaching from vegetable soils can reach up to 50% of nitrogen fertilizer application rate (Zhao *et al.*, 2010; Min *et al.*, 2011; Yong-xia *et al.*, 2015), while nitrogen loss via leaching from paddy fields, plowed twice a year, accounts for only 2% of total nitrogen loss (Xing and Zhu, 2000; Zhu and Chen, 2002). The risk of nitrogen losses through leaching is even higher in the Tailake region due to the higher annual precipitation (over 1,000 mm).

Vegetable production often requires a larger input of nitrogen and irrigation water (Shi *et al.*, 2009; Qiu *et al.*, 2010). Low nutrient retention capacity and high nitrogen leaching loss limits the soil mineral nitrogen content for vegetable plant uptake. Hence, vegetable farmers usually apply excessive nitrogen fertilizer into soils to meet the demand of vegetable nutrient requirements. Excessive nitrogen fertilizer application is not sustainable and cannot maintain high vegetable crop yields in the long-term. In addition, excessive nitrogen fertilizer application causes other environmental problems such as high nitrogen leaching (Camargo and Alonso, 2006; Ju *et al.*, 2007; Shi *et al.*, 2009), soil acidification (Kemmitt *et al.*, 2006; Liang *et al.*, 2013) and soil fertility decline (Ju *et al.*, 2007; Darilek *et al.*, 2009; Vitousek *et al.*, 2009). In order to alleviate these problems and maintain high vegetable yields, it is necessary to develop approaches (methods) to promote nitrogen retention in the soil and reduce nitrogen loss through leaching, in vegetable production fields.

Applying organic matter directly (Zhang *et al.*, 2014) or reducing the chemical nitrogen fertilizer application (Agostini *et al.*, 2010; Min *et al.*, 2012) can meet this demand to some extent. However, restoring soil structure and aggregate properties is a complicated and slow process that requires a relatively long period (decades or even hundreds of years) (Diacono and Montemurro, 2010). In addition, nitrate nitrogen is the form of available nitrogen for most vegetable crops, and nitrate-N is also prone to leaching. Nitrogen losses via leaching can be decreased in the short term after reducing fertilizer application, but also may decrease yields if improperly managed (Ju *et al.*, 2009; Min *et al.*, 2012).

The addition of biochar into vegetable soils could offer an alternative for addressing the problems of poor nutrient retention and nitrogen loss through leaching by enhancing soil nitrogen retention capacity and decreasing leaching losses simultaneously (Steiner *et al.*, 2008; Lehmann, 2009; Novak *et al.*, 2009; Zheng *et al.*, 2013). Biochar is a fine-grained and porous substance, similar to charcoal. However, unlike charcoal, biochar is produced through modern pyrolysis processes under oxygen-free or anoxic conditions at a relatively low temperature (450^{o}C – 650^{o}C) (Brown, 2009), from a wide range of biomass sources including woody materials and agricultural residues (Bird *et al.*, 2011; Agrafioti *et al.*, 2013). In recent years, biochar has received much attention with regard to optimizing production conditions (Sun *et al.*, 2014) and raw materials (Zhao *et al.*, 2013). Although biochar has a variety of physical-chemical characterizations because of different manufacturing processes, it has the primary characteristic of high stability against decomposition (Lehmann *et al.*, 2009; Kuzyakov *et al.*, 2014) and an excellent ability to absorb ions (Qiu *et al.*, 2008; Gai *et al.*, 2014) compared to other forms of soil organic matter. This is due to its greater surface area, negative surface charge, and charge density (Liang *et al.*, 2006; Lehmann, 2007). Biochar could serve as a type of soil amendment in agricultural systems to increase crop yield by regulating nitrogen processes (Major *et al.*, 2009; Clough and Condron, 2010; Singh *et al.*, 2010; Steiner *et al.*, 2010; Zhang *et al.*, 2010; Dempster *et al.*, 2012a; Zheng *et al.*, 2013) and ameliorating the soil environment

(Novak *et al.*, 2009; Zhang *et al.*, 2010). Studies on the effect of biochar addition on soil nitrogen leaching found that ammonium concentration of leachate decreased and this was attributed to adsorption by biochar (Major *et al.*, 2009; Laird *et al.*, 2010; Hale *et al.*, 2013). Furthermore, other studies also reported that biochar provided a fine water- retaining capacity (Spokas *et al.*, 2012; Bruun *et al.*, 2014; Ulyett *et al.*, 2014).

According to previous studies, biochar may be a potential soil amendment for improving nitrogen retention in vegetable production systems. Nitrogen is lost mainly through leaching in the form of nitrate nitrogen (Min *et al.*, 2011). However, the effects of biochar on nitrate nitrogen of leachate are inconsistent (Ding *et al.*, 2010; Laird *et al.*, 2010; Dempster *et al.*, 2012b; Yao *et al.*, 2012; Hale *et al.*, 2013). The effect of biochar addition on leachate volume has been ignored to some extent. It is still unknown whether the mineral nitrogen retained by biochar can be re-used by plants. The data on biochar addition to soils used for vegetable production under intensive cultivation systems, with excessive nitrogen application rates, has not been well documented. Therefore, there is an urgency to study the effect of biochar addition on soils used for vegetable production under intensive cultivation systems and to determine the effect on nitrogen retention (including soil mineral nitrogen content, the bioavailability of retained mineral nitrogen by biochar and nitrogen losses occurring as a result of leaching) in vegetable fields.

The objectives of this study were (1) to investigate the effect of biochar on soil mineral nitrogen retention, (2) to determine the bioavailability of mineral nitrogen retained by biochar, (3) to investigate the effect of biochar addition on nitrogen leaching loss.

3.2 Materials and methods

3.2.1 Soil description

Soil used for the pot experiment in this study was collected from a vegetable field (31°17'N, 119°54'E) in Yixing City, Jiangsu Province, China. This vegetable field was located in the Tailake region, with a subtropical monsoon climate, with an average annual temperature and rainfall of 15.7 ℃ and 1,177 mm, respectively.

This vegetable field has been under paddy production for hundreds of years before being converted to vegetable production in the past 10 years. In Tailake Region, vegetables are usually planted 3-4 times (seasons) in a year. Urea and compound fertilizer are commonly applied to supply nitrogen at the rate of 900 -1300 kg/ha per year (Zhu and Chen, 2002; Huang *et al.*, 2006; Min *et al.*, 2011). The soil is an Hydragric Anthrosols evolved from lacustrine deposits, with a pH (H_2O) of 5.56; an organic matter (SOM) content of 18.2 g/kg; total N (TN) and phosphorus (TP) contents of 1.21and 0.62 g/kg, respectively; and mineral N, available phosphorus and potassium contents of 64.77, 73.0 and 152.3 mg/kg, respectively.

3.2.2 Planting material

Pakchoi (*Brassica chinensis L.*) is a type of Chinese cabbage, popular in southern China and Southeast Asia. The typical growing period for pakchoi is 20-35 days in a moderate climate (around 25 °C), and relatively prolonged to 40-50 days in cold weather (below 10 °C). Due to one month growth cycle, pakchoi can ensure market supply and also requires a lot of nitrogen input. The nitrogen applied on vegetable fields for the production of pakchoi planting is nearly 200 kg/ha every season (Yuan *et al.*, 2010) in the Tailake region.

3.2.3 Biochar characterization

Biochar used in this study was produced from wheat straw using a biogas-energy slow pyrolysis system. The reactor was heated via a step-wise procedure under oxygen-limited conditions. The temperature was increased to 450 °C at a rate of 5 °C per minute and was then maintained for over 5 hours until no visible smoke was emitted from the gas vent. The biochar properties in this study are as follows: total nitrogen (TN) and total carbon (TC) contents were 12.5 and 503.1 g kg^{-1}, respectively; ammonium and nitrate nitrogen contents were 1.8 and 3.0 mg kg^{-1}, respectively; pH 8.9; and BET 7.4 m^2 g^{-1}. The biochar was milled to pass through a 0.25-mm sieve prior to experimental application.

3.2.4 Pot experiment

The pot experiment was carried out in the greenhouse at the Jiangsu Agricultural Academy of Sciences, with the temperature maintained between 25°C -35°C (The temperature outside ranged from 15°C -40°C during this period.). Two hundred and fifty kilograms of soil were sampled from the 0-20 cm profile depth from a vegetable field (described in 3.2.1) two months after the harvesting of a celery crop. The collected soil was air-dried and 2 kg was used to fill pots with the following dimensions: 28 cm in height, 15 cm in width and 10 cm in depth. One pot was considered as an individual unit for sampling, harvesting and data analysis. The vegetable pakchoi was planted for four growing seasons beginning in April 2016 until November 2016.

The experiment comprised three biochar addition levels (0, 1% w/w, 5% w/w) in the two nitrogen conditions (no nitrogen and nitrogen). The details of treatment are presented in Table 3.1. The replicates for six treatments were different because of sampling requirements (Table 3.1).

Table 3.1 Treatments and their replicates in pot experiment with four growing seasons

Treatments	Rates of biochar addition (% w/w)	Rates of nitrogen fertilizer application (mg N/kg soil)
CK	0	0
1%BC	1	0
5%BC	5	0
CKU	0	100
U1%BC	1	100
U5%BC	5	100

Replicates:

CK and CKU maintained 3 replicates (pots) for four seasons.

1%BC, 5%BC, U1%BC and U5%BC had 12 replicates for 1st season, 9 replicates for 2nd season, 6 replicates for 3rd season and 3 replicates for 4th season. The cost of each treatment is 3 replicates for biochar sampling.

Experiment implemented with the process of growing season presented in Fig. 3.1.

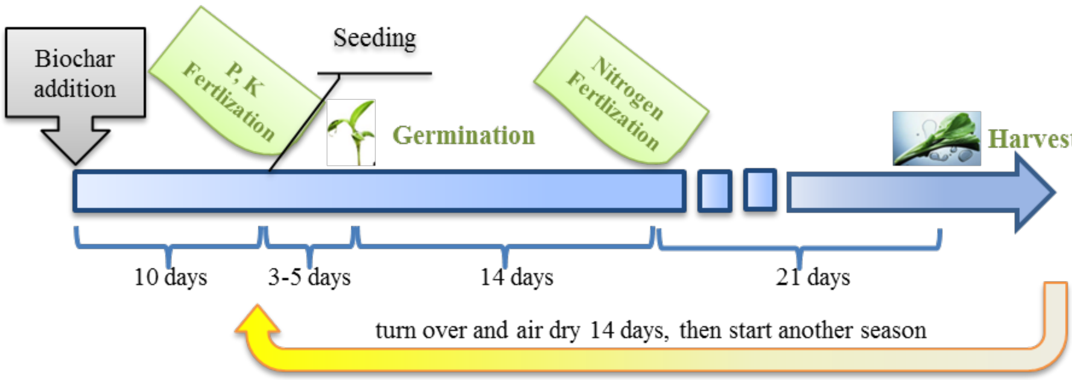


Fig. 3.1 Process of one growing season (nitrogen fertilizer only applied in 1st to 3rd growing seasons)

Biochar was weighted as the additional rate for each pot (20 g biochar for each pot of 1%BC and U1%BC treatments and 100 g biochar for each pot of 5%BC and U5%BC treatments). Three grams of biochar was separated, divided into three equal parts and then packed into three non-woven bags (1g/bag) which allowed water, nutrients and microbes, but not soil or biochar particles, to pass through. The rest of the biochar (17 g biochar for 1%BC and U1%BC treatments and 97 g biochar for 5%BC and U5%BC treatments) was mixed through with 2 kg air-dried soil (Fig. 3.2). All of the packs were buried 3 cm below surface soil at the beginning of pot experiment.

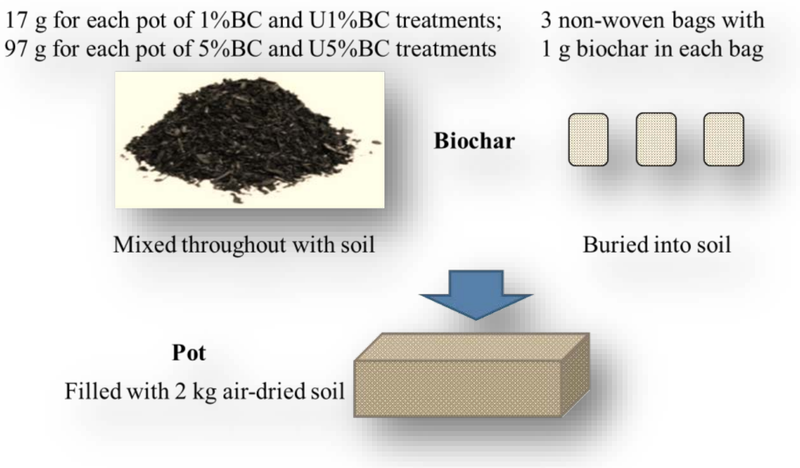


Fig. 3.2 Method for biochar addition

Soil and biochar were left standing for 10 days in a state of steady soil microbial activity with moisture being maintained by irrigation.

After that, 85 mg P/kg and 120 mg K/kg chemical fertilizers were applied as base fertilizers and 0.2 g (about 50-60 seeds) seeds were sown into each pot containing soil (P, K fertilizer application repeated every growing season). The germination time was calculated from planting date until more than 35 seeds had germinated (3-5 days after sowing).

^{15}N-labeled urea with 10 atom% ^{15}N excess was used as the nitrogen chemical fertilizer. During 1st – 3rd seasons, 100 mg N/kg was applied into the pots of CKU, U1%BC and U5%BC treatments at the 14th day every season but no more nitrogen fertilizer was applied to any treatment in the 4th season.

Soil moisture was maintained at 28% (60% of the maximum water holding capacity) by irrigating with deionized water every two days. The amount of water for irrigation was determined by the data from the soil moisture analyser (TZS-II, Tuopu Instrument Co.).

Pakchoi was harvested on the 35th day, and another growing season began after pre-treatment.

3.2.5 Simulation of leaching

Trays were placed under each pot to collect all the leachate flowing from the three pores at the base of the pots (Fig. 2.3). Since there was no natural rainfall in the greenhouse, excess irrigations were implemented four times (on the 7th, 14th, 21st and 28th days) during every growing season. An amount of 1.05 L deionized water was added for every irrigation event (4.2 L every season) to each pot (equivalent to 25 mm precipitation per event and 100 mm precipitation in one growing season). Deionized water was added frequently in small quantities to avoid water flowing down along the inner wall. The process of irrigation was carried out over two hours.

3.2.6 Sampling

3.2.6.1 Soil sampling

One composite soil sample was collected from each pot by mixing four soil cores after the pakchoi harvest in each growing season. The soil samples were air dried and then divided into two subsamples. One subsample was passed through a 2-mm sieve to remove large organic debris and then stored in plastic bags at 4 °C for subsequent determination of soil pH (data presented in Chapter 4), mineral nitrogen (ammonium and nitrate nitrogen) content, soil nitrogen mineralization and nitrification rates. The other subsample was oven dried at 105 °C to a constant mass and then ground to pass through a 0.149-mm sieve; this subsample was analyzed for soil organic matter content and bases content (data presented in Chapter 4)

3.2.6.2 Biochar sampling

Biochar was sampled from 1%BC, 5%BC, U1%BC and U5%BC treatments by taking back the 3 buried non-woven bags after the pakchoi harvest. Three pots in each of these treatments would be used for biochar sampling every season and cannot be used for pakchoi planting for the next season. That is the reason for the decrease in pot replicates in these treatments (Table 3.1). The biochar in the 3 non-woven bags was taken out and stored in plastic bags at 4 °C for subsequent determination of mineral nitrogen (ammonium and nitrate nitrogen) content.

3.2.6.3 Leachate sampling

Leachate was collected 6 hours after each excess irrigation event from the tray under each pot.

3.3 Sample analysis

The soil and leachate samples were collected from every pot with pakchoi in a specific season. Due to the decrease in replicates of biochar relative treatments (1%BC, 5%BC, U1%BC and U5%BC treatments), the number of soil and leachate samples changed with deceasing replicates. The mean value (and SD) of data from soil and leachate analysis was calculated based on all the samples collected in a specific season. However, biochar analysis was always based on the samples from the 3 replicates.

3.3.1 Soil and biochar

Mineral nitrogen in the soil or mineral nitrogen retained by biochar was extracted using a 2 M KCl solution at a ratio of sample and solution=1:10, followed by shaking for 1 hour on the reciprocating shaker, and then filtering the extract. The extract was analyzed using an auto analyser (Traacs 800, Bran & Luebbe, Hamburg) to determine the mineral nitrogen content in soils and the mineral nitrogen retained by biochar.

The amount of the mineral nitrogen retained by biochar per kilogram soil was calculated using the following Equation 3.1, 3.2 and 3.3:

$$w_{(AN\ on\ BC)} = w_{(BC\ AN)} \times r \qquad \text{(Equation 3.1)}$$

Where, $w_{(AN\ on\ BC)}$=ammonium nitrogen retained by biochar per kilogram soil (mg/kg), $w_{(BC\ AN)}$ = ammonium nitrogen content per kilogram biochar(mg/kg), r =biochar additional rate (1% w/w and 5%w/w in this study)

$$w_{(NN\ on\ BC)} = w_{(BC\ NN)} \times r \qquad \text{(Equation 3.2)}$$

Where, $w_{(NN\ on\ BC)}$=nitrate nitrogen retained by biochar per kilogram soil (mg/kg), $w_{(BC\ NN)}$ = nitrate nitrogen content per kilogram biochar(mg/kg)

$$w_{(MN\ on\ BC)} = w_{(AN\ on\ BC)} + w_{(NN\ on\ BC)} \qquad \text{(Equation 3.3)}$$

Where, $w_{(MN\ on\ BC)}$=mineral nitrogen retained by biochar per kilogram soil (mg/kg)

The percentages of the mineral nitrogen retained by biochar to the mineral nitrogen in soil were calculated with the Equation 3.4, 3.5 and 3.6:

$$P_{A(BC\ to\ soil)} = w_{(AN\ on\ BC)}/w_{(AN\ in\ S)} \qquad \text{(Equation 3.4)}$$

Where, $P_{A(BC\ to\ soil)}$ =the percentages of ammonium nitrogen from biochar, $w_{(AN\ in\ S)}$ =the ammonium nitrogen content in soil

$$P_{N(BC\ to\ soil)} = w_{(NN\ on\ BC)}/w_{(NN\ in\ S)} \qquad \text{(Equation 3.5)}$$

Where, $P_{N(BC\ to\ soil)}$ =the percentages of nitrate nitrogen from biochar, $w_{(NN\ in\ S)}$ =the nitrate nitrogen content in soil

$$P_{M(BC\ to\ soil)} = w_{(MN\ on\ BC)}/w_{(MN\ in\ S)} \qquad \text{(Equation 3.6)}$$

Where, $P_{M(BC\ to\ soil)}$ =the percentages of mineral nitrogen from biochar, $w_{(MN\ in\ S)}$ =the mineral nitrogen content in soil

Soil nitrogen mineralization and nitrification were determined by the incubation over a 35-day period at 30°C. Nitrogen mineralization rates were calculated as the difference between final and initial soil mineral nitrogen content divided by 35 days (Stanford and Smith, 1972).

Nitrification rates were calculated as the difference in soil nitrate nitrogen content divided by the number of incubating days (Drury *et al.*, 2008).

3.3.2 Leachate

Leachate volumes were measured and recorded immediately after sampling from each pot. For the ammonium and nitrate analysis, every leachate sample was filtered through 0.45 lm membranes respectively and the ammonium and nitrate concentrations were determined using a continuous-flow analyzer (Skalar Corp., Netherlands). The amount of nitrogen lost via leaching was calculated with the Equation 3.7 and 3.8:

$$m_{n\ (leaching\ loss)} = \rho_{n\ (leachate\ N)} \times V_{n\ (leachate)} \qquad \text{(Equation 3.7)}$$

Where, $m_{n\ (leaching\ loss)}$= amount of nitrogen loss via leaching in *n* time (mg/pot), $\rho_{(leachate\ N)}$ =mineral nitrogen concentrations (ammonium concentration and nitrate concentration) of leachate in *n* time (mg/L), $V_{(leachate)}$ = volume of leachate in *n* time (L/pot) and n=1,2,3,4 means the data from 1st, 2nd, 3rd and 4th leaching in one growing season.

$$m_{(leaching\ loss)} = \sum_{n=1}^{4} m_{n\ (leaching\ loss)} \qquad \text{(Equation 3.8)}$$

Where, $m_{(leaching\ loss)}$ = amount of nitrogen loss via leaching in one growing season (mg/pot).

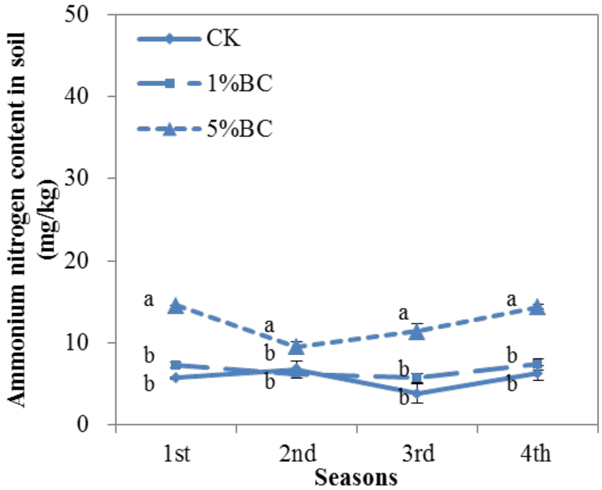
3.3.3 Statistical analyses

The mean and standard differences (presented in figures), of three replications were used to ascertain soil mineral nitrogen contents, soil nitrogen mineralization and nitrification rates, the amount of mineral nitrogen retained by biochar and the amount of nitrogen loss. Significant differences were tested using the standard analysis of variance (ANOVA) by Duncan’s multiple-range test at the 5% level (SPSS ver. 16.0 for Windows, SPSS Inc., USA).

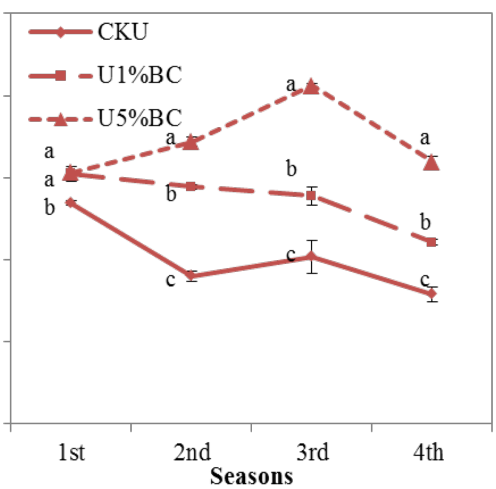
3.4 Results

3.4.1 Mineral nitrogen contents in soils

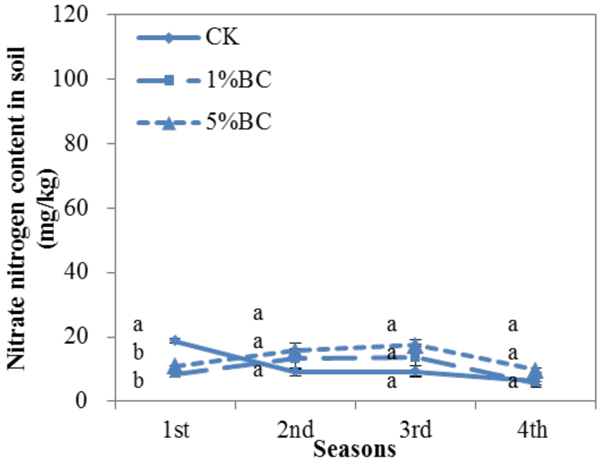
In the no nitrogen condition, biochar addition with 5% (5%BC treatment) significantly increased ammonium nitrogen content by 121% compared to no biochar treatment (CK treatment). The ammonium nitrogen contents in the soil during growing seasons were on average 5.64 mg/kg, 6.61 mg/kg, 12.47 mg/kg for CK, 1%BC and 5%BC treatments, respectively (Fig. 3.3 a). The ammonium nitrogen content showed slight changes over four continuous growing seasons. The nitrate nitrogen content in the soil were on average 10.88 mg/kg, 10.25 mg/kg, 13.49 mg/kg for CK, 1%BC and 5%BC treatments, respectively (Fig. 3.3 c). No significant differences were observed in nitrate nitrogen content of treatments in the no nitrogen condition.



