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# Effects of biochar on soil available inorganic nitrogen: A review and meta-analysis

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ABSTRACT

The interaction between biochar and soil changes nitrogen (N) dynamics in different ecosystems. Although multiple studies have reported influences of biochar on soil inorganic N (SIN) including ammonium ($NH_4^+$-N) and nitrate ($NO_3^-$-N), the influences reported are contradictory. We undertook a meta-analysis to investigate how biochar properties and the interaction among biochar, soil and fertilisation affect SIN. This quantitative analysis used 56 studies with 1080 experimental cases from manuscripts published between 2010 and 2015. Overall, we found that biochar reduced SIN regardless of experimental conditions (approximately $-11 \pm 2\%$ of $NH_4^+$-N and $-10 \pm 1.6\%$ of $NO_3^-$-N); however, 95% of cases were observed within one year after biochar application. SIN was best explained by residence time of biochar in soil, pyrolysis temperature, application rate, fertiliser type, and soil pH. The effects of biochar were complex due to the interaction of biochar with environmental factors. Most biochar trials used wood as a feedstock, but woody biochar did not decrease SIN as much as other plant-derived biochars. When biochar was used with $NH_4$-based fertilisers, SIN decreased compared to biochar with no fertiliser. In contrast, adding organic fertiliser with biochar increased SIN compared to biochar alone. SIN was clearly reduced after one month of biochar application, suggesting that biochar should be applied at least one month prior to planting so plants are not affected by decreased N. Our results revealed that the interactions between biochar and environmental factors, pyrolysis temperature of biochar and biochar surface properties are the main driving factors affecting SIN. There were limited long-term studies of >1 year, thus the long-term effects of biochar on SIN still remain unclear.



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## 1. Introduction

Nitrogen (N) is one of the most critical elements for plant growth and productivity (Atkinson et al., 2010; Bai et al., 2012; Reverchon et al., 2014; Bai et al., 2016). In particular, soil inorganic nitrogen (SIN) is an important N source for plants because plants uptake inorganic N directly through the rooting system (Lynch, 1995). However, N loss via leaching and volatilisation leads to reduced crop productivity, eutrophication, excess nitrate in groundwater, and increased nitrous oxide ($N_2O$) emissions (Overrein, 1969; Bradbury et al., 1993; Xing and Zhu, 2000; Mikkelsen and Hartz, 2008).

Biochar is a promising soil additive to reduce N loss and improve soil fertility (Lal, 2009; Joseph et al., 2013). Biochar is a carbon (C) rich material produced by pyrolysis of biomass at relatively low temperatures (<700 °C) without oxygen ($O_2$) (Lehmann and Joseph, 2009). There are contradictory reports regarding N availability when biochar is applied including decrease, increase and no effect (Blackwell et al., 2009; Clough et al., 2013; Bai et al., 2015b; Xu et al., 2015). However, these studies have not yet been synthesised; therefore, a systematic analysis of the relationship between biochar and SIN is necessary. This study aimed to (a) investigate possible mechanisms influencing SIN when biochar is applied through a short review of available published studies and (b) use a meta-analysis to explore the general trends in $NH_4^+$-N and $NO_3^-$-N across multiple studies in the presence of biochar.

## 2. Overview of the mechanisms affecting soil inorganic N after biochar application

### 2.1. Abiotic mechanisms - adsorption/desorption

Chemisorption of SIN by biochar is based on functional groups (Lehmann and Joseph, 2009). Acid functional groups include carboxylic, hydroxyl, lactone and lactol groups on the surface of biochar (Brennan et al., 2001; Amonette and Joseph, 2009). Carboxylic groups are strong Bronsted acids; less acidic groups include phenols and carbonyls. They have a negative charge and adsorb $NH_4^+$-N by electrostatic attraction (Montes-Morán et al., 2004; Zheng et al., 2010). In general, $NO_3^-$-N adsorption by biochar is weak because biochar carries greater negative surface charges than positive surface charges (Kameyama et al., 2012). However, the existence of base functional groups including chromenes, ketones and pyrones on biochar can facilitate $NO_3^-$-N adsorption to biochar (Montes-Morán et al., 2004; Amonette and Joseph, 2009). $NO_3^-$-N adsorption is also possible via unconventional H-bonding between $NO_3^-$-N ions and the biochar surface (Mukherjee et al., 2011; Lawrinenko, 2014; Kammann et al., 2015).

