8

Environmental Applications of Hydrothermal Carbonization Technology: Biochar Production, Carbon Sequestration, and Waste Conversion

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8.1 Introduction

The motivation for the development and use of hydrothermal carbonization (HTC) in the last decade came primarily from the desire to create sustainable carbon nanomaterials/nanostructures (e.g., [1–6]) for use in applications ranging from hydrogen storage to chemical adsorption (e.g., [7, 8]). These were already pointed out in Chapter 7.

The potential environmental benefits of this process [9–13] were quickly recognized, and research was expanded to include the carbonization of biomass and organic waste streams for environmental applications. The carbon-rich material, often referred to as hydrochar,

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resulting from the carbonization of these feedstocks in the presence of water may be used in a variety of environmental applications, such as a soil amendment [11] and as an adsorbent in environmental remediation processes [14]. HTC has also shown promise as a sustainable waste stream conversion technique, ultimately converting waste materials to value-added products, while promoting integration of carbon in the solid phase (e.g., [9, 11, 12, 15]).

Waste streams, such as municipal solid waste (MSW), animal wastes (e.g., pig, cow, poultry), and human wastes (e.g., wastewater), may be sustainably converted to a stable, sterile, carbon-rich, high-energy-density material via HTC (e.g., [9–12]). Utilization of HTC as a conversion technique may substantially reduce fugitive greenhouse gas emissions from MSW landfills, composting facilities, animal manure pits, and wastewater treatment plants by promoting carbon integration within the hydrochar. In addition, the resulting hydrochar may serve as a source of renewable solid fuel. Another advantage associated with using HTC as a waste management tool is that it results in considerable waste volume and mass reduction, requiring less ultimate storage/disposal space.

Perhaps one of the most advantageous aspects of using HTC for waste stream conversion is the generation of value-added products. The ability to recover and reuse waste materials promotes the desired waste management hierarchy (e.g., reuse, recycle) prevalent in many countries. As illustrated in Figure 8.1, hydrochar resulting from the carbonization of wastes has the potential to be used as an adsorbent in environmental remediation applications, a novel carbon material, a storable solid fuel for energy generation (via cocombustion or use in carbon fuel cells), and possibly as a soil amendment.

Using hydrochar as a soil amendment is a topic of recent exploration. There has been a recent surge in exploring land application of biochar (terminology commonly used to denote char application in soils) to increase soil fertility, while providing a long-term carbon sink

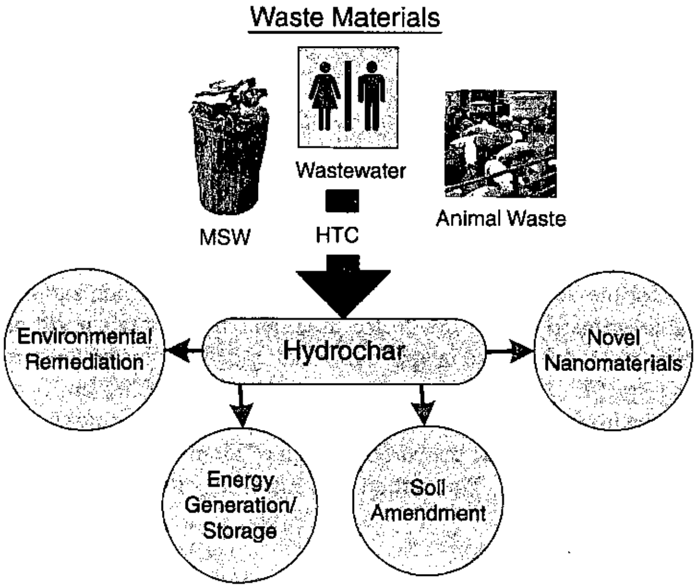

Figure 8.1 *Potential uses of hydrochar resulting from the HTC of waste streams.*

(e.g., [16]). The source of the biochar in the majority of reported studies, however, has been from the dry pyrolysis of different types of biomass. Hydrochar also has the potential to serve as a valuable soil amendment. Land application of hydrochar may increase the carbon content of degraded soils, ultimately improving soil fertility [11]. Research regarding the application of hydrochar in soils is still in its infancy [11].

Utilization of HTC in environmentally relevant applications is fairly new, and there is much additional research required to fully explore the potential and subsequent use of the process in such applications. This chapter describes the current knowledge associated with environmentally relevant HTC applications. The use of HTC as a waste management tool is first examined, followed by an overview of char applications, with a focus on char as a soil amendment. In addition, the current commercial status and research needs required to implement carbonization at the field-scale are discussed.

