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A Review of Biochar's Applications in the Soil Nitrogen Cycle

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Abstract

Biochar is an emerging soil amendment technology which is increasingly attracting the attention of researchers. Biochar is produced in an environmentally friendly manner by recycling plant waste into fertilizer. Nitrogen is a significant factor in crop growth, and the use of biochar as a source of soil nitrogen has been a subject of much study. The direct application of biochar as nitrogenous fertilizer is inefficacious because biochar contains more carbon than nitrogen. Instead, the porosity and large surface area of biochar is effective at retaining nitrogen compounds and inhibiting its leaching by runoff. Further study into the interplay between biochar and soil chemistry is needed because the characteristics of biochar is greatly influenced by the pyrolytic conditions used to produce biochar and the type of soil it is used in.

Key words: biochar, nitrogen, soil, amendment

1. Introduction

Biochar is produced by pyrolyzing biomass. In general, biomass is treated in a high temperature, anoxic environment; the resultant vapors are removed by a nitrogen stream, and the liquid bio-oil products is collected for biofuel, leaving behind a solid material known as biochar. The main component of biochar is carbon, hydrogen, nitrogen and other trace elements.

Biochar is considered a better soil amender than other forms of organic matter. When used in soil, biochar promotes plant growth and reduces the biological availability of heavy metals and organic pollutants. Because biochar is slow to decompose, soils treated with biochar retain these properties for many years. Thus, biochar is an effective sequestration and bioremediation tool in reducing the emission of pollutants while improving soil quality[1].

For crops, nitrogen is one of the most important nutrients. In soil, the majority of nitrogen exists in complex organic forms; before it can be incorporated by the plant, it must be ammonified to NH_4^+ and then nitrified to NO_3^-[2]. Thus, it is inevitable that the nitrogen cycle will remove much of the soil's nitrogen before the plant can even use it through either the discharge of gaseous nitrogen dioxide or the leaching of nitrates by water runoff.

According to the research to date, biochar has the potential to control the rates of nitrogen cycling in the following three ways: (i) enhancing the soil content of NH_4^+ and NO_3^- through direct adsorption by the biochar; (ii) reducing the emission of N_2O and losses of nitrogen leaching; (iii) increasing the population of nitrifying soil bacteria for biological N retention[3]. i) and ii) is improved when the biochar has a smaller particle size and a larger surface area; iii) is improved by both surface area and high pH.

In this article, we will focus on the nitrogen mass balance in both slow and fast pyrolysis processes from different feedstocks and reaction conditions as well as biochar's effect on soil nitrogen amendment. Finally, we will identify the changes to the nitrogen cycle after the application of biochar in the soil.

2. Characteristics and Mass Balance of Nitrogen in Biochar

Overall, the main element in biochar is carbon (70-80% by weight); the nitrogen content is significantly lower (<3% by weight). At low temperatures (below 200°C), pyrolysis will result in an increase in the percentage of nitrogen over the unreacted material as water vapor and volatile organic compounds (VOCs) are removed from the material. Nitrogen begins to volatilize above 200°C, with some of the NH_4^+ being oxidized into NO_3^-, which is further converted into various nitrous oxides that are emitted in the gas outflow. However, since the production of VOCs continues until around 400°C, the percentage of nitrogen by weight in this temperature region is material dependent[4]. At still higher temperatures (500°C and higher), with lessened production of VOCs, the nitrogen percentage begins to decrease as any remaining nitrogen begins to condense with carbon to form N-heterocyclic aromatic structures. This leads to a C:N ratio of at least 32:1[5]. As Table 1 shows, even when the raw materials and reaction conditions were nearly identical, a slightly different setting resulted in biochar with very different physical and chemical properties[6].