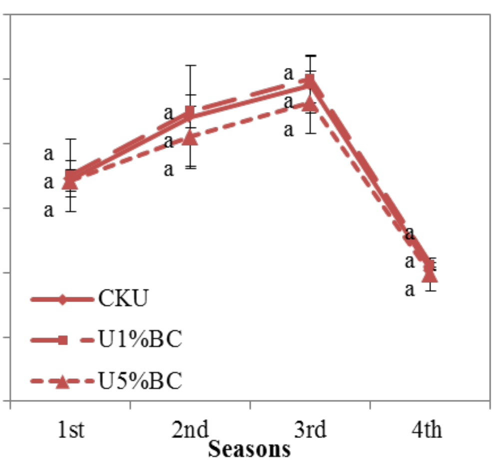
(a) Ammonium nitrogen content in the no nitrogen condition



(b) Ammonium nitrogen content in the nitrogen condition



(c) Nitrate nitrogen content in the no nitrogen condition



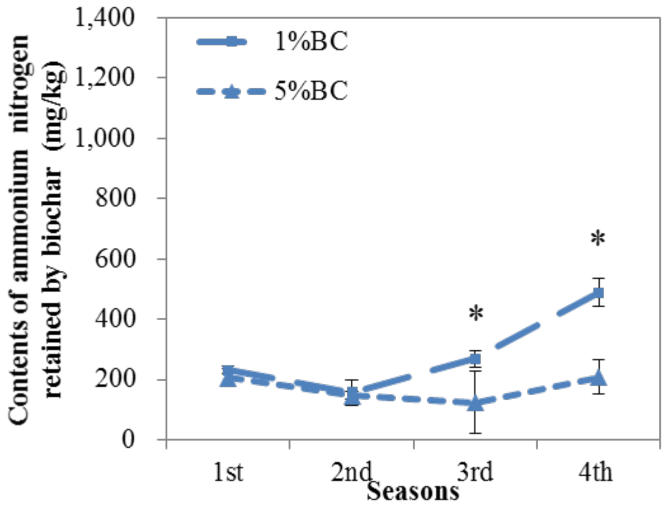
(d) Nitrate nitrogen content in the nitrogen condition

Fig. 3.3 Mineral nitrogen content in soils during four growing seasons. CK=treatment with no biochar and no nitrogen fertilizer; 1%BC= treatment with 1% biochar addition; 5%BC= treatment with 5% biochar addition; CKU=treatment with nitrogen fertilizer application; U1%BC= treatment with 1% biochar addition and nitrogen fertilizer application; U5%BC= treatment with 5% biochar addition and nitrogen fertilizer application. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). SD in the same letters in one season are not significantly different, determined by Duncan's multiple-range test ($p<0.05$).

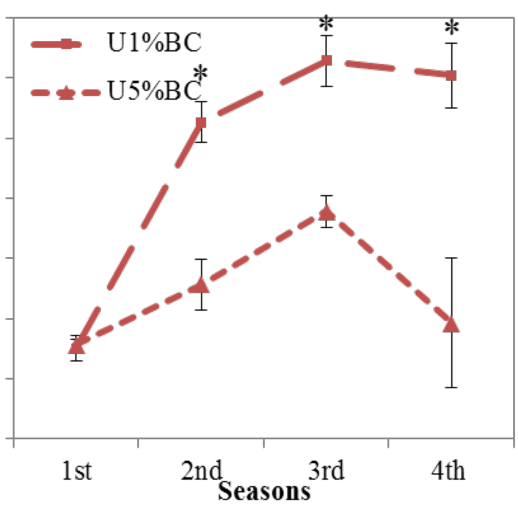
Nitrogen fertilizer application increased both ammonium nitrogen and nitrate nitrogen content in the soil (Fig. 3.3 b, Fig. 3.3 d). Similar to the trend in the no nitrogen condition, biochar addition significantly promoted ammonium nitrogen content in soil in the nitrogen condition. The ammonium nitrogen content of U5%BC treatment was at a higher level than that of 1%BC treatment from the 2nd growing season. Ammonium nitrogen contents in the soil during the growing season were on average 20.28 mg/kg, 27.34 mg/kg, 34.54mg/kg for CKU, U1%BC and U5%BC treatments, respectively (Fig. 3.3 b). The differences of nitrate nitrogen in soil of CKU, U1%BC and U5%BC treatments were not significant during the 4 growing seasons, but showed similar trends. Nitrate nitrogen content of treatments with nitrogen fertilizer all sharply decreased in the 4th growing season (Fig. 3.3 d). Nitrate nitrogen content in the soil during the growing season were on average 74.10 mg/kg, 75.77 mg/kg, 70.79 mg/kg for CKU, U1%BC and U5%BC treatments, respectively.

3.4.2 Mineral nitrogen retained by biochar

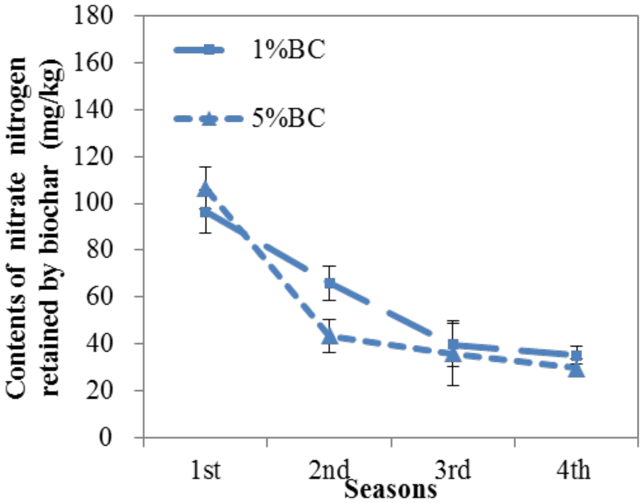
The quantities of ammonium nitrogen retained by biochar attained maximum values in the 4th season and 3rd season under a no nitrogen and nitrogen condition, respectively (Fig. 3.4 a & b) and the quantities of nitrate nitrogen reached the maximum values in the 1st season and 2nd season under a no nitrogen and nitrogen condition, respectively (Fig. 3.4 c & d). Ammonium nitrogen retained by biochar maintained 200 mg/kg in the no nitrogen condition (Fig. 3.4 a), while the ammonium content could be up to 600 mg/kg in the U5%BC treatment and 1200 mg/kg in the U1%BC treatment. This decreased to 300 mg/kg in the 4th growing season (Fig. 3.4b). Nitrate nitrogen retained by biochar showed a decreasing trend during four growing seasons (expect for the U1%BC treatment) (Fig. 3.4 c & d). Nitrate nitrogen retained by biochar was around 40 mg/kg and 80 mg/kg in the no nitrogen and nitrogen conditions, respectively. The significances between two addition rates were found in the ammonium and nitrate content in the 2nd, 3rd and 4th seasons in the nitrogen condition (Fig. 3.4 b & d) and merely in the ammonium content in the 3rd and 4th seasons in the no nitrogen condition (Fig. 3.4 a).



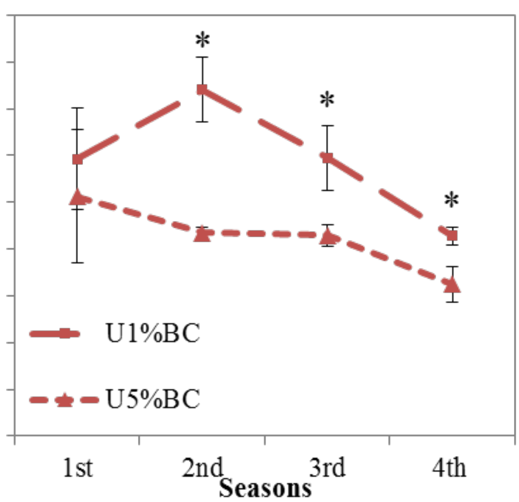
(a) Ammonium nitrogen content in the no nitrogen condition



(b) Ammonium nitrogen content in the nitrogen condition



(c) Nitrate nitrogen content in the no nitrogen condition



(d) Nitrate nitrogen content in the nitrogen condition

Fig. 3.4 Contents of mineral nitrogen retained by biochar during four growing seasons. Plots represent the SD of the means (n=3)

The percentages represent how much mineral nitrogen was retained by biochar in the soils (Table 3.2). Generally, the percentages of ammonium, nitrate and mineral nitrogen were all higher in the no nitrogen condition than those in the nitrogen condition. Biochar retained 21.25%-44.13% of the mineral nitrogen in the soil in the no nitrogen condition and 9.97%-27.18 in the nitrogen condition. Furthermore, the percentages increased with the biochar addition rates. The treatment with a 5% biochar addition (44.13%) had a significantly higher percentage than that of other treatments ($p<0.05$); this was the lowest percentage represented in the 1%BC treatment (9.97%). On average, the percentages of ammonium ranged from 33.77% to 72.34% of ammonium nitrogen, which consisted of 1.63% to 22.06% of nitrate nitrogen. The percentages of ammonium nitrogen of 5%BC and U5%BC treatments were around 70%, which was on average 38% for 1%BC and U1%BC treatments.

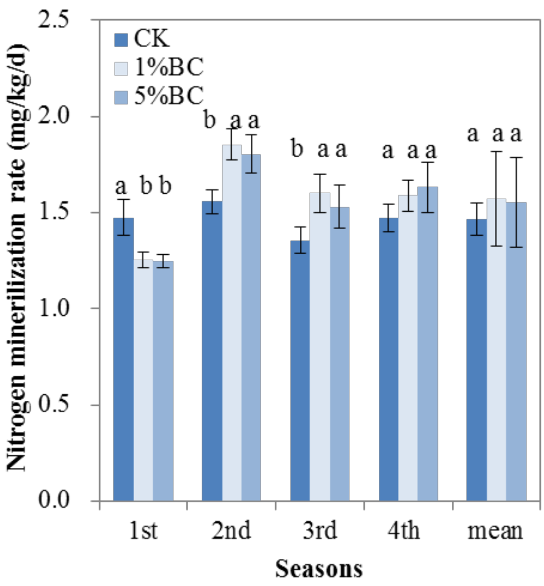
Table 3.2 Percentages of mineral nitrogen retained by biochar to mineral nitrogen in the soil in the forms of ammonium, nitrate and mineral, respectively

	Ammonium nitrogen	Nitrate nitrogen	Mineral nitrogen
1%BC	42.67%±18.73%ab	6.38±3.62%b	21.25±11.26%b
5%BC	68.97%±10.13%a	22.06%±18.00%a	44.13%±14.58%a
U1%BC	33.77%±14.10%b	1.63%±0.34%b	9.94%±2.71%c
U5%BC	72.34%±20.21%a	6.40%±1.72%b	27.81%±7.88%b

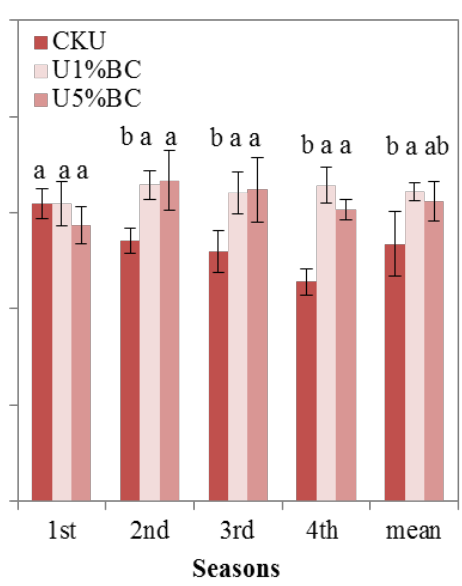
Data value was represented by mean ± SD (n = 4, data from four seasons) and SD was represented across the columns. SD with the same letters are not significantly different, determined by Duncan's multiple-range test ($p<0.05$).

3.4.3 Nitrogen mineralization and nitrification rates in soils

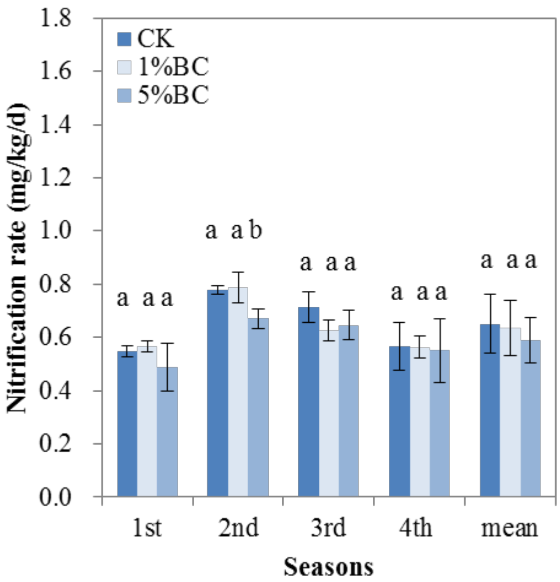
Biochar addition increased nitrogen mineralization rates in the 2nd and 3rd seasons in the no nitrogen condition (Fig.3.5 a) and in the 2nd, 3rd and 4th seasons in the nitrogen condition (Fig.3.5 b). However, a significant decrease in mineralization rates was observed in the treatments with biochar addition in the 1st season (Fig.3.5 a). Nevertheless, nitrification rates of U1%BC and U5%BC were higher than that of CKU treatment during four seasons (only significant in the 3rd and 4th seasons) (Fig. 3.5 d), but the rates were similar among the treatments in the no nitrogen condition.



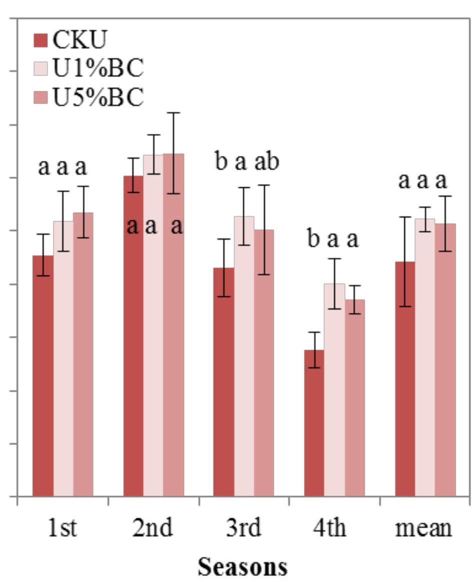
(a) Nitrogen mineralization rates in the treatments in the no nitrogen condition



(b) Nitrogen mineralization in the treatments in the nitrogen condition



(c) Nitrification rates in the treatments in the no nitrogen condition



(d) Nitrification rates in the treatments in the nitrogen condition

Fig. 3.5 Nitrogen mineralization rates and nitrification rates of soils during four growing seasons. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). SD with the same letters in same season are not significantly different, determined by Duncan's multiple-range test ($p<0.05$).

3.4.4 Nitrogen leaching loss

Leachate volumes were affected by the biochar addition but not with the nitrogen conditions. Similar values of leachate volume was observed between CK and CKU treatments, 1%BC and U1%BC treatments, 5%BC and U5%BC treatments, respectively (Fig. 3.6).

Biochar significantly reduced leachate volumes, and the reduction was higher at the 5% biochar addition rate. On average, 1% biochar addition (1%BC and U1%BC treatments) reduced leachate volume by 17%-48% and 5% biochar addition (5%BC and U5%BC treatments) reduced by 28%-58% compared to no biochar treatments (CK and CKU treatments).

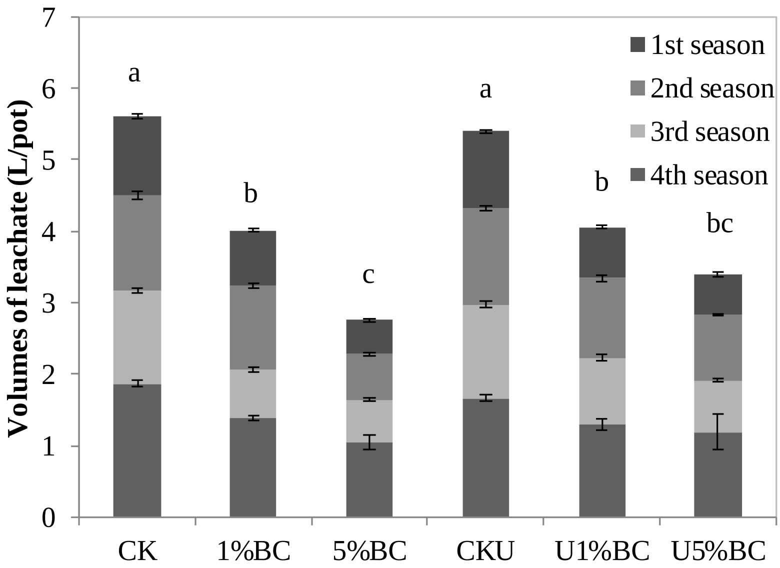
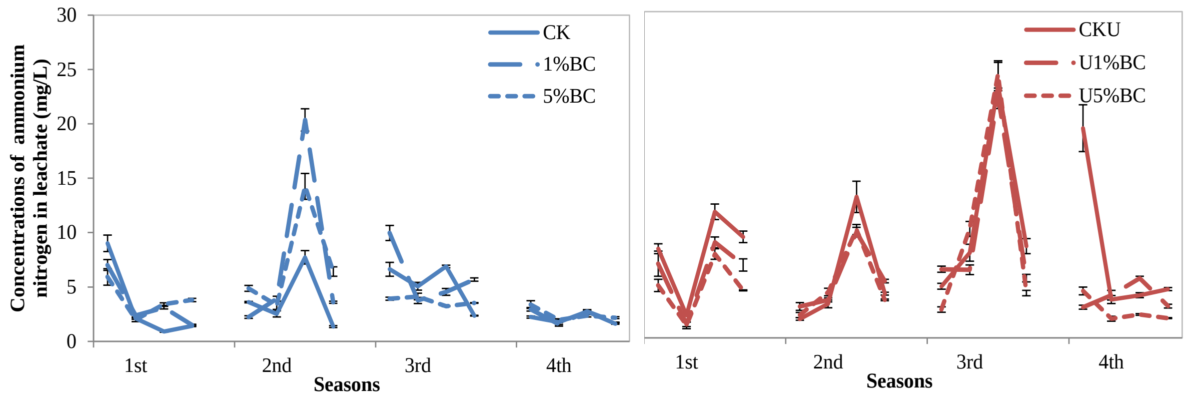


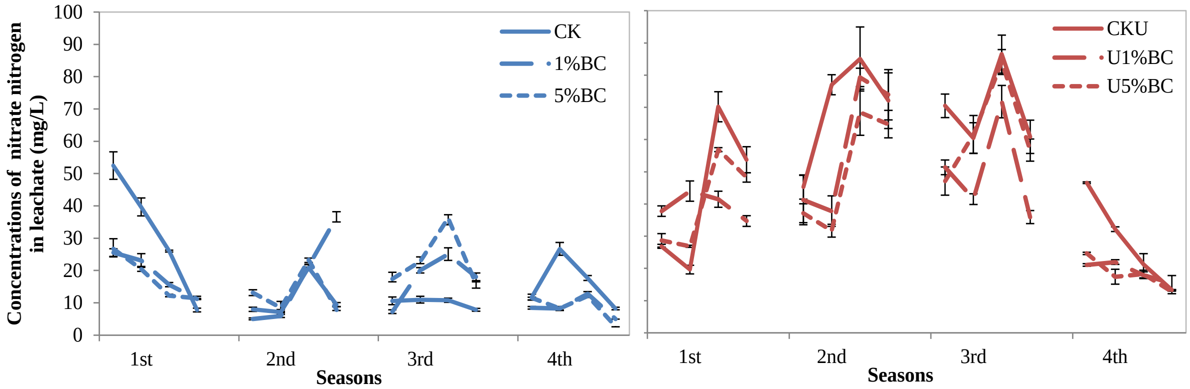
Fig. 3.6 Volume of leachate in four growing seasons. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). Duncan's multiple-range test was used to determine the difference of the sum of leachate volume from four seasons. The same letters are not significantly different ($p<0.05$).

In the no nitrogen condition, biochar addition increased ammonium nitrogen contents in the 2nd and 3rd growing seasons (Fig. 3.7 a) and its effect on nitrate nitrogen was different (Fig. 3.7 c) during the four growing seasons. However ammonium nitrogen in leachate was reduced by 9%-51% in response to 1% biochar addition and 10%-68% in response to 5% biochar addition (Fig. 3.7 b), and nitrate nitrogen was reduced by 7%-33% in response to 1% biochar addition and 6%-35% in response to 5% biochar addition (Fig. 3.7 d) in the nitrogen condition. Furthermore, the effect of biochar on ammonium and nitrate concentrations leachate was more pronounced in the 4th season than those in the first three seasons



(a) Ammonium nitrogen concentration in the no nitrogen condition

(b) Ammonium nitrogen concentration in the nitrogen condition



(c) Nitrate nitrogen concentration in the no nitrogen condition

(d) Nitrate nitrogen concentration in the nitrogen condition

Fig. 3.7 Dynamics of mineral nitrogen concentrations in leachate. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.).

Typically, nitrogen leaching loss in the nitrogen condition was 2.6-3.1 times higher than that in the no nitrogen condition (Fig. 3.8). The addition of biochar also reduced nitrogen loss via leaching by 37% and 55% in the 1%BC and 5%BC treatments compared to CK treatment.

While U1%BC reduced 42% and U5%BC reduced 52% nitrogen loss via leaching compared to CKU treatment.

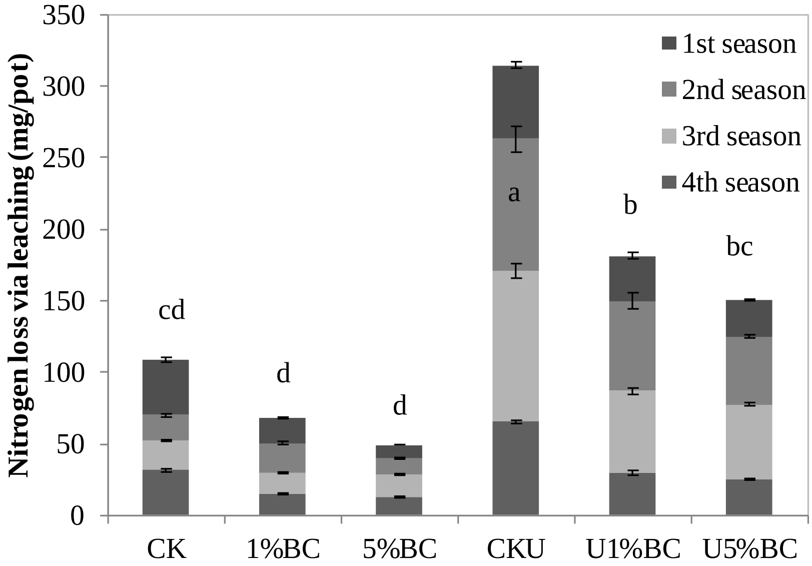


Fig. 3.8 Mineral nitrogen loss from leaching. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). Duncan's multiple-range test was used to determine the difference of the sum of leachate volume from four seasons. The same letters are not significantly different ($p<0.05$).

