Plant Soil (2012) 350:35–42
DOI 10.1007/s11104-011-0930-8

COMMENTARY

Biochar's role as an alternative N-fertilizer: ammonia capture

Kurt A. Spokas · Jeff M. Novak · Rodney T. Venterea

Received: 11 July 2011 / Accepted: 19 July 2011 / Published online: 3 August 2011

Abstract
Background Biochar's role as a carbon sequestration agent, while simultaneously providing soil fertility improvements when used as an amendment, has been receiving significant attention across all sectors of society, ranging from academia, industry, government, as well as the general public. This has lead to some exaggeration and possible confusion regarding biochar's actual effectiveness as a soil amendment. One sparsely explored area where biochar appears to have real potential for significant impact is the soil nitrogen cycle.
Scope Taghizadeh-Toosi et al. (this issue) examined ammonia sorption on biochar as a means of providing a nitrogen-enriched soil amendment. The longevity of the trapped ammonia was particularly remarkable; it was sequestered in a stable form for at least 12 days under laboratory air flow. Furthermore, the authors observed increased ^{15}N uptake by plants grown in soil amended with the ^{15}N-enriched biochar, indicating that the ^{15}N was not irreversibly bound, but, was plant-available.
Conclusions Their observations add credence to utilizing biochar as a carrier for nitrogen fertilization, while potentially reducing the undesired environmental consequences through gas emissions, overland flow, and leaching.

Keywords Biochar · Black carbon · Nitrogen fertilization · Nitrogen cycle

Background

Innovative agricultural management systems are needed to fulfill the future global demand for food, feed, and fiber products while minimizing negative atmospheric, soil, and water quality impacts (Hayati et al. 2011; Lal 2000; Lambin and Meyfroidt 2011). One such proposed management innovation is the use of biochar as a soil amendment (Laird 2008; Lehmann 2007). Before addressing some of the details and implications of the Taghizadeh-Toosi et al. (2011) study, it is important to provide some background on biochar.

Varying definitions have been applied to the term *biochar* (Cabrera-Mesa and Spokas 2011) and *black carbon* (Jones et al. 1997). For the purposes of this article, we will use biochar to describe the solid residual resulting from the thermal-chemical conversion of renewable biomass feedstocks created specif-

Responsible Editor: Johannes Lehmann.

K. A. Spokas (✉) · R. T. Venterea
USDA-ARS, Soil and Water Management Unit,
1991 Upper Buford Circle – 439 Borlaug Hall,
St. Paul, MN 55108, USA
e-mail: kurt.spokas@ars.usda.gov

J. M. Novak
USDA-ARS, Coastal Plains Soil, Water,
and Plant Research Center,
2611 W. Lucas Street,
Florence, SC 29501, USA

ically for carbon sequestration (Goldberg 1985; Kuhlbusch and Crutzen 1995; Lehmann 2007). On the other hand, black carbon is the term for the spectrum of carbon thermal-chemical conversion products, regardless of the creation purpose (i.e., naturally produced or anthropogenic for energy, fuel, or carbon sequestration) or source of material (i.e., biomass or fossil fuels) (Jones et al. 1997; Schmidt and Noack 2000). As shown in Fig. 1, black carbon as a term describes a range of thermal-chemical solid by-products, from graphite to chars, as a function of the oxygen to carbon ratio in the residual product (Fig. 1). By examining the chemical characteristics of a variety of biochars, biochar spans black carbon materials (Fig. 1), from soot to char (Spokas 2010). Soot formation, which is a function of the conditions during the thermal-chemical conversion process, can occur from biomass and is not exclusive to fossil fuel sources (e.g., Zamperlini et al. 1997). One particuar property of soot is that it contains no residual relic structures of the original feedstock material, due to the formation through combustion condensation reactions, typically from gas phase (Hedges et al. 2000). On the other hand, char and charcoal do possess relic structures as combustion residues (Hedges et al. 2000). However, the universaility in this black carbon terminology and analytical quantification of these divisions in the black carbon continuum are lacking (e.g., Hammes et al. 2007; Jones et al. 1997).

Black carbon materials have been applied to soils throughout human history to improve soil fertility and crop productivity (Lefroy 1883). One example is soil application of *wood ash* (solid residuals from fire pits or wood fired boilers) (Pitman 2006). Depending on the conditions of the reactions, wood ash can contain high carbon residuals, which would be classified as chars or charcoals in the black carbon continuum (Muse and Mitchell 1995; Pitman 2006). However, both negative and positive agronomic effects have been observed following amendments of black carbon materials to soils (Atkinson et al. 2010; Lehmann et al. 2003; Lehmann et al. 2011; Major et al. 2010; Novak et al. 2009; Spokas et al. 2011a). This suggests that current biochar application to soil is not a 'one-size fit-all paradigm', but instead requires careful consideration of the properties associated with each particular black carbon material and how those properties might remedy a specific soil deficiency (Novak and Busscher 2011).