Table 1: Select physical and chemical composition data for Pinus spp. biochar created under nearly equivalent pyrolysis conditions[6]

Production Temperature (°C)	pH (H_2O)	C ($g\ kg^{-1}$)	O	N	Surface Area ($m^2\ g^{-1}$)	Reference
500	8.3	817		2		(Gaskin et al. 2008)
500		827	114	1	16	(Amutio et al. 2011)
500		800	150	60		(Garcia-Perez et al. 2008)
500		814		34	2	(Kwapinski et al. 2010)
550	9.8	777	167	6	235	(Hina et al. 2010)
500	5.6					(Rajkovich 2010)
500	7.7	678		3		(Warnock et al. 2010)
465	6.8	750	90	3	0.1	(Spokas et al. 2011b)
500	7.3	733		2		(Spokas et al. 2011b)
500		819	145	1	196	(Keiluweit et al. 2010)
500	6.6	826		2		(Taghizadeh-Toosi et al. 2011)
525		806	140		206	(Zimmerman 2010)

2.1 Fast pyrolysis and Slow Pyrolysis

According to Bruun's experiment, biochar was produced from wheat straw decomposed at 525°C by slow pyrolysis (SP) in a nitrogen stream and by fast pyrolysis (FP) using a Pyrolysis Centrifuge Reactor (PCR). From Table 2, we can see that the nitrogen content of SP- and FP-biochar are both higher than the content in the soil and feedstock, but the nitrogen content of the SP-biochar was little higher than that of the FP-biochar. Thus, SP-biochar have more favorable pH, particle size, and surface area characteristics[7].

Table 2: Chemical characteristics of slow pyrolysis (SP) and fast pyrolysis (FP) biochar as compared with the feedstock material (wheat straw) and soil[7].

	Unit	Soil	SP-biochar	FP-biochar	Straw
C	%	1.20	69.6	49.3	43.7
H	%	—	2.1	3.7	5.6
O[a]	%	—	7.1	24.1	43.9
N	%	0.14	1.5	1.2	0.9
H/C		—	0.02	0.06	0.12
O/C		—	0.08	0.38	0.94
C/N		8.7	47	40	50
Ash fraction	%	—	19.8	21.6	5.9
Cellulose	%	—	0	7.4	40.3
Hemicellulose	%	—	0	1.4	22.8
pH		—	10.1	6.8	—

[a] Oxygen determined by difference (100% − C, H, N and ash %).

Similar results were obtained in *Dr. Brewer's* (2009) research[8]. In her study, corn stover and switchgrass were treated with slow and fast pyrolysis. The temperature for both was 500°C. From Table 3, we observe that the nitrogen content of pyrolyzed switchgrass was lower (less than 1% by weight) than that of the pyrolyzed corn stover, especially the SP-corn biochar (1.3% by weight). However, just as in Table 2, for both types of feedstock, the SP-biochar contained more nitrogen than the corresponding FP-biochar. Similarly, from Table 4, the composition analysis of biochar combustion showed the samples of switchgrass and corn stover FP-biochar had higher N+O content than the other biochars, implying that the FP-biochar, like in Table 2, has higher oxygen content[8].

Table 3: Composition of representative biochars[8]

Char	C (wt%)	H (wt%)	N (wt%)
Switchgrass S.P.	39.4	1.3	0.7
Switchgrass F.P.	38.7	0.5	0.6
Switchgrass gasification	42.8	1.6	0.8
Corn stover S.P.	62.8	2.9	1.3
Corn stover F.P.	37.8	2.5	0.8
Corn stover gasification	38.5	1.3	0.7
Hardwood	65.3	2.6	0.6

Table 4: Elemental analysis of switchgrass and corn stover biochars from NMR and combustion[8]

Char	C (wt %)	H (wt %)	O + N (wt %)
Switchgrass S. P.	(39.4 ± 0.4)	1.53 (1.31 ± 0.01)	4.9 (~6.3)
Switchgrass F. P.	(38.7 ± 0.2)	1.63 (2.49 ± 0.03)	10.1 (~5.7)
Switchgrass gasification	(42.8 ± 0.1)	1.18 (1.60 ± 0.02)	7.9 (~3.9)
Corn stover F. P.	(37.8 ± 0.6)	1.82 (2.48 ± 0.05)	11.3 (~10.5)
Corn stover gasification	(38.5 ± 0.2)	1.08 (1.29 ± 0.01)	8.2 (~7.2)

S.P., slow pyrolysis; F.P., fast pyrolysis.

