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Review Article

Biochar: A Tool for Mitigating Climate Change - A Review

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Abstract

Biochar, a recalcitrant form of carbon made by the thermo-chemical conversion of biomass is increasingly discussed as a potential tool in areas such as climate change mitigation, carbon negative emission technologies, soil quality and food security (Lehmann and Joseph, 2009). The production and use of biochar as a soil additive may offer an opportunity to tackle a number of these issues simultaneously (Lee *et al*., 2010).The conversion of biomass carbon to biochar leads to sequestration of about 50% of the initial carbon compared to the low amounts retained after burning (3%) and biological decomposition (less than 10-20% after 5-10 years) (Lehmann *et al*. 2006). Rondon *et al*. (2005) reported a 50% reduction in N_2O emissions from soybean plots and almost complete suppression of CH_4 emissions from biochar amended acidic soils in the Eastern Colombian Plains. Biochar is produced by thermal decomposition of organic material in a low-oxygen environment, called pyrolysis. This stable charcoal-like material has the potential to contribute to the mitigation of climate change by increasing soil carbon (C) (Lehmann, 2007; Woolf *et al.*, 2010). In addition, biochar can increase crop yields (Biederman *et al.*,2013) and reduce water stress, which helps to adapt to climate change. Biochar also controls nitrogen (N) cycling (Clough *et al.*, 2013), especially N_2O emissions from soil are reduced on average by 54 % in lab studies and 28 % in field measurements (Cayuela *et al.*, 2014). Biochars are often alkaline and therefore increase soil pH after application (Joseph *et al.*, 2010). Denitrifying bacterial communities have the potential to increase their N_2Oreducing activity with increasing pH, which may reduce N_2O emissions from soils. Spokas and Reicosky (2009) also reported mitigation of net methane emissions in the forest nursery soil by the application of biochar.

Keywords: Biochar, Climatic Change, Green House Gases, Carbon Sequestration

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Introduction

Climate change which is the burning issue of twenty first century is largely caused by the increased concentrations of GHGs in the atmosphere which are occurring as a result of actions such as fossil-fuel burning and deforestation (IPCC, 2013). Atmospheric carbon dioxide (CO_2) concentrations have increased by 40 % from pre-industrial levels, reaching 391 ppm in 2011, with CO_2 accounting for 76 % of total anthropogenic GHG emissions in 2010 (IPCC, 2013). Increased GHG concentrations in the atmosphere affect the Earths radiative balance. Changes in this radiative balance cause temperature changes in the atmosphere and can cause subsequent changes in other climate systems. Climate change is likely to have impacts which will vary spatially and temporally, and will also be dependent on the manifestation and the magnitude of the changes. The potential impacts of increased GHGs on the climate system are projected, to different levels of certainty and understanding, in the latest report of the Intergovernmental Panel on Climate Change (IPCC) which assesses the current scientific knowledge and evidence on climate change. Warming of the climate has already been detected, with resulting reductions in cover of snow and ice and increased sea-level (IPCC, 2013). The future severity of climate change will depend on the concentrations of greenhouse gases reached, and the sensitivity of the climate to these concentrations. The potential manifestations of climate change, in addition to an increase in global mean surface temperature, include more frequent and more intense extreme weather events (including droughts and storms), increased or decreased precipitation locally and increased variability in weather. These impacts are expected to vary spatially and temporally with, for example, some regions expected to see impacts such as increased precipitation and other regions facing greater risk of drought. Changes in global mean surface temperature are already impacting food production systems, with, for example, reductions identified in production of wheat and maize in some main production regions.

The United Nations Framework Convention on Climate Change (UNFCCC) aims to develop international mechanisms to tackle climate change, with 195 parties to the convention. Mechanisms such as the Kyoto Protocol have been developed to achieve international goals such as emissions reductions and the development of adaptation funds. There is often a sluggish response to the forecasts of climate scientists with many national and international targets to reduce emissions falling short of the reductions deemed necessary by scientists. In light of the often slow response of governments, businesses and communities to reduce emissions, a number of methods of climate engineering have been proposed and are at varied levels of research and development. In terms of the engineering and physical impacts of the geoengineering technologies, they are often divided into two categories; solar radiation management and carbon dioxide removal technologies. Solar radiation management (SRM) technologies aim to reduce the amount of incoming short wave radiation through various methods including reflectors in space, surface albedo modification and stratospheric aerosol injection. SRM technologies do not reduce the build-up of CO_2 in the atmosphere so other effects such as ocean acidification would still occur, and the SRM technology would need to be continually deployed otherwise an abrupt change in climate may occur. Carbon dioxide removal (CDR) technologies aim to reduce the amount of CO_2 in the atmosphere, through negative emission technologies such as bioenergy with carbon capture and storage (BECCS), biochar, ocean fertilization and enhanced rock weathering. As mentioned previously, these SRM and CDR technologies are in different stages of research and development, with a number of potential regulatory barriers to deployment also existing. Biochar is one method of CDR which is currently deployed on the small scale, mainly for soil amendment purposes rather than CO_2 removal. The impact on soil and CO_2 sequestration potential of biochar is not currently fully understood with research into areas such as production methods, soil and plant effects, and the potential for larger scale deployment for CS currently dominating the biochar literature.