8.2 Waste Conversion to Useful Products

HTC of waste streams is an attractive alternative waste management strategy for biomass residuals such as agricultural residues and municipal wastes. In HTC, the feedstock is heated in subcritical water to between 150 and 250 °C at autogenic pressures for reaction times ranging from 1 to 20 h. The feedstock is decomposed by reaction mechanisms similar to those in dry pyrolysis, which include hydrolysis, dehydration, decarboxylation, aromatization, and recondensation [11]. In contrast to dry pyrolysis, however, HTC produces higher solid (i.e., hydrochar) yields, more water-soluble organic compounds, and mainly CO_2 as a major gaseous product. Furthermore, the chemical structure of the solid products more closely resemble natural coals than pyrolysis-derived chars [11, 17].

Since, during HTC, the majority of the carbon remains integrated within the solid material, successful carbonization of wastes could substantially reduce fugitive greenhouse gas emissions from current management/treatment processes. Approximately 36% of the estimated anthropogenic CH_4 emitted in the United States in 2008 was related to waste management activities (including landfills and composting [18, 19]). Waste management-related activities also accounted for approximately 8% of US N_2O emissions (a much more potent greenhouse gas). Berge [15] reports that carbon emissions resulting from HTC of MSW may be lower than those expected from landfilling (over a range gas collection efficiencies), composting, or incinerating (over a range of waste conversion efficiencies) the same waste materials.

There are many additional advantages associated with carbonizing waste streams. HTC of waste materials may require less solids processing/treatment (such as chemical or mechanical dewatering of biosolids). Ramke *et al.* [12], for example, evaluated the dewaterability of sewage sludge prior to and following carbonization, and concluded that carbonization significantly improved the dewaterability of the solids. Another significant potential advantage associated with this process is that emerging compounds, such as pharmaceuticals, personal care products, and endocrine-disrupting compounds, which currently pose significant environmental concerns in landfills (e.g., [20–22]), animal wastes (e.g., [23, 24]), and wastewater (e.g., [25, 26]), may be thermally degraded or transformed during carbonization.

The conversion of wastes to a valuable resource adds to the attractiveness of this approach. The hydrochar may be used in applications such as environmental remediation, feedstock for energy generation (via cocombustion or use in carbon fuel cells), and soil augmentation. To date, recovering waste materials (or transformed waste materials) as an energy source or other value-added product has been limited. Many of the studies that have evaluated the conversion of waste streams via HTC have been focused on creating an energy-rich hydrochar material. Use of the hydrochar as a solid fuel has been explored by Berge *et al.* [9], Ramke *et al.* [12], and Hwang *et al.* [27]. These studies report the hydrochar has characteristics similar to lignite coal. Work evaluating the burning of the char to produce energy has also been conducted. The benefits include a significant reduction in coal ignition temperature through the blending of hydrochar with coal [28], as well as a homogenized and stabilized fuel. Converting wastes (some components classified as renewable) to a source of non-fossil-fuel-derived energy has many significant potential environmental advantages.

To date, there have been a limited number of studies evaluating the carbonization of waste materials. The purpose of this section is to review the current state of knowledge associated with using HTC as a waste conversion tool, including associated environmental implications, hydrochar characteristics, and research needs.

8.2.1 Conversion of Municipal Solid Waste

8.2.1.1 MSW Characteristics

MSW is broadly defined as wastes originating from residential (i.e., product packaging, newspapers, magazines, food waste, grass clippings, yard waste, recyclables), institutional (i.e., schools, prisons), and commercial sources (i.e., restaurants). Construction and demolition debris and combustion ash are not generally characterized as MSW.

Waste properties that are important during HTC include the chemical composition, volatile fraction, combustible fraction, moisture content, particle size, and energy content. Typical ranges associated with these parameters are presented in Table 8.1 and are highly dependent on waste composition. MSW is generally comprised of a mixture of organics, inorganics, putrescibles, combustibles, and recyclables [29, 30]. Typical unsorted

Table 8.1 *Typical unsorted MSW properties relevant to carbonization [29, 30].*

Waste property	Value
Elemental analysis (%, dry ash free)	
Carbon	27–55
Hydrogen	3–9
Oxygen	22–44
Nitrogen	0.4–1.8
Sulfur	0.04–0.18
Volatile fraction (%, dry weight)	40–60
Moisture content (%, wet weight)	15–40
Noncombustible fraction (%, weight)	10–30
Particle size[a]	average: 18–20 cm range: 0.02–60 cm
Energy content (MJ $kg_{dry\ weight}^{-1}$)[a]	2–14

[a] Neglecting bulky items.

Table 8.2 Comparison of MSW composition in the United States, European Union, and developing countries. (Adapted with permission from [37]. © 2009 Elsevier.)