2.2 Temperature, Residence Time and Other Factors

Laidy's (2014) experiment on SP bamboo biochar showed that while yield decreased with the increase in reaction temperature (from 80% of dry weight at 300°C to 30% of dry weight at 600°C), the percentage of nitrogen by weight was highest at 500°C (at 2.12%)[9]. Similar results were found by *Kloss, S., et al.* (2012). In their "high temperature" treatment (HTT) of wheat straw, spruce wood, and poplar wood, they found that an increase from 400°C to 460°C led to an increase in the carbon and nitrogen weight percentage of all their samples, but a further increase to 525°C led to a slight decrease. HTT did not significantly change the C:N ratio, however[10].

Not all experiments support our model of a peak in nitrogen percentage by weight as temperature increases. *Qianfeng Zhang* (2013) showed in his experiment that feedstock material and residence time are the two most important factors that affect biochar characteristics. He chose three different types of crop waste as test materials: corn cobs, soybean stalks, and rice husks. Among these three kinds of raw materials, soybean had the highest nitrogen content. Because the raw materials were different, the resulting nitrogen content showed different behavior as pyrolysis temperature and residence times increased from 300°C to 500°C and 3-9 hours, respectively. Only soybean showed a consistent negative trend at 3, 6, and 9 hours, while corn and rice showed no significant changes at 3 hours. With the increase in temperature, the percentage of nitrogen by weight of soybean and corn biochar decreased steadily while the percentage for rice's biochar increased[11]. This result is consistent with *Novak's* (2009) conclusion. In that experiment, the nitrogen loss rate of corn cob, soybean stalk, and rice husk were respectively 27.28%-66.33%, 21.07%-75.14% and 5.31%-38.26%[12].

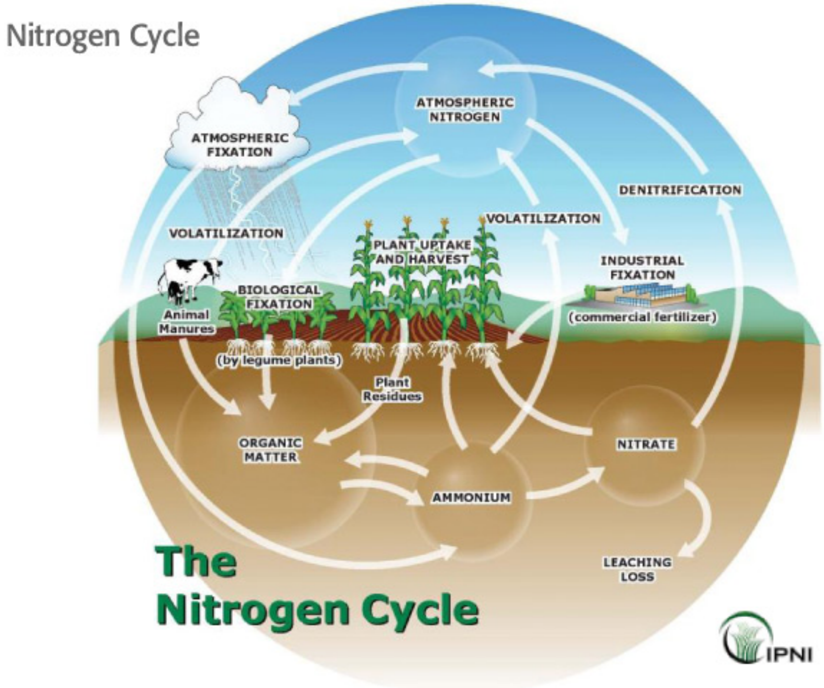
3. Effect of Biochar Amendment on Soil

The low uptake efficiency (an international average of 33%) of nitrogen fertilizer by crops is a global environmental problem. Unabsorbed nitrogen fertilizer is carried away by water runoff into lakes and rivers, resulting in eutrophication, or is converted into gaseous nitrous oxide by soil bacteria, contributing to acid rain[13]. The economic losses caused by these processes is in excess of 150 million dollars a year[14]. However, since biochar consists mostly of recalcitrant aromatics rather than bioavailable amines, it cannot directly provide nitrogen to crops as most conventional fertilizers do[12]. Instead, biochar inhibits the leaching of nitrogen compounds and affects the availability of nitrates and ammonia in the soil.