3.5 Discussion

Our results show that biochar addition significantly increased soil mineral nitrogen contents mainly in ammonium nitrogen (Fig. 3.3). It may be attributed to biochar nitrogen retention (Fig. 3.4), the improvement of nitrogen mineralization (Fig. 3.5) and the reduction of nitrogen leaching loss (Fig. 3.8).

3.5.1 Biochar nitrogen retention

It was found that the biochar added with different rates show quite difference in the mineral nitrogen retentions (Fig. 3.4). The total amount of mineral nitrogen retained by biochar in soil was increased by the increased biochar addition rate (Table 3.2) but the amount of mineral nitrogen retained by one unit biochar was lower in the treatments with higher biochar addition rate (Fig. 3.4). It was implied that the part of mineral nitrogen, which could be retained by biochar in soil, was limited and less than the maximum of biochar nitrogen retention.

Additionally, adsorption conditions were different in the two nitrogen conditions (no nitrogen and nitrogen condition). In the no nitrogen condition, the content of ammonium nitrogen retained by biochar was 13-42 times higher than that in the soil (Fig. 3.4a). There was no significant decrease in the content of ammonium nitrogen retained by biochar, and also in the soil in the no nitrogen condition after planting pakchoi for four seasons. This indicates that (1) this part of ammonium nitrogen (200-400 mg N/kg biochar) was bonded relatively strongly and (2) soil nitrogen mineralization replenished ammonium nitrogen supply. In the nitrogen condition, there was 14-33 times the content of ammonium nitrogen retained by biochar than that in the soil (Fig. 3.4b). The ammonium nitrogen retained by biochar reached up to 1000 mg/kg after the 1st growing season, but the content did not grow as much with further nitrogen fertilizer applications. It suggests that the available adsorption sites on biochar were being quickly saturated (Sarkhot *et al.*, 2013). Contrary to the stable retention in the no-nitrogen soil, a sharp decrease (from 1200 mg/kg to 300 mg/kg) was observed when fertilization was stopped in the 4th season. It implies that there was more than one mechanism for biochar retention of ammonium nitrogen. Studies reveal that biochar's surface is full of different functional groups which could attract positive ions (Mukherjee *et al.*, 2011; Jiang *et al.*, 2012). The large surface (Lehmann, 2007) with proper pore diameter (Spokas *et al.*, 2012) could also supply space for ammonium ions and intermolecular forces could assist biochar bonding of ammonium ions (Du *et al.*, 2016). In this study, it is difficult to specify the contribution of each individual mechanism to the ammonium nitrogen retained on biochar. However, these functions had different strengths for ammonium retention, contributing some ammonium nitrogen that was steadily retained by biochar, even in an environment of low content, but the other would release when pakchoi completing for that.

Retention of mineral nitrogen by biochar has been widely reported. However, most referred findings were based on column leaching experiments (Ding *et al.*, 2010; Laird *et al.*, 2010; Yao *et al.*, 2012; Gai *et al.*, 2014) or solution adsorptive experiments (Sarkhot *et al.*, 2013). In this study, some biochar was re-collected from soil to test the mineral nitrogen content directly. It was interesting to find the enrichment of biochar on both ammonium and nitrate nitrogen resulting in 9.94-44.13% of mineral nitrogen in soil actually retained by biochar (Table 3.2). However, the content of ammonium and nitrate nitrogen retained by biochar (from U1%BC and U5%BC, Fig. 3.4) decreased in the 4th season (no nitrogen fertilizer applied in that season). It might indicate that mineral nitrogen retained by biochar still displayed bio-availability. Previous studies also revealed the potential use of biochar as a fertilizer with some of adsorbed nutrient recovery (Streubel *et al.*, 2011; Spokas *et al.*, 2012; Taghizadeh-Toosi *et al.*, 2012). To some extent, the recovery of mineral nitrogen content from biochar (nitrate nitrogen in the no nitrogen condition and both ammonium and nitrate nitrogen in the 4th season) could be regarded as the response of biochar to the demands of vegetables or crops growing when the soil nitrogen supplement is low. The dynamic of mineral nitrogen content between soil and biochar reflected the continual transfer between soil-biochar environment and other nitrogen reservoirs. Compared to the decrease of nitrate nitrogen content in the soil, the change of nitrates retained by biochar was more significant. It was speculated that pakchoi might be inclined to assimilate nitrates from biochar. Further work is still needed to study the details of nitrogen source preference.

3.5.2 Effect of biochar addition on nitrogen mineralization and nitrification

The response of the mineralization process to biochar addition was inconsistent and changed with growing seasons under the two nitrogen conditions (Fig.3.6 a & b). The negative effect of biochar addition on nitrogen mineralization was observed in the 1st season (only significant in the no nitrogen condition). The high C:N ratio of biochar may be one reason to explain the decline of mineralization in the no nitrogen condition (Steiner *et al.*, 2008; Streubel *et al.*, 2011); however, in the nitrogen condition, soil C:N ratio may not have changed much due to the fertilizer application and therefore no significant effect was found in the 1st season.

The promotion of nitrogen mineralization was found from 2nd to 4th seasons (only significant in the nitrogen condition), providing more mineral nitrogen for soil retention. The trends of the treatments with different biochar additional rates were always similar. It indicated that biochar addition had no direct effect on these processes in the short term. Instead, long-term use of biochar could affect soil aeration (Clough and Condron, 2010; Ulyett *et al.*, 2014), soil microbial biomass (Dempster *et al.*, 2012a; Veksha *et al.*, 2014), soil pH (Chan *et al.*, 2008; Atkinson *et al.*, 2010; Spokas *et al.*, 2012), and then indirectly affect the nitrogen process. The long-term effects of biochar addition on vegetable soil need to be tested in further work.

Furthermore, the effect of biochar on soil nitrification rate was merely observed in the nitrogen condition (Fig. 3.5). It was speculated that soil nitrification rate might related to the soil pH value (data and information of soil pH value would be provided in the next chapter). Previous study reported that soil acidity significantly reduce nitrification (de Boer and Kowalchuk, 2001) and Evidence for the influence of soil pH on nitrification was confirmed by Nicol *et al.* (2008), who demonstrated a positive correlation between soil pH and ammonia oxidizer (the dominant microbe to soil nitrification) abundance. Thus, the effect of biochar on soil acidity may be an important benefit of biochar addition to microbial biomass, especially for ammonia oxidizer, contributing the improvement of soil nitrification rate in the nitrogen condition.

3.5.3 Effect of biochar addition on nitrogen leaching loss

Unexpectedly, biochar addition increased the average ammonium concentrations of leachate in the no nitrogen condition but decreased nitrate concentrations in both nitrogen conditions. Promotion of nitrogen mineralization and weakening of nitrification may be possible explanations for the increased ammonium concentration. The adsorption may partly explain the decrease in nitrate concentration of leachate in previous studies (Mizuta *et al.*, 2004; Cheng *et al.*, 2008; Yao *et al.*, 2012). However, the nitrate retained directly by biochar was slight (Table 3.2) and easily lost (Fig 3.5 d) implying directly retaining did not possibly reduce the nitrate concentration of leachate by 21% in the nitrogen condition. Dempster *et al.* (2012a) attributed the decrease in nitrate concentration to the decrease in nitrification but the nitrification was promoted in some seasons in this study (Fig 3.6 d). It was believed that biochar addition increased the residence time of nitrate nitrogen in the root zone of plants and provided a greater opportunity for plant assimilation and thus decreased the nitrate loss via leaching (Kameyama *et al.*, 2012; Bruun *et al.*, 2014). In this study, the decline of leachate volumes due to biochar plays an important role in decreasing nitrogen leaching loss. Biochar is known to be highly porous with a good water retention capacity (Spokas *et al.*, 2012; Bruun *et al.*, 2014; Ulyett *et al.*, 2014). A great reduction in leachate volumes was observed and the effect of biochar on decreasing leachate volumes was more pronounced at higher biochar application rate (Fig. 3.6).

3.5.4 Biochar additional rates

In this study, 5% biochar addition significantly increased soil ammonium content and had the lower leachate volume compared to 1% and no biochar addition. However, the difference between 1% and 5% biochar additions was not significant with respect to soil mineral nitrogen content, nitrogen mineralization and nitrification and leaching loss. Similar findings were also reported previously (Chan *et al.*, 2008; Zhang *et al.*, 2010; Biederman and Harpole, 2013). A negative effect of high biochar addition was also pronounced on ammonia volatilization (Feng *et al.*, 2017). Determining the optimal biochar addition rate needs further exploration (Biederman and Harpole, 2013). Correspondingly, the correct addition rate of biochar should be studied by considering its effects on other nitrogen processes and on the soils' properties.

3.6 Conclusion

Biochar increased soil mineral nitrogen content by enhancing nitrogen retention in soils and soil nitrogen mineralization. Part of the mineral nitrogen retained by biochar was still bioavailable for plant uptake in the soil. Biochar significantly reduced nitrogen leaching loss by decreasing leachate volumes and nitrate concentrations in the leachate. The mitigation of leachate due to biochar addition was mainly attributed to the enhanced water retention capacity, nitrate adsorption and increased residence time of nitrate nitrogen for assimilation by pakchoi. These results indicate that biochar addition could enhance soil nitrogen retention and decrease nitrogen losses through leaching, and thus may decrease nitrogen fertilizer application rates necessary for maintaining high vegetable yields.

References

Agostini, F., Tei, F., Silgram, M., Farneselli, M., Benincasa, P., Aller, M., 2010. Decreasing nitrate leaching in vegetable crops with better N management. Genetic engineering, biofertilisation, soil quality and organic farming. Springer, pp. 147-200.

Agostini, F., Tei, F., Silgram, M., Farneselli, M., Benincasa, P., Aller, M., 2010. Decreasing nitrate leaching in vegetable crops with better N management. Genetic engineering, biofertilisation, soil quality and organic farming. Springer, pp. 147-200.

Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. Journal of Analytical and Applied Pyrolysis 101, 72-78.

Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337, 1-18.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta‐analysis. GCB Bioenergy 5, 202-214.

Bird, M.I., Wurster, C.M., de Paula Silva, P.H., Bass, A.M., De Nys, R., 2011. Algal biochar–production and properties. Bioresource Technology 102, 1886-1891.

Brown, R., 2009. Biochar Production Technology. Biochar for environmental management: Science and technology, 127-146.

Bruun, E.W., Petersen, C.T., Hansen, E., Holm, J.K., Hauggaard‐Nielsen, H., 2014. Biochar amendment to coarse sandy subsoil improves root growth and increases water retention. Soil Use and Management 30, 109-118.

Camargo, J.A., Alonso, Á., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environment International 32, 831-849.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2008. Agronomic values of greenwaste biochar as a soil amendment. Soil Research 45, 629-634.

Cheng, C.H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72, 1598-1610.

Clough, T.J., Condron, L.M., 2010. Biochar and the nitrogen cycle: introduction. Journal of Environmental Quality 39, 1218-1223.

Darilek, J.L., Huang, B., Wang, Z., Qi, Y., Zhao, Y., Sun, W., Gu, Z., Shi, X., 2009. Changes in soil fertility parameters and the environmental effects in a rapidly developing region of China. Agriculture, Ecosystems & Environment 129, 286-292.

De Boer, W., Kowalchuk, G., 2001. Nitrification in acid soils: micro-organisms and mechanisms. Soil Biology and Biochemistry 33, 853-866.

Dempster, D., Gleeson, D., Solaiman, Z.i., Jones, D., Murphy, D., 2012a. Decreased soil microbial biomass and nitrogen mineralisation with Eucalyptus biochar addition to a coarse textured soil. Plant and Soil 354, 311-324.

Dempster, D.N., Jones, D.L., Murphy, D.V., 2012b. Clay and biochar amendments decreased inorganic but not dissolved organic nitrogen leaching in soil. Soil Research 50, 216-221.

Diacono, M., Montemurro, F., 2010. Long-term effects of organic amendments on soil fertility. A review. Agronomy for Sustainable Development 30, 401-422.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, & Soil Pollution 213, 47-55.

Drury, C., Hart, S., Yang, X., 2008. Nitrification techniques for soils. Soil sampling and methods of analysis, 2e éd., Société canadienne de la Science du sol, CRC Press, Taylor and Francis Group, Boca Raton (FL).

Du, J., Sun, P., Feng, Z., Zhang, X., Zhao, Y., 2016. The biosorption capacity of biochar for 4-bromodiphengl ether: study of its kinetics, mechanism, and use as a carrier for immobilized bacteria. Environmental Science and Pollution Research 23, 3770-3780.

Feng, Y., Sun, H., Xue, L., Liu, Y., Gao, Q., Lu, K., Yang, L., 2017. Biochar applied at an appropriate rate can avoid increasing NH 3 volatilization dramatically in rice paddy soil. Chemosphere 168, 1277-1284.

Gai, X., Wang, H., Liu, J., Zhai, L., Liu, S., Ren, T., Liu, H., 2014. Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PloS one 9, e113888.

Hale, S., Alling, V., Martinsen, V., Mulder, J., Breedveld, G., Cornelissen, G., 2013. The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere 91, 1612-1619.

Huan, H., Zhou, J., Duan, Z., Wang, H., Gao, Y., 2007. Contributions of greenhouse soil nutrients accumulation to the formation of the secondary salinization: a case study of Yixing City, China. Agrochimica 51, 207-221.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Jiang, T.Y., Jiang, J., Xu, R.K., Li, Z., 2012. Adsorption of Pb (II) on variable charge soils amended with rice-straw derived biochar. Chemosphere 89, 249-256.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X.T., Kou, C.L., Christie, P., Dou, Z., Zhang, F., 2007. Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain. Environmental Pollution 145, 497-506.

Kameyama, K., Miyamoto, T., Shiono, T., Shinogi, Y., 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. Journal of Environmental Quality 41, 1131-1137.

Kemmitt, S.J., Wright, D., Goulding, K.W., Jones, D.L., 2006. pH regulation of carbon and nitrogen dynamics in two agricultural soils. Soil Biology and Biochemistry 38, 898-911.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14 C analysis. Soil Biology and Biochemistry 70, 229-236.

Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D., 2010. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158, 436-442.

Lehmann, J., 2007. A handful of carbon. Nature 447, 143-144.

Lehmann, J., 2009. Terra Preta Nova—where to from here. Amazonian Dark Earths: Wim Sombroek's vision. Springer Science, Dordrecht, 473-486.

Lehmann, J., Czimczik, C., Laird, D., Sohi, S., 2009. Stability of biochar in soil. Biochar for environmental management: Science and technology, 183-206.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F., Petersen, J., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Liang, L., Zhao, X., Yi, X., Chen, Z., Dong, X., Chen, R., Shen, R., 2013. Excessive application of nitrogen and phosphorus fertilizers induces soil acidification and phosphorus enrichment during vegetable production in Yangtze River Delta, China. Soil Use and

Management 29, 161-168.

Major, J., Steiner, C., Downie, A., Lehmann, J., 2009. Biochar effects on nutrient leaching. Biochar for environmental management: Science and technology 271.

Min, J., Shi, W., Xing, G., Zhang, H., Zhu, Z., 2011. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems. Nutrient Cycling in Agroecosystems 91, 31.

Min, J., Zhang, H., Shi, W., 2012. Optimizing nitrogen input to reduce nitrate leaching loss in greenhouse vegetable production. Agricultural Water Management 111, 53-59.

Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. Bioresource Technology 95, 255-257.

Mukherjee, A., Zimmerman, A., Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. Geoderma 163, 247-255.

Nicol, G. W., Leininger, S., Schleper, C., Prosser, J. I., 2008. The influence of soil pH on the diversity, abundance and transcriptional activity of ammonia oxidizing archaea and bacteria. Environmental Microbiology 10, 2966-2978.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A., 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Science 174, 105-112.

Qi, Y., Wang, Y., Liu, J., Yu, X., Zhou, C., 2011. Comparative study on composition of soil aggregates with different land use patterns and several kinds of soil aggregate stability index. Transactions of the Chinese Society of Agricultural Engineering 27, 340-347.

Qiu, S., Ju, X., Ingwersen, J., Qin, Z., Li, L., Streck, T., Christie, P., Zhang, F., 2010. Changes in soil carbon and nitrogen pools after shifting from conventional cereal to greenhouse vegetable production. Soil and Tillage Research 107, 80-87.

Qiu, Y., Cheng, H., Xu, C., Sheng, G.D., 2008. Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. Water Research 42, 567-574.

Sarkhot, D., Ghezzehei, T., Berhe, A., 2013. Effectiveness of biochar for sorption of ammonium and phosphate from dairy effluent. Journal of Environmental Quality 42, 1545-1554.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.

Singh, B.P., Hatton, B.J., Singh, B., Cowie, A.L., Kathuria, A., 2010. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. Journal of Environmental Quality 39, 1224-1235.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of Environmental Quality 41, 973-989.

Stanford, G., Smith, S., 1972. Nitrogen mineralization potentials of soils. Soil Science Society of America Journal 36, 465-472.

Steiner, C., Das, K., Melear, N., Lakly, D., 2010. Reducing nitrogen loss during poultry litter composting using biochar. Journal of Environmental Quality 39, 1236-1242.

Steiner, C., Glaser, B., Geraldes Teixeira, W., Lehmann, J., Blum, W.E., Zech, W., 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. Journal of Plant Nutrition and Soil Science 171, 893-899.

Streubel, J., Collins, H., Garcia-Perez, M., Tarara, J., Granatstein, D., Kruger, C., 2011. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Science Society of America Journal 75, 1402-1413.

Sun, Y., Gao, B., Yao, Y., Fang, J., Zhang, M., Zhou, Y., Chen, H., Yang, L., 2014. Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. Chemical Engineering Journal 240, 574-578.

Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M., 2012. Biochar adsorbed ammonia is bioavailable. Plant and Soil 350, 57-69.

Ulyett, J., Sakrabani, R., Kibblewhite, M., Hann, M., 2014. Impact of biochar addition on water retention, nitrification and carbon dioxide evolution from two sandy loam soils. European Journal of Soil Science 65, 96-104.

Veksha, A., McLaughlin, H., Layzell, D.B., Hill, J.M., 2014. Pyrolysis of wood to biochar: Increasing yield while maintaining microporosity. Bioresource Technology 153, 173-179.

Vitousek, P.M., Naylor, R., Crews, T., David, M., Drinkwater, L., Holland, E., Johnes, P., Katzenberger, J., Martinelli, L., Matson, P., 2009. Nutrient imbalances in agricultural development. Science 324, 1519-1520.

Wang, H., Guan, D., Zhang, R., Chen, Y., Hu, Y., Xiao, L., 2014. Soil aggregates and organic carbon affected by the land use change from rice paddy to vegetable field. Ecological

Engineering 70, 206-211.

Xing, G., Zhu, Z., 2000. An assessment of N loss from agricultural fields to the environment in China. Nutrient Cycling in Agroecosystems 57, 67-73.

Yan, Y., Tian, J., Fan, M., Zhang, F., Li, X., Christie, P., Chen, H., Lee, J., Kuzyakov, Y., Six, J., 2012. Soil organic carbon and total nitrogen in intensively managed arable soils. Agriculture, Ecosystems & Environment 150, 102-110.

Yao, Y., Gao, B., Zhang, M., Inyang, M., Zimmerman, A.R., 2012. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere 89, 1467-1471.

Yong,X., L., Bo, G., X.Y., Y., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Yuan, W., Dong, Y.h., Wang, H., 2010. Response of Greengrocery (Brassica chinensis) to Fertilization Patterns and Its Ecological Stoichiometry. Journal of Ecology and Rural Environment 26, 273-278.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D., 2010. Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. Agriculture, Ecosystems & Environment 139, 469-475.

Zhang, P., Wei, T., Jia, Z., Han, Q., Ren, X., 2014. Soil aggregate and crop yield changes with different rates of straw incorporation in semiarid areas of northwest China. Geoderma 230, 41-49.

Zhao, C., Hu, C., Huang, W., Sun, X., Tan, Q., Di, H., 2010. A lysimeter study of nitrate leaching and optimum nitrogen application rates for intensively irrigated vegetable production systems in Central China. Journal of Soils and Sediments 10, 9-17.

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. Journal of Hazardous Materials 256, 1-9.

Zheng, H., Wang, Z., Deng, X., Herbert, S., Xing, B., 2013. Impacts of adding biochar on nitrogen retention and bioavailability in agricultural soil. Geoderma 206, 32-39.

Zhu, Z., Chen, D., 2002. Nitrogen fertilizer use in China–Contributions to food production, impacts on the environment and best management strategies. Nutrient Cycling in Agroecosystems 63, 117-127Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. Journal of Analytical and Applied

Pyrolysis 101, 72-78.

Zheng, H., Wang, Z., Deng, X., Herbert, S., Xing, B., 2013. Impacts of adding biochar on nitrogen retention and bioavailability in agricultural soil. Geoderma 206, 32-39.

Zhu, Z., Chen, D., 2002. Nitrogen fertilizer use in China–Contributions to food production, impacts on the environment and best management strategies. Nutrient Cycling in Agroecosystems 63, 117-127.

CHAPTER 4: EFFECTS OF BIOCHAR ADDITION ON SOIL ACIDITY IN SOIL USED FOR VEGETABLE PRODUCTION

Abstract

Accelerated soil acidification in vegetable fields in China could possibly be due to the intensive vegetable cultivation systems. Alkaline biochar could provide a new approach for mitigating acidity in soil used for vegetable production because it benefits both the nitrogen and carbon processes. However, few studies have examined the changes in soil acidity, with different acid-indicating indices, after biochar addition. The objective was to determine the effect of biochar addition on vegetable soil acidity. Soil samples were collected from a four season's pot experiment. In this pot experiment, biochar was added to soil in which pakchoi was grown over four seasons. Soil samples were tested for soil pH value, pH buffering capacity, acidification rate and base contents in soil. Results showed that biochar addition increased soil pH values 0.06-0.10 in the no nitrogen condition and significantly retarded soil acidification in the nitrogen condition. Soil pH buffering capacity was promoted by 13%-32% and acidification rate was reduced by 3.42 to 4.24 kmol H^+/ha a after biochar addition. The mitigation of soil acidity was not only as a result of biochar's natural alkalinity but could also be attributed to some soil nitrogen processes such as promotion of plant nitrate uptake, reduction of nitrification and nitrate leaching, maintaining soil base contents, which are relative to soil acidity, but were changed by the addition of biochar. It was concluded that biochar could mitigate vegetable soil acidity. But effect of biochar on soil acidifying processes should be studied based on specific soil conditions.