	Percentage of total composition						
	Paper	Textiles	Plastics	Glass	Metals	Organics	Other
United States	35	5	11	5	8	30	6
European Union	26	2	8	6	5	28	25
Developing countries[a]	13	2	11	3	5	54	12

[a] Based on average values from 19 developing countries; see source for specific countries included in the analysis.

MSW consists of 40–50% cellulose, 9–12% hemicellulose, and 10–15% lignin [31]. The biodegradable fraction of unsorted MSW varies and is dependent on waste composition. Approximately only 45% of typical unsorted MSW in the United States is biodegradable [29]. The percent biodegradability is typically larger in developing counties (see Table 8.2). Approximately 90% of the biodegradable fraction is typically comprised of cellulose plus hemicellulose [31]. In general, waste is fairly combustible (70–90% by weight) and contains a large fraction of volatile solids (40–60% by weight). The heterogeneous nature of MSW (in terms of composition, chemical properties, and particle size), particularly unsorted MSW, complicates its use as a feedstock for thermochemical conversion processes, potentially requiring the waste be processed (i.e., shredded, sorted) prior to introduction to such processes to minimize operation and maintenance issues, and to result in a consistent conversion product (e.g., oil, gas) [7, 29, 30, 32–34].

An attractive feature of carbonizing MSW for future use is that it is a continuously generated feedstock (always abundant) containing appreciable masses of renewable resources (i.e., food, paper, wood products [35]). Waste generation rates and composition vary with location and have been shown to correlate with average income, ranging from 0.1 (low-income countries) to more than 0.8 metric tons per person-year (high-income countries [36]). In 2007, approximately 0.745, 0.522, and 0.548 metric tons per person-year of waste were generated in the United States, European Union, and Malaysia, respectively [35, 37, 38]. Variations in waste generation rates and composition can be attributed to several different factors, including country gross national product, population (and population density), collection frequency, affluence, cost of disposal, legislation, and public attitudes [29, 30, 36, 37, 39, 40]. Table 8.2 presents a comparison between typical waste composition from developed (United States and European Union) and developing countries. It should also be noted that current waste management practices also differ between countries. In the United States, the majority of waste discarded resides in MSW landfills (54% [35]), while the majority of waste discarded in Japan is incinerated (75% [41]) and in Germany is recycled or incinerated (70% and 30%, respectively [42]).

8.2.1.2 *Carbonization Studies*

MSW has been successfully used as a feedstock in several high-temperature, wet and dry conversion processes, such as pyrolysis, incineration, and gasification [34, 43–49]. Fewer studies evaluating the conversion of this waste stream via HTC have been conducted.

In comparison to other, more traditional thermal conversion processes, HTC occurs at comparatively lower temperatures, is simpler (e.g., compared to fluidized-bed gasification), requires the presence of water, and the main process product is a carbon-rich, high energy-density char. Oily and tar products may also result, depending on the feedstock and reaction temperature and time. Gaseous oxidation products, particularly CO_2, are limited during HTC because unlike combustion, exposure to oxygen is limited to that initially present in the reactor headspace and any dissolved oxygen in the water or initial feedstock.

Table 8.3 contains a summary of investigations evaluating the HTC of typical components of MSW and/or mixed MSW. Information, and in many cases the lack of, in Table 8.3 illustrates the current need for additional in-depth experimental studies to fully evaluate the use of HTC in this manner. What is apparent from the studies conducted is that the majority of carbon does remain in the solid material, despite variations in solids concentration, temperature, and reaction times. All studies report a fraction of carbon is transferred to the liquid-phase, and a smaller fraction of carbon is transferred to the gas phase (all studies report the majority of this gas is CO_2).

Ramke *et al.* [12] carbonized several different waste materials, most notably organics and green waste (grass cuttings). Results demonstrated that carbonization is feasible. Similarly to that observed when carbonizing pure substances, the majority of carbon remained within the hydrochar material (75–80%, see Table 8.3). Hwang *et al.* [27] also explored the HTC of components of MSW, specifically shredded paper and dog food, at different temperatures (Table 8.3). They determined that at all temperatures the majority of carbon remained within the solid-phase (greater than 80%). It was also determined that as the temperature increased, less carbon remained within the solid and solid yields decreased. Carbon balances from experiments conducted by Berge *et al.* [9] reveal results similar to those reported by others.

In all studies, an appreciable fraction of carbon is transferred to the liquid. When considering the use of this technique as a waste management tool, management/treatment of the liquid is necessary. Ramke *et al.* [12] measured gross organics in the liquid phase and reported that the BOD_5 ranges from 10 000 to 14 000 mg l^{-1} and the COD ranges from 14 000 to 70 000 mg l^{-1}. Experiments on the liquid-phase conducted by Ramke *et al.* [12] suggest that the organics in the liquid are degradable (COD approached 90% removal). Berge *et al.* [9] also identified several different organics in the leachate stream (using gross characterization and identification via GC-MS). BOD and COD results were similar to that reported by Ramke *et al.* [12]. Hwang *et al.* [27] tracked chloride and reported that the majority of the chloride remained within the char (at the tested temperatures).