SIN adsorption by biochar is also time dependent and varies with the temperature and feedstock used to produce biochar. Over time, oxygen-containing acid functional groups (e.g. carboxyl and hydroxyl) are formed on the biochar surface leading to increased biochar CEC and the potential to adsorb more $NH_4^+$-N than fresh biochar. During the ageing of biochar in the soil, $NO_3^-$-N chemisorption through H-bonding may be enhanced because biochar becomes more hydrophilic (Hammes and Schmidt, 2009). The effect of feedstock on $NO_3^-$-N adsorption and the mechanisms of $NO_3^-$-N adsorption by aged biochar through H-bonding remain unclear and need further research (Clough et al., 2013; Kammann et al., 2015).

Sorption capacity of biochar decreases with increased pyrolysis temperature (Mukherjee et al., 2011; Gai et al., 2014). At high temperatures (>600 °C), acidic functional groups (mainly carboxyl) are converted to neutral or basic fused aromatic groups due to the loss of oxygen-containing functional groups, leading to decreased CEC (Cheng et al., 2008; Gaskin et al., 2008; Kookana et al., 2011; Gai et al., 2014). Therefore, aged biochar produced at lower temperatures are expected to adsorb more $NH_4^+$-N compared to the fresh and high temperature biochar.

The feedstock used to produce biochar influences acid (carboxylic) functional groups in biochar to adsorb $NH_4^+$-N (Kookana et al., 2011). For example, grassy biochars (produced from cordgrass) have a higher concentration of carboxylic groups than woody biochars (produced from honey mesquite and loblolly pine), and thus the sorption capacity of the grassy biochars is higher than the woody biochar (Harvey et al., 2012). The higher concentration of carboxylic functional groups is probably because of a high concentration of cellulose, alkali salts and alkali metal oxides in their feedstock (Harvey et al., 2012). Lignocellulose fragments in grassy feedstocks are oxidised more efficiently during pyrolysis and cycloreversion oxidation occurs more rapidly to carboxylic acids. These processes are less efficient in woody feedstocks, owing to a reduced surface charge at any pyrolysis temperature compared with grassy feedstocks (Harvey et al., 2012).

Additionally, physisorption happens inside the pores and on the inner surface of biochar (Lehmann and Joseph, 2009; Saleh et al., 2012; Clough et al., 2013). The inner-surface area of biochar has a positive correlation with the adsorption capability of biochar (Zhang et al., 2012). A commonly used surface area measurement is BET surface area, calculated by determining the adsorption of gases in multimolecular layers (Brunauer et al., 1938). For example, the BET surface area of biochar from beet-root chips and spent brewer's grains is 10 times higher than BET of hydrochar from the same feedstocks, leading to increased $NH_4^+$-N adsorption due to increased physisorption (Bargmann et al., 2014). Generally, biochars produced from high temperatures and slow pyrolysis possess higher BET and pore volume, and have a higher physisorption capacity (Lua et al., 2004; Downie et al., 2009; Kookana et al., 2011; Bruun et al., 2012). At high temperature (>600 °C), biochar surface area and pores are enhanced due to the enhancement of crystallites and their ordered structure (Downie et al., 2009). However, when the temperature reaches a threshold (e.g. pine biochar at 750 °C, wheat residue biochar at 700 °C), deformation occurs, micropore structure is destroyed and surface area decreases (Chun et al., 2004; Brown et al., 2006; Downie et al., 2009). Slow pyrolysis