Bio-energy in the black

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At best, common renewable energy strategies can only offset fossil fuel emissions of CO_2 – they cannot reverse climate change. One promising approach to lowering CO_2 in the atmosphere while producing energy is biochar bio-energy, based on low-temperature pyrolysis. This technology relies on capturing the off-gases from thermal decomposition of wood or grasses to produce heat, electricity, or biofuels. Biochar is a major by-product of this pyrolysis, and has remarkable environmental properties. In soil, biochar was shown to persist longer and to retain cations better than other forms of soil organic matter. The precise half-life of biochar is still disputed, however, and this will have important implications for the value of the technology, particularly in carbon trading. Furthermore, the cation retention of fresh biochar is relatively low compared to aged biochar in soil, and it is not clear under what conditions, and over what period of time, biochar develops its adsorbing properties. Research is still needed to maximize the favorable attributes of biochar and to fully evaluate environmental risks, but this technology has the potential to provide an important carbon sink and to reduce environmental pollution by fertilizers.

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The energy demands of modern societies are steadily increasing. Today, much of this demand is satisfied by fossil fuels, such as gas, oil, and coal, energy resources that are not renewable, and which will eventually be exhausted. The first glimpse of the energy crisis to come has been the price increases at the gas station. Additional concerns include the dependence on regionally concentrated supplies and related international conflicts, and the emission of greenhouse gases associated with the use of fossil fuels (IPCC 2001). There is ample evidence to show that the Earth is warming due to anthropogenic emissions of greenhouse gases, with climatic consequences including desertification, a rise in ocean levels, and increased numbers of hurricanes (IPCC 2001).

In addition to urgently needed energy conservation, alternative forms of energy are required to decrease dependence on fossil fuel reserves and to avoid or decrease CO_2 emissions. Wind and solar energy, hydropower, geothermal energy, and bio-energy can all help society to reach these goals (Turner 1999). However, none of these technologies will be able to reverse climate change.

A variant of bio-energy may not only be carbon-neutral, but carbon-negative. Use of this type of energy would not only avoid contributing to climate change, but may actually draw CO_2 from the atmosphere, thereby reducing global warming. Using pyrolysis in combination with a land application of a biochar residue, carbon sequestration, and renewable energy, are not alternatives to one another (Turner 1999), but may become a joint strategy.

In a nutshell:

- Current plans to replace fossil fuels with renewable energy may reduce emissions, but will not reverse climate change
- A new strategy obtains energy from gases produced by thermally degrading trees, shrubs, grasses, or organic wastes – very similar to charcoal production – in a process called pyrolysis, with charcoal, or "bio-char", as the end product
- The proposed approach of combining pyrolysis for energy production with bio-char additions to soil takes advantage of bio-char's proven longevity and ability to retain cations, actively draw CO_2 from the atmosphere, regenerate degraded lands, and reduce environmental pollution
- To evaluate the economic and environmental benefits of bio-char, precise knowledge of its longevity, and of the time and conditions needed to develop its adsorptive properties, is needed
- A full environmental risk assessment should be conducted to show the level of emissions and the impacts on soil associated with this technology

The basic concept of biochar bio-energy

Pyrolysis is one of many technologies to produce energy from biomass (Bridgwater 2003). What distinguishes pyrolysis from alternative ways of converting biomass to energy is that pyrolysis produces a carbon-rich, solid by-product, biochar (Figure 1). Under complete or partial exclusion of oxygen, biomass is heated to moderate temperatures, between about 400 and 500°C (giving the process the name "low-temperature pyrolysis"), using a variety of different reactor configurations. At these temperatures, biomass undergoes exothermic processes and releases a multitude of gaseous components in addition to heat (Czernik and Bridgwater 2004). Both heat and gases can be captured to produce energy carriers such as electricity, bio-oil, or hydrogen for household use or powering cars. In addition to energy, certain valuable co-products