Carbon in the gas phase has also been measured. As seen in many of the studies (Table 8.3), a small fraction of carbon is transferred to the gas phase. Ramke *et al.* [12] report that CO_2 is the predominant gas and represents 70–90% of the total gas produced, while trace hydrocarbons represented the balance. Berge *et al.* [9] conducted a more detailed analysis of the gas-phase components. They identified, in addition to CO_2, several trace gases, such as CH_4, hydrogen, and propene. Of environmental concern is the detection of furans. Additional studies are required to understand the furan concentrations and their associated implications (see Berge *et al.* [9]).

The carbon fractionation reported by these carbonization studies suggests that the hydrochar produced via MSW carbonization may serve as a significant carbon sink. Berge *et al.* [9] report that the carbon sequestered during carbonization of paper, food waste, and mixed MSW is greater than that currently achieved when landfilling the materials.

Table 8.3 *Studies evaluating MSW conversion via HTC.*

	HTC conditions			Char characteristics							Liquid		Gas		
Feedstock	Temperature (°C)	Reaction time (h)	Solids content (% weight)	% Carbon[a]	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Energy content (KJ kg^{-1})	Yield (%)	^{13}C NMR	% Carbon[a]	Composition information	% Carbon[a]	Composition information	Source
Organics	180	12	>20	74.9	NR	NR	NR	15 000	NR	no	19	BOD; TOC; COD; some composition information	6.1	not provided	[12]
Green waste (grass cuttings)	180	12	>20	75.3	NR	NR	NR	NR	NR	no	19.7	BOD; TOC; COD; some composition information	5	not provided	[12]
Paper	234–294	NR	25	80–90	25–50	~15	<5	~20 000 –25 000	NR	no	<5	TOC; chloride	<10	CO_2, CO, CH_4 only	[27]
Dog food	234–294	NR	25	80–90	35–55	~15	~10	25 000	NR	no	5–10	TOC; chloride	10–20	CO_2, CO, CH_4 only	[27]
Paper	250	20	20	48.8	52.8	19.8	24.2	23 900	29.2	yes	37.4	BOD; COD; TOC; composition via GC-MS	10.8	composition via GC-/MS	[9]
Food waste	250	20	20	75	53.5	29.7	11.2	29 100	43.8	yes	20.1	BOD; COD; TOC; composition via GC-MS	9	composition via GC-MS	[9]
Mixed MSW	250	20	20	74.8	33.6	14.6	46	20 000	63.2	yes	27.7	BOD; COD; TOC; composition via GC-MS	8.3	composition via GC-MS	[9]
Rabbit food	200–300	50–150 s	NR	NR	NR	NR	NR	NR	30–45	no	NR	yes; glucose, acetic acid	NR	NR	[50]
Japanese MSW	220	0.5	50	NR	70.9	12.3	16.8	16 400	NR	no	NR	no	NR	none	[51]
Indian MSW	220	0.5	50	NR	63.6	17.5	18.9	17 900	NR	no	NR	no	NR	none	[51]
Chinese MSW	220	0.5	50	NR	57.9	27.1	15.0	24 900	NR	no	NR	no	NR	none	[51]

[a] Percentage of initially present carbon.

NMR, nuclear magnetic resonance; NR, not reported; BOD, biochemical oxygen demand; COD, chemical oxygen demand; TOC, total organic carbon; GC-MS, gas chromatography-mass spectrometry.

Barlaz [31] developed carbon storage factors (CSFs: mass of carbon remaining in the solid following biological decomposition in a landfill/dry mass of feedstock) as a means to compare the mass of carbon remaining (stored) within solid material following biological decomposition in landfills. The estimated CSFs from hydrothermally carbonized office paper, food, and model mixed MSW are greater than those reported for landfilling of the same materials. This suggests that more carbon remains stored within the solid material following carbonization than if the materials had been landfilled, providing evidence that carbonization may be a promising process for mitigating carbon emissions associated with management of MSW. Berge [15] reports that retention of carbon in the char creates a carbon sink far surpassing that of current waste management processes (e.g., landfilling, composting, and incineration).