Biochar

Biochar is a fine-grained, carbon-rich, porous product remaining after plant biomass has been subjected to thermo-chemical conversion process (pyrolysis) at low temperatures (~350–600°C) in an environment with little or no oxygen (Amonette and Joseph, 2009). Biochar is not a pure carbon, but rather mix of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S) and ash in different proportions. The central quality of biochar and char that makes it attractive as a soil amendment is its highly porous structure, potentially responsible for improved water retention and increased soil surface area. It is important to note that there is a wide variety of char products produced industrially. For applications such as activated carbon, char may be produced at high temperature, under long heating times and with controlled supply of oxygen. In contrast, basic techniques for manufacture of charcoal (such as clay kilns) tend to function at a lower temperature, and reaction does not proceed under tightly controlled conditions. Traditional charcoal production should be more accurately described as ‘carbonization’, which involves smothering of biomass with soil prior to ignition or combustion of biomass whilst wet. Drying and roasting of biomass at even lower temperatures is known as ‘torrefaction’. Biochar from pyrolysis, and conventional charcoal and char share key characteristics which are related to carbon sequestration (long residence time) and soil fertility (soil conditioning effect). Intensive study of biochar-rich dark earths in the Amazon (terra preta), has led to a wider appreciation of biochar’s unique properties as a soil enhancer.

Preparation of Biochar

For as long as human history has been recorded, heating or carbonizing wood for the purpose of manufacturing biochar has been practiced (Emrich, 1985). There are different ways to make biochar, but all of them involve heating biomass with little or no oxygen to drive off volatile gasses, leaving carbon behind. This simple process is called thermal decomposition usually achieved from pyrolysis or gasification. Pyrolysis is the temperature driven chemical decomposition of biomass without combustion. In commercial biochar pyrolysis systems, the process occurs in three steps: first, moisture and some volatiles are lost; second, unreacted residues are converted to volatiles, gasses and biochar, and third, there is a slow chemical rearrangement of the biochar (Demirbas, 2004). Biochar can be produced at scales ranging from large industrial facilities down to the individual farm (Lehmann and Joseph, 2009), and even at the domestic level (Whitman and Lehmann, 2009), making it applicable to a variety of socioeconomic situations. Various pyrolysis technologies are commercially available that yield different proportions of biochar and bio-energy products, such as bio-oil and syngas. The gaseous bio-energy products are typically used to generate electricity; the bio-oil may be used directly for low-grade heating applications and, potentially, as a diesel substitute after suitable treatment (Elliott, 2007). To make biochar technology popular among the farmers, it is imperative to develop low cost biochar kiln at community level or low cost biochar stove at individual farmer's family level.The various methods which are in vogue are as under:

Heap Method

It is one of the traditional practices to generate income in various parts of India. In traditional method, a heap of pyramid like structure (earth kiln) is prepared by keeping wood logs and roots of plants for making charcoal. To allow the combustion products to escape, vents are opened starting from the top and working downwards. When smoke production is stopped, the cooling process is started by covering stack with a layer of moist earth. The cooling process takes several days before the earth is removed and the biochar produced is separated from the surrounding carbonized portions. Earth-mound kilns equipped with a chimney are most advanced among earth kilns. The ability to alter the chimney diameter according to the oxygen demand, and precise control of the draft of the chimney, which is dependent on height, results in better control of the pyrolysis process. Mostly fibre wastes of coconut, paddy straw or any available agriculture waste are used to prepare paste mixed with clay soil to cover the heap structure containing wood logs. Finally, it is covered with sand from outside and water is applied over it. Entire wood logs are converted into charcoal after burning inside the heap for 3-4 days.

Drum Method

Kilns that are built in place, typically are constructed from soil or other local materials, are located close to biomass resources and are small. They are economically viable if the cost of construction and transportation of biochar is lower than the cost of transporting and processing of biomass. In a modified method, char production is done by pyrolysis kiln. Venkatesh et al. (2010) developed a low-cost charring kiln by modifying oil drums at CRIDA, Hyderabad. A cylindrical metal oil drum (200 L capacity) with both sides intact was procured from local market and was modified for use as charring kiln. A square shaped hole of 16 cm x 16 cm was made on the centre of top side of the drum for loading the crop residues. On the opposite side (bottom) of the oil drum, a total of 36 holes each measuring 4 cm2 were made in concentric circles with a 5 cm2 hole at the center covering 20% of the total surface area of the bottom portion of the oil drum to facilitate uniform circulation of air from below.