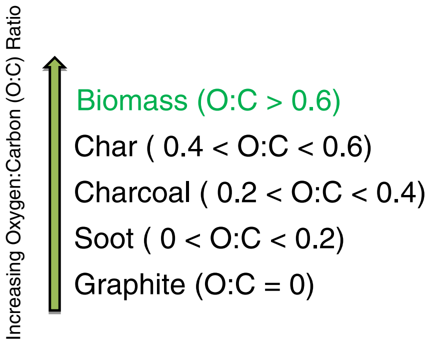

Fig. 1 Illustration of the various material forms within the black carbon continuum as defined by the range in the oxygen to carbon (O:C) ratio. Figure is adapted from Elmquist et al. (2006) and Hedges et al. (2000)

As previously stated, the name biochar does not provide information on the chemical nature or composition of the actual material, which varies widely. Biochar is composed of a heterogeneous collection of carbonized structures with random entrained inorganic elements as well as potential relic chemical structures from the parent feedstock, associated sorbed volatiles and ash (Brewer et al. 2009; Keiluweit et al. 2010; Spokas et al. 2011b). This variability is evident when one examines the organic and inorganic compositional data across biochar forms reported in the literature (Spokas 2010). Even biochar created from the same feedstock under equivalent pyrolysis conditions but in different units can result in chemically dissimilar black carbon materials (Table 1). Furthermore, different chemical and physical properties can exist as a function of particle size of the same black carbon material (Francioso et al. 2011; Nocentini et al. 2010). However, elemental compositional data of black carbon material does not adequately describe the variability in surface chemical functional groups (Boehm 1966; Boehm et al. 1964; Rodriguez-Reinoso et al. 1992) or core-structure that can occur (Novak et al. 2009; Novak and Busscher 2011).

Scope

Carbon surface functional groups will determine interactions between black carbon material and elements in the environment (Boehm 1994). Recent studies have hypothesized relationships in black

Table 1 Select physical and chemical composition data for *Pinus spp.* biochar created at nearly equivalent pyrolysis conditions

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)

pH was measured in water; surface area listed was determined by BET-N_2 gas

carbon sorption capacities of various compounds with respective general physical properties of the black carbon material, such as surface area and pore structure (Chen and Chen 2009; Chen et al. 2008; Chun et al. 2004; Kasozi et al. 2010; Lammirato et al. 2011). However, the actual chemical make-up of the surface groups on black carbon materials can exert more direction over chemical sorption than the previously mentioned physical parameters (Ania et al. 2007; Biniak et al. 1997; Fletcher et al. 2007; Franz et al. 2000; Hina et al. 2010; Mattson et al. 1969; Pereira et al. 2003; Pesavento et al. 2003; Qiu et al. 2008; Uchimiya et al. 2011). Only a limited number of recent studies (e.g., Azargohar and Dalai 2011; Cheng et al. 2006; Chun et al. 2004; Hina et al. 2010; Mukherjee et al. 2011; Nguyen et al. 2008; Qiu et al. 2009; Singh et al. 2010; Zhou et al. 2010) have characterized groups responsible for surface acidity. The composition of the surface groups is an important characteristic for the successful implementation of black carbon materials as a soil amendment at field scales, and could aid in understanding the aged or delayed response to biochar amendments occasionally observed (Ascough et al. 2011; Cheng et al. 2008; Major et al. 2010). Therefore, understanding a priori the interaction of black carbon materials on nitrogen is desirable, otherwise, it may have properties that could infringe on soil nitrogen availability (Atkinson et al. 2010) and inadvertently reduce crop yields (Van Zwieten et al. 2010).

It is becoming evident that black carbon materials have particular properties that can influence the soil nitrogen cycle and hence, nitrogen availability (Bailey et al. 2011; Clough and Condron 2010; Smith et al. 2010). Sorbed organic compounds on black carbon have been postulated to interfere with soil microbial nitrification and denitrification reactions (Clough et al. 2010; Spokas et al. 2010; Spokas et al. 2011b). Furthermore, black carbon has been observed to react with various nitrogen compounds (Guo et al. 2001; Singoredjo et al. 1993). In the recent study, Taghizadeh-Toosi et al. (2011) provided data showing the sorption of ammonia to black carbons produced at different conditions from the same pine species (*Pinus radiata*). This work is important, if not unique, from the standpoint of utilizing stable N isotopes to track its movement through the entire system (i.e., biochar, soil, and plant), which illustrated plant availability of the trapped nitrogen.