Key words:

Soil acidity, biochar addition, pH values, pH buffering capacity, acidification rate, base contents

4.1 Introduction

Soil acidification is a natural process; however, intensive agriculture speeds up acidification through many processes, such as nitrification, increased leaching and biomass removal. In China, a study by Guo *et al.* (2010) reported that over 90% of 154 agricultural fields showed soil pH decreased around 0.5 units from the 1980s to 2000s. Nitrogen fertilizer application has been considered the main contributor to soil acidification (Qu *et al.*, 2014; Tian and Niu, 2015). Soil acidification in vegetable production systems is more significant (Yin *et al.*, 2004; Sun *et al.*, 2006; Shen *et al.*, 2016; Yang *et al.*, 2016) due to larger bases loss via leaching or bases removed with the plant biomass harvest (Duan *et al.*, 2004; Hicks *et al.*, 2008). The soil acidification would directly or indirectly affect plant growth, nutrient availability, organic matter and microbial activity (Kemmitt *et al.*, 2006), and ultimately affect agricultural ecosystem sustainability.

The optimal soil pH range for planting most crops is between 5.5 and 8 (Seufert *et al.*, 2012). Lime is commonly applied to raise soil pH values in different ecosystems (Rengel, 2003; Fageria and Baligar, 2008). In China, large amounts of ammonium fertilizer are added into soils each year. Theoretical calculations show that each kg of applied ammonium, leached as nitrate, demands 7 kg lime to neutralize (Porter, 1981). The continuous application of lime causes other problems, such as parched soils and acceleration of other cations leaching losses. Recently, it has been found that when lime rates exceed a certain amount, soil nitrification process are inhibited (Guo *et al.*, 2017). This implies that lime application might not be the appropriate approach for dealing with soil acidification in the long term. Hence, in order to prevent soil acidification in agricultural fields used for vegetable production, lime should be applied with caution.

Biochar, produced by pyrolysis of plant-derived biomass, contains alkaline substances and normally has an alkaline pH (Lehmann *et al.*, 2007). The sole application of biochar, or application of biochar combined with lime, showed significant effects on controlling acidification of the soil (Masud *et al.*, 2015). A meta-analysis revealed the alkalinity of biochar was one of the main mechanisms for improving crop productivity (Jeffery *et al.*, 2011). In addition, alkaline biochar is more effective at increasing biomass and at changing soil pH in acidic soils (Biederman and Harpole, 2013).

However, the improvement of soil pH values following biochar addition was not found in every study. Other nitrogen processes affected by biochar addition may also have an effect on soil pH values. The acidifying effect of enhanced nitrification due to biochar addition may offset the liming effect of biochar (Zhao *et al.*, 2014). The alkalinity of biochar may contribute to an increase in soil pH in the short term due to the interaction with soil compounds (Fidel, 2012). The long-term pH effect of biochar could be attributed to the interaction of insoluble organic functional groups on biochar surfaces with the soil solution (Joseph *et al.*, 2010). This implies that the effect of biochar on soil pH values may change as the growing season continues. On the other hand, most studies using pH unit to measure soil acidity. Soil pH is a calculation of hydronium ion concentration in the soil solution. But soil pH is buffered by several components of the solid phase, such as soil organic matter, bases, hydroxyl Al^{3+} and undissolved carbonate compounds (Eckert and Sims, 1995). When biochar is added, these buffering components may release acid to maintain the initial equilibrium. The change in soil pH value due to biochar addition may be much less than predicted.

Therefore, with the aim to determine the effect of biochar on soil acidity, soil was collected during four continuous growing seasons with different biochar additions and then different acid-indicating indices were tested to comprehensively evaluate the effects of biochar addition on soil acidity.

4.2 Material and Methods

4.2.1 Soil and biochar description and characterization

Soil used for the pot experiment in this study was collected from vegetable fields in the Tailake region of China. A detailed description of the soil was presented in Chapter 3-3.2.1. Biochar used in this study was produced from wheat straw. The method of pyrolysis was described in Chapter 3-3.2.3. The properties of soil and biochar were shown in Table 4.1.

Table 4.1 Main properties of soil and biochar

	Soil	Biochar
TN (g/kg)	1.21	12.50
TP (g/kg)	0.62	4.94
Ammonium N (mg/kg)	9.73	1.81
Nitrate N (mg/kg)	55.03	3.02
Available P (mg/kg)	72.98	48.43
Available K (mg/kg)	152.34	1836.40
Exchangeable K (mmol/kg)	7.26	58.70
Exchangeable Na (mmol/kg)	8.51	0.57
Exchangeable Ca(mmol/kg)	52.57	310.40
Exchangeable Mg (mmol/kg)	17.70	7.14
Exchangeable Al (mmol/kg)	1.59	0.02
Organic matter (g/kg)	18.20	443.12
pH	5.56	8.90
BET (m^2/g)	--	7.63

4.2.2 Experimental design

A pot experiment was conducted under two nitrogen conditions with three biochar additional level: CK=treatment with no biochar and no nitrogen fertilizer; 1%BC= treatment with 1% biochar addition; 5%BC= treatment with 5% biochar addition; CKU=treatment with nitrogen fertilizer application; U1%BC= treatment with 1% biochar addition and nitrogen fertilizer application; U5%BC= treatment with 5% biochar addition and nitrogen fertilizer application (details showed in Chapter 3-Table 3.1). The former three treatments were grown without fertilization (no nitrogen addition); the latter three treatments were grown with fertilization (nitrogen addition). Pakchoi was planted for four growing seasons with simulated leaching (Chapter 3-3.4.1, 3.4.2 and Fig. 3.1). Nitrogen fertilizer was applied in the CKU, U1%BC and U5%BC treatments in the 1^{st}, 2^{nd} and 3^{rd} seasons and none was applied in the 4^{th} season.

4.2.3 Soil sampling

Soil samples were collected from each pot by mixing four soil cores in each growing season after the pakchoi harvest. The soil samples were air-dried and then passed through a 2-mm sieve to remove large organic debris and then stored in plastic bags at 4 °C for subsequent testing.

4.3 Sample analysis

Each pot was considered as an independent experimental unit. Due to the decrease in pots of biochar relative treatments (1%BC, 5%BC, U1%BC and U5%BC treatments), the number of soil samples changed with decreasing replicates (details shown in Chapter 3-Table 3.1). The mean value (and SD) of measured data from soil analysis was calculated based on all treatments with all soil samples collected in a specific season. Soil pH values were determined after each growing season. Soil pH buffering capacity, acidification rate, organic matter content and base contents were measured once after the 4^{th} season with three replicates.

4.3.1 Soil pH value, soil organic matter content and base contents

Soil pH value was determined by using a sample of air-dried soil mixed with deionized water with a ratio of 1:2.5 (soil: water) and the pH value of the clear supernatant was measured by means of a pH electrode (Hach Corp., Italy).

Soil organic matter content was calculated by multiplying the data of total organic carbon by 1.724. The content of total organic carbon (TOC) was measured by means of a TOC analyzer (Thermo Finnigan, Elk Grove Village, IL).

Extraction of the soil sample was done with 1.0 m KCl, and titrated to pH 7.0 with 0.25 m NaOH to measure soil exchangeable Al^{3+} content (Lu, 2000).

Soil exchangeable base contents in extraction of soil sample were done with 1.0 m ammonium acetate (Lu, 2000). Contents of K^+ and Na^+ were determined by flame photometry (Sherwood Corp., UK) and contents of Ca^{2+} and Mg^{2+} by atomic absorption spectrometry (Shimadzu Corp., Japan).

4.3.2 Soil pH buffering capacity

The pH buffer capacities were determined by titrating 50 g of each soil sample in sealable polyethylene bags with H_2SO_4 and $CaCO_3$ at rates of 0、1×10^{-2}、2×10^{-2}、4×10^{-2}、6×10^{-2} and 8×10^{-2} mol/L mol (H^+ or $1/2CO_3^{-2}$)/L/kg. The rates of $CaCO_3$ were added to the soils as a suspension in distilled water (Magdoff and Bartlett, 1985; Tarkalson *et al.*, 2006). After H_2SO_4 or $CaCO_3$ were thoroughly mixed with soil, deionized water was added to each soil to reach 60% of water holding capacity. The bags were sealed and stored in a dark incubator at a temperature of 25 ℃ for 30 days. The soils were then air-dried and the pH values determined. Regression analysis using the linear range of the titration curve was calculated with the Equation 4.1.

$$pHBC=1/a \times 10 \qquad \text{(Equation 4.1)}$$

Where, *pHBC*=pH buffer capacity of the soil in the 4th season (mmol H+/kg/pH), 1=one unit pH range used in calculation, *a*=slope of linear.

4.3.3 Acidification rate

Acidification rate was defined as the rate of acid acceleration calculated with the Equation 4.2.

$$AR= \Delta pH\times pHBC\times BD\times Vol/10^6 \qquad \text{(Equation 4.2)}$$

Where, *AR*=acidification rate (10^3 mol H^+ /ha), ΔpH=difference value of the soil pH between present soil samples and the original soil sample (pH unit), BD=bulk density of the soil (kg/m^3), *Vol*=volume of soil per unit area (m^3/ha), $BD\times Vol=2.4\times10^6$ kg/ha in the soil type.

4.3.4 Statistical analyses

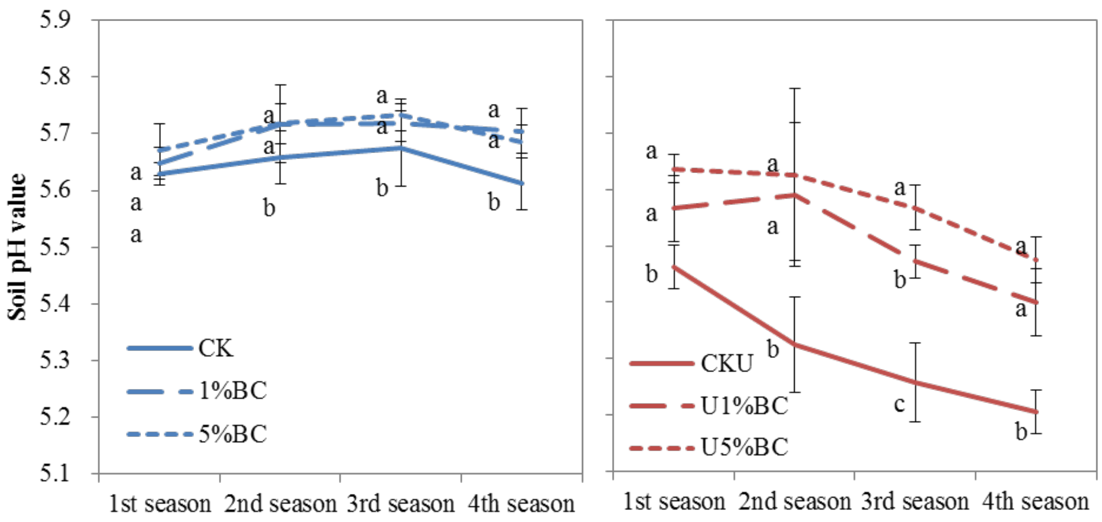
Duncan multiple-range test was used to determine the significant difference in soil pH value, pH buffering capacity, acidification rate, organic matter content and bases content among treatments in one season or among four growing seasons for one treatment at a 5% level. The analysis of correlation relationships among soil acid-indicating indices and contents of organic matter, bases and aluminum were conducted by bivariate correlation analysis with significance levels of 5% or 1%(SPSS ver. 16.0 for Windows, SPSS Inc., USA).

4.4 Results

4.4.1 Soil pH among different treatments

Nitrogen fertilizer application significantly decreased pH values of soils (*P*=0.001) with the pH values ranging from 5.61 to 5.73 in the no nitrogen condition and 5.21 to 5.62 in the nitrogen condition (Fig. 4.1).

In the no nitrogen condition, pH values of soils were increased by 0.06-0.10 unit due to biochar addition from the 2nd season and no significant change was observed in the 1st season (Fig. 5.1a). The effect of biochar addition on pH values was significant in four seasons in the nitrogen condition (Fig. 5.1b). The difference caused by 1% and 5% biochar additional rates were only found in the 3rd season.



(a) In no nitrogen condition (b) In nitrogen condition

Fig. 4.1 Dynamic of soil pH values. CK=treatment with no biochar and no nitrogen fertilizer; 1%BC= treatment with 1% biochar addition; 5%BC= treatment with 5% biochar addition; CKU=treatment with nitrogen fertilizer application; U1%BC= treatment with 1% biochar addition and nitrogen fertilizer application; U5%BC= treatment with 5% biochar addition and nitrogen fertilizer application. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in 1st, 2nd, 3rd and 4th season, respectively.). SD with the same letters in same season are not significantly different, determined by Duncan multiple-range test ($p<0.05$).

The trends of pH values during four seasons were quite different in the six treatments (Fig. 4.2). The pH values were significantly reduced ($p<0.05$) in the CKU and U1%BC treatments from 5.46 and 5.57 in the 1st season to 5.21 and 5.40 in the 4th season, respectively. But the reduction of pH values in the CKU treatment was 0.25 unit, 0.08 unit higher than that (0.17 unit) in the U1%BC treatment. The pH value was significantly increased from 5.64 to 5.72 in the 2nd and 3rd season in the 1%BC treatment. There were no significant differences with respect to pH values between the 1st and 4th seasons. No significant change was found in the CK, 5%BC and U5%BC treatments during four growing seasons, ranging from 5.61 to 5.67, from 5.65 to 5.72 and from 5.47 to 5.60 ($P>0.05$), respectively.

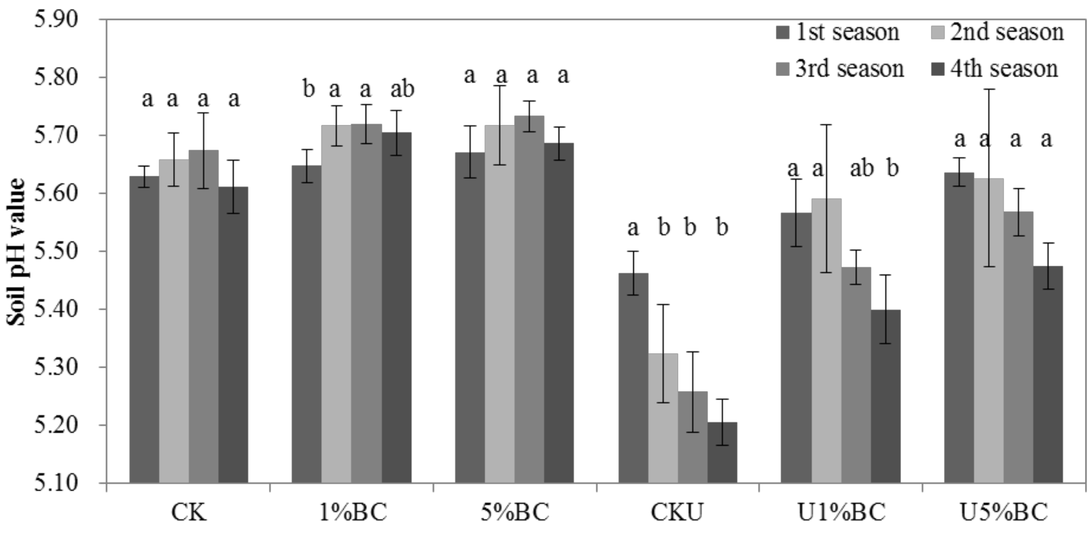
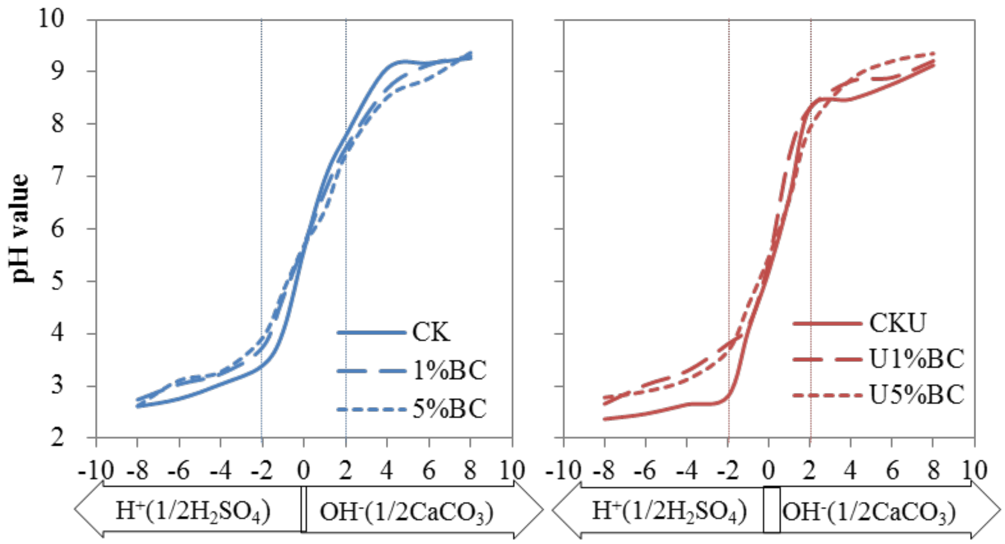


Fig. 4.2 Soil pH values during four growing seasons. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in 1st, 2nd, 3rd and 4th season, respectively.). SD with the same letters in one treatment are not significantly different, determined by Duncan multiple-range test ($p<0.05$).

4.4.2 Soil pH buffering capacity and acidification rates

As shown in Fig. 4.3 the curves produced by H^+ and OH^- added had different slopes due to biochar addition. In the range of -2 (2mmol H^+ /kg) to +2 (2mmol OH^- /kg), pH values of soils changed rapidly from 3.39 to 8.23 in the no nitrogen condition and 2.08 to 8.30 in the nitrogen condition. In comparison to CK and CKU treatments, there was less change in pH value found in the 1%BC, 5%BC treatments (Fig. 4.3 a) and U1%BC, U5%BC treatments (Fig. 4.3 b) with the same H^+ or OH^- added.



(a) In no nitrogen condition (b) In nitrogen condition

Fig. 4.3 Titration curves of soil pH value regulated by acidic and alkaline solutions. The positive and negative values in x-axis were corresponding to acid addition and base addition, respectively. The range between -2 (2mmol H^+ /kg) to +2 (2mmol OH^- /kg) is the area where soil pH values changed rapidly.

The pH buffering capacity for soils was calculated from the slope of lines in the buffer curves. Biochar addition significantly decreased the slope in the two nitrogen conditions and the effect of biochar on the slope was more significant in the treatments with 5% biochar addition than that with 1% biochar addition. With the same biochar addition, nitrogen fertilizer application increased the slope with the slope ranging from 0.86 to 1.14 in the no nitrogen condition and 1.02 to 1.28 in the nitrogen condition (Table 4.2).

Table 4.2 Soil pH buffering capacities and acidification rates after four growing seasons

	Slope	ΔpH	pHBC mmol/ kg/pH	AR kmol H^+/ha
CK	1.14±0.03b	0.09±0.03a	8.77±0.21b	-1.87±0.70c
1%BC	0.98±0.02cd	0.11±0.04a	10.17±0.19a	-2.72±0.98c
5%BC	0.86±0.03d	0.14±0.11a	11.56±0.34a	-3.82±3.01c
CKU	1.28±0.07a	-0.30±0.06c	7.80±0.41c	5.53±0.83a
U1%BC	1.14±0.09b	-0.10±0.05b	8.82±0.67b	2.11±0.91b
U5%BC	1.02±0.07c	-0.05±0.05b	9.87±0.78ab	1.17±1.08b
original	1.11±0.04 b		9.00±0.44 b	

Data value was represented by mean ± SD (n = 3). SD with the same letters are not significantly different, determined by Duncan multiple-range test ($p<0.05$).

Compared to the soil pH value before this experiment (Table 4.1), the treatments in the no nitrogen fertilizer increased pH values (ΔpH was positive in Tables) while the treatments in the no nitrogen fertilizer decreased (ΔpH was negative in Table) after four growing seasons. The CKU treatment had a 0.30-unit decrease in pH value and biochar addition significantly decreased the difference resulting in 0.1 and 0.05 unit decreases in pH values of U1%BC and U5%BC treatments, respectively. No significant effect was found on the differences in the pH values in the no nitrogen condition with the addition of biochar.

Soil pH buffering capacity was significantly decreased by fertilization between the CK and CKU treatments. Biochar addition increased soil pH buffering capacity by 16%-32% and 13%-27% in the no nitrogen and nitrogen conditions, respectively. The highest rate of soil pH buffering capacity was observed in the 5%BC treatment.

The calculated acidification rate for treatments in the no nitrogen condition (CK, 1%BC, 5%BC) was negative, and suggested the pH of soil was becoming less acidic. Treatments in the nitrogen condition (CKU, U1%BC, U5%BC) were positive and suggested the soil was becoming acidic. Out of all the treatments, biochar addition reduced soil acidification rates significantly ($p<0.05$), and the reduction of acidification rates were enhanced by higher rates of added biochar. Biochar addition reduced acidification rates by 3.42 and 4.24 kmol H^+/ha at U 1%BC and U5%BC treatment, respectively.

4.4.3 Soil organic matter content and major base content

The organic matter content showed an increased trend following biochar addition, but was not significant (Table 4.3). Biochar addition significantly increased more base contents in the two nitrogen conditions. The contents of exchangeable K^+, Na^+ and Mg^{2+} in the 1%BC and 5%BC treatments were significantly higher than that in the CK treatment. The exchangeable contents of K^+, Na^+, Ca^{2+} and Mg^{2+} in the U1%BC and U5%BC treatments were significantly higher than those in the CKU treatment. Further promotion of base contents was found in exchange of K^+ between the 1%BC and 5%BC treatments. However, no significant effect between the 1% and 5% biochar additional rates (between the 1%BC and 5%BC treatments or between the U1%BC and U5%BC treatments) were found in exchangeable Na^+, Ca^{2+} and Mg^{2+}.The content of exchangeable Al^{3+} was not affected by biochar and showed an insignificant difference throughout the six treatments.

4.4.4 Relationships among soil pH value, pH buffering capacity, acidification rate and bases contents

Close relationships were found among soil pH value, pH buffering capacity and acidification rate (Table 4.4). In addition, only soil pH buffering capacity was significantly related to all the contents of exchangeable bases, while soil pH value was related to exchangeable K^+ and Na^+ and acidification rate was related to exchangeable K^+ and Ca^{2+}. Organic matter content showed significant relationships with Ca^{2+} and Mg^{2+}.

Table 4.3 Contents of organic matter, base cations and exchangeable aluminum

	Organic matter (g/kg)	Base cation (mmol/kg)				Exchangeable Al^{3+} (mmol/kg)
		Exchangeable K^{+}	Exchangeable Na^{+}	Exchangeable Ca^{2+}	Exchangeable Mg^{2+}	
CK	16.65±2.44a	4.02±1.26c	3.15±0.37b	52.57±4.11a	9.97±0.72c	3.66±0.63a
1%BC	17.42±2.03a	5.95±0.76b	9.03±0.42a	40.11±2.19ab	14.71±3.87ab	3.90±0.21a
5%BC	17.57±2.02a	8.43±1.00a	8.47±0.91a	37.75±3.68b	17.31±0.62b	3.54±0.22a
CKU	16.21±1.69a	1.94±0.18d	3.31±0.34b	27.79±0.65c	8.57±0.50c	3.24±0.19a
U1%BC	18.09±1.99a	6.16±0.89b	7.68±0.63a	42.24±2.13ab	19.79±4.08a	3.56±0.67a
U5%BC	18.46±2.03a	4.87±0.78bc	8.16±0.95a	40.33±5.35ab	17.63±3.25ab	3.57±0.33a
original	18.20±0.88	7.26±1.36	8.51±0,46	52.57±4.11	17.70±1.39	3.59±0.26a

Data value was represented by mean ± SD (n = 3). SD with the same letters are not significantly different, determined by Duncan multiple-range test ($p<0.05$).