3.1 Inhibition of the Leaching of Nitrogen Compounds

Leaching is the main cause of nitrogen depletion in soil. Soil nitrogen is mainly of the form of nitrates (NO_3-N). Although the decomposition of all living things produces NH_4-N, in warm and aerated soil, microorganisms convert the former to nitrate so quickly that nitrate often accumulates in soil in excess of what plants can absorb. These nitrate solutes dissolve into the water contained in the soil's pores. This nitrogen-rich water subsequently infiltrates below the plant's roots or flows into aboveground bodies of water, thereby depriving the soil of nitrogen[15]. The N cycling process in agriculture and environment is shown in Figure 1.

Figure 1: N Cycling Process in Agriculture and Environment[15]



There have been several studies showing the effectiveness of biochar in inhibiting nitrogen loss from leaching. *Zhou Z. and Lee X.* (2011) tested the effectiveness of corn biochar in preventing nitrogen leaching in both purple soil and chrenozem. They found that that biochar had significantly stronger protective qualities in the looser purple soil, but that using minimal amounts (10 t/ha) actually exacerbated nitrogen loss. Most significantly, they found that beyond 130mm of rain, no amount of biochar tested had any effectiveness in preventing leaching[16]. This likely explains biochar's uselessness in boosting rice production[17]. In addition, biochar is more effective at retaining organic nitrogen compounds (88% retention) than it is at retaining nitrate (68% retention)[16]. This was later corroborated by the results of *Chen Xinxiang's* (2014) leaching experiment where soil containing various amounts of biochar was rinsed by water up to 10 times. Throughout the leaching process, the main form of nitrogen loss was from nitrates, which accounted for 97.3%-98% of the total nitrogen losses. As the amount of biochar applied to the soil was increased, the amount of nitrogen lost to leaching for both NH_4-N and NO_3-N were reduced. At the maximum tested amount of 80t·hm^{-2}, the losses after 10 rinses were minimized (a retention rate of 41%). One reason for this reduction is that biochar itself has high porosity and surface area, which can absorb NH_4-N and NO_3-N physically. Furthermore, biochar applied soils also see an increase in their overall porosity and water retention, both of which are factors in nitrogen retention[18]. Lehmann suggests that the high surface area and porosity: (i) provides sites for electrostatic adsorption; (ii) has the ability to retain the soil's water and dissolved nutrients[19].

3.2 The Effect on NH_4^+ and NO_3^-

The porous structure of biochar has been the subject of many absorption studies. Biochar is selective in its sorption; although nitrate and ammonium are both nitrogenous compounds, the effect of biochar on nitrogen leaching varies greatly between these two types of nutrients, as well as between different types of biochar. *Ying Yao* (2012) tested the NH_4^+ and NO_3^- sorption ability of thirteen types of biochar. Nine types were effective at absorbing ammonium in solution, but most types had little effect on nitrate in solution. Further tests in a soil leaching study showed that the biochar of pepperwood, pyrolyzed at 600°C, reduced nitrate and ammonium leaching by 34% and 34.7%, respectively[20]. The C:N ratio is another factor that influences the effect of biochar in soil. Inorganic nitrogen will be effectively converted to organic nitrogen when the biochar used has a C:N ratio of at least 32:1. At the same time, such a C:N ratio reduces the rate of biochar decomposition because the nitrogen in the biochar has been condensed into biologically unavailable heterocyclic aromatic compounds. This longevity increases the long-term effect of high C:N biochar[21].