The ability of black carbon materials to sorb ammonia has been known for some time (Holmes and Beebe 1957). Previous work has shown a range of ammonia sorption capacities from <1 mg ammonia g^{-1} for non-oxidized black carbons to >60 mg ammonia g^{-1} for dry oxidized black carbon materials (Seredych and Bandosz 2007), compared with an average of 6 mg ammonia g^{-1} observed by Taghizadeh-Toosi et al. (2011). Sorbed ammonia at ambient conditions can exist in multiple forms on black carbon, which range from physical (e.g., aqueous dissolution, trapped in pores, intercalated between graphitic sheets) to chemical adsorption/reaction mechanisms (Boehm et al. 1994; Petit et al.

2009; Seredych and Bandosz 2007; Seredych et al. 2009; Seredych et al. 2010).

A review of the potential reactions between ammonia and black carbon materials are given in Jansen and van Bekkum (1994). Briefly, ammonia sorption on oxidized black carbon surfaces is known to react with surface oxygen groups leading to the formation of amines and amides at ambient conditions (Seredych and Bandosz 2007) and potential chemical ring structure development (e.g., pyrroles, pyridines, quaternary ammonium) at elevated temperatures (Jansen and van Bekkum 1994). Liquid water and water vapor can compete with ammonia for sorption sites (Seredych and Bandosz 2007; Seredych et al. 2009), whereas the water films present on black carbon increase dissolution of ammonia into the water film, creating ammonium ions (Seredych and Bandosz 2007).

At ambient conditions, ammonia can act as a Brownsted and/or Lewis acid, which leads to the formation of an ammonium salt or an amide following reaction with a surface carboxyl group (Fig. 2). After considering the reactions shown in Fig. 2, one can conceptualize the reasons for hysteresis in the desorption of ammonia (Holmes and Beebe 1957). Since ammonium salts could dissociate in water, the nitrogen would then be available as ammonium. On the other hand, additional chemical reactions would be required to liberate the nitrogen from the amide (Fig. 2). The presence of amides and amines on the surface of black carbon following exposure to ammonia was confirmed by X-ray photoelectron (XPS) and spectroscopic methods (Petit et al. 2009). In addition, the presence of sulfur groups (Petit et al. 2010; Seredych et al. 2010), alkali earth metals (Bandosz and Petit 2009), and other metals (Petit and Bandosz 2011) entrained within the black carbon structure increase sorption of ammonia and other compounds by catalyzing chemical reactions.

Since ammonia is an alkaline gas, the presence of acidic groups on the surface, and thus the pH of the carbon surface, would directly impact the removal processes (Bandosz 2006; Le Leuch and Bandosz 2007). Similar observations were reported by Taghizadeh-Toosi et al. (2011). In their study, the black carbon with the least impact on plant growth (presumably through the lowest contribution of nitrogen to the plant-soil system) possessed the highest pH. This means that there was an increase in hydroxyl ion (OH^-) availability, thus deprotonation of the carboxyl surface group occurs forming a resonance stabilized carboxyl anion (March 1992). This stabilized anion suppresses potential ammonia acidic reactions (Fig. 2). Additional studies have reported similar findings; ammonia sorption on black carbon was correlated to the quantity of surface acidic groups (Holmes and Beebe 1957; Huang et al. 2008; Molina-Sabio et al. 2011; Seredych and Bandosz 2007). Therefore, black carbon can sorb ammonia through several sorption and reaction pathways that are pH dependent.

Sorption of compounds on black carbon surfaces at low (ambient) temperatures are generally considered reversible (Leon and Radovic 1994). Holmes and Beebe (1957) suggested the reversibility of the ammonia sorption, and in fact, this reversibility is the basis for the use of black carbon as a chemical sensor for ammonia detection (Suehiro et al. 2003). This reversibility of ammonia trapping through the formation of ammonium salts could be the underlying mechanism explaining a portion of ^{15}N presence as ammonium in solution that was plant available as reported in Taghizadeh-Toosi et al. (2011), since the ^{15}N was detected in the plant roots and tissue