Biochar Stove

More than two billion people in developing world still cook and heat their homes with primitive stoves or open fires by burning wood, straw, dung, or coal. These inefficient technologies cause air pollution that can harm respiratory and cardiac health, and exacerbate global warming. New stove technologies can produce both heat for cooking and biochar for carbon sequestration and soil building. Limited testing indicates that these stoves are much more efficient and emit less gas. The UN Environment Program now recognizes that Atmospheric Brown Clouds (ABCs) are a major contributor to climate change (UNEP, 2008). ABCs are caused by particulate emissions from inefficient combustion of biomass and fossil fuels and they include both black particles (soot) that heat the atmosphere by absorbing sunlight, and white particles that reflect sunlight and contribute to cooling. There are two basic types of stoves that can be used to produce charcoal and heat, the Top-Lit Updraft Gasifier (TLUD) and the Anila stove. There are many variations on the TLUD, but the biggest distinction is between natural draft TLUDs and fanforced TLUDs. The TLUD operates as a gasifier by creating a stratified pyrolysis/combustion regime with four basic zones: raw biomass, flaming pyrolysis, gas combustion and charcoal combustion (Anderson and Reed, 2004). The charcoal can be retained if it is removed at the proper time and quenched. Biomass fuel is placed between the two cylinders and a fire is ignited in the centre. Heat from the central fire pyrolyzes the concentric ring of fuel. The gases escape to the centre where they add to the cooking flame as the ring of biomass turns to char. The centre combustion chamber can be configured as either a rocket stove design (with a side opening door) or as a TLUD with primary combustion air entering from the bottom. The modern Anila stove was developed by U.N. Ravikumar, an environmentalist and engineer with the Centre for Appropriate Rural Technology (CART) at India's National Institute of Engineering. The key aims of the design are to reduce the indoor air pollution that results from cooking and to take advantage of the abundance of bio-residues found in rural areas in developing countries. The engineering principle the underlines the Anila stove is top lit updraft gasification, which essentially means that the hardwood fuel burns from the top down and simultaneously combusts the syngas that is released by the biomass. However, the yield of biochar is less in this method as compared to other methods of biochar preparation.

Figure 1 Drum method of biochar production. Source: https://www.pinterest.com/pin/61994932348630789/

Figure 2 Drum method of biochar production.Source: https://charcoalkiln.wordpress.com/2012/11/10/55-gallon-drum-charcoal-retort/

Methods of application

Like any other organic amendments, Biochar can be applied to soil by different methods including broadcasting, band application, spot placement, deep banding etc. However, the method of biochar application in soil depends on the farming system, available machinery and labor. Application of biochar by hand is well known, but is not viable on large-scale because of labor intensity and human health concerns due to prolonged contact with airborne biochar particulates. In developed countries, several large scale biochar trials have been conducted using a tractor propelled lime spreader. While the technology lends itself to careful calibration of output and uniform application, there are significant concerns surrounding environmental air quality and product loss due to wind and water erosion. Similarly, deep banding of biochar has been successfully implemented in several wheat fields in Western Australia. This low-impact application method deposits biochar directly into the rhizosphere, and may be viable for previously established crops, and perennial cropping systems. However, relatively low rates of application are technically possible with one pass (3 t/ha), and the process is relatively labour intensive. Additionally, issues with pneumatic clogging due to biochar particle size distribution and air quality remain. Mixtures may be applied for uniform topsoil mixing, or top-dressed in tree plantations without incorporation. Although the airborne dust fraction would be minimized, the tonnages of biochar application may be relatively low per ha, and additional equipment would be needed to incorporate applied compost into top soils thereby increasing costs and carbon footprint. Line trenching and backfilling may lend itself to high biochar application rates in soil for carbon sequestration while still increasing the agronomic performance of soils. Though labor and carbon intensive, the combination of high saturation rates and improved agronomic productivity may make the practice viable. However, like deep banding, it is unknown how well biochar migrates vertically through the soil profile.

Rate of application

It depends on many factors including the type of biomass used, the degree of metal contamination in the biomass, the types and proportions of various nutrients (N, P, etc.). Experiments have found that rates between 5-50 t/ha (0.5-5 kg/m^2) have often been used successfully. While no recommended application rates for biochar can be given, biochar should be applied in moderate amounts to soil. Rates around 1% by weight or less have been used successfully so far in field crops (Major, 2013). Research suggests that even low rates of biochar application can significantly increase crop productivity assuming that the biochar is rich in nutrients which that soil lacks (Winsley, 2007). In the case of piggery and poultry manure biochar, the biochar works both as an organic fertilizer and soil conditioner with agronomic benefits observed at low application rates (10 t/ha) (Chan et al. 2007). Application to soils of higher amounts of biochar may increase the carbon credit benefit; but, in nitrogen-limiting soils it could fail to assist crop productivity as a high C/N ratio leads to low N availability. Crop productivity benefits of higher biochar application rates can be maximized only if the soil is rich in nitrogen, or if the crops are nitrogen-fixing legumes. Therefore, application of biochar to soils in a legume-based (e.g. peanut and maize) rotational cropping system, clovers and lucernes is more beneficial. Biochar application rates also depend on the amount of dangerous metals present in the original biomass. The chance of bio-magnification also depends on the amount of a given metal in the soil.

Soil quality and fertility improvement

Biochar is a high carbon containing material (more than 50%) produced by heating of biomass in absence of oxygen. Biochar application to soil leads to several interactions mainly with soil matrix, soil microbes, and plant roots (Lehmann and Joseph, 2009). The types and rates of interactions depend on different factors like composition of biomass as well as biochar, methods of biochar preparation, physical aspect of biochar and soil environmental condition mainly soil temperature and moisture. Biochar can act as a soil conditioner by improving the physical and biological properties of soils such as water holding capacity and soil nutrients retention, and also enhancing plant growth (Sohi et al., 2010). The application of biochar in soils is based on its properties such as: (i) agricultural value from enhanced soils nutrient retention and water holding capacity, (ii) permanent carbon sequestration, and (iii) reduced GHG emissions, particularly nitrous oxide (N_2O) and methane (CH_4) release (Bracmort, 2010; Brown, 2009). Farmers will be motivated to apply biochar on their farms if these benefits can be demonstrated explicitly. At the local scale, soil organic carbon levels shape agro-ecosystem function and influence soil fertility and physical properties, such as aggregate stability, water holding capacity and cation exchange capacity (CEC) (Milne et al., 2007). The ability of soils to retain nutrients in cation form that are available to plants can be increased using biochar. The addition of biochar to agricultural soils is receiving considerable interest due to the agronomic benefits it may provide (Quayle, 2010). Several authors have reported that biochar has the potential to: (i) increase soil pH, (ii) decrease aluminum toxicity, (iii) decrease soil tensile strength, (iv) improve soil conditions for earthworm populations, and (v) improve fertilizer use efficiency.