A few other studies evaluating the hydrothermal treatment of MSW have been conducted for purposes other than those described previously. Goto *et al.* [50] carbonized rabbit food at temperatures ranging from 200 to 300 °C. The objective of the experiments was to determine yields of smaller organic molecules, such as glucose and acetic acid. They measured glucose yields as high as 33%, up to 2.6% for acetic acid, and 3.2% yield of lactic acid. Onwudili and Williams [52] studied the catalytic (base catalyst: sodium hydroxide) gasification of refuse-derived fuel (material composed of MSW with recyclables removed) at temperatures ranging from 330 to 375 °C and placed emphasis on understanding how the produced gas composition varies with catalyst addition and temperature. The carbon content of the residues resulting from their studies ranged from 48 to 72%. Onwudili and Williams [52] also gasified glucose, starch, and cellulose for comparison, and reported differences in char properties and gas production.

8.2.2 Conversion of Animal Manure

"Confined animal feeding operations" in the United States and many other countries over the last few decades have undergone extensive expansions and consolidations [53]. This shift of animal production agriculture toward fewer, but larger operations has created environmental concerns in recycling and disposing of surplus animal manure because traditional manure management systems may not adequately dispose/recycle the surplus animal manure and pose potential environmental threat [54–56]. HTC of animal manure may provide a viable alternative for managing surplus animal manure and simultaneously produce value-added hydrochar.

8.2.2.1 Animal Manure Characteristics

Animal manures have widely different physical and chemical properties (Table 8.4). The dry manures such as chicken litter and feedlot manures have a moisture content ranging from 10.2 to 20.3%, whereas wet manures such as swine and dairy manures can have a moisture content greater than 96%. Except for the paved-surface feedlots, most poultry and feedlot operations collect a mixture containing manure, bedding, waste feed, and underlying soil. These mixtures generally have high ash contents. Furthermore, both volatile matter and fixed carbon content of soil-containing manure decrease, negatively affecting the higher heating value (HHV). Dairy and swine feeding operations typically produce a dilute solids waste stream comprised primarily of discharged wash water, but also manure, urine, and undigested feed. Discharged swine and dairy manure characteristics are highly dependent

Table 8.4 *Characteristics of animal manures.*

	Dry manures			Wet manures	
Parameters	Chicken litter [59]	Soil-surfaced feedlot manure [60]	Paved-surfaced feedlot manure [60]	Pit-recharge liquid swine manure	Flushed dairy manure
Proximate analyses					
Moisture contents (%)	10.2	19.8	20.3	98.0 [61]	96.2 [62]
Volatile matter ($\%_{db}$)	51.1	33.8	64.6	68.7	83.8
Ash ($\%_{db}$)	30.6	58.7	20.2	31.3[a]	16.2[a]
Fixed C ($\%_{db}$)	8.2	7.5	15.2	NA	NA
HHV (MJ kg^{-1})	13.0	7.9	16.8	17.2	18.2
Ultimate analyses					
C ($\%_{db}$)	34.4	21.7	43.1	45.7 [63]	44.7 [64]
H ($\%_{db}$)	4.1	2.62	5.22	6.45	5.85
N ($\%_{db}$)	3.27	1.94	3.11	3.45	2.05
S ($\%_{db}$)	0.81	0.42	0.67	0.38	0.31
O ($\%_{db}$)	23.4	14.6	27.7	31.4	38.2

[a] Reported as "fixed solid," which is a combination of ash and fixed carbon.

on the type of manure handling and collection system (flush or pit-recharge) and the amount of added water [57]. Compared to the poultry- and cattle-based manures, dairy and swine manures have higher volatile matter and greater HHV. In a preliminary wet gasification analysis, Ro *et al.* [58] reported that swine manure among the five major types of animal manure would produce product gases with the highest energy per kilogram of dry matter [58].

8.2.2.2 *Animal Manure Carbonization*

The chemical structure of the solid products from HTC resembles natural coals more closely than chars from dry pyrolysis [11, 17]. Pyrochars also usually have a higher carbon and lower hydrogen content than hydrochars (likely due to temperature differences). In order to investigate how the structures differ, Cao *et al.* [65] compared two chars made from carbonizing swine manure via the two types of pyrolysis using ^{13}C solid-state NMR spectroscopy. Raw swine manure was converted into hydrochar (designated as "HTC-swine A") by anaerobically heating the manure solution (20% solid) to 250 °C under its autogenic pressure for 20 h and washed with acetone to remove mobile compounds adsorbed on hydrochar. Pyrochar was produced by pyrolyzing dried swine manure at 620 °C for 2 h with a heating rate of 13 °C min^{-1} [59].

As shown in Table 8.5, fixed carbon and ash contents of pyrochar increased dramatically from that of raw swine manure. While carbon contents in both hydrochar and pyrochar increased slightly, both hydrogen and oxygen contents of the pyrochar decreased substantially, indicating the increase in aromaticity due to pyrolysis. The NMR spectra of these chars and raw swine manure clearly showed the increase in aromaticity of the pyrochar

Table 8.5 Proximate and ultimate analyses of raw swine manure and its chars. (Reproduced with permission from [65]. © 2011 American Chemical Society.)