Table 4.4 Significance of the relationships among soil acid-indicating indices and contents of organic matter, base cations and aluminum

	pH values	pH buffering capacity	Acidification rate	Organic matter	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}
pH values	1.00	0.72**	-0.91**	-0.10	0.65**	0.49*	0.17	0.27	0.40
pH buffering capacity		1.00	-0.77**	0.34	0.77**	0.73**	0.47*	0.54*	0.40
Acidification rate			1.00	0.09	-0.62**	-0.43	-0.52*	-0.25	-0.48
Organic matter				1.00	0.36	0.19	0.56*	0.57*	-0.12
K^+					1.00	0.69**	0.21	0.72**	0.21
Na^+						1.00	-0.04	0.84**	0.31
Ca^{2+}							1.00	0.12	0.30
Mg^{2+}								1.00	0.15
Al^{3+}									1.00

* means $p<0.05$ and ** means $p<0.01$ determined by Duncan multiple-range test.

4.5 Discussion

4.5.1 Factors affecting soil acidity by biochar

Alkalinity is a direct way for biochar to affect soil acidity and biochar also can change soil properties (such as water holding capacity and base contents) and nitrogen processes (such as nitrification, denitrification, nitrate uptake by plant and nitrate leaching loss), which could indirectly influence soil acidity. Most studies found that the effect of biochar addition on agricultural soils were related to the liming effect of biochar (Jeffery et al., 2011; Yuan and Xu, 2011; Feng et al., 2017).

In this study, the mitigation of soil acidity can be mainly attributed to biochar addition. While nitrate uptake and assimilation by plants (Marschner et al., 1991; Imsande and Touraine, 1994) and denitrification by soil microorganisms(Li et al., 2003) also act various effects on soil acidity changes. On the other hand, acceleration of soil acidity can be caused by several factors such as nitrification of ammonium-based fertilizers (Zhao et al., 2007), leaching of nitrate (Rengel et al., 2000) and removal of bases from the soil in the harvested plant (Duan et al., 2004). These process related to pH changes were studies widely in previous study, but in our study, biochar addition clearly was the most significant factor that improve soil pH environment.

4.5.2 Effect of biochar addition on soil pH values in two nitrogen conditions

In the no nitrogen condition, pH values were always higher than that of original soil samples. Mitigation of soil acidity can be explained by nitrate uptake and assimilation by pakchoi. This is an ongoing process lasting throughout pakchoi's growth. Although no nitrogen fertilizer was applied in this condition, pakchoi also took up an amount of nitrates from the soil for biomass production. This explanation can be supported by the fact that soil nitrate content continued decreasing (Chapter 3 Fig 3.5 c) with an increasing trend of soil pH values (Fig 4.2). On the other hand, biochar addition significantly promoted soil pH values significantly in a short period during the experiment. No difference in soil pH among treatments was observed in the 1st season and the effect of biochar addition rate on soil acidity was not significantly different in the no nitrogen condition (Fig 4.1a), indicating that the natural alkalinity of biochar may not be enough to change the hydrogen ion concentration in the soil solution. However, biochar addition promoted nitrogen (nitrate) uptake by pakchoi (data will be listed in chapter 5) thus mitigating soil acidity. Furthermore, the nitrification from the 1st to 3rd seasons was reduced to some extent by biochar addition, although not significantly (Chapter 3 Fig 3.6 c). As a result, the acidifying effect of nitrification was weakened because of biochar addition. In addition, the amount of exchangeable K^+, Na^+ and Mg^{2+} in the CK treatment were lower than those in the 1%BC and 5%BC treatments (Table 4.3) indicating that biochar addition retained more bases in the soil. This is consistent with the report of Xu *et al.* (2012), in which biochar addition with 5% w/w increased cation exchange capacity (CEC) 50%-80%, without leaching.

In the nitrogen condition, a decreasing trend of soil pH values was observed during the four growing seasons suggesting nitrogen fertilizer application acidified vegetable soils in this study. Compared to treatments in the no nitrogen condition, nitrogen fertilizer application enhanced soil nitrification (Chapter 3 Fig 3.6 c and d) and increased nitrogen loss in CKU, U1%BC and U5%BC treatments, when compared with that in CK, 1%BC and 5%BC treatments, respectively (Chapter 3 Fig 3.9). In addition, higher biochar addition rate seems to more effectively maintain soil pH values although the significant difference between two biochar addition rates observed only in the 3rd season in the nitrogen condition (Fig. 4.1). It could be supposed as a cumulative effect from the difference in biochar addition rate and also indicated that the reduction in nitrogen leaching loss had a great impact on soil acidity. Thus, it is suggested that the acidifying effect of nitrification and leaching contributed to soil acidity in the nitrogen condition.

Biochar addition effectively reduced soil acidity in the no nitrogen condition and maintained soil pH values in the nitrogen condition (Fig 4.1 & 4.2). The change of soil acidity due to biochar addition was a result of the combined effects of different processes. In the nitrogen condition, the change in soil acidity could be attributed to four processes: (1) enhancing nitrification (Chapter 3 Fig 3.6 d), (2) decreasing nitrate leaching loss (Chapter 3 Fig 3.9) and bases loss (Table 4.3), (3) promoting soil pH buffering capacity (Table 4.2) and (4) increasing nitrate uptake by pakchoi (Chapter 5 Fig 5.2). Enhanced nitrification is the process accelerating soil acidification; however, it seems to be compensated for by the other three processes.

The significant increase of soil pH value (compared to original soil) was not observed at the beginning of 1st season in this study (Fig. 4.1), indicating the high buffering capacity of soil itself. However, differences between two nitrogen conditions were significant. Obia *et al.* (2015) reported 1.2 and 2.6 pH value increases after 1% and 5% biochar addition and held the opinion that the response of soil pH value to biochar addition were determined by soil buffering capacity. Moreover, after pakchoi planting and leaching happening, differences among treatments became evident. It was implied that nitrogen process might play a more pronounced than soil property.

4.5.3 Effect of biochar addition on soil pH buffering capacity and acidification rate

Soil pH, pH buffering capacity and acidification rate were the three indices used to assess soil acidity in this study. Different from soil pH value, pH buffering capacity is a soil characteristic determining the stability of soil pH values and acidification rates and is an indices predicting the trend of soil pH value in a changing environment. These three acid-indicating indices were significantly related to each other (Table 4.4).

After four growing seasons, soil pH buffering capacity was increased on average by 20% and the acidification rate was significantly reduced due to biochar addition (Table 4.2). There was a close relationship between soil pH buffering capacity and bases contents (Table 4.4). Liang *et al.* (2006) showed that biochar addition could increase soil CEC. It was attributed to the oxygen-containing functional groups (e.g. –COO– and –O–) on biochar which could contribute considerably to a negative surface charge for adsorbing more bases (Yuan *et al.*, 2011). It indicated that biochar addition increased soil pH buffering capacity via increasing soil base contents. Moreover, no significance of exchangeable Al^{3+} content was observed implying that soil acidification process in this study was still in the level of primary buffering system (Liao and Dai, 1991) and bases with charge of plus one or two (K^+, Na^+, Ca^{2+} and Mg^{2+}) was already enough to respond to the change of soil acidity. On the other hand, studies found biochar could absorb and provide hydrogen ions through association reactions in a low pH condition and dissociation reactions in a high pH condition (Xu *et al.*, 2012) and thus buffered the change of soil pH values.

4.5.4 How to evaluate the effect of biochar on soil acidity?

The alkalinity of biochar was not the main factor for directly increasing soil pH values, because no significant difference were found between treatments with different biochar additional rates in the no nitrogen condition. Instead, many processes in the soil affected soil acidity in this study, as discussed above. Soil pH values may not reflect the change of soil acidity caused by soil processes (Fidel, 2012). Soil pH buffering capacity should be chosen as assistant indices for assessing biochar's effect on soil acidity (Eckert and Sims, 1995). Additionally, the contributions of each individual process to soil acidity will be different with the various soil types and rates of nitrogen fertilizer application (Clough *et al.*, 2013). The effect of biochar addition on soil acidity was not definite. The effects of biochar on each acidifying process of soil should be studied before biochar is used as an amendment for acid soils.

4.6 Conclusion

Soil pH value, pH buffering capacity and acidification rate were three acid-indicating indices chosen in this study to assess biochar effect on soil acidity. It was found that biochar addition increased soil pH values in the no nitrogen condition and reduced soil acidification in the nitrogen condition. Biochar also significantly enhanced soil pH buffering capacity in the two nitrogen conditions and significantly reduced acidification rate in the nitrogen condition. Additionally, increasing the biochar addition rate could enhance the effect of reducing soil acidification in the nitrogen condition but with no significant effect on soil pH buffering capacity and acidification rate. Compared to soil pH values, soil pH buffering capacity was more sensitive to soil acidity in this study. Furthermore, biochar's effect on soil acidity was partly dependent on its effect on soil properties (such as base contents) and processes (such as nitrification, nitrate leaching and plant nitrate uptake) rather than its natural alkalinity. Plant nitrate uptake was promoted by biochar and resulted in soil acidity mitigation. Biochar could relatively reduce nitrification in the no nitrogen condition and significantly reduce nitrate leaching in the nitrogen condition, which also reduced soil acidification. In addition, biochar maintained soil base contents and thereby promoted soil pH buffering capacity. It was suggested that biochar could mitigate acidity in vegetable soil but each soil acidifying process should be studied separately, based on specific soil conditions, before biochar can be used as a soil acid amendment.

References

Aitken, R., Moody, P., McKinley, P., 1990. Lime requirement of acidic Queensland soils. I. Relationships between soil properties and pH buffer capacity. Soil Research 28, 695-701.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5, 202-214.

Clough, T.J., Condron, L.M., Kammann, C., Müller, C., 2013. A review of biochar and soil nitrogen dynamics. Agronomy 3, 275-293.

Duan, L., Huang, Y., Hao, J., Xie, S., Hou, M., 2004. Vegetation uptake of nitrogen and base cations in China and its role in soil acidification. Science of the Total Environment 330, 187-198.

Eckert, D., Sims, J.T., 1995. Recommended soil pH and lime requirement tests. Recommended soil testing procedures for the northeastern United States. Northeast Regional Bulletin 493, 11-16.

Fageria, N., Baligar, V., 2008. Ameliorating soil acidity of tropical Oxisols by liming for sustainable crop production. Advances in agronomy 99, 345-399.

Feng, Y., Sun, H., Xue, L., Liu, Y., Gao, Q., Lu, K., Yang, L., 2017. Biochar applied at an appropriate rate can avoid increasing NH 3 volatilization dramatically in rice paddy soil. Chemosphere 168, 1277-1284.

Fidel, R.B., 2012. Evaluation and implementation of methods for quantifying organic and inorganic components of biochar alkalinity. Iowa State University.

Guo, A.N., Duan, G.L., Zhao, Z.qQ Tang, Z., Wang, Y.yY Wang, B.X., 2017. Effect of $CaCO_3$ application on microbial nitrogen cycling in acid soil Environmental Science 38, 3483-3488.

Guo, J.H., Liu, X.J., Zhang, Y., Shen, J., Han, W., Zhang, W., Christie, P., Goulding, K., Vitousek, P., Zhang, F., 2010. Significant acidification in major Chinese croplands. Science 327, 1008-1010.

Hicks, W.K., Kuylenstierna, J.C., Owen, A., Dentener, F., Seip, H.M., Rodhe, H., 2008. Soil sensitivity to acidification in Asia: status and prospects. Ambio: A Journal of the Human Environment 37, 295-303.

Imsande, J., Touraine, B., 1994. N demand and the regulation of nitrate uptake. Plant Physiology 105, 3.

Jeffery, S., Verheijen, F.G., Van Der Velde, M., Bastos, A.C., 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agriculture, Ecosystems & Environment 144, 175-187.

Joseph, S., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C., Hook, J., Van Zwieten, L., Kimber, S., Cowie, A., Singh, B., 2010. An investigation into the reactions of biochar in soil. Soil Research 48, 501-515.

Kemmitt, S.J., Wright, D., Goulding, K.W., Jones, D.L., 2006. pH regulation of carbon and nitrogen dynamics in two agricultural soils. Soil Biology and Biochemistry 38, 898-911.

Lehmann, J., Kern, D.C., Glaser, B., Woods, W.I., 2007. Amazonian dark earths: origin properties management. Springer Science & Business Media.

Li, H., Han, Y., Cai, Z., 2003. Nitrogen mineralization in paddy soils of the Taihu Region of China under anaerobic conditions: dynamics and model fitting. Geoderma 115, 161-175.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F., Petersen, J., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719-1730.

Liao, B.H., Dai Z.H., 1991. Soil buffering capacity to acid precipitation and weathering characteristics of soil minerals. Acta Scientiae Circumstantiae 11, 425-431.

Lu, R.K., 2000. Soil agricultural chemistry analysis. Beijing: Agriculture Press.

Magdoff, F., Bartlett, R., 1985. Soil pH buffering revisited. Soil Science Society of America Journal 49, 145-148.

Marschner, H., Häussling, M., George, E., 1991. Ammonium and nitrate uptake rates and rhizosphere pH in non-mycorrhizal roots of Norway spruce [*Picea abies (L.) Karst.*]. Trees-Structure and Function 5, 14-21.

Masud, M.M., Li, J.Y., Xu, R.K., 2015. Application of alkaline slag and phosphogypsum for alleviating soil acidity in an Ultisol profile: a short-term leaching experiment. Journal of Soils & Sediments 15, 365-373.

Obia, A., Cornelissen, G., Mulder, J., Dörsch, P.. Effect of Soil pH increase by Biochar on NO, N_2O and N_2 Production during Denitrification in Acid Soils. Plos One, 2015, 10(9):e0138781.

Porter, W., 1981. Soil acidification-the cause. Proceedings Riverina Outlook Conference: 3l-46.

Qu, Z., Wang, J., Almøy, T., Bakken, L.R., 2014. Excessive use of nitrogen in Chinese agriculture results in high $N_2O/(N_2O+ N_2)$ product ratio of denitrification, primarily due to acidification of the soils. Global Change Biology.

Rengel, Z., 2003. Handbook of soil acidity. CRC Press.

Rengel, Z., Tang, C., Raphael, C., Bowden, J., 2000. Understanding subsoil acidification: effect of nitrogen transformation and nitrate leaching. Soil Research 38, 837-849.

Seufert, V., Ramankutty, N., Foley, J.A., 2012. Comparing the yields of organic and conventional agriculture. Nature 485, 229-232.

Shen, W., Ni, Y., Gao, N., Bian, B., Zheng, S., Lin, X., Chu, H., 2016. Bacterial community composition is shaped by soil secondary salinization and acidification brought on by high nitrogen fertilization rates. Applied Soil Ecology 108, 76-83.

Sun, R.J., wang, D.J., Lin, J.H., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.

Tarkalson, D.D., Payero, J.O., Hergert, G.W., Cassman, K.G., 2006. Acidification of soil in a dry land winter wheat-sorghum/corn-fallow rotation in the semiarid US Great Plains. Plant and Soil 283, 367-379.

Tian, D., Niu, S., 2015. A global analysis of soil acidification caused by nitrogen addition. Environmental Research Letters 10, 024019.

Xu, R.k., Zhao, A.z., Yuan, J.h., Jiang, J., 2012. pH buffering capacity of acid soils from tropical and subtropical regions of China as influenced by incorporation of crop straw biochars. Journal of Soils and Sediments 12, 494-502.

Yang, L., Huang, B., Mao, M., Yao, L., Niedermann, S., Hu, W., Chen, Y., 2016. Sustainability assessment of greenhouse vegetable farming practices from environmental, economic, and socio-institutional perspectives in China. Environmental Science and Pollution Research 23, 17287-17297.

Yin, R., Zhang, H.y., Huang, J.f., Lin, X.g., Wang, J.h., Cao, Z.h., 2004. Comparsion of microbiological properties between soils of rice-wheat rotation and vegetable cultivation. Plant Nutrition and Fertilizing Science 10, 57-62.

Yuan, J.H., Xu, R.K., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource Technology 102, 3488-3497.

Yuan, J.H., Xu, R.K., 2011. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic Ultisol. Soil Use and Management 27, 110-115.

Zhao, W., Cai, Z.c., Xu, Z.h., 2007. Does ammonium-based N addition influence nitrification and acidification in humid subtropical soils of China? Plant and Soil 297, 213-221.

Zhao, X., Wang, S., Xing, G., 2014. Nitrification, acidification, and nitrogen leaching from subtropical cropland soils as affected by rice straw-based biochar: laboratory incubation and column leaching studies. Journal of Soils and Sediments 14, 471-482

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CHAPTER 5: EFFECTS OF BIOCHAR ADDITION ON VEGETABLE (PAKCHOI) NITROGEN UPTAKE AND RECOVERY EFFICIENCY IN VEGETABLE PRODUCTION SYSTEMS

Abstract

Nitrogen uptake by plants is an important process closely related to yield. Considering the amount of nitrogen lost during cultivation farmers are likely to apply excessive nitrogen fertilizer to ensure soil mineral nitrogen for vegetables. The nitrogen recovery efficiency (NRE) of vegetables is usually less than 40%, which leads to a high loss of nitrogen and large amounts of nitrogen being left in the soil.

In order to promote vegetable nitrogen uptake and NRE in vegetable production systems, biochar was applied as a soil amendment. During four continuous growing seasons, pakchoi was planted with biochar addition at the levels of 0, 1% and 5%, to determine the effects on vegetable nitrogen uptake and NRE. By using the technique of stable isotope ^{15}N-traced, the amount of nitrogen fertilizer in pakchoi soil and leachate was quantified and two major nitrogen sources (fertilization and soil mineralization) were separated.

The results showed that with biochar addition, the pakchoi yield and nitrogen uptake in treatments remained unchanged during four growing seasons, whereas the yield and nitrogen uptake in treatments without biochar addition decreased after the 2nd season. The NRE and recovery of nitrogen fertilizer in the soil was promoted, and the recovery in leachate was reduced due to the biochar addition. Nitrogen from fertilizer was the major source for pakchoi nitrogen uptake (60.12%-76.00%), soil residual nitrogen (67.21%-97.97%) and nitrogen leaching loss (78.13%-97.50%). However, nitrogen from soil mineralization was the major nitrogen source for biochar retention (64.31%-86.40%). It was concluded that biochar addition could increase nitrogen uptake by plants, and its NRE, through decreasing nitrogen loss in continuous growing seasons. However, the effect of biochar on ammonia volatilization needs to be further studied.

Key words:

Nitrogen uptake by plant, ^{15}N, nitrogen recovery efficiency, nitrogen sources, nitrogen processes, vegetable production systems

5.1 Introduction

Crop yields are strongly correlated with nitrogen uptake by plants (Schnier *et al.*, 1990). Maintaining high crop yields and nitrogen uptake are important for improved agricultural productivity. Nitrogen uptake by plants was the main index used to evaluate the effects on yield (Lukina *et al.*, 2001; Masclaux-Daubresse *et al.*, 2010). Nitrogen recovery efficiency (NRE) is defined as the ratio of the nitrogen uptake by plant to fertilizer nitrogen input. The index also measured both nitrogen uptakes by crops and environmental impact on crop growth (Dobermann, 2005; Liu *et al.*, 2010; Qiao *et al.*, 2012).

In consideration of nitrogen loss, farmers in China always apply excessive nitrogen fertilizer in vegetable production fields to ensure sufficient nitrogen in the soil for plant uptake, leading to high losses and low NRE in plants (Cassman *et al.*, 2002; Ju *et al.*, 2007). The rate of nitrogen fertilizer application has reached 1100-1500 kg N/ha in Northern China (Ma *et al.*, 2000; Ju *et al.*, 2009) and 900-1300 kg N /ha in the Tailake region of China (Huang *et al.*, 2006; Zhu *et al.*, 2006; Min and Shi, 2009). Typical NRE of plants range from 20% to 40% (Cassman *et al.*, 2002; Zhu *et al.*, 2005; Huang *et al.*, 2006). Many studies focus on reducing the rate of nitrogen fertilizer application in vegetable production fields (Ju *et al.*, 2004; Li *et al.*, 2007; Min *et al.*, 2011a; Min *et al.*, 2012). NRE could be promoted with reducing fertilizer application, but nitrogen uptake could then possibly decrease Nitrogen uptake by vegetables is influenced by the dynamic equilibrium status of vegetable production systems. Nitrogen in these systems are divided into several processes and are in a dynamic equilibrium status (Clough and Condron, 2010; Haynes, 2012). Because nitrogen is a limited nutrient in vegetable production, different types of nitrogen fertilizer and application rates would affect nitrogen processes and influence the dynamic equilibrium status. According to our study in the previous chapters, fertilization would immediately increase soil mineral nitrogen content (Chapter 3 Fig. 3.3). The active mineral nitrogen from fertilizer would accelerate the nitrification process, ammonia volatilization process and affect other related nitrogen processes in vegetable soils.

When excessive nitrogen fertilizer is applied, the vegetable crop may utilize a certain quantity and the rest would be left in the soil or lost (Zhu *et al.*, 2005; Huang *et al.*, 2006; Shi *et al.*, 2009). The low NRE in vegetable production systems indicates that 35% of fertilizer nitrogen is residual or lost from ecosystems in various ways (Cao *et al.*, 2008; Liu *et al.*, 2010), and the remaining nitrogen in vegetable soils subsequently gets lost into the water system, causing non-point source pollution (Camargo and Alonso, 2006; Ju *et al.*, 2007) and soil acidification (Guo *et al.*, 2010; Liang *et al.*, 2013). Some studies report that nitrogen loss from vegetable fields contribute more aquatic nitrogen to agricultural non-point pollution than conventional crop fields (Ju *et al.*, 2007; Zhao *et al.*, 2010; Min *et al.*, 2011a; Luo *et al.*, 2015). A significant decline in soil pH values has been found after conventional crop fields are converted to vegetable production fields (Yin *et al.*, 2004; Sun *et al.*, 2006), and soil acidification was greatly accelerated with excessive nitrogen fertilizer application (Liang *et al.*, 2013). On the other hand, high nitrogen leaching loss and large amounts of nitrogen left in the soil may limit the NRE in vegetable production systems (Ding *et al.*, 2010). Therefore, a comprehensive approach to promoting NRE should be developed considering nitrogen leaching loss and amounts of nitrogen left in the soil of vegetable production systems.

Biochar is a potential energy product, but when applied to soils it could provide a stable carbon pool (Kuzyakov *et al.*, 2014) and improve soil quality (Novak *et al.*, 2009). For these reasons, the use of biochar as a soil amendment has gained interest worldwide. The positive effect of biochar on nitrogen uptake of crops and NRE has been widely reported, and is mainly attributed to a liming effect and high nitrogen retention (Atkinson *et al.*, 2010; Ding *et al.*, 2010; Basso *et al.*, 2013; Biederman and Harpole, 2013). It has also been shown that biochar addition could effectively decrease N_2O emissions in vegetable production systems (Jia *et al.*, 2012). It was believed that biochar addition would have a positive impact on nitrogen processes and thereby increase NRE and nitrogen uptake by vegetables. .