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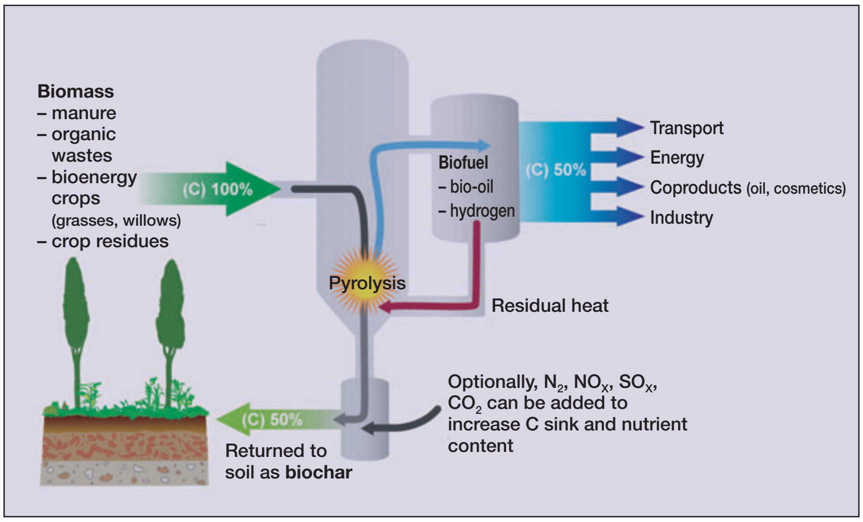

Figure 1. *Concept of low-temperature pyrolysis bio-energy with biochar sequestration. Typically, about 50% of the pyrolyzed biomass is converted into biochar and can be returned to soil.*

can be obtained, including wood preservative, meat browning, food flavoring, adhesives, or specific chemical compounds (Czernik and Bridgwater 2004). Both slow and fast pyrolysis can be used. High-temperature pyrolysis (typically above 700°C), which is more commonly called gasification, is less appropriate in this context, as it yields much lower amounts of biochar, or none at all.

Biochar is the residue of pyrolysis and is often used to pre-dry biomass feedstock or is sold as charcoal briquettes. A novel approach is to explore the value of this by-product when added to soil. Two aspects of biochar make it valuable for this purpose: (1) its high stability against decay and (2) its superior ability to retain nutrients as compared to other forms of soil organic matter. Three environmental benefits arise from these properties: (1) mitigation of climate change, (2) improvement of soils, and (3) reduction of environmental pollution. These benefits, and the specific properties of biochar that yield them, are described below. Important constraints include the long time periods and specific conditions required for the biochar to become an efficient adsorber; these are discussed below. Future research needs are also identified.

Biochar properties

Stability

Biochar has long been used to date archaeological deposits by quantifying its carbon-14 decay (Arnold and Libby 1951), since biochar and other, more aromatic black carbons persist in the environment longer than any other form of organic carbon. Finely divided biochar has even remained in soils in humid tropical climates, such as the Amazon, for thousands of years (Sombroek *et al.* 2003), resisting the rapid rates of mineralization common to organic matter in these environments and producing a distinct black color (Figure 2). Such biochar is typically older than any other form of carbon in soils (Pessenda *et al.* 2001).

Despite this high level of resistance, we know that biochar will ultimately be mineralized to CO_2; otherwise, soil organic matter would be dominated by biochar accumulated over geological time scales (Goldberg 1985). Very little is known about the half-life of biochar for two reasons: first, the recalcitrance of biochar greatly depends on a multitude of factors, including the type of biomass used for pyrolysis, the production conditions, soil properties, and climate (Lehmann *et al.* 2006). Some biochars may decompose relatively rapidly in soils, while others persist for millennia, so that more information is needed about the behavior of biochars in soil. Secondly, quantification of long-term stability requires long-term observations, exceeding the periods feasible in traditional experiments. Extrapolations from short-term incubation or field experiments are hampered by:

- *The heterogeneous chemical nature of biochar.* Charred biomass consists not only of recalcitrant aromatic ring structures, but also of more easily degradable aliphatic and oxidized carbon structures (Schmidt and Noack 2000). The range of carbon forms within a biochar particle may depend on the carbon properties of the plant cell structure, on the charring conditions, and on the formation process (by either condensation of volatiles or by direct charring of plant cells). The consequence of this heterogeneity is that some portions of biochar may indeed be mineralized very rapidly, as are aliphatic carbon forms (Cheng *et al.* 2006). An extrapolation from relatively easily mineralizable carbon forms to the entire biochar may therefore lead to erroneous projections.
- *The particulate form of biochar* (Figure 3). Because biochar exists as particulates, biotic or abiotic decay must be initiated on its surface. Such surface oxidation may be initiated quite rapidly (ie within a few months; Cheng *et al.* 2006), but is restricted to the outer areas of a particle, even after several hundred years in soils (Lehmann *et al.* 2005b). Quantification of the decomposition of fresh biochar by short-term experiments may therefore lead to an overestimation of long-term decay.

Biochar's particulate form also clearly distinguishes it from other stable forms of organic matter, which are commonly perceived as macromolecules or macromolecular associations entrapped in fine pores, adsorbed to mineral surfaces, or occluded in aggregates. Particulate organic matter, on the other hand, is mostly unprotected by mineral association and is therefore easily mineralizable

(Golchin *et al.* 1994). Although biochar is present in particulate form, it is very recalcitrant to microbial decomposition (Schmidt and Noack 2000). A preferential occurrence of biochar within aggregates (Brodowski *et al.* 2006) suggests physical protection by minerals (Figure 3), in addition to chemical recalcitrance, but there is, as yet, no quantitative evidence of this. It is not yet known whether complexation with mineral surfaces also plays a role in biochar stabilization (Glaser *et al.* 2000; Rumpel *et al.* 2005).

The particulate form may serve in itself as a protection mechanism against decay for the interior of the biochar particle, by compartmentalization; this is similar to the mechanism proposed for the protection of organic matter by aggregation. Whether biochar pores are accessible to microorganisms or their enzymes remains to be shown. Specific microorganisms probably specialize in biochar environments in soils (Yin *et al.* 2000). Whether this also results in a different ecology of biochar degradation is unclear. Vastly different principles may control biochar reactions in comparison to other organic matter; the science of soil–biochar dynamics is still in its infancy.

Nutrient retention

Nutrients are retained in soil and remain available to plants mainly by adsorption to minerals and organic matter. While we are usually unable to change the mineralogy of a given soil, we can change the amount of soil organic matter. Typically, the ability of soils to retain cations in an exchangeable and thus plant-available form (cation exchange capacity [CEC]) increases in proportion to the amount of soil organic matter, and this holds for biochar as well. However, 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 (Figure 4), although the mechanism for this process is not fully understood. These properties make biochar a unique substance, retaining exchangeable and therefore plant-available nutrients in the soil, and offering the possibility of improving crop yields while decreasing environmental pollution by nutrients.

There is typically little or no cation exchange capacity of soil organic matter at very low pH, but this increases with higher pH. Biochar is no exception, but the point at which the CEC of biochar is zero (point of zero net charge [PZNC]) depends on the temperature at which the biochar is produced, the potential CEC (standardized for pH 7) increasing with temperature (Figure 5). Also, pH and surface area of fresh biochar appear to increase with production temperature, as carbon yield decreases (Figure 5), so that the optimum temperature is probably 450–550°C. It should be noted, however, that biochar properties change considerably during exposure to the environment, and interactions between production procedures and environmental effects have not been investigated to date.