Effect of biochar on different soil properties

Factor Impact Source Cation exchange capacity 50% increase (Glaser et al., 2002) Fertilizer use efficiency 10-30 % increase (Gaunt and Cowie, 2009) Liming agent 1 point pH increase (Lehman and Rondon, 2006) Soil moisture retention Up to 18 % increase (Tryon, 1948),Crop productivity 20-120% increase (Lehman and Rondon, 2006), Methane emission 100% decrease (Rondon et al, 2005), Nitrous oxide emissions 50 % decrease (Yanai et al., 2007), Bulk density Soil dependent (Laird, 2008), Mycorrhizal fungi 40 % increase (Warnock et al., 2007), Biological nitrogen fixation 50-72% increase (Lehman and Rondon, 2006).Black carbon may significantly affect nutrient retention and play a key role in a wide range of biogeochemical processes in the soil, especially for nutrient cycling. Chan et al. (2007) studied the influence of rate and type of biochar produced from poultry litter under different conditions on soil quality parameters. Biochar addition to the hard-setting soil resulted in significant but different changes in soil chemical and physical properties, including increase in C, N, pH and available P, and reduction in soil strength. The different effects of the two biochars (one produced at 450°C and the other at 550°C) could be related to their different characteristics. Significantly different changes in soil biology in terms of microbial biomass and earthworm preference properties were observed between the two biochars. Mankasingh et al. (2011) conducted a plot-scale evaluation of biochar application to agricultural soils in Tirunelveli, Tamil Nadu, India, to investigate the potential of biochar to improve soil fertility and moisture content. Several locally available feed stocks (rice husk, cassia stems, palm leaves and sawdust) were analysed as proposed soil amendments so that no single biomass material is depleted. The biochars from different biomass feedstock contained >20% C and were high in macro- and micronutrients. The results suggest that an application rate of 6.6 metric tons cassia biochar/ha was enough to initiate C-accumulation, which is reflected in an increase in organic matter and a net reduction in soil bulk density. Significant changes in soil quality, including increase in pH, organic carbon and exchangeable cations as well as reduction in tensile strength were observed at higher rates of biochar application, i.e. > 50 t/ha. Reduction in tensile strength and increase in field capacity of hard-setting soil were the most significant findings (Chan et al., 2007). Biochars can potentially increase the cation exchange capacity (CEC) of soils especially for highly weathered, nutrient-poor sandy soils; however, this is dependent on biochar properties and aging of applied biochar in the soil. The published data suggest that biochars from woody materials tend to provide low CEC values, while non-woody plant materials such as sugarcane trash (leaf) or tree bark tend to have higher CEC values.

Biochar can be used by farmers to control the pH of soil and also to reduce lime applications (Rodriguez et al., 2002).When mixed with organic matter, biochar can result in enhanced retention of soil water as a result of its pore structure which contributes to nutrient retention because of its ability to trap nutrient rich water within the pores (Oguntunde et al., 2008).Biochar has an even greater ability than other soil organic matter to adsorb cations per unit carbon (Sombroek et al., 1993), due to its greater surface area, greater negative surface charge, and greater charge density (Liang et al., 2006). In contrast to other organic matter in soil, biochar also appears to be able to strongly adsorb phosphate, even though it is an anion, although the mechanism for this process is not fully understood. Thus, biochar application could provide a new technology for both soil fertility and crop productivity improvement, with potential positive and quantifiable environmental benefits, such as carbon trading (Bracmort, 2010 and Yeboah et al. 2009).Biochar has a relatively structured carbon matrix with a medium-to high surface area, suggesting that it may act as a surface sorbent which is similar in some aspects to AC. Black carbon surfaces are porous with apolar and aromatic surfaces. They have a high surface to volume ratio and a strong affinity to non-polar substances such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans (PCDD/Fs), PCBs, and PBDEs.