It is claimed that by increasing the soil's retention and absorption of NH_4^+ and NO_3^-, biochar can effectively reduce nitrogen loss and the emission of N_2O, thereby improving soil quality. However, *Yu Luo's* (2014) study yielded a different result. He compared the effects on soil of biochar made from *Miscanthus* giganteus (a grass used for biofuel production) pyrolyzed at 350°C and 700°C. As with the above experiments, he found that biochar had a greater affinity for ammonia than for nitrate and that the higher temperature biochar had a higher pH and a greater affinity for nitrogenous compounds in general. As a result, the soil containing low temperature biochar contained higher ammonia and nitrate levels compared with the soil containing high temperature biochar. This demonstrated biochar's self-antagonistic effects: although higher pH biochar produces more alkaline soil (which in turn promotes nitrification) and biochar in general aerates the soil (nitrifying bacteria are heavy consumers of oxygen), higher pH biochars tend to absorb more ammonia. Past the necessary levels needed to promote bacterial growth, the excess adsorption will deplete the soil of ammonia, thereby starving the population of nitrifying bacteria[22]. *Prommer* (2014) also obtained similar results: when biochar is applied to soil, the rate of organic nitrogen transformation was reduced by 50-80% with no effect on the mineralization of organic nitrogen. However, biochar promoted microbial biochemical reactions that increased nitrification rates. Thus, biochar can decelerate the loss of organic nitrogen and decrease the emissions of inorganic nitrogen, but could potentially increase water runoff. To remedy this problem, the author suggested that biochar should be used with inorganic nitrogen fertilizer to compensate for the loss of organic nitrogen in soil[23].

3.3 Interaction between roots and biochar

Compared to the soil amendment research, the research of the effect of biochar on plant roots is few. The first to draw this connection was *Prendergast-Miller* (2013), who summarized two mechanisms for biochar's effects on roots: (i) biochar was a nutrient source; (ii) biochar improved nutrient availability. He compared two kinds of biochar made from *Miscanthus* straw and *Salix* wood chips in three soil conditions: bulk, rhizosphere and rhizosheath soil. He also modulated the temperature of the fresh biochar (between -10^oC and 30^oC) artificially to imitate the natural weathering biochar would receive in soil. After weathering, the nitrogen content of the biochar was lost. In his conclusion, except when biochar was a direct source of nutrients, biochar increased nitrogen retention in the rhizosphere and bulk soils through indirect interactions. The roots grew towards the biochar, while the biochar altered the nutrient content of the soil closest to itself. In addition, by reducing the nitrogen content of the biochar, weathering also reduced the nitrogen retained in the soil, indicating that the nutrient content of biochar is an important factor in root-biochar interaction[24].

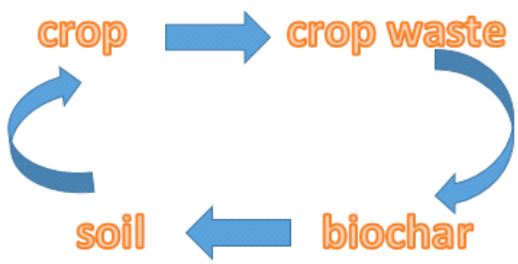
4. Conclusion

Overall, the characteristics and nitrogen content of biochar is influenced by the type of feedstock and the conditions of pyrolysis. The ideal biochar, with high pH, surface area, and porosity is formed by slow pyrolysis (SP) or under high temperature conditions where most of the bioavailable nitrogen has been volatilized or condensed into N-heterocyclic aromatic compounds. Increased residence time is more likely to yield consistent results, though certain materials, such as rice and soybean stalks, require further investigation, as they seem to defy trends exhibited by other materials.

Since biochar's nitrogen is not bioavailable, biochar enhances the soil's nitrogen content by changing the soil's nitrogen cycle. The adsorption and cation exchange ability of NH_4^+ and NO_3^- of biochar can effectively inhibit the leaching of nitrates and retain nitrogen. Biochar also provides a home for nitrifying bacteria to convert NH_4^+ into NO_3^- and aerates the soil. However, these changes may not be entirely beneficial as biochar is not be universally effective while changes to the nitrogen cycle may result in unintended consequences. More study is needed on the function of biochar in soil so we can learn how to best apply biochar (maybe together with fertilizer) in crops to maximize yields and minimize environmental damage.

Ideally, we can build a new nitrogen cycle with biochar in soil. We starting with crop waste to make biochar, which is returned to the soil as fertilizer to produce more crops (Figure 2). Since the properties of biochar is changeable, we should create custom biochars to match the characteristics of a given field, crop, and climate.

Figure 2: the cycle of nitrogen with biochar



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