Parameters	Raw swine manure solid	HTC-swine A[a]	Pyrochar
Proximate analyses			
Moisture content (%)	12.8 ± 0.3	3.4 ± 0.8	3.4 ± 0.1
Volatile matter ($\%_{db}$)[b,c]	60.6 ± 1.1	59.1 ±1.5	14.1 ± 2.5
Ash ($\%_{db}$)	18.5 ± 0.2	27.8 ± 0.3	44.7 ± 1.2
Fixed C ($\%_{db}$)[d]	8.1 ± 0.6	13.1 ±1.3	41.2 ± 1.3
HHV (MJ kg^{-1})	19.5 ± 0.2	NA	18.3 ± 0.4
Ultimate analyses[e]			
C ($\%_{db}$)	47.3 ± 0.2	49.5 ± 2.8	50.7 ± 0.6
H ($\%_{db}$)	5.9 ± 0.1	5.7 ± 0.0	1.9 ± 0.3
N ($\%_{db}$)	4.58 ± 0.13	1.92 ± 0.95	3.26 ± 0.08
O ($\%_{db}$)	20.1 ± 0.4	16.5 ± 6.0	<0.01
S ($\%_{db}$)	0.93 ± 0.04	NA	0.66 ± 0.01
P (mg g^{-1} dry matter)[f]	23.7 ± 0.8	47.7	71.5 ± 1.3

[a] Hydrochar washed with acetone.
[b] ASTM D3175-07.
[c] Calculated as 100 – volatile matter – ash.
[d] ASTM D3172.
[e] ASTM D3176-02.
[f] USEPA Method 3052.

(Figure 8.2). Figure 8.2 also shows the NMR spectra of HTC-swine W, HTC-AW-swine A, and HTC-AC-swine A, which are water-washed hydrochar, acid-prewashed hydrochar, and acid-catalyzed hydrochar, respectively. When the raw swine manure was carbonized via HTC, the signals from aromatic or olefinic carbons around 130 ppm increased, indicating the increase in aromaticity, while the signals from COO/N—C═O functionalities decreased simultaneously. Proteins or peptides are one of the major constituents of swine manure along with carbohydrates as indicated by significant signals in the regions of 48–112 and 165–190 ppm. Furthermore, there was a substantial increase in mobile —$(CH_2)_n$— groups in HTC-swine W char, as indicated by the dominant band around 30 ppm in its dipolar-dephased spectrum. It suggested that the acetone wash removed some mobile —$(CH_2)_n$— groups in the hydrochar.

In contrast to hydrochar, the pyrochar spectra (Figure 8.2f, l, and r) showed that the pyrochar was predominantly aromatic, with only very small peaks in the alkyl region (0–48 ppm). The dipolar-dephased spectrum of the pyrochar showed a very pronounced signal from nonprotonated aromatic carbons with signals from the mobile —$(CH_2)_n$— and CCH_3 components. The absence of carbohydrates in pyrochar was evident with the complete disappearance of the signals assigned to anomeric O—C—O carbons around 103 ppm in the chemical shift anisotropy (CSA)-filtered spectrum.

The ^1H–^{13}C long-range recoupled dipolar dephasing experiments infer the information about the size of aromatic fused rings. The larger the ^1H–^{13}C distance, the slower the dephasing of the ^{13}C signal and the larger the aromatic cluster size. Figure 8.3 shows the dephasing times of HTC-swine A ranging from 0.29 to 0.86 ms, while those of pyrochar