Biochar for climate change mitigation

Carbon sequestration

Soil Carbon sequestration is the removal of atmospheric CO_2 through photosynthesis to form organic matter, which is ultimately stored in the soil as long-lived, stable forms of C. The global carbon cycle is made up of flows and pools of carbon in the Earth’s system. The important pools of carbon are terrestrial, atmospheric, ocean, and geological. The carbon within these pools has varying lifetimes, and flows take place between them all. Carbon in the active carbon pool moves rapidly between pools (Lehmann, 2007). In order to decrease carbon in the atmosphere, it is necessary to move it into a passive pool containing stable or inert carbon. Biochar provides a facile flow of carbon from the active pool to the passive pool. In comparison to burning, controlled carbonization converts even larger quantities of biomass organic matter into stable C pools which are assumed to persist in the environment over centuries. The conversion of biomass carbon to biochar leads to sequestration of about 50% of the initial carbon compared to the low amounts retained after burning (3%) and biological decomposition (less than 10-20% after 5-10 years) (Lehmann et al. 2006). This efficiency of carbon conversion of biomass to biochar is highly dependent on the type of feedstock, but is not significantly affected by the pyrolysis temperature (within 350-500°C common for pyrolysis). According to Gaunt and Lehmann (2008), terra preta soils suggest that biochar can have carbon storage permanence in the soil for many hundreds to thousands of years. Large amounts of carbon in biochar may be sequestered in the soil for long periods estimated to be hundreds to thousands of years While biochar mineralizes in soils, a fraction of it remains in a very stable form (Schmidt and Noack, 2000); this property of biochar provides it the potential to be a major carbon sink. Compared with other terrestrial sequestration strategies, such as afforestation or re-forestation, carbon sequestration in biochar increases its storage time (Ogawa et al. 2006 and Sohi et al. 2010). About 12% of the total anthropogenic carbon emissions by landuse change (0.21 Pg C) can be offset annually in the soil, if the slash-and-burn system is replaced by the slash-and-char system. The principal mechanisms operating in soils through which biochar entering the soil is stabilized and significantly increase its residence time in soil are intrinsic recalcitrance, spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces (Sollins et al., 1996).Among the biochars, maize biochar showed lowest carbon mineralization suggesting its greater potential for long-term carbon sequestration. Application of biochar showed highest amount of carbon in soil under wheat-pearl millet cropping system. The findings of a recent modeling study (Woolf et al., 2010) reported that biochar amendments to soil, when carried out sustainably, may annually sequester an amount of C equal to 12% the current anthropogenic CO_2 emissions. They estimate that the maximum sustainable technical potential for carbon abatement from biochar is 1-1.8 giga ton (Gt) C per year by 2050. Technical estimates of the potential for biomass pyrolysis coupled with soil storage to sequester carbon suggest that several hundred giga tons of carbon emissions could be sequestered or offset by 2100, which is a large fraction of the total needed to mitigate global climate disruption. Furthermore, it is relatively simple to verify the benefits that can be derived from the application of biochar as soil amendment. It is also easy to monitor carbon sequestration as a climate change mitigation measure for national carbon accounting (Lehmann et al. 2006).This can be done by using the income generated and the quantity of carbon that has been sequestered. Production and application of biochar to farm soils can tackle many global and domesticpolicy issues. Nevertheless, the application of biochar at the farm level is discouragingly slow, largely due to financial constraints.

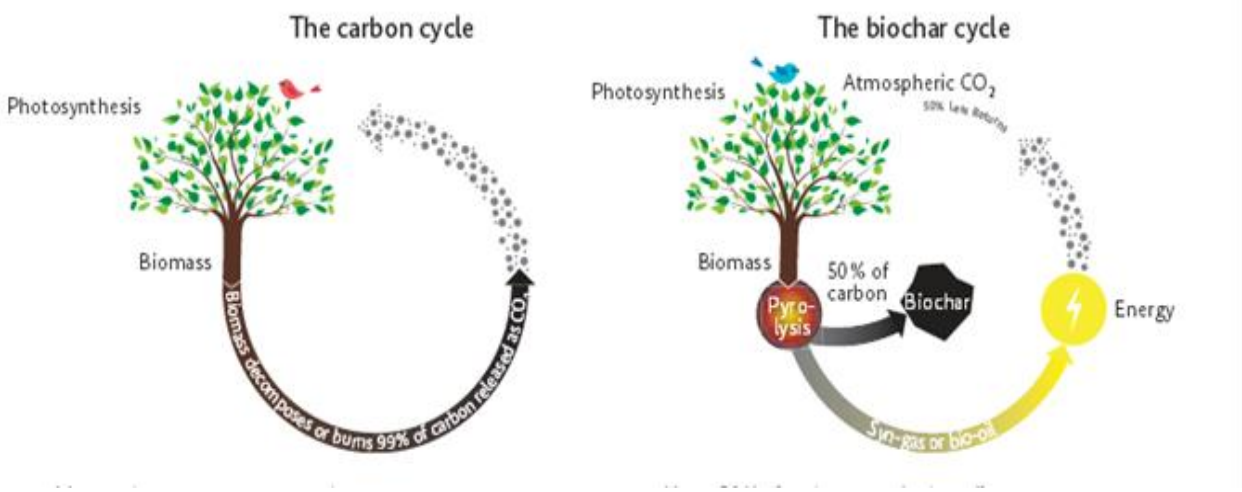

Figure 3 Carbon cycle versus the biochar cycle. Source: adapted from Wilson(2013) based on Biochar Solutions Inc. (2011)