Studies on crop nitrogen uptake and NRE in vegetable production systems are limited. Existing studies found that different biochar addition rates might result in different responses in plant nitrogen uptake (Zhang *et al.*, 2011; Jia *et al.*, 2012). Given the variety of nitrogen uptake responses to biochar addition, this indicates that a number of interrelated nitrogen processes are involved. Few studies have investigated vegetable nitrogen uptake, nitrogen left in the soil and nitrogen loss. Furthermore, vegetable production systems are strongly modified by human activities and therefore the effect of biochar addition on nitrogen processes should be assessed under continuous growing conditions.

A pot experiment was conducted with three biochar addition levels (0, 1% w/w and 5% w/w). Pakchoi was planted during four continuous growing seasons and in the 1^{st}, 2^{nd} and 3^{rd} seasons ^{15}N-labeled urea was applied and in the 4^{th} season no nitrogen fertilizer was added. Stable isotope ^{15}N-traced fertilizer was used to (1) determine the effect of biochar on plant nitrogen uptake and plant yield, (2) investigate the recovery of nitrogen fertilizer in plants, soil and leachate with different biochar addition rates and (3) ascertain the sources of nitrogen (fertilization and soil mineralization) associated with vegetable nitrogen uptake, nitrogen left in the soil and nitrogen loss. These results would provide information to determine the effect of biochar addition on nitrogen uptake by vegetable plants, its recovery efficiency and increase our understanding of nitrogen processes related to biochar addition to soil used for vegetable production.

5.2 Material and Methods

5.2.1 Soil and biochar description and characterization

Soil used for this study was collected from a vegetable field in the Tailake region of China. A detailed description of soil properties has been presented in Chapter 3-3.2.1 and Chapter 4-4.2.1. Biochar was produced by slow pyrolysis of wheat straw, with procedure details and properties presented in Chapter 3-3.2.3 and Chapter 4-4.2.1.

5.2.2 Planting material

In this study Pakchoi (*Brassica chinensis L.*) was chosen as a typical planted vegetable. A detailed description has been presented in Chapter 3-3.2.2. The length of one single growing season for pakchoi was 35 days.

5.2.3Use of ^{15}N tracing in comparing nitrogen sources

A pot experiment consisted of six treatments: No nitrogen (CK, 1%BC, 5%BC), nitrogen (CKU, U1%BC and U5%BC) (details in Chapter 3-Table 3.1). Pakchoi was planted for four growing seasons with simulated leaching (Chapter 3-3.4.1, 3.4.2 and Fig. 3.1). The ^{15}N labeled urea (urea-^{15}N) at 10.18% abundance level (supported by Shanghai Research Institute of Chemical Industry) was used as nitrogen fertilizer applied in CKU, U1%BC and U5%BC treatments in the 1st, 2nd and 3rd seasons and no more nitrogen fertilizer was applied in the 4th season.

5.2.4 Crop harvesting and biochar sampling

Pakchoi was harvested on the 35th day of the growing season. The yield was determined based on the fresh aboveground biomass (Y, g/pot). Soil (or soil-biochar mixture) and biochar samples were collected from each pot after the harvest at the end of each growing season using the methods presented in Chapter 3.2.6.1 and 3.2.6.2. Leachate was collected from the tray placed under each pot after excessive irrigations.

5.3 Analysis

5.3.1 Plant tissue analysis

The plant samples were then oven dried at 70 °C to a constant mass, weighed ($R_{dry\text{-}plant}$, %), ground to pass through a 0.149-mm sieve and rolled in a ball mill to analyse the nitrogen content ($w_{N\text{-}plant}$,mg/g) (Flash EA 1112 series; Thermo Finnigan, Elk Grove Village, IL) and abundance of ^{15}N(A, %) (Isotope mass spectrometer, MAT-251, USA). The amount of the nitrogen uptake by pakchoi per pot was calculated with the Equation 5.1:

$$N_{plant}=Y\times R_{dry\text{-}plant}\times w_{N\text{-}plant} \quad \text{(Equation 5.1)}$$

Where, N_{plant}=the amount of pakchoi nitrogen (mg/pot), Y= the pakchoi yield in one pot (g/pot), $R_{dry\text{-}plant}$ = the ratio of dry matter content (%), $w_{N\text{-}plant}$= the nitrogen content per dry matter of pakchoi.

The nitrogen utilization efficiency was calculated with the equation (Equation 5.2) (Moll *et al.*, 1982):

$$NUE= (N_{plant\text{-}U}- N_{plant\text{-}CK})/F\times 100\% \quad \text{(Equation 5.2)}$$

Where, NUE=the nitrogen utilization efficiency (%), $N_{plant\text{-}U}$ = the amount of pakchoi nitrogen in CKU, U1%BC or U5%BC treatment (mg/pot), $N_{plant\text{-}CK}$=the amount of pakchoi nitrogen in CK treatment(mg/pot), F=the amount of nitrogen applied (mg/pot)=200 mg/pot in the 1st, 2nd, 3rd growing seasons and 600 mg/pot in the four growing seasons.

5.3.2 Soil and biochar analysis

The soil and biochar samples were air dried, passed through a 2-mm sieve to remove large organic debris and then stored in plastic bags at 4 °C to analyze the mineral nitrogen content in the soil ($w_{N\text{-}soil}$) and the mineral nitrogen content retained by biochar($w_{N\text{-}BC}$), with the method described in Chapter 3-3.3.1. The amount of mineral nitrogen left in the soil per pot was calculated with the Equations 5.3:

$$N_{soil}= (w_{n\ N\text{-}soil}- w_{n\text{-}1\ N\text{-}soil}) \times m \quad \text{(Equation 5.3)}$$

If n=1, $N_{soil}= (w_{1\ N\text{-}soil}- w_{original\ N\text{-}soil}) \times m$

Where, N_{left}= the amount of soil mineral nitrogen left (mg/pot), $w_{n\ N\text{-}soil}$ = mineral nitrogen content in soil from n season (mg/kg), n=1, 2, 3 or 4, m= weight of soil in one pot=2 kg/pot.

5.3.3 Leachate analysis

Nitrogen leaching loss ($N_{leaching}$) was calculated with the method described in Chapter 3-3.3.2.

5.3.4 ^{15}N testing

The principal method of analysis for stable isotopes is mass spectrometry and the abundance of an element is the percentage of the number of atoms in the stable nuclide divided by the total number of atoms of the element. All 15N abundances in this study were measured with an isotope mass spectrometer (MAT-251, USA, with analytic error ± 0.02%). The difference between the abundance of the stable nuclide (A) and the natural abundance ($A_{natural}$) is the atom percent excess of the element, which is also called enrichment.

The ^{15}N abundance of plants (A_{plant}) were directly determined. However, the ^{15}N abundance of mineral nitrogen in leachate ($A_{leaching}$), soil (A_{soil}) or biochar (A_{BC}) were determined using the crystal prepared with the method referred to by Zhang *et al.* (2009) and Lu (2000).

5.3.5 Calculations

The parameters related to ^{15}N in this study are listed in Table 5.1 below. The parameter of N was obtained with the methods in 5.3.1, 5.3.2 and 5.3.3. The parameter of A was measured by an isotope mass spectrometer (5.3.4). The other parameters (P_f , P_s, N_f, N_s and NR) were all calculated with the values of N and A.

The percentages of nitrogen from fertilizer and soil were calculated with the Equation 5.4 and 5.5 (Zhang *et al.*, 2012).

$$P_f = (A - A_{natural})/(A_{fertilizer} - A_{natural}) \times 100\% \qquad \text{(Equation 5.4)}$$

$$P_s = 1 - P_f \qquad \text{(Equation 5.5)}$$

Where P_f = the percentage of nitrogen in plant, soil mineral, leachate and biochar from fertilizer (%), A is the abundance of plant, soil, leachate or biochar (%). $A_{fertilizer}$ = the abundance of ^{15}N in the labeled urea (%) =10.18% in this study, $A_{natural}$= natural abundance of ^{15}N (%)= 0.365%. P_s is the percentage of nitrogen from soil (%).

Table 5.1 Parameters related to ^{15}N in this study

		Nitrogen uptake by pakchoi	Mineral residual nitrogen in soil	Nitrogen loss	Nitrogen loss via leaching	Nitrogen loss via other pathways	Nitrogen retained by biochar
Amount of nitrogen	(N, mg/pot)	N_{plant}	N_{soil}	N_{loss}	$N_{leaching}$	$N_{other\ loss}$	
^{15}N abundance	(A,%)	A_{plant}	A_{soil}		$A_{leaching}$		A_{BC}
Percentage of nitrogen from fertilizer	(P_f, %)	$P_{f\text{-}plant}$	$P_{f\text{-}soil}$		$P_{f\text{-}leaching}$		$P_{f\text{-}BC}$
Percentage of nitrogen from soil	(P_s, %)	$P_{s\text{-}plant}$	$P_{s\text{-}soil}$		$P_{s\text{-}leaching}$		$P_{s\text{-}BC}$
Amount of nitrogen from fertilizer	(N_f, mg/pot)	$N_{f\text{-}plant}$	$N_{f\text{-}soil}$	$N_{f\text{-}loss}$	$N_{f\text{-}leaching}$	$N_{f\text{-}other\ loss}$	
Amount of nitrogen from soil	(N_s, mg/pot)	$N_{s\text{-}plant}$	$N_{s\text{-}soil}$	$N_{s\text{-}loss}$	$N_{s\text{-}leaching}$	$N_{s\text{-}other\ loss}$	
Nitrogen recovery of fertilizer	(NR, %)	NR_{plant}=NRE	NR_{soil}		$NR_{leaching}$		

The amounts of nitrogen from fertilizer and soil were calculated with the Equation 5.6 and 5.7.

$$N_f = P_f \times N \quad \text{(Equation 5.6)}$$

$$N_s = N - N_f \quad \text{(Equation 5.7)}$$

Where, N_f = the amount of nitrogen in plant, soil, leachate and biochar from fertilizer (mg/pot), N= the total amount of nitrogen obtained with the methods in 5.3.1, 5.3.2 and 5.3.3 (mg/pot), N_s = the amount of nitrogen from soil (mg/pot).

The recovery efficiencies of ^{15}N-urea were calculated with the Equation 5.8.

$$NR = N_f / F \quad \text{(Equation 5.8)}$$

Where, *NR= the* recovery of applied ^{15}N labeled urea in plant tissue, soil, leachate and biochar and *F*= the amount of nitrogen applied (mg/pot)=200 mg/pot in 1st, 2nd , 3rd growing seasons and 600 mg/pot in the four growing seasons.

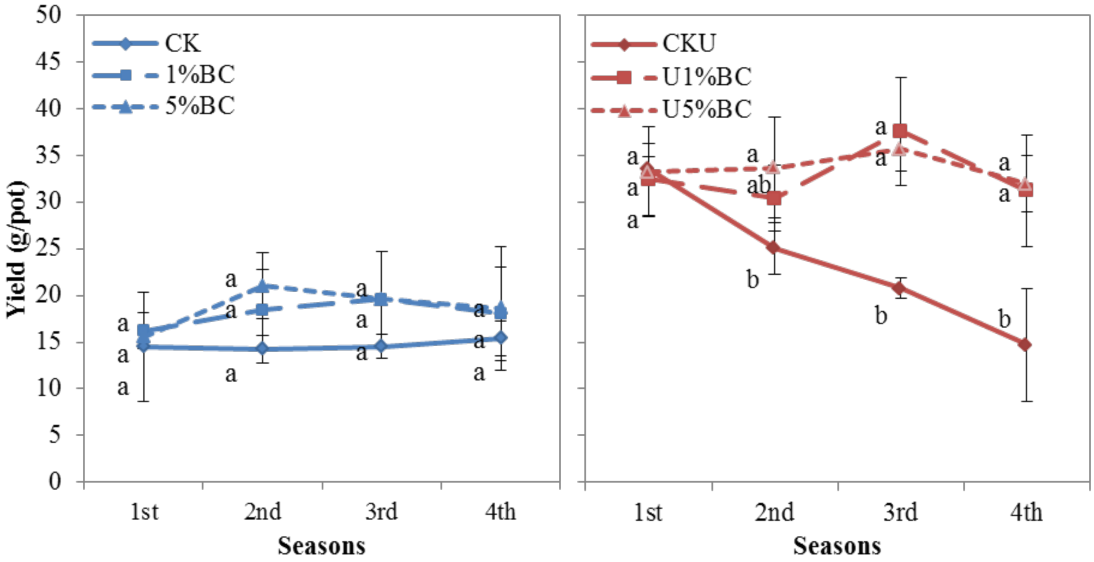
5.3.6 Statistical analyses

The significant differences in yield, nitrogen uptake by pakchoi and NUE among treatments for four growing seasons and were the parameters related to ^{15}N in plant, soil, leachate or biochar among treatments all analyzed using the Duncan multiple-range test at a 5% level, respectively (SPSS ver. 16.0 for Windows, SPSS Inc., USA).

5.4 Results

5.4.1 Yields of pakchoi

Biochar did not significantly affect pakchoi yields in the no nitrogen condition and yields were unchanged during the four growing seasons (Fig. 5.1a). Pakchoi yields were increased after nitrogen addition in the 1st growing season. However, the yield of the treatment, without biochar addition (CKU treatment), gradually decreased in the subsequent growing seasons (Fig. 5.1b). Biochar additions (U1%BC and U5%BC treatments) maintained pakchoi yields in the four growing seasons, with average yields of biochar addition treatments for 1st 2nd, 3rd, 4th being 32.87, 32.05, 32.64 and 31.59 g/pot, respectively. The difference with respect to pakchoi yields between CKU and U1%BC / U5%BC treatments were significant in the 3rd (P=0.002) and 4th (P=0.007) seasons, while biochar addition rates did not show significant effect on yield.

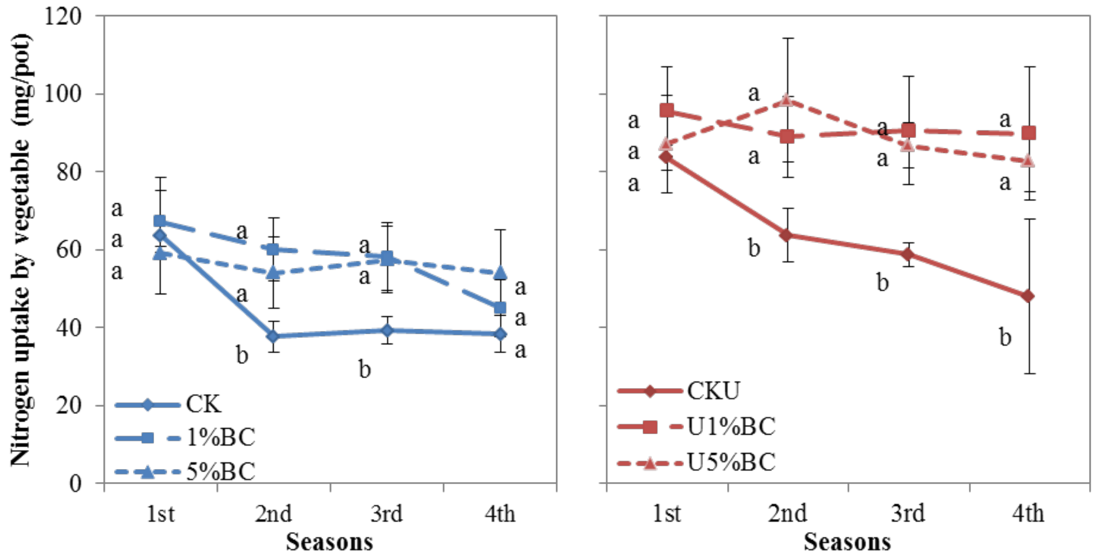


(a) In the no nitrogen condition (b) In the nitrogen condition

Fig. 5.1 Yields of pakchoi in four growing seasons. CK=treatment with no biochar and no nitrogen fertilizer; 1%BC= treatment with 1% biochar addition; 5%BC= treatment with 5% biochar addition; CKU=treatment with nitrogen fertilizer application; U1%BC= treatment with 1% biochar addition and nitrogen fertilizer application; U5%BC= treatment with 5% biochar addition and nitrogen fertilizer application. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). SD with the same letters in same season are not significantly different, determined by Duncan's test ($p<0.05$).

5.4.2 Nitrogen uptake by pakchoi and NUE

The differences in nitrogen uptake by pakchoi were significantly different between the treatments (Fig. 5.2). Nitrogen uptake by vegetables in U1%BC and U5%BC were higher than that in 1%BC and 5%BC treatments. The calculated nitrogen uptake between U1%BC and U5%BC were similar during four growing seasons. Pakchoi nitrogen uptake decreased after the 1st growing season for the treatments (CK and CKU treatments) without biochar addition. Significant differences between treatments with and without biochar were observed in the 2nd and 3rd growing seasons in the no nitrogen condition (Fig. 5.2 a), and in the 2nd, 3rd and 4th growing seasons in the nitrogen condition (Fig. 5.2 b). There were no significant differences found between treatments in 1% and 5% biochar addition rates.



(a) In no nitrogen condition (b) In nitrogen condition

Fig. 5.2 Nitrogen uptake by pakchoi in four growing seasons. Bars represent the SD of the means (n=3 for CK and CKU treatments; n = 12, 9, 6 and 3 for four biochar addition treatments in the 1st, 2nd, 3rd and 4th season, respectively.). SD with the same letters in same season are not significantly different, determined by Duncan's test ($p<0.05$).

In the 1st, 2nd and 3rd seasons, the NUE was on average 10.92%, 22.39% and 21.95% in CKU, U1%BC and U5%BC treatments, respectively (Table 5.2). The NUE in the four seasons was higher than the average means of the 1st, 2nd and 3rd seasons, due to no nitrogen being applied in the 4th season. Biochar addition significantly increased nitrogen utilization efficiencies in U1%BC and U5%BC treatments.

Table 5.2 NUE in treatments with nitrogen fertilizer

	CKU	U1%BC	U5%BC
1st season	10.02%±2.34% a	15.94%±1.89% a	11.78%±0.34% a
2nd season	13.00%±1.34% b	25.63%±3.43% a	30.35%±5.15% a
3rd season	9.74%±0.87% b	25.61%±3.82% a	23.73%±3.51% a
The four seasons	12.51%±1.50% b	30.95%±4.97% a	29.36%±5.98% a

Data value was represented by mean ± SD (n=3 for CKU treatments; n = 12, 9, 6 and 3 for U1%BC and U5%BC treatments in the 1st season, the 2nd season and the 3rd season and the four seasons, respectively.) and SD was represented across the rows. SD with the same letters are not significantly different, determined by Duncan's test (P<0.05).

5.4.3 Nitrogen uptake by Pakchoi plants from two nitrogen sources (labeled fertilizer and soil mineralization) in soils amended using biochar

In this study, the nitrogen uptake by pakchoi left in the soil, lost via leaching and adsorbed by biochar were mainly from ^{15}N fertilizer and soil mineralization. Labeled fertilizer was applied during 1st, 2nd and 3rd seasons. As Fig. 5.3 shows, nitrogen from the fertilizer was the major source of nitrogen for pakchoi uptake, soil residual nitrogen and leaching loss during 1st, 2nd and 3rd seasons, contributing 60.12%- 76.00% of the total pakchoi nitrogen uptake (Fig. 5.3 a), 67.21%-97.97% of the total mineral nitrogen change in the soil (or soil-biochar mixture) (Fig. 5.3 b) and 78.13%-97.50% of the total nitrogen leaching loss (Fig. 5.3 c). However, soil mineralized nitrogen was the major source of mineral nitrogen retained by biochar; merely 13.60%-35.69% of the mineral nitrogen retained by biochar was from fertilizer (Fig. 5.3 d).

From the 1st to 3rd seasons, biochar addition increased the amount and ratio of fertilizer nitrogen in pakchoi and the soil but decreased the amount and percentage in leaching loss. The amount of fertilizer nitrogen in pakchoi was decreased in the CKU treatment from the 1st season to the 3rd season, while no significant difference was found in U1%BC and U5%BC treatments (Fig. 5.3 a). In addition, the amount of mineral nitrogen left by fertilizer in the soil decreased from the 1st season to the 3rd season. Biochar addition retained mineral nitrogen from fertilizer and the amount of mineral nitrogen from fertilizer was increased by increasing the biochar addition rate (The amount of mineral nitrogen from fertilizer in U5%BC was higher than that in U1%BC.) (Fig. 5.3 b). Furthermore, more nitrogen from fertilizer was lost via leaching in the 2nd and 3rd seasons compared to the 1st season (Fig. 5.3 c). Biochar addition indicated a potential to reduce the percentage of fertilizer nitrogen lost via leaching.

In the 4th season, no labeled fertilizer was applied. The amount of ^{15}N found in pakchoi, leachate and biochar were all from the remaining fertilizer in the 1st, 2nd and 3rd seasons. The amount of nitrogen fertilizer in pakchoi was maintained in U1%BC and U5%BC treatments due to biochar addition in the 4th season, while the amount was quite low in the CKU treatment (Fig. 5.3 a). In addition, biochar addition decreased the percentage of nitrogen fertilizer lost via leaching in U1%BC and U5%BC treatments compared to the CKU treatment (Fig. 5.3 c). However, the change in soil mineral nitrogen content in the 4th season was mainly attributed to the decrease in mineral nitrogen from fertilizer (Fig. 5.3 b). Treatments with biochar addition (U1%BC and U5%BC) showed a higher amount and percentage of nitrogen fertilizer decrease in the 4th season. A similar condition was observed in the mineral nitrogen retained by biochar. Most nitrogen released by biochar was the nitrogen from fertilizer rather than the nitrogen from soil mineralization in the 4th season (Fig. 5.3 d).