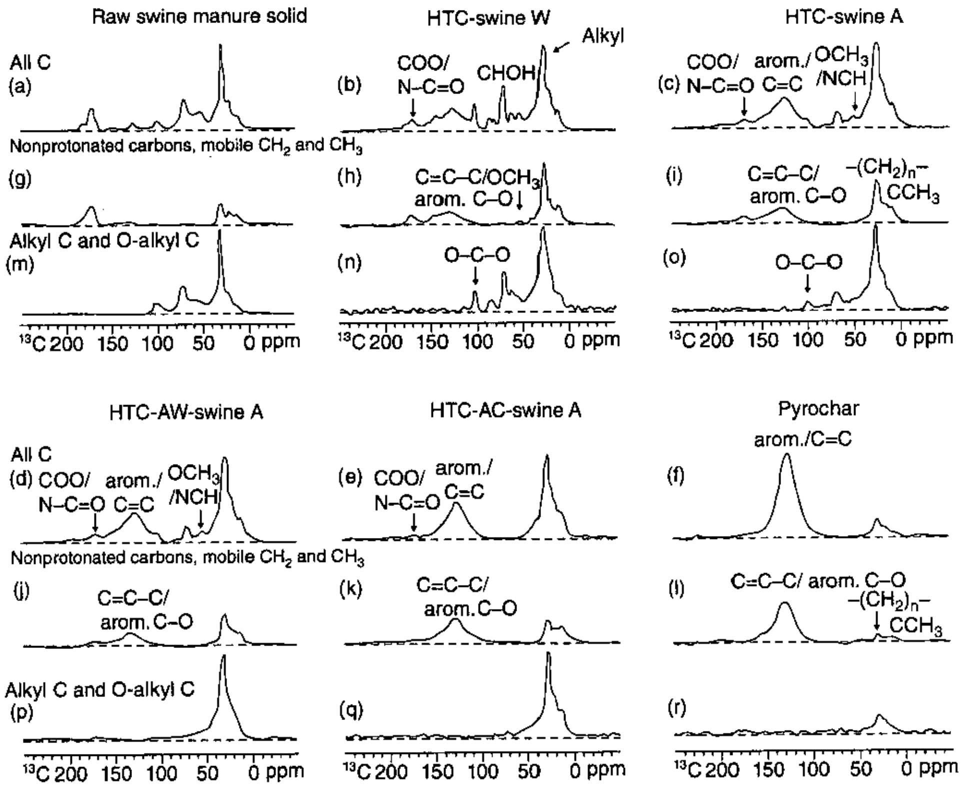

Figure 8.2 *^{13}C NMR spectral editing for identification of functional groups in raw swine manure solid (a, g, and m), HTC-swine W (b, h, and n), HTC-swine A (c, i, and o), HTC-AW-swine A (d, j, and p), HTC-AC-swine A (e, k, and q), and pyrochar (f, l, and r). (a–f) Unselective cross-polarization (CP)/total sideband suppression (TOSS) spectra. (g–l) Corresponding dipolar-dephased CP/TOSS spectra. (m–r) Selection of sp^3-hybridized carbon signals by a ^{13}C CSA filter. (Reproduced with permission from [65]. © 2011 American Chemical Society.)*

ranging from 0.29 to 1.43 ms. Comparison of the dephasing curves of HTC-swine A, pyrochar, and lignin suggested the presence of fused or more substituted aromatic rings in both hydrochar and pyrochar than lignin, but a more condensed character of aromatics in pyrochar than hydrochar (Figure 8.3c).

The quantitative structural compositions of the carbons of the swine chars are shown in Table 8.6. These chars were produced from different pyrolysis and postprocessing conditions based on ^{13}C direct polarization/magic-angle spinning NMR experiments. The dominant structural component in the raw swine manure was alkyl (62.7%), followed by *O*-alkyl (12.6% excluding O—CH$_3$), COO/N—C=O (11.0%), and NCH (5.7%) groups. These functionalities decreased as the swine manure was carbonized, but aromatic components increased. Raw swine manure underwent substantially deeper carbonization during