Mitigation of greenhouse gas emissions

Effect of biochar on N_2O emission

The flux of N_2O from soil is controlled by biological and abiotic processes and is the net result of production and consumption. Butterbach-Bahl et al (2013) reviewed key processes that contribute to N_2O formation in soils. These include: (i) chemical decomposition of hydroxylamine during autotrophic and heterotrophic nitrification; (ii) chemodenitrification of soil NO_3 - and abiotic decomposition of ammonium nitrate in the presence of light, humidity and reactive surfaces; (iii) nitrifier-denitrification within the same nitrifying microorganism; (iv) coupled nitrification–denitrification by distinct microorganisms (production of nitrate [NO_3 -] by nitrite [NO_2 -] oxidizers, which is immediately denitrified in situ by denitrifiers); (v) denitrification conducted by organisms capable of using nitrogen oxides as alternative electron acceptors under oxygen (O_2)-limiting environmental conditions; (vi) co-denitrification of organic N compounds with NO; and (vii) NO_3 - ammonification or dissimilatory NO_3 - reduction to ammonium (NH4 +). It is known that metal cations, particularly iron (Fe) and tin (Sn), can catalyse chemodenitrification The importance of these additional transformation pathways for typical soils has been historically assumed to be trivial due to the low concentrations of these metals. In summary, the relative contribution of each of these processes to the total N_2O emissions depends on soil characteristics (texture, available carbon (C), pH, microbial activity), temperature and water content. Biological denitrification is often regarded as the principal source of N_2O emissions, which has been described as a biologically 'broad process' involving nitrifiers, N2 -fixers (symbiotic as well as non-symbiotic), thiosulfate oxidizers, methylotrophs, aerobic and anaerobic taxa, heterotrophs, autotrophs, photosynthetic bacteria and extremophiles. During denitrification, NO_3 - is sequentially reduced to N_2 via a set of four enzymes; nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor) and nitrous oxide reductase (Nos). These are usually induced under increasingly anaerobic conditions.The enzymes sequentially convert NO_3 - to NO_2 - (Nar), NO_2 - to NO (Nir), NO to N_2O (Nor) and N_2O to N_2(Nos), respectively.

The role of biochar in controlling N_2O emissions

The biotic and abiotic mechanisms responsible for biochar induced mitigation of soil N_2O emissions remain elusive. These mechanisms will most likely be a function of both the biochar and soil properties and their interaction. Biochar application in soil may affect N_2O emissions by changing: (i) soil physical properties (e.g. gas diffusivity, aggregation, water retention) (Quin et al, 2014); (ii) soil chemical properties (e.g. pH, Eh, availability of organic and mineral N and dissolved organic C, organomineral interactions); and (iii) soil biological properties (e.g. microbial community structure, microbial biomass and activity, macrofauna activity, N cycling enzymes). Such changes in soil properties could influence N mineralization-immobilization, turnover and nitrification or denitrification processes in the soil. Many of these potential effects on soil properties may relate to the chemical composition of biochar (low molecular weight organic compounds, aliphatic to aromatic C ratio, intrinsic N content and form, ash content, acid neutralizing capacity) and physical characteristics (specific surface area, sorption properties, particle size). Over time, the developing negative charge on biochar surfaces (Cheng et al 2006) and subsequent interactions with native organic matter and clay minerals may further contribute to the mitigation of soil N_2O emissions. Specific mechanisms that may decrease or increase N_2O emissions following biochar application to soil are described below. The relative change (i.e. decrease, increase or no change compared to a control) in N_2O emissions resulting from biochar application will depend on the net effect of several abiotic and biotic mechanisms operating concurrently. The mechanisms of biochar interactions with N_2O have rarely been critically evaluated and have generally been proposed as ‘hypotheses’.

Biochar limits N availability in soil

Biochar is generally a high C-to-N ratio material; it comprises relatively labile, low molecular weight organic compounds, albeit in much smaller quantities cf. parent feedstock, and its porous structure may provide a suitable habitat for microorganisms. These characteristics are suitable for biochar to support microbial growth and activity and may induce N immobilization in soil as the microorganisms utilize C from the volatile or labile components within biochar. This mechanism would decrease bioavailable N in soil, thus decreasing N_2O emissions via limiting substrates for nitrification and denitrification processes. Biochar may also tighten the soil N cycling through a range of other mechanisms such as: (i) direct sorption of NO_3 -, NH_4 +, organic N species and enzymes on biochar surfaces and within pores and (ii) biochar induced organo-mineral associations. These effects may be a function of feedstock type and production conditions, which can influence the pore structure and the charge characteristics of biochars. Particularly the electrostatic adsorption of NH4 + on biochar may increase as negatively charged functional groups develop on biochar surfaces during oxidation in soil. Singh et al (2010) found a significant decrease in the leaching of NH4 +-N following some ageing of biochar in soil. Furthermore, biochar induced organo-mineral associations may stabilize or decrease mineralization of native or added organic matter in soil which may reduce bioavailability of organic N in soil. Biochar changes bioavailable C supply in soil. The reduction of NO_3 - by denitrifiers requires a readily available C supply with 30 moles of C required for the complete denitrification of 24 moles of NO_3 - (Saggar et al, 2013). Biochar is generally not an important source of bioavailable (labile) or soluble organic C, relative to that of uncharred organic matter. The intrinsic labile C in biochars varies with feedstock type and production conditions, with manure-based or lower temperature biochars possessing higher labile C than plant-based or higher temperature biochars. Biochar can also contain a variety of other organic compounds sorbed to the biochar. The intrinsic and sorbed labile organic compounds in biochar may support microbial denitrification to some extent. However, the post-production handling also greatly impacts these sorbed species, with longer storage times typically resulting in lower quantities of labile C observed on the biochar (Spokas et al, 2011). On the other hand, biochar may decrease native labile organic C in soil by enhancing microbial growth and respiration and consequently causing positive priming of soil organic C.The rapid increases in microbial respiration caused by biochar could potentially induce localized sites of anaerobiosis to favour denitrification (Harter et al, 2013). This could be particularly important for situations of nearto-full anaerobic conditions, which could otherwise affect the activity of O_2 -sensitive N_2O reductases. Wang et al, 2013 observed significantly increased gene and transcript copy numbers of the nosZ-encoded bacterial N_2O reductase in a composting incubation study. Similarly, Harter et al (2013) found that addition of biochar to a soil changed the denitrifier community composition by promoting the growth and activity of N_2O-reducing bacteria expressing nosZ relative to nirS- and nirK-containing denitrifiers. Harter et al (2013) concur that conditions, such as decreased bioavailability of key electron acceptor (NO_3 -) and donor (NH_4 +, dissolved organic C) species and an increase in soil pH, together with the electron shuttling property of biochar would enhance the abundance and gene expression activity of nosZ and consequently promote reduction of N_2O to N_2 in biochar-amended soil. The impact of biochars on nosZ gene abundance was, however, dependent upon soil and biochar propertiesas the increased nosZ gene abundance was only observed in a sandy soil, with little if any impact observed on more fertile soil types. This emphasizes the importance of understanding mechanisms across different soils to draw conclusions on the potential for biochar to mitigate N_2 O emissions.