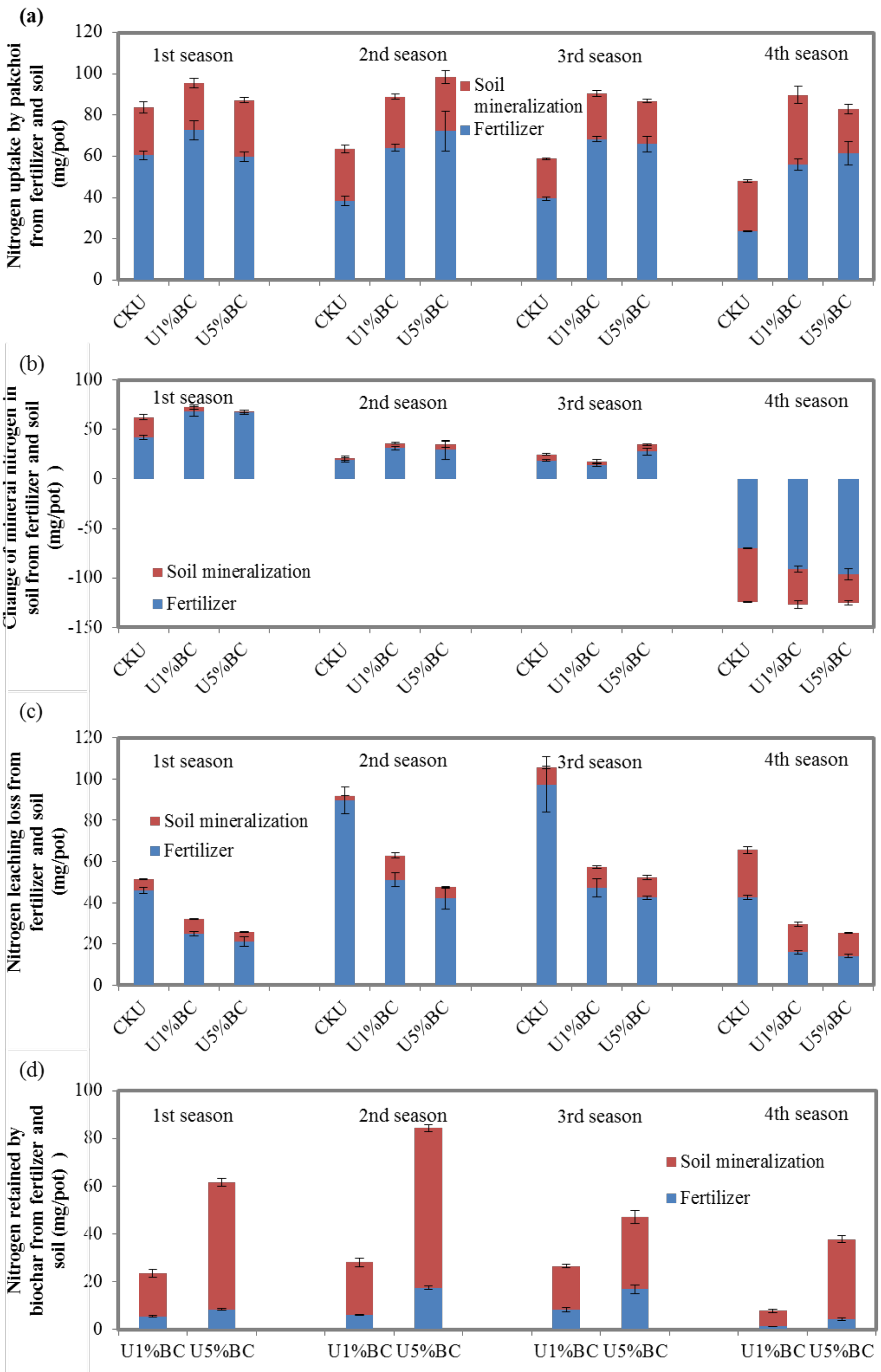


Fig. 5.3 Two sources of nitrogen (from fertilizer and from soil mineralization) in pakchoi, soil, leachate and biochar. Bars represent the SD of the means (n=3 for CKU treatment; n = 12, 9, 6 and 3 for U1%BC and U5%BC treatments in the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} season, respectively). The positive data in (c) means soil mineral

nitrogen content increased and the negative data means soil mineral nitrogen content decreased. The differences between two sources of nitrogen were significant for all treatments and all seasons.

5.4.4 Recovery of fertilizer nitrogen (^{15}N)

The nitrogen recovery (NR) in pakchoi, soil and leachate ranged from 19.14% to 43.51%, from 1.58% to 33.58% and from 10.62% to 48.67%, respectively and the rate of the total nitrogen loss ranged from 29.45%-71.73% (Table 5.3). The effect of biochar addition on NRE (NR in pakchoi) and NR in soil and leachate was similar over the four seasons. Biochar addition increased NRE and NR in soil and decreased NR in leachate, and the total rate of nitrogen loss. As Table 5.3 shows, the NRE in CKU treatment was less than 20% in the 2nd and 3rd season, while the NRE in biochar addition treatments (U1%BC and U5% BC) were over 30% in the 2nd and 3rd season and exceeded 40% in the four seasons. The NR in soil decreased sharply in the absence of fertilizer and merely 1.58%-4.60% of fertilizer nitrogen was left in the soil after four growing seasons. The rate of total nitrogen loss in the CKU treatment increased from 48.86% to 71.26% in the 2nd season, while biochar addition significantly decreased the NR in nitrogen loss to approximately 50%. The NR in leachate ranged from 22.95% to 48.67% in the CKU treatment, and from 10.62% to 25.58% in U1%BC and U5% BC treatment, respectively. However, besides leaching loss, fertilizer nitrogen loss from other pathways accounted for 16.97%-35.24%. The rate of nitrogen loss via other pathways was increased with the 5% biochar addition.

The fertilizer nitrogen balance was calculated after ^{15}N tracing. The part of ^{15}N not found in the experiment system was treated as nitrogen loss from other pathways (Table 5.3). The rate of nitrogen loss might be overestimated because some of the undetermined ^{15}N might by immobilized by microbes and restored in an organic nitrogen form in the soil. The ^{15}N abundance in total soil nitrogen content was tested in this study (data was not presented) but no statistical significant difference was found compared to natural abundance.

Table 5.3 Recovery of fertilizer nitrogen in pakchoi, soil and leachate and rate of nitrogen loss during the four growing seasons

Growing seasons	Treatments	^{15}N application (mg/pot)	NR in pakchoi (%)	NR in soil (%)	Rate of nitrogen loss(%)		
					NR in leachate	Unfound[(1)]	Total[(2)]
1st season	CKU	200	30.21%±2.60% a	20.92%±2.77% b	22.95%±3.37% a	25.91%±3.42% a	48.86%±3.39% a
	U1%BC	200	36.30%±3.28% a	34.25%±1.72% a	12.49%±1.55% b	16.97%±1.34% b	29.45%±1.46% c
	U5%BC	200	29.83%±2.54% a	33.58%±4.85% a	10.62%±1.34% b	25.97%±2.76% a	36.58%±2.31% b
2nd season	CKU	200	19.14%±1.77% b	9.6%±1.06% b	44.80%±4.34% a	26.46%±2.67% a	71.26%±3.87% a
	U1%BC	200	32.09%±3.75% a	15.51%±2.10% a	25.58%±1.55% b	26.82%±2.84% a	52.40%±2.13% b
	U5%BC	200	36.12%±5.14% a	14.7%±1.15% a	21.10%±2.60% b	28.07%±1.66% a	49.18%±2.07% b
3rd season	CKU	200	19.71%±2.19% b	9.37%±0.95% b	48.67%±6.82% a	22.25%±1.81% b	70.91%±5.36% a
	U1%BC	200	34.19%±2.76% a	7.06%±1.64% b	23.51%±3.14% b	35.24%±1.90% a	58.75%±2.40% b
	U5%BC	200	32.96%±2.05% a	13.77%±0.85% a	21.21%±2.68% b	32.06%±4.52% a	53.27%±3.64% b
Four seasons	CKU	600	26.96%±2.30% b	1.58%±0.34% c	45.90%±5.82% a	25.56%±2.41% b	71.73%±5.08% a
	U1%BC	600	43.51%±4.18% a	3.75%±0.89% b	23.18%±2.46% b	29.55%±1.62%ab	52.74%±2.03% b
	U5%BC	600	43.23%±5.33% a	4.60%±1.27% a	20.01%±1.91% b	32.16%±1.74% a	52.17%±1.82% b

Notes: (1) 'Unfound' is the part of labeled nitrogen not found in the experiment system (soil, vegetable plant and leachate) and considered as the nitrogen loss from other pathways (such as nitrogen gas loss and nitrogen immobilization) not directly detected in this experiment. It is calculated by the difference value between mineral nitrogen applied from fertilizer and the other outputs (including mineral nitrogen uptake by vegetables, left in soil and leaching loss). (2) Total loss is calculated by sum of the data in leaching and unfound. Data value was represented by mean ± SD (n=3 for CKU treatment; n = 12, 9, 6 and 3 for U1%BC and U5%BC treatments in the 1st season, the 2nd season and the 3rd season and the four seasons, respectively.). SD with the same letters are not significantly different, determined by Duncan's test (P<0.05).

5.4.5 Nitrogen outputs and their sources

Nitrogen uptake by pakchoi, left in the soil and lost (including leaching) were the three pathways of nitrogen output that was the focus of this study (Table 5.4). In the no nitrogen condition the nitrogen uptake by pakchoi plants and in the leachate, was all from soil mineralized nitrogen. Biochar addition significantly increased nitrogen uptake by pakchoi plants and decreased losses via leaching. However, the effect of biochar addition on soil mineral nitrogen content was not significant. In the nitrogen condition, nitrogen taken up by pakchoi from soil mineralization was lower than that in the no nitrogen condition, and fertilizer contributed more nitrogen for pakchoi uptake and loss. Although part of fertilizer nitrogen was left in soil, it was found that the decrease in soil mineralized nitrogen was greater and thus the change of mineral nitrogen content ranged from -16.34 to 13.30 mg/pot.

Table 5.4 Nitrogen outputs from two sources during four growing seasons

(mg/pot)	Nitrogen uptake by pakchoi		Mineral nitrogen left in soil [1]		Nitrogen loss		
					Leaching		Other loss
Sources	from fertilizer	from soil mineralization	from fertilizer	from soil mineralization	from fertilizer	from soil mineralization	from fertilizer
CK		179.09 b		-104.34 a		108.93 a	
1%BC		230.47 a		-103.54 a		68.47 b	
5%BC		224.67 a		-81.36 a		49.32 b	
CKU	161.76 (*b*)	92.40 (*b*)	9.46 (*b*)	-25.80 (*b*)	275.39 (*a*)	39.02 (*a*)	153.39 (*b*)
U1%BC	261.08 (*a*)	103.72 (*a*)	22.49 (*a*)	-22.93 (*b*)	139.10 (*b*)	42.52 (*a*)	177.33 (a*b*)
U5%BC	259.35 (*a*)	95.89 (*b*)	27.60(*a*)	-14.30 (*a*)	120.00 (*b*)	30.77 (*b*)	193.05 (*a*)

Notes:(1) The positive data in the column 'Mineral nitrogen left in soil' means soil mineral nitrogen content increased and the negative date means soil mineral nitrogen content decreased. Data value was represented by mean (n=3). Statistical analysis was made in the no nitrogen and nitrogen conditions and represented by 'letter' and '(*letter)*', respectively. Means followed by same letters were not significantly different, determined by Duncan's test (P<0.05).

5.5 Discussion

Nitrogen uptake by plants is determined by the status of the ecosystem balance (Haynes, 2012). In this study, the amount of mineral nitrogen supplied to the vegetables came from chemical commercial fertilizer and soil mineralized nitrogen. Although the mineral nitrogen content in organic soil was up to 64.77 mg/kg (5.2.1), nitrogen fertilizer application still noticeably increased pakchoi nitrogen uptake (Fig. 5.2). The same trend between yield and nitrogen uptake by pakchoi was found in Fig. 5.1 and Fig.5.2. In the no nitrogen condition, the soil mineralized nitrogen had become the major nitrogen input and the stable yield (Fig. 5.1a) and mineral nitrogen content (Fig. 3.3 a & c) implied that the system had reached a nitrogen balance. Furthermore, biochar addition significantly increased nitrogen uptake by pakchoi (Fig. 5.2 a) in the no nitrogen condition while no significant change was observed with respect to yield (Fig. 5.1 a). Previous studies reported consistent findings that nitrogen content in plant tissue would increase with increasing amount of nitrogen application and yield might non-significant or delayed response to that due to other factors such as tillage practice or fertilizer applied timing (Ahmad *et al.*, 2009; Halvorson *et al.*, 2006). It seemed that plant nitrogen uptake was more sensitive than yield to the increase in soil mineral nitrogen content than pakchoi yields. This implied that nitrogen uptake by plants could be used to estimate plant yield when the soil mineral content was changed.

In this study, it was found that pakchoi was more inclined to use nitrogen supplied by the fertilizer than from soil mineralized nitrogen (Fig. 5.3); in the treatments where nitrogen fertilizer was applied, both yield and nitrogen uptake by pakchoi was increased by fertilizer in the 1st season. But in the treatment without biochar addition, both yield and nitrogen uptake of pakchoi decreased from the 2nd season. This suggests that (1) nitrogen fertilizer application contributed to the high pakchoi yield and nitrogen uptake; (2) soil nitrogen processes (such as nitrogen mineralization, nitrogen loss) and some properties (such as organic matter content, pH and CEC, Chapter 2) could be changed by continuous planting, leading to a decrease in pakchoi yield and nitrogen uptake.

Excessive nitrogen fertilizer application is one of the most important challenges for Chinese vegetable production systems (Ju *et al.*, 2007; Ding *et al.*, 2010; Liang *et al.*, 2013); however, the decisive role of nitrogen fertilizer in yield cannot be discounted (Zhu and Chen, 2002; Mosier *et al.*, 2004). Reduction in nitrogen fertilizer application could only be feasible if plant yield and nitrogen uptake were not significantly affected.

Thus, improving NRE is a key approach in maintaining plant yield.

Nitrogen uptake by plants is one of the processes in the vegetable production system and can be influenced by residual soil nitrogen, nitrogen losses and retention by biochar.

It was interesting to find that there were almost no significant change in the soil mineral nitrogen content in treatments with nitrogen applied in the 1st, 2nd and 3rd seasons (CKU, U1%BC and U5%BC treatments). Previous studies observed nitrate nitrogen as the main form of fertilizer nitrogen left in the soil (Guo *et al.*, 2008; Min *et al.*, 2011b), which could easily be lost when leaching occurs. Compared to the 1st season, higher percentage loss in the 2nd and 3rd seasons via leaching loss (Fig. 5.3c and Table 5.3). It was believed the increase nitrogen loss via leaching was partly from the fertilizer nitrogen left in soil profile in the prior season because the percentage of nitrogen left in soil should be double after the 2nd season corresponding to the same loss. Actually, 20% of fertilizer nitrogen was found in soil after the 1st season, while only about 9% was found after the 2nd and 3rd season (Table 5.3). The delay of fertilizer nitrogen loss could also be confirmed by the nitrogen leaching loss in the 4th season when no more nitrogen fertilizer application (Fig. 5.3c). The planting of catch crops (Thorup-Kristensen *et al.*, 2003; Guo *et al.*, 2008; Shi *et al.*, 2009) could also decrease residual nitrogen in the soil. In this study, pakchoi played a similar role as catch crops which were planted without nitrogen fertilizer application in the 4th season. Furthermore, leaching was triggered by excessive irrigations. As a result, the mineral residual nitrogen in soil from the first three fertilizer applications during the three seasons was depleted after the 4th season (Chapter 3, Fig. 3.3 d). It indicated that fertilizer nitrogen left in the soil did not affect nitrogen uptake by plants in this study. In addition, the amount of nitrogen retained by biochar was very slight and 48.70%-76.81% of the nitrogen was released in the 4th season (Fig. 5.3 d and Chapter 3, Fig. 3.4). The restriction of biochar retaining nitrogen on plant nitrogen uptake was negligible. Therefore, nitrogen loss was the main restriction influencing plant nitrogen uptake in this study.

The decrease in NRE in pakchoi was found in the 2nd season corresponding to a large increase in nitrogen loss (Table 5.3). The decrease in pakchoi nitrogen uptake could be partly explained by the increased nitrogen loss. Some studies suggest that nitrogen losses through leaching limits the improvement of nitrogen efficiency (Rathke *et al.*, 2006; Ding *et al.*, 2010). However, it was also likely that pakchoi assimilated less fertilizer nitrogen in the soil environment with pH values of 5.32 in the 2nd season (The original soil pH value was 5.56 at the beginning of the pot experiment, Chapter 4, Fig. 4.1) and thus more fertilizer nitrogen was left in the soil inducing an increase in nitrogen loss. Similar results were reported that plant growth was affected by soil acidification resulting in low nitrogen uptake by plants (Ju *et al.*, 2007; Shi *et al.*, 2009; Liang *et al.*, 2013). Li *et al.* (2007) concluded that improving NRE could effectively reduce nitrogen leaching.

In this study, biochar addition improved nitrogen uptake by pakchoi vegetable plants through ameliorating soil acidity (Chapter 4) and decreasing nitrogen loss (Table 5.3). The maintenance of yield and nitrogen uptake by pakchoi plants (Fig. 5.1 and Fig. 5.2) could be attributed to the stable pH environment of the soil (Chapter 4 Fig. 4.1) in the treatments with biochar addition. Furthermore, from the data in Chapter 3, it was thought that biochar increased pakchoi nitrogen uptake by prolonging nitrogen retention time in the soil (Kameyama *et al.*, 2012), which could partly be supported by the improved soil water holding capacity (Spokas *et al.*, 2012; Bruun *et al.*, 2014), and the significant decrease in volume and nitrogen concentration of leachate (Chapter 3 Fig.3.7 and Fig. 3.7). However, the nitrogen loss via other pathways was relatively increased by biochar addition (Table 5.3 'Unfound'). It was speculated that the part of ^{15}N loss via other pathways might consist of nitrogen loss via gas and nitrogen immobilization (from mineral nitrogen to organic nitrogen). Feng *et al.* (2017) reported that biochar addition at the rate of 3% would significantly enhance ammonia volatilization due to the increase in soil pH value. It may be a possible explanation for the increased nitrogen loss via gas in this study because the pH value in U1%BC and U5%BC treatments were significantly higher than that in CKU treatment (Chapter 4, Fig. 4.1). On the other hand, some studies reported biochar addition stimulated fertilizer nitrogen immobilization and thus reduced nitrogen availability (Clough and Condron, 2010; Bruun *et al.*, 2012). The results in this study may be different. The mineral nitrogen from soil mineralization did not achieve a balance in both nitrogen conditions (Table 5.4). The decrease in mineral nitrogen from soil mineralization in agricultural soil was much lower than the amount of mineral nitrogen uptake by plant and leaching loss. This implies that soil mineralization contributed 100-200 mg/pot nitrogen for plant assimilation and loss. There was certainly some ^{15}N (fertilizer nitrogen) immobilized and restored in an organic form in the soil but much more nitrogen was produced by soil mineralization due to biochar addition.

5.6 Conclusion

Biochar addition effectively maintained pakchoi yields and nitrogen uptake. The NR of ^{15}N in pakchoi and soil ranged from 19.14% to 43.51% and from 1.58% to 33.58%, respectively and the rate of ^{15}N loss ranged from 29.45% to 71.73%. Biochar addition increased the NR in pakchoi and soil and decreased the NR in leachate and the rate of nitrogen loss. Compared to nitrogen left in the soil and retained by biochar, nitrogen loss had an obvious effect on plant nitrogen uptake in this study.

Fertilizer nitrogen was the major source for pakchoi nitrogen uptake, residual soil nitrogen and nitrogen leaching loss; contributing 60.12%- 76.00% of the pakchoi nitrogen uptake, 67.21%-97.97% of the mineral nitrogen change in soil and 78.13%-97.50% of the nitrogen leaching loss. However, soil mineralized nitrogen was the major source for biochar retaining nitrogen. In the absence of nitrogen fertilizer, the nitrogen fertilizer left in the soil from the 1st, 2nd and 3rd seasons decreased sharply and most fertilizer nitrogen retained by biochar was subsequently released .

In conclusion, biochar can regulate the distribution of nitrogen fertilizer by decreasing nitrogen loss through leaching and thus increase nitrogen uptake by plants and maintain plant yield under intensive vegetable production systems, characterized by the continuous application of chemical commericial nitrogen fertilizers. However, biochar may increase the risk of nitrogen loss via ammonia volatilization. Further research on the effect of biochar on plant growth and nitrogen losses via various processes is still needed before biochar can be applied in vegetable production systems to mitigate the effect of excessive N fertilisier application by Chinese farmers

References

Ahmad, I., Iqbal, M., Ahmad, B., Ahmad, G., Shah, N.H., 2009. Maize yield, plant tissue and residual soil N as affected by nitrogen management and tillage system. Journal of Agriculture & Biological Sciences 1,19-29.

Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337, 1-18.

Basso, A.S., Miguez, F.E., Laird, D.A., Horton, R., Westgate, M., 2013. Assessing potential of biochar for increasing water - holding capacity of sandy soils. GCB Bioenergy 5, 132-143.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta - analysis. GCB Bioenergy 5, 202-214.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biology and Biochemistry 46, 73-79.

Bruun, E.W., Petersen, C.T., Hansen, E., Holm, J.K., Hauggaard - Nielsen, H., 2014. Biochar amendment to coarse sandy subsoil improves root growth and increases water retention. Soil Use and Management 30, 109-118.

Camargo, J.A., Alonso, Á., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environment International 32, 831-849.

Cao, B., Xu, Q., He, F., Cai, G., 2008. Nitrogen use efficiency and fate of N fertilizers applied to open field vegetables. Acta Agriculturae Nucleatae Sinica 22, 343-347.

Cassman, K.G., Dobermann, A., Walters, D.T., 2002. Agroecosystems, nitrogen-use efficiency, and nitrogen management. AMBIO: A Journal of the Human Environment 31, 132-140.

Clough, T.J., Condron, L.M., 2010. Biochar and the nitrogen cycle: introduction. Journal of Environmental Quality 39, 1218-1223.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, & Soil Pollution 213, 47-55.

Dobermann, A.R., 2005. Nitrogen use efficiency–state of the art.

Feng, Y., Sun, H., Xue, L., Liu, Y., Gao, Q., Lu, K., Yang, L., 2017. Biochar applied at an appropriate rate can avoid increasing NH3 volatilization dramatically in rice paddy soil. Chemosphere 168, 1277-1284.

Guo, J.H., Liu, X.J., Zhang, Y., Shen, J., Han, W., Zhang, W., Christie, P., Goulding, K., Vitousek, P., Zhang, F., 2010. Significant acidification in major Chinese croplands. Science 327, 1008-1010.

Guo, R., Li, X., Christie, P., Chen, Q., Jiang, R., Zhang, F., 2008. Influence of root zone nitrogen management and a summer catch crop on cucumber yield and soil mineral nitrogen dynamics in intensive production systems. Plant and Soil 313, 55-70.

Halvorson, A.D., Mosier, A.R., Reule, C.A., Bausch, W.C., 2006. Nitrogen and tillage effects on irrigated continuous corn yields. Agronomy Journal 98, 63-71.

Haynes, R., 2012. Mineral nitrogen in the plant-soil system. Elsevier.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Jia, J., Li, B., Chen, Z., Xie, Z., Xiong, Z., 2012. Effects of biochar application on vegetable production and emissions of N2O and CH4. Soil Science and Plant Nutrition 58, 503-509.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X., Liu, X., Zhang, F., Roelcke, M., 2004. Nitrogen fertilization, soil nitrate accumulation, and policy recommendations in several agricultural regions of China. AMBIO: A Journal of the Human Environment 33, 300-305.

Ju, X.T., Kou, C.L., Christie, P., Dou, Z., Zhang, F., 2007. Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain. Environmental Pollution 145, 497-506.

Kameyama, K., Miyamoto, T., Shiono, T., Shinogi, Y., 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. Journal of Environmental Quality 41, 1131-1137.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14 C analysis. Soil Biology and Biochemistry 70, 229-236.

Li, X., Hu, C., Delgado, J.A., Zhang, Y., Ouyang, Z., 2007. Increased nitrogen use efficiencies as a key mitigation alternative to reduce nitrate leaching in north china plain. Agricultural Water Management 89, 137-147.

Liang, L., Zhao, X., Yi, X., Chen, Z., Dong, X., Chen, R., Shen, R., 2013. Excessive application of nitrogen and phosphorus fertilizers induces soil acidification and phosphorus enrichment during vegetable production in Yangtze River Delta, China. Soil Use and Management 29, 161-168.