Courtesy of J Thies

Figure 2. *Dark earth from the Amazon, with biochar which accumulated about 800 years before present and still shows a distinctly black color, indicating the high stability of biochar (compare black topsoil with the yellow underlying material in the pit).*

The effects of biochar on biological processes (Lehmann and Rondon 2006) or water relationships in soil have not been thoroughly investigated, but could potentially lead to important returns. For example, biological fixation of atmospheric nitrogen by common beans was found to be enhanced by the addition of biochar to a highly weathered savanna soil, most likely through the mechanism of greater micronutrient availability (Rondon *et al.* 2007). Higher bacterial growth rates with biochar were explained by better attachment and, possibly, physical protection of microorganisms within the pore structure (Pietikäinen *et al.* 2000). Similar explanations were put forward for greater levels of infection by mycorrhizal fungi (Saito and Marumoto 2002). A greater surface area (Liang *et al.* 2006) is likely to result in greater water-holding capacity, but has not yet been investigated.

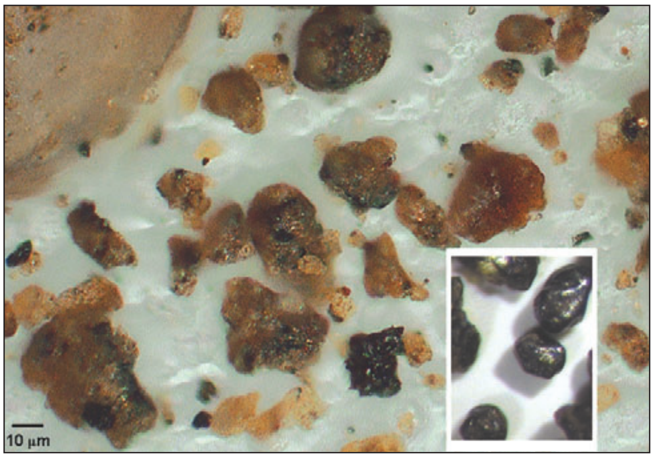

Figure 3. *Biochar particles in a dark earth from the Amazon, with dimensions of several tens of microns to submicrons. Upper left side shows a quartz grain, inset shows separated biochar particles. Note the coatings of biochar particles with minerals in their natural assemblage.*

Environmental benefits

Combating climate change

The most straightforward effect of combining pyrolysis with biochar application to soil is a net withdrawal of CO_2 from the atmosphere. Carbon dioxide is assimilated by plants through photosynthesis, then pyrolyzed, producing energy from the captured gases while the biochar residue is retained and subsequently stored in soil (Figure 1). If new CO_2 is fixed by plants, the biochar burial becomes a net sink of carbon. The proportion of carbon retained in biochar during pyrolysis varies both with pyrolysis temperature and with the type of feedstock (Lehmann *et al.* 2006; Figure 5). Within the range of temperatures suitable for energy production through pyrolysis of about 400–550°C, the effects of temperature are negligible (Figure 5) compared to the effects of different types of feedstock, which changes the recovery of the initial carbon from 39 to 64% (Lehmann *et al.* 2006). An achievable level of typical carbon recovery is around 50% (Lehmann *et al.* 2003, 2006). The reason that this recovery is relatively high (62% for the example in Figure 5) lies in the fact that the carbon concentration increases from the original wood (containing 45% carbon) to biochar (containing about 85% carbon; at 700°C for the example shown in Figure 5).

As discussed above, biochar is not inert and will eventually decompose and release CO_2. However, the time scale over which this occurs is very long compared to other organic carbon forms in soil and to uncharred organic additions (Baldock and Smernik 2002). The total amount of carbon that can be stored is not limited by soil properties such as clay content and mineralogy, as is typically found for other soil organic matter. A portion of biochar can be mineralized very rapidly. The magnitude of this mineralization needs to be better understood, since opportunities exist to reduce, but not avoid, these losses.

Preliminary results indicate that biochar bio-energy not only leads to a net sequestration of CO_2, but that the presence of biochar in soil may decrease emissions of two even more potent greenhouse gases, nitrous oxide (NO_x) and methane. In greenhouse experiments, NO_x emissions were reduced by 80% and methane emissions were completely suppressed with biochar additions of 20 g kg^{-1} to a forage grass stand (Rondon *et al.* 2005). The reason for the reductions in methane and NO_x emissions is not currently known. Lower nitrification is one potential mechanism, possibly due to lower mineralization resulting from a higher C:N ratio or lower carbon quality. However, in forest soils, additions of biochar were recently found to increase nitrogen mineralization due to adsorption and resultant inactivation of secondary plant compounds, which would normally decrease microbial activity (DeLuca *et al.* 2006). The effects of biochar on the soil nitrogen cycle and the associated emissions of greenhouse gases clearly require more attention.