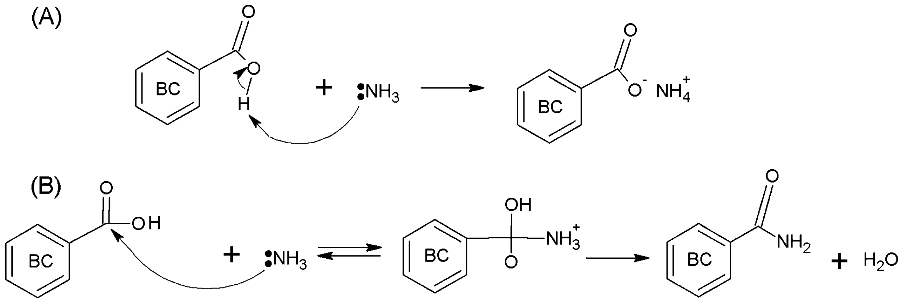

Fig. 2 Example reactions of a black carbon material (represented by the benzene ring labeled with BC) carboxyl surface group reacting with ammonia, with ammonia acting as **a** Brownsted or **b** Lewis acid. Figure is adapted from Jansen and van Bekkum (1994) and Seredych and Bandosz (2007)

materials. However, there was no detailed evaluation of other ^{15}N forms (i.e., nitrogen gas, nitric oxide, nitrous oxide, pyridines, amines, amides, etc.), besides extractable ammonium and nitrate.

Despite not investigating the eventual end form of the incorporated ^{15}N, Taghizadeh-Toosi et al. (2011) did demonstrate the stability of the total sorbed ^{15}N under a gas stream (of unknown humidity). Further chemical characterization or leaching potential of the ^{15}N was not performed. Therefore, the potential forms of the sorbed ^{15}N on the black carbon were not fully elucidated. However, mass balance calculations did reveal that the ^{15}N atom was not fully incorporated into the nitrogen pools associated with ammonium and nitrate (Taghizadeh-Toosi et al. 2011). In other words, the ^{15}N from ammonia is distributed among other nitrogen containing inorganic or organic compounds that have not been accounted for or identified.

Another noteworthy observation from Taghizadeh-Toosi et al. (2011) was the disappearance of extractable nitrate following exposure of the black carbon to ammonia (Fig. 3 in original manuscript), which could be a vital clue in the interaction of black carbon with the soil N cycle. Black carbon has been observed to sorb nitrate from solution (Mizuta et al. 2004). The exact mechanism for this disappearance is not known. However, the reaction of nitrate with black carbon materials should not be surprising, since it is the chemical basis for black powder (gunpowder) (Russel 2009). In addition, black carbon materials react with other nitrogen oxide forms (Guo et al. 2001; Singoredjo et al. 1993). The most critical component of this observation is the potential explanation for the observed reductions in nitrous oxide production (Spokas and Reicosky 2009; Van Zwieten et al. 2010; Yanai et al. 2007), which could be directly linked to reduced nitrate availability for denitrification. This interaction between black carbon and nitrate is speculative. However, the extreme economic and environmental value of potentially harnessing the ability of black carbon materials to reduce nitrous oxide formation requires further study.

Conclusions

In summary, certain nitrogen compounds can react with black carbon materials, even at ambient conditions. Past research has shown that ammonia can be sorbed to black carbon with hysteric effects on its release. The sorption and reaction potential of black carbon with nitrogen depends on the surface oxygen groups. Taghizadeh-Toosi et al. (2011) have demonstrated that some portion of sorbed ammonia on black carbon is plant available. The differences in the surface group chemistry of black carbon materials may be the main reason for mixed results in the literature with respect to black carbon's effects on the soil nitrogen cycle, but further studies are needed. However, higher concentrations of surface oxygen groups results in a black carbon with decreased carbon sequestration potential (Spokas 2010). Suggesting, a balance might be needed between the potential carbon sequestration length and the reactivity of the black carbon material with nitrogen compounds for current biochar efforts. Regardless, there needs to be an improved insight into the intricacies of black carbon's effect on the soil system, which would lead to consistent and predictable results for best management guidance for black carbon applications.

This knowledge begins with the recognition that biochar needs to be evaluated in context of the black carbon continuum, since biochar as a material is not new and is comprised of various forms of black carbon (Fig. 1). This recognition will extend our understanding to optimize biochar production and perhaps lead to the tailoring of the chemical surface properties to insure that we can effectively use biochar to improve the overall health and fertility of our soil resources. As highlighted by Clough and Condron (2010) and the observations of plant avaiable nitrogen in Taghizadeh-Toosi et al. (2011), the potential role of black carbon materials in the soil nitrogen cycle offers attractive opportunities for agriculture to reduce the environmental footprint of food, feed, fiber and renewable energy production. However, we need to understand the fundamental mechanisms behind these interactions in order to optimize new agricultural management systems to take advantage of black carbon's potential as an effective soil amendment.

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