Liu, J., You, L., Amini, M., Obersteiner, M., Herrero, M., Zehnder, A.J., Yang, H., 2010. A high-resolution assessment on global nitrogen flows in cropland. Proceedings of the National Academy of Sciences 107, 8035-8040.

Lu, R.k., 2000. Soil agricultural chemistry analysis. Beijing: Agriculture Press.

Lukina, E., Freeman, K., Wynn, K., Thomason, W., Mullen, R., Stone, M., Solie, J., Klatt, A., Johnson, G., Elliott, R., 2001. Nitrogen fertilization optimization algorithm based on in-season estimates of yield and plant nitrogen uptake. Journal of Plant Nutrition 24, 885-898.

Luo, Y.x., Gao, B., Yan, X.y., Jiang, X.s., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Ma, W., Mao, D., Zhang, F., 2000. Nutrients accumulation within vegetable awning (green house) in Shandong province. Phosphate & Compound Fertilizer 3, 028.

Masclaux-Daubresse, C., Daniel-Vedele, F., Dechorgnat, J., Chardon, F., Gaufichon, L., Suzuki, A., 2010. Nitrogen uptake, assimilation and remobilization in plants: challenges for sustainable and productive agriculture. Annals of Botany 105, 1141-1157.

Min, J., Shi, W.m., 2009. Effects of different N rates on the yield, N use efficiency andfruit quality of vegetables cultivated in plastic greenhouse in Taihu lake region. Plant Nutrition and Fertilizer Science 15, 151-157.

Min, J., Shi, W., Xing, G., Zhang, H., Zhu, Z., 2011a. Effects of a catch crop and reduced nitrogen fertilization on nitrogen leaching in greenhouse vegetable production systems. Nutrient Cycling in Agroecosystems 91, 31.

Min, J., Zhang, H., Shi, W., 2012. Optimizing nitrogen input to reduce nitrate leaching loss in greenhouse vegetable production. Agricultural Water Management 111, 53-59.

Min, J., Zhao, X., Shi, W.M., Xing, G.X., Zhu, Z.L., 2011b. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.

Mosier, A., Syers, J.K., Freney, J.R., 2004. Agriculture and the nitrogen cycle: assessing the impacts of fertilizer use on food production and the environment. Island Press.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A., 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Science 174, 105-112.

Qiao, J., Yang, L., Yan, T., Xue, F., Zhao, D., 2012. Nitrogen fertilizer reduction in rice production for two consecutive years in the Taihu Lake area. Agriculture, Ecosystems & Environment 146, 103-112.

Rathke, G.W., Behrens, T., Diepenbrock, W., 2006. Integrated nitrogen management strategies to improve seed yield, oil content and nitrogen efficiency of winter oilseed rape (Brassica napus L.): A review. Agriculture, Ecosystems & Environment 117, 80-108.

Schnier, H., Dingkuhn, M., De Datta, S., Mengel, K., Faronilo, J., 1990. Nitrogen fertilization of direct-seeded flooded vs. transplanted rice: I. Nitrogen uptake, photosynthesis, growth, and yield. Crop Science 30, 1276-1284.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of Environmental Quality 41, 973-989.

Sun, R.j., wang, D.j., Lin, J.h., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.

Thorup-Kristensen, K., Magid, J., Jensen, L.S., 2003. Catch crops and green manures as biological tools in nitrogen management in temperate zones. Advances in agronomy 79, 227-302.

Yin, R., Zhang, H.y., Huang, J.f., Lin, X.g., Wang, J.h., Cao, Z.h., 2004. Comparsion of microbiological properties between soils of rice-wheat rotation and vegetable cultivation. Plant Nutrition and Fertilizing Science 10, 57-62.

Zhang, J., Cai, Z., Cheng, Y., Zhu, T., 2009. Denitrification and total nitrogen gas production from forest soils of Eastern China. Soil Biology and Biochemistry 41, 2551-2557.

Zhang, Q., Yang, Z., Zhang, H., Yi, J., 2012. Recovery efficiency and loss of 15 N-labelled urea in a rice–soil system in the upper reaches of the Yellow River basin. Agriculture, Ecosystems & Environment 158, 118-126.

Zhang, W.J., Li, Z.F., Zhang, Q.Z., Du, Z.L., Ma, M.Y., Wang, Y.d., 2011. Impacts of biochar and nitrogen fertilizer on spinach yield and tissue nitrate content from a pot experiment. Journal of Agro-Environment Science 10, 7.

Zhao, C., Hu, C., Huang, W., Sun, X., Tan, Q., Di, H., 2010. A lysimeter study of nitrate leaching and optimum nitrogen application rates for intensively irrigated vegetable production systems in Central China. Journal of Soils and Sediments 10, 9-17.

Zhu, J., Li, X., Christie, P., Li, J., 2005. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (Capsicum frutescens L.) cropping systems. Agriculture, Ecosystems & Environment 111, 70-80.

Zhu, Z., Chen, D., 2002. Nitrogen fertilizer use in China–Contributions to food production, impacts on the environment and best management strategies. Nutrient Cycling in Agroecosystems 63, 117-127.

Zhu, Z., Norse, D., Sun, B., 2006. Policy for reducing non-point pollution from crop production in China. China Environmental Science Press, Beijing, 135-161

CHAPTER 6: GENERAL CONCLUSIONS

6.1 Introduction

With the pace of economic development, fields used for vegetable planting have increased considerably over the past decades in order to meet the large consumer demand in China (NBS, 2015). Maintaining high vegetable yields is of great significance because the land area available for vegetable cultivation is limited (Chen, 2007; Chen *et al.*, 2013).

Farmers apply large amounts of nitrogen fertilizer to ensure sufficient nitrogen is available in the soil for vegetable growth (Huang *et al.*, 2006; Ju *et al.*, 2007; Shi *et al.*, 2009). Intensive cultivation is very common in vegetable production systems in China but excessive application of nitrogen fertilizer can change nitrogen processes (Zhu *et al.*, 2005; Cao *et al.*, 2008; Min *et al.*, 2011; Luo *et al.*, 2015) and some soil chemical properties(Yin *et al.*, 2004; Sun *et al.*, 2006), which can hamper sustainable production. However, neither reducing chemical nitrogen fertilizer application nor using organic nitrogen fertilizer can comprehensively address the existing problems (such as high nitrogen loss and soil acidity) in vegetable production fields (Ju *et al.*, 2009; Xue *et al.*, 2010; Wei *et al.*, 2012). Therefore, there is a need to consider new approaches with regard to soil chemical properties and nitrogen processes that could affect the nitrogen supply to the soil (including soil nitrogen retention, nitrogen mineralization and nitrogen loss) in vegetable production systems, to ensure better yields and higher nitrogen uptake and use efficiency.

Biochar is a carbon rich product derived from biomass pyrolysis under low oxygen conditions, resulting in a porous, low density carbon rich material (Lehmann, 2009). It has been widely studied as a soil amendment fueled because of its potential to change soil conditions and improve crop yields (Atkinson *et al.*, 2010; Ding *et al.*, 2010; Spokas *et al.*, 2012; Biederman and Harpole, 2013; Jeffery *et al.*, 2015). The effects of biochar addition on soil nitrogen content and soil nitrogen transformation processes have been reported (Clough and Condron, 2010; Bruun *et al.*, 2012; Dempster *et al.*, 2012; Feng *et al.*, 2017). Biochar may be an option for regulating nitrogen processes and mitigating soil acidity in vegetable soils due to its adsorption and alkalinity properties (Lehmann, 2007). In China, there are sufficient agricultural residues which can serve as raw materials for biochar production, and biochar production industries are increasing in Chinese rural areas.

However, studies on biochar addition to soils used for vegetable production have not been well documented (Jia *et al.*, 2012). It is still unknown whether the positive effect of biochar on soil nitrogen processes and soil chemical properties, found in short term experiments or incubation studies, can be consistent in the long-term. Information on the bioavailability of nitrogen retained by biochar is still lacking. It is not well understood whether biochar addition and its effect on nitrogen retention, plant uptake, residual soil nitrogen and nitrogen losses are influenced by the sources of nitrogen (nitrogen from soil mineralization processes or nitrogen from chemical fertilizer). Research is needed to study and assess the effects of biochar addition on nitrogen retention and uptake by vegetables produced under continuous and intensive cultivation systems in China.

Therefore, the study was carried out as a pot experiment over a time period of four continuous growing seasons using the technique of stable isotope ^{15}N-traced, with the aim of determining the effects of biochar addition on soil nitrogen retention and uptake by vegetables (pakchoi) in the intensive cultivation systems in China.

6.2 Responses of major findings to the objectives of this study

Objectives	Major findings
➢ To determine the differences of soil chemical properties and nitrogen dynamics between vegetable soils and paddy soils.	➢ Chapter 2 (summarized in 6.2.1)
➢ To determine the effect of biochar addition on soil nitrogen retention in	➢ Chapter 3 (summarized in 6.2.2)

soils used for vegetable production in China.	
➢ To determine the effect of biochar addition on soil acidity in soils used for vegetable production in China.	➢ Chapter 4 (summarized in 6.2.3)
➢ To determine the effect of biochar addition on nitrogen uptake by vegetable (pakchoi) and yields.	➢ Chapter 5 (summarized in 6.2.4)
➢ To examine the ratios of nitrogen fertilizer to total nitrogen (fertilizer nitrogen + soil mineralized nitrogen) and the recovery of nitrogen fertilizer in plants, soil and leachate with different biochar addition rates.	➢ Chapter 5 (summarized in 6.2.5)

6.2.1 Differences in nitrogen processes and soil chemical properties between paddy soils and vegetable soils

A pot experiment was conducted in the absence of nitrogen fertilizer to compare three pairs of soil samples (every pair included one paddy soil and one vegetable soil) collected from the Tailake region of China. The major findings were:

- Soil pH values and organic matter content was lower in the vegetable soils compared with those in the paddy soils.
- Nitrogen leaching loss from the vegetable soils was higher than that from the paddy soils and was attributed to the higher soil mineral nitrogen content of vegetable soils
- Pakchoi nitrogen uptake in the vegetable soils was lower than that in the paddy soils due to the soil acidity and high nitrogen leaching loss in the vegetable soils.

6.2.2 Effect of biochar addition on soil nitrogen retention in vegetable soil

Nitrogen retention in vegetable soils was studied by taking into consideration soil mineral nitrogen content, nitrogen retained and released by biochar and nitrogen leaching losses at three biochar additional rates (0, 1% and 5 %) over four continuous growing seasons. The major findings were:

- Biochar addition significantly increased the soil mineral nitrogen content by enhancing nitrogen retention in soils and soil nitrogen mineralization.
- The mineral nitrogen retained in soils amended with biochar could be reused by plants.
- Biochar addition reduced nitrogen leaching losses in soils by decreasing the volume and nitrate concentration of leachate.

6.2.3 Effect of biochar addition on vegetable soil acidity

The soil pH value, pH buffering capacity, acidification rate and bases contents in soil were tested after planting the vegetable pakchoi in soils amended with biochar and used for vegetable production over four continuous seasons . The major findings were:

- Biochar addition increased soil pH values or retarded soil acidification.
- Biochar addition promoted soil pH buffering capacity and reduced acidification rate.
- Biochar addition maintained soil bases content under leaching conditions.

6.2.4 Effect of biochar addition on plant nitrogen uptake and yield

Pakchoi nitrogen uptake and yield was measured in the four continuous seasons with nitrogen fertilizer being applied in the 1^{st}, 2^{nd} and 3^{rd} seasons. The major findings were:

- Biochar addition maintained pakchoi yield and nitrogen uptake, while pakchoi yield decreased in the treatments without biochar from the beginning of the 2^{nd} season.

6.2.5 Amount of nitrogen from two sources and nitrogen recovery efficiency of plant nitrogen uptake, nitrogen residue in soil and nitrogen loss

The technique of stable isotope ^{15}N-traced was used to identify fertilizer nitrogen sources in plant nitrogen uptake, nitrogen residue in soil and nitrogen loss in four seasons (with labeled nitrogen fertilizer applied in the 1st, 2nd and 3rd seasons and no nitrogen fertilizer applied in the 4th season). The major findings were:

- Chemical fertilizer provided the major source for pakchoi nitrogen uptake, soil residual nitrogen and nitrogen leaching loss, while soil mineralization processes provided the major source of nitrogen retained by the biochar.
- Biochar addition increased the NRE of pakchoi and the recovery of fertilizer nitrogen in soil and reduced the recovery of fertilizer nitrogen in leachate.
- In the absence of nitrogen fertilizer, the nitrogen fertilizer left in the soil from the 1st, 2nd and 3rd seasons decreased sharply. Most nitrogen fertilizer retained by biochar was also released during this time.

6.3 General conclusion

The effects of biochar addition on nitrogen retention in soils used for vegetable production and nitrogen uptake by vegetable plants (pakchoi) were investigated. Based on the major findings, it can be concluded that:

The effective soil output for plant uptake was reduced and the unusable output via leaching loss was increased after the conversion from paddy to vegetable cultivation. Biochar addition could promote soil nitrogen retention, decrease nitrogen fertilizer loss, retarded soil acidification and hence increased plant nitrogen uptake in continuous growing seasons in vegetable production systems. The use of biochar as an amendment for vegetable soil could maintain high vegetable yields and make it possible to reduce nitrogen fertilizer application rates.

6.4 Advices for future work

There are plenty of study needed before extensive utilization of biochar in vegetable production systems. As the findings in the thesis were concluded from pot experiments, the effect of biochar on nitrogen processes should be assessed in the special field for several growing seasons. The additional method of biochar is the fields where studies are urgently needed now.

6.4.1 How to determine whether the soil should be added biochar?

It is important to define the role of biochar before answer this question. Biochar was firstly studied as a carbon-rich product for fixing atmospheric carbon in soil system. When biochar is used as a carbon storage material, it can be returned to any soils in natural systems.

In recent years, increasing attentions have paid with regard the amending capacities of biochar (Seen detail in 1.5 Chapter 1). The characteristics of biochar produced from different original materials or pyrolysis conditions are different attributing to various amending functions. When biochar is treated as a soil amendment, its proper producing condition is the key to determine its effect on soil problem. Furthermore, biochar may not as effective as other specific amendments for certain soil problem (such as heavy metal pollution) and lots of biochar will be needed when biochar is the only amendment used for that problem. The expense, efficiency and the potential negative effect of biochar should be considered for determining whether biochar is the optimal choice. However, the problems in most cultivated soils are various and correlative and biochar addition could settle several soil problems at once. For example, high leaching loss, low nitrogen retention are the major two constraints for plant uptake nitrogen in this study. A significant promotion of plant nitrogen uptake was found in treatments with biochar addition in continuous growing seasons, which was contributed to the comprehensive effects of biochar on soil nitrogen retention, leaching loss and even soil pH maintaining (6.2 in Chapter 6). It was economical and environmentally friendly to use biochar as the soil amendment.

In our opinion, there is no need to add biochar to all kinds of fields. There are some questions that we suggest to ask before adding biochar to soil listed as below:

What is biochar used as?

A soil amendment	*A carbon storage material*	*Other roles*
(1) What is the problem about the soil?	*(1) Where is the biochar from?*	*(1) Why choose biochar for it?*
(2) Can the problem be alleviated / amended by biochar?	*(2) Is the producing technique low-carbon?*	*(2) What advantages does biochar have compared with previous methods?*
(3) How much biochar should be added for the problem?	*(3) Will the system be affected by biochar addition?*	…
(4) Is there any negative effect or risks along with biochar addition rate?	…	
(5) Is it economical to use biochar as the amendment for this problem?		
…		

6.4.2 How to determine the optimal biochar addition rate and frequency?

When biochar treated as an amendment, its addition rate should be determined by the amending function of certain problem in theory. Unfortunately, the effect of biochar addition on problem amending is not commonly linear growth. For example, two addition rates (1% and 5% biochar) were used in this study. Soil leaching loss was further reduced by more biochar addition but no significant effect was found on soil mineral nitrogen content, total nitrogen loss, soil pH value and plant nitrogen uptake between 1% and 5% biochar addition. Furthermore, Kammann *et al.* (2012) found quinoa growth was retarded with a high biochar addition and Feng *et al.* (2017) reported a significant increase in ammonia volatilization in paddy soil with 3% biochar addition. However, meta-analysis of biochar addition rates provided little insight into how biochar should best be applied (Biederman and Harpole, 2013).

Furthermore, the frequency of biochar addition is another problems in practical application. For the field agricultural residue returned as the form of biochar, it will be added after every growing season. The rate of biochar addition may be low for one time but the rate of cumulated addition will be high and the long-term effects of multiple additions are still lack of study.

In this study, it was found soil pH buffering capacity could be used to determine biochar addition rates by using the linear relationship between slope of titration curve and biochar addition rate. Additionally, biochar should be added again when soil pH values decrease and no significant difference was shown in the pH of the soil without the addition of biochar. Findings in Chapter 4 suggest that multiple additions of biochar are necessary to prevent acidification.

Therefore, the proper biochar addition rate should be in the range of high efficiency rather than best effect on the aiming problem. The indicators related the aiming problem could be used to determine the time for adding biochar again. Moreover, the long-term effects on other soil physical / chemical characteristics and the response of plant to biochar addition need to be taken account and also studied further.

6.4.3 Use biochar as a carrier for nitrogen transport

The availability of mineral nitrogen retained by biochar has been demonstrated in this study. In addition, Taghizadeh-Toosi *et al.* (2012) has reported that the ammonia adsorbed on biochar could be utilized by plants again, thus implying that biochar could be used as a carrier for transporting nitrogen.

Non-point pollution is a serious problem in China and nitrogen from agricultural fields contributes approximately 40% of the nitrogen in the water system (Yang *et al.*, 2013). If biochar could be replaced with an environmental material to retain or adsorb nitrogen from the water system, it could be taken back and returned to the fields as a type of fertilizer.

However, there is limited data available for the nitrogen adsorbing capacity of biochar in open water systems and the technology of collecting biochar from water systems is still unknown.

References

A tkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337, 1-18.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta ‐ analysis. GCB Bioenergy 5, 202-214.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biology and Biochemistry 46, 73-79.

Cao, B., Xu, Q., He, F., Cai, G., 2008. Nitrogen use efficiency and fate of N fertilizers applied to open field vegetables. Acta Agriculturae Nucleatae Sinica 22, 343-347.

Chen, J., 2007. Rapid urbanization in China: a real challenge to soil protection and food security. Catena 69, 1-15.

Chen, W.F., Zhang, W.m., Meng, J., 2013. Advances and Prospects in Research of Biochar Utilization in Agriculture. Scientia Agricultura Sinica 46, 3324-3333.

Clough, T.J., Condron, L.M., 2010. Biochar and the nitrogen cycle: introduction. Journal of Environmental Quality 39, 1218-1223.

Dempster, D., Gleeson, D., Solaiman, Z.i., Jones, D., Murphy, D., 2012. Decreased soil microbial biomass and nitrogen mineralisation with Eucalyptus biochar addition to a coarse textured soil. Plant and Soil 354, 311-324.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, & Soil Pollution 213, 47-55.

Feng, Y., Sun, H., Xue, L., Liu, Y., Gao, Q., Lu, K., Yang, L., 2017. Biochar applied at an appropriate rate can avoid increasing NH 3 volatilization dramatically in rice paddy soil. Chemosphere 168, 1277-1284.

Huang, B., Shi, X., Yu, D., Öborn, I., Blombäck, K., Pagella, T.F., Wang, H., Sun, W., Sinclair, F.L., 2006. Environmental assessment of small-scale vegetable farming systems in peri-urban areas of the Yangtze River Delta Region, China. Agriculture, Ecosystems & Environment 112, 391-402.

Jeffery, S., Meinders, M.B., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F., Mommer, L., van Groenigen, J.W., 2015. Biochar application does not improve the soil hydrological function of a sandy soil. Geoderma 251, 47-54.

Jia, J., Li, B., Chen, Z., Xie, Z., Xiong, Z., 2012. Effects of biochar application on vegetable production and emissions of N2O and CH4. Soil Science and Plant Nutrition 58, 503-509.

Ju, X.T., Xing, G.X., Chen, X.P., Zhang, S.L., Zhang, L.J., Liu, X.J., Cui, Z.L., Yin, B., Christie, P., Zhu, Z.L., 2009. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences 106, 3041-3046.

Ju, X.T., Kou, C.L., Christie, P., Dou, Z., Zhang, F., 2007. Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain. Environmental Pollution 145, 497-506.

Kammann, C., Ratering, S., Eckhard, C., Müller, C., 2012. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from soils. Journal of Environmental Quality 41, 1052-1066.

Lehmann, J., 2007. A handful of carbon. Nature 447, 143-144.

Lehmann, J., 2009. Biochar for environmental management: An introduction. In 'Biochar for environmental management: Science and technology'.(Eds J Lehmann, S Joseph) pp. 1–12. International Biochar Initiative: Westerville, OH, USA.

Luo, Y.X., Gao, B., Yan, X.y., Jiang, X.S., 2015. Estimating contribution of agricultural sources to aquatic nitrogen load in Taihu Lake Region: A case study of Yili River catchment. Journal of Agro-Environment Science 34, 2318-2326.

Min, J., Zhao, X., Shi, W.M., Xing, G.X., Zhu, Z.L., 2011. Nitrogen balance and loss in a greenhouse vegetable system in Southeastern China. Pedosphere 21, 464-472.

NBS, 2015. China Statistical Yearbook. . China Statistic Press, Beijing., National Bureau of Statistics of China,.

Shi, W.M., Yao, J., Yan, F., 2009. Vegetable cultivation under greenhouse conditions leads to rapid accumulation of nutrients, acidification and salinity of soils and groundwater contamination in South-Eastern China. Nutrient Cycling in Agroecosystems 83, 73-84.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of

Environmental Quality 41, 973-989.

Sun, R.j., wang, D.j., Lin, J.h., 2006. Evolution of soil fertility in Taihu region and its causes. Soils 38, 106-109.

Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M., 2012. Biochar adsorbed ammonia is bioavailable. Plant and Soil 350, 57-69.

Wei, H.q., Lv, J.l., Xu, M.g., Cai, Z.j., Wang, B.r., 2012. Alkalinity of organic manure and its mechanism for mitigating soil acidification. Plant Nutrition and Fertilizer Science 18, 1159-1167.

Xue, F., Yan, T.m., Yang, L.z., Qiao, J., 2010. Influences of organic fertilizer application on soil biological properties. Chinese Journal of Eco-Agriculture 18, 1372-1377.

Yang, L.z., Shi, W.m., Xue, L.h., Song, X.f., Wang, S.q., Chang, Z.z., 2013. Reduce-Retain-Reuse-Restore technology for the controlling the agricultural nno-point source pollution in countryside in China: general countermeasures and technologies. Journal of Agro-Environment Science 32, 1-8.

Yin, R., Zhang, H.y., Huang, J.f., Lin, X.g., Wang, J.h., Cao, Z.h., 2004. Comparsion of microbiological properties between soils of rice-wheat rotation and vegetable cultivation. Plant Nutrition and Fertilizing Science 10, 57-62.

Zhu, J., Li, X., Christie, P., Li, J., 2005. Environmental implications of low nitrogen use efficiency in excessively fertilized hot pepper (Capsicum frutescens L.) cropping systems. Agriculture, Ecosystems & Environment 111, 70-80.