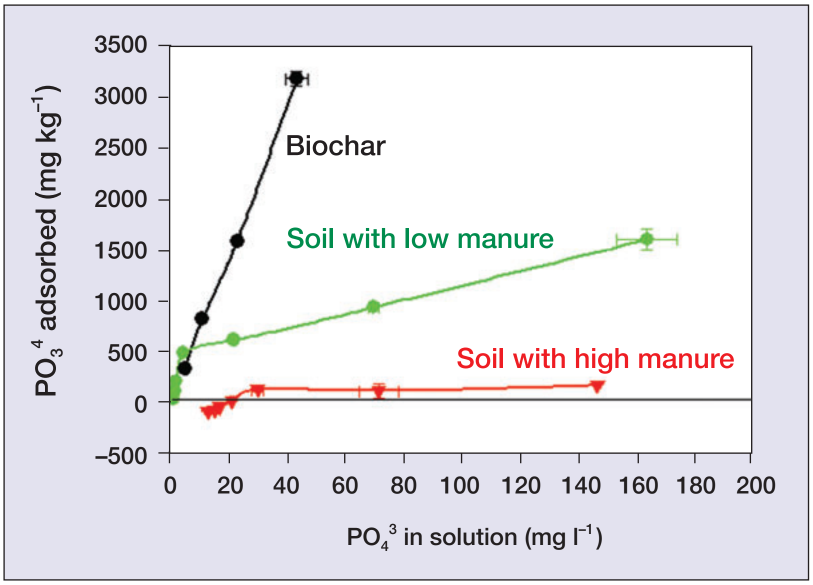

Figure 4. *Adsorption of phosphate to biochar (produced from* Robinia pseudoacacia *L at 350°C for 16 hours; Cheng* et al. *2006) in comparison to soil after short- and long-term application of animal manure (phosphate adsorption to soil from Lehmann* et al. *[2005a]). Means and standard errors are shown; n = 3.*

Several carbon costs are associated with the land-based production of biomass, transport to the bio-energy plant, pyrolysis itself, and land application of biochar (the latter is much less costly for biochar than for biomass, due to the fact that the mass per unit carbon of biochar is about 60% that of biomass). Our preliminary calculations take all of these carbon costs into account and suggest that the energy balance for various feedstocks, such as corn or switchgrass, is very favorable, with approximately 3–9 kg C energy yield for every kg C energy invested, even with the proposed use of biochar as a carbon sink instead of an energy source (Gaunt and Lehmann unpublished data). Comparable ratios for ethanol currently amount to 0.7–2.2 kg C (kg C)$^{-1}$ (Pimentel and Patzek 2005; Metzger 2006) and, for biomass burning, to 10–13 kg C (kg C)$^{-1}$ (willow; Keoleian and Volk 2005), with the caveat that the latter produces only heat, not liquid fuel. This means that pyrolysis produces 3–9 times more energy than is invested in generating the energy. At the same time, about half of the carbon can be sequestered in soil. Such a carbon-negative technology would lead to a net withdrawal of CO_2 from the atmosphere, while producing and consuming energy. These numbers need to be substantiated using a wider range of scenarios, including the actual use of the bio-energy in, for example, transportation or household consumption, and with better data for fertilizer savings, biochar stability, and greenhouse gas emissions.