Bioavailable C in biochar is oxidized by N_2O

Avdeev et al (2005) reported that a range of aromatic and aliphatic compounds are oxidized by N_2O. It is hypothesized that an O atom is transferred through the 1,3-dipolar cyclo-addition of N_2O to the C=C bond with the resulting intermediate decomposing to yield a ketone and N_2. Biochar contains a range of aromatic and non-aromatic compounds on their internal and external surfaces. Therefore, it is feasible that these compounds may be oxidized as described by Avdeev et al (2005), resulting in the reduction of N_2O. However, these organic compounds are not particularly stable and are degraded in soil. Therefore, the long-term benefits of this N_2O mitigation mechanism would decline over time as these compounds are oxidized or metabolized by soil microbiota. However, biochar is also capable of sorbing organic compounds in soil, thus potentially extending the efficacy of this proposed mechanism by replenishing the supply of aromatic compounds on the biochar surface.

Biochar increases soil pH

Biochar can be alkaline and the extent of alkalinity varies depending on feedstock type and pyrolysis temperature. Oxygen-containing organic functional groups, ash (metal oxides) and carbonate minerals are the main forms of alkalinity in biochars (Yuan et al, 2011). Biochar may also contain significant amounts of soluble base cations. More recently, fused-ring aromatic structures and aromatic C-O groups have been shown to correlate positively with the pH of biochar. Thus, biochar possessing significant alkalinity can be used to ameliorate acidity and increase soil pH. Through the combined addition of alkalinity and low-molecular organic compounds to soil through biochar, together with biochar enhanced soil microbial respiration and its electron shuttling property biochar may increase the activity of nosZ-containing microorganisms. These changes in the denitrifying community were observed by Harter et al (2013), thus facilitating completion of denitrification ($N_2O \rightarrow N_2$) and decreasing the N_2O product ratio of denitrification.

Biochar affects gas diffusivity and aeration

Soil structure, in particular porosity and pore architecture, regulates movement and storage of water and gas into and within soil. Biochar can increase soil porosity directly by reducing bulk density.Using micro computer tomography (µCT scanner), Quin et al (2014) similarly demonstrated that a wood-based biochar increased porosity over time with concurrent increases in pore size and connectivity in two clayey soils, but not in a sandy soil. The increase in soil aeration as a function of biochar type and application rate, reduces anaerobic micro-sites and consequently may result in decreases in N_2O emissions by minimizing denitrification.

Microbial inhibitors

Sorbed organic compounds on biochar may transiently inhibit the activity of nitrifiers and denitrifiers and decrease N_2O emissions. Biochar is known to possess a very complex and heterogeneous assortment of sorbed organic compounds and can change the bioavailability of organic compounds present in soil (Martin et al, 2012). These compounds are assumed to sorb to the biochar as a result of their formation during pyrolysis and can have both positive and negative impacts on plants and microbial populations. Understanding the role of trace organic compounds in altering soil processes is still in its infancy. A current hypothesis from research on natural wood smoke and fires is that there are chemical compounds that are plant stimulants present on charred materials. These stimulatory compounds are produced during the thermal pyrolysis of biomass, which can correspondingly trigger/ stimulate seed germination. On the other hand, some of the compounds associated with biochar can also be inhibitory to both plant and microbial activity and could be linked to the positive suppression of plant pathogens. Nevertheless, these sorbed species are not the sole mechanism behind the emission mitigating actions of biochar in soils as other soil chemical, physical and microbial alterations also occur which are specific to the particular soil type, biochar and environment.

Sorption of N_2O onto biochar

Biochar has been shown to directly sorb gases including N_2O. Cornelissen et al (2013) found under sterilized and anhydrous conditions binding of N_2O was an order of magnitude higher than either metal oxides or organic matter (extracted organic matter or plant litter). They also found that Langmuir maximum sorption capacities (Qmax; cm3 g-1) were greatest for the biochars produced above 350°C and sorption affinities increased on pine wood biochars between 350°C and 700°C. It is important to note that the surface area of the low-temperature pine biochar was 60m2 g-1 whereas the high temperature biochar was 176m2 g-1. Due to the high concentration of functional groups associated with biochars produced at 350°C the mechanisms of N_2O sorption are probably different to those of a high temperature biochar. The authors noted that these sorption capacities would change in a moist environment where nanometer pores become filled with water. Water has a high solubility for N_2O (ca. 0.12g in 100 mL at 20°C) and it will be important to determine whether this solubility and mechanism for transportation of N_2O impacts on surface emissions. More importantly soil water will have a range of cations and anions, colloidal clay particles and dissolved organic matter that have high concentrations of functional groups. These components in soil water may interact with biochar and consequently influence its N_2O sorption capacity.