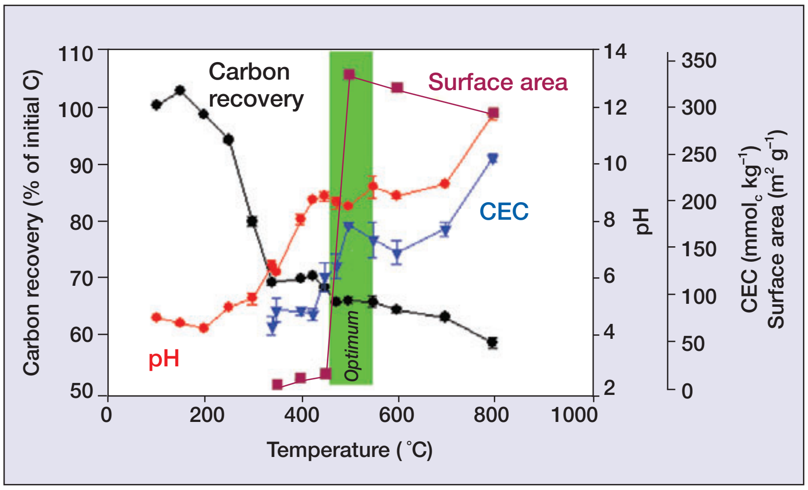

Figure 5. *The properties of biochar greatly depend on the production procedure. Temperature effects on carbon recovery, cation exchange capacity (CEC; measured at pH 7), pH, and surface area are shown here. Twenty grams of air-dried wood from* Robinia pseudacacia L *were pyrolyzed in closed containers (0.025 m^3) with a heating rate of 0.4˚C per minute (1-hr stabilization at each end point) in triplicate; means and standard errors are shown; carbon contents were determined by dry combustion (Europa ANCA GSL, PDZEuropa, Crewe, England), cation exchange capacity by ammonium acetate at pH 7, pH in 1N KCl at 1:20 (w/v) ratio twice, and surface area by the BET N_2 method on an automated surface area analyzer (Tristar 3000, Micromeritics Instruments Corp, Norcross, GA).*

Improving soil

Any bio-energy production will lead to a maximum removal of biomass from land. This highly extractive procedure potentially leads to widespread soil degradation, with negative effects on soil productivity, habitats, and off-site pollution. Pyrolysis, coupled with an organic matter return through biochar applications, addresses this dilemma, because about half of the original carbon can be returned. In addition, the biochar is extremely effective in restoring soil fertility. Several overviews have presented evidence for the improvement of soil productivity by biochar (see Glaser *et al.* [2002] and Lehmann and Rondon [2006]). The extraordinary persistence of biochar makes it possible to extend its application beyond the area from which the biomass was obtained to generate the bio-energy. Once applied to a certain location, additions do not need to be repeated annually, as exemplified by the persistently high fertility of Amazonian Dark Earths over several hundred to thousands of years, as well as by remnants of historic charcoal production (Glaser *et al.* 2002; Lehmann and Rondon 2006). This allows application to areas which were not harvested for bio-energy production, but which would benefit from improved soil fertility or reduced pollution by agro-chemicals.

Reducing pollution of waterways

When applied to soil, biochar may reduce off-site pollution in two ways: first, by retaining nutrients such as nitrogen and phosphorus in the soil, and lowering the amount of soil nutrients leached into groundwater or eroded into surface waters. Secondly, biochar would reduce pollution by improving nutrient retention in the topsoil, thereby reducing the amount of fertilizer needed to grow a crop. Reduced leaching has been demonstrated in greenhouse studies (Lehmann *et al.* 2003) and can be expected from adsorption behavior (Figures 4 and 5). The reductions in erosion have not been tested; erosion reductions based on the movement of nutrients adsorbed to sediments are debatable, whereas reductions in soluble nutrients can be expected (Figure 4).

A substantial reduction in the phosphorus mobility of animal manures may be achievable by directly pyrolyzing the manures (He *et al.* 2000). This would not only reduce the volume and weight of the manures that need to be disposed of, but could presumably also convert the soluble inorganic phosphate contained in manure into adsorbed phosphate in biochar. The properties and behavior of charred manure in soil need more attention, especially with respect to phosphorus dynamics.

Scrubbing air pollutants

Pyrolysis appears to offer additional opportunities to decrease greenhouse gas emissions, namely through the ability of biochar to scrub CO_2, nitrous oxides, and sulfur dioxide from flue gas (Day *et al.* 2005; Figure 1). The CO_2 is precipitated onto the biochar surfaces during an exothermic process (Lee *et al.* 2003). Such a procedure could be used to reduce net emissions by fossil fuels, for example in conjunction with coal firing. At the same time, the precipitate creates a highly nitrogen-rich biochar that could be used instead of nitrogen fertilizer additions (Day *et al.* 2005). Such benefits would need to be more fully investigated.

Pitfalls and impediments to successful adoption

As mentioned above, biochar properties vary greatly, depending on the biomass used to produce biochar and the production conditions (such as pyrolysis temperature). Biochar produced below 400°C has a low pH, low CEC, and small surface area (Figure 5), and may therefore not be suitable for improving soil fertility. Similar assessments for the stability of biochar in the environment are not yet available, but should show important effects of both production procedure and biomass type. A rapidly decaying form of biochar would be neither a sustainable improver of soil nor a long-term carbon sink. Until these dependencies are sufficiently understood and unless they are taken into consideration, biochar applications will, in certain situations, fail to produce the desired effects.

Under any production scenario, the CEC of freshly produced biochar is relatively low (Figure 5). Only aged biochar shows high cation retention, as in Amazonian Dark Earths (Liang *et al.* 2006). At high temperatures (30–70°C), cation retention occurs within a few months (Lehmann *et al.* 2003; Cheng *et al.* 2006). The production method that would attain high CEC in soil in cold climates is not currently known. If certain types of biochar under certain environmental conditions require decades of exposure to microbial and abiotic oxidation to develop the cation retention properties that justify their application, then the technology would not be successful at such sites.

If not incorporated into soil, biochar may be prone to erosion. Eventual burial in river or ocean sediments may increase the mean residence time of the biochar in the environment, but also jeopardizes any intended soil improvement and may even increase net losses of adsorbed nutrients. Suitable technology for soil injection or incorporation still need to be developed.

The type of biomass and production conditions also have a major impact on the amount and composition of phytotoxic and potentially carcinogenic organic materials that are produced during pyrolysis (Lima *et al.* 2005). Production in typical charcoal kilns has been shown to yield a form of biochar that has positive effects on plant growth (Lehmann and Rondon 2006). Yet this cannot be generalized without experimental evidence. A full environmental risk assessment, including human health considerations, is necessary before widespread adoption could be recommended.

Conclusions

Bio-energy through pyrolysis in combination with biochar sequestration holds promise for obtaining energy and improving the environment in multiple ways. The technology has the potential to be carbon negative, which means that, for every unit of energy produced or possibly even consumed, greenhouse gases would be removed from the atmosphere. This could be the beginning of a biochar revolution that is not only restricted to a bio-energy combination, but applicable to a range of different land-use systems (Lehmann *et al.* 2006). Compared to the limited amount of CO_2 that can be removed from the atmosphere by other land-based sequestration strategies, such as no-tillage or afforestation (Jackson and Schlesinger 2004), a biochar sink has the advantage of easy accountability and multiple other environmental benefits.

There are, however, possible pitfalls as well as gaps in our understanding of the science of biochar behavior in soil and how different pyrolysis conditions affect biochar ecology in the environment. Pyrolysis is currently being developed with the primary goal of maximizing the quantity and quality of the energy carrier, such as bio-oil or electricity. The optimization of biochar properties within a pyrolysis system has not been the focus of research to date, and biochar can have very different properties depending on the type of organic residue from which it is obtained and how it is produced. Certain production conditions and feedstock types can make the biochar completely ineffective in retaining nutrients and affecting atmospheric CO_2, or susceptible to microbial decay. Efforts similar to the development of fertilizers over the past century need to be undertaken to provide the underlying scientific information for biochar ecology that contributes to cleaner air and water while producing energy. The evidence overwhelmingly suggests that exploration and development of biochar bio-energy is highly promising.

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