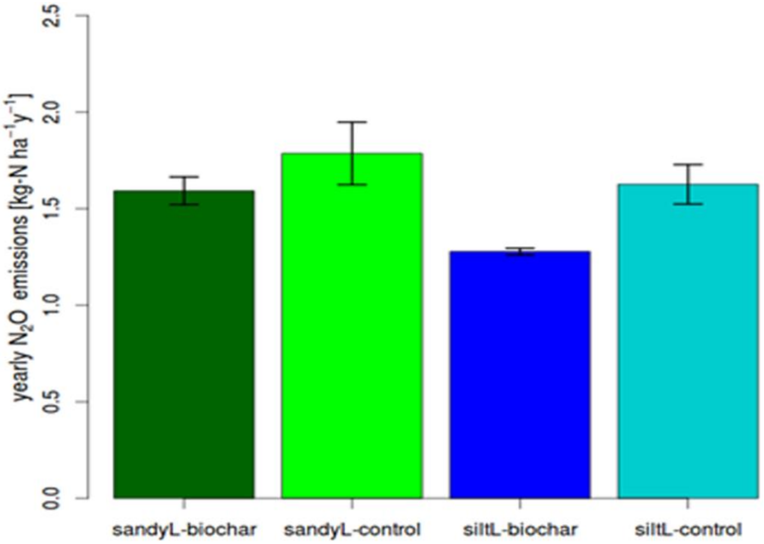

Figure 4 Effect of biochar on the N_2O emission. Source: http://iopscience.iop.org/article/10.1088/1748-9326/11/8/084013/meta

Biochar impacts net CH_4 fluxes

Biochars with a higher number of carboxyl groups can also adsorb NH_3, lowering the NH_4 concentration in soils. Thus alleviation of NH_4 + inhibition of the methane monooxygenase (MMO, the first enzyme of the methanotrophic pathway) may have been prevented by the presence of biochar to a larger extent than in the control (Karhu et al, 2011). biochar addition include changes in the Archaeal methanogenic or bacterial methanotrophic community and activity. Feng et al (2012) investigated microbial abundance and activity in rice mesocosms over one growing season. They found that methanogenic activity and abundances were unchanged, but that methanotrophic abundances were greatly increased, explaining the observed lowering in net CH_4 emissions. Soil methanotrophs are the only known biological sink for atmospheric CH_4, which oxidise CH_4 and produce CO_2 as a by- product. Biochar addition has been observed to increase soil methanotrophic activity in one published study; Karhu et al., (2011) observed increased soil CH_4 uptake within an arable soil following biochar amendment that they put down to increased soil aeration. Soil methanotrophs require oxygen as a terminal electron acceptor and their activity is highest at around 60% WFPS and decreases above this moisture content (Karhu et al., 2011). As previously discussed, biochar addition to soil may decrease soil albedo and has been hypothesised to increase soil temperature and typically, high pH biochar increases the pH of the soil it is added to (Lehmann et al., 2011). Methanogenic activity increases with temperature (up to 40°C) and is at a maximum at close- to- neutral pH, while soil methanotrophy increases with temperature up until 10°C, (Castro et al., 1995) and methanotrophic activity is at a maximum at a close- to- neutral pH. Biochar amendment affects the methanogenic archaeal community compositions in paddy soils. No statistically significant differences in methanogenic activities are noted in the rhizosphere of biochar amended and control soil during the rice growing seasons. But in a field experiment biochar addition at the rate of 9 t ha−1 significantly decreased CH_4 emission without affecting the CO_2 and N_2O emissions (Karhu et al. 2011). But in a laboratory incubation experiment the CH_4 emission from paddy soil was completely inhibited compared with the non-amendment control soil. It has been observed that soil CH_4 emission in response to the biochar amendment may vary with biochar types and properties. Most of the studies supported that decreasing methanogenic activity in paddy soil amended with biochar could be due to the increase in porosity of soil in presence of biochar that may inhibit the growth and multiplication of anaerobic methanogens.

Conclusion

Climate change is one of the burning issue of 20^{ist} century discussed along the length and breadth of the world and there is a huge concern among the scientific community of the world in this regard. It not only have a detrimental effect on the animal kingdom but also plant kingdom is worst victim of it. This has ignited the minds of nature lovers and think tanks all across the world and a number of combating strategies have been put on table to solve this grave problem. Biochar is one such strategy which can act as a revolutionary tool in mitigating the climatic change. The escape of three potent greenhouse gases viz $CO_{2,}$ CH_4 and N_2O into the atmosphere can be curtailed by incorporating biochar into the soil. It not only traps the carbon into the soil by the process of carbon sequestration but also minimizes the production of methane gas from marshy and inundated soils like paddy fields. Besides these, it also helps in the sorption of N_2O and there by restricts its escape into the atmosphere. Besides the above mentioned facts it also improves the physical, chemical and biological properties of soil and also its production and application does not require too much expertise and even a lay man can practice it at ground level. But at the same time a deep research has to be done in this regard so that it can be proved as a unique tool for climate change mitigation.

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