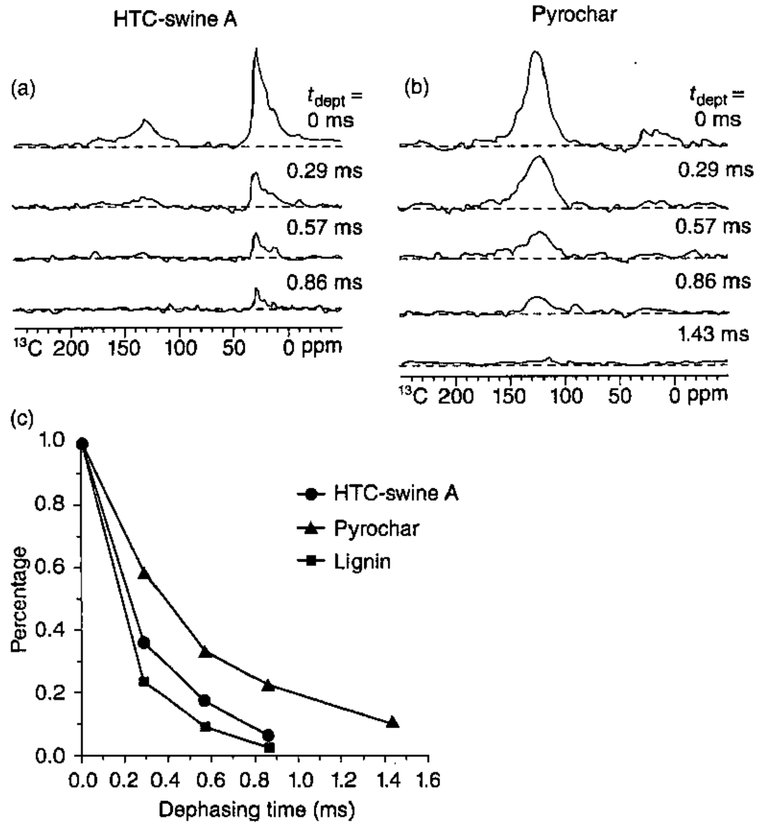

Figure 8.3 Series of direct polarization/TOSS spectra after ^1H–^{13}C recoupled long-range dipolar dephasing of the indicated durations t_{deph} of (a) HTC-swine A and (b) pyrochar. (c) Long-range dipolar dephasing curves for HTC-swine A and pyrochar. The aromatic signals were integrated between 107 and 142 ppm. Circles: HTC-swine A; triangles: pyrochar; squares: lignin. For reference, data for lignin are also shown. The data points have been corrected for regular T_2 relaxation. (Reproduced with permission from [65]. © 2011 American Chemical Society.)

pyrolysis than HTC as indicated by higher aromatics and low alkyl groups in pyrochar. In pyrochar, aromatic carbons (82.0%) became the predominant components, with the remainder being mostly alkyl hydrocarbons (11.0%). As observed by Ro *et al.* [59], nitrogen from peptides/proteins (NCH and COO/N—C═O groups) was substantially lost during swine manure pyrolysis.

8.2.3 Potential Hydrochar Uses

A variety of applications for both pyro- and hydrochars have been proposed in numerous fields, ranging from innovative materials to renewable energy. This diversity stems partly from the wide range of researchers and companies currently exploring the potential of char

Table 8.6 *Quantitative structural information obtained from ^{13}C NMR of raw swine manure and its chars. (Adapted with permission from [65]. © 2011 American Chemical Society.)*

	ppm								
	190–220	165–190	165–145	112–145		112–60	60–48		48–0
Sample	Aldehyde ketone	COO/N—C=O	Aromatic C—O	Nonprotonated aromatic/ olefinic C	Protonated aromatic/ olefinic C	*O*-alkyl C	NCH	O-CH$_3$	Alkyl
Raw swine manure	1.1	11.0	0.5	3.2	1.7	12.6	5.9	1.2	62.7
HTC-swine A[a]	1.8	5.6	5.2	14.1	7.0	1.8	1.8	0	62.6
Pyrochar	0.9	2.8	6.4	54.9	20.7	2.2	1.1	0	11.0

[a] Hydrochar washed with acetone.

applications as well as from its flexibility. The advantages of hydrochar use over pyrochar are that heterogeneous wet organic residues and waste streams can be processed without preliminary separating and drying, and with the HTC process there is a greater flexibility to design innovative carbon materials to fulfill a specific function. The structure, size, and functionality of the hydrochar can be varied by changing the carbonization time, feedstock type, and concentration, as well as by using additives and stabilizers. For example, the type of functional groups on the hydrochar can be modified by the addition of certain compounds to make the materials more hydrophilic and highly dispersible in water [66, 67].

The potential uses of hydrochar as an innovative material range from bulk applications such as adsorbents, especially for water purification purposes or soil amendments for the improvement of soil characteristics and plant growth, to specialty applications such as catalysts in chemical processing or for energy storage in batteries. Further uses for hydrochar are in energy production as a substitute for fossil fuels in conventional combustion processes or in novel fuel cells and engines. The possibility of using hydrochar as a method for carbon sequestration is also being investigated: the transformation of easily biodegradable waste streams to stable, more recalcitrant hydrochars may offer a means to store carbon, either in soil amendments (i.e., carbon storage by increase of the soil carbon pool size) or in storage vessels.

8.2.3.1 Adsorbents

In order to increase their capacity to adsorb compounds, chars are normally subjected to an activation step, thus becoming "activated carbon." The sorption properties of activated carbons in general are extremely versatile, and can be used in production and environmental protection processes to remove a variety of inorganic and organic constituents from water or gases. Chars are effective in removing heavy metals [68], arsenates [69], organic dyes [70], as well as many other toxic substances [71].

Chars made from carbonizing biomass and animal manures have been found to have high surface area and sorption capacity after activation. Lima *et al.* reported that the poultry- and turkey-based activated pyrochars had greater sorption capacity toward copper than commercial activated carbon [72–74]. Recently, Sun *et al.* [14] found that hydrochars made from hydrothermally carbonizing chicken litter and swine manure showed more effective sorption capacity for endocrine-disrupting chemicals than pyrochars. Hydrochars' logarithmic single-point organic carbon normalized distribution coefficients ($\log K_{OC}$) of bisphenol A and 17α-ethinyl estradiol were higher than that of pyrochars. For nonpolar compounds such as phenanthrene, sorption capacities of both hydrochar and pyrochar were similar, demonstrating that manure-based hydrochar could adsorb a wide spectrum of both polar and nonpolar organic contaminants. Further research on this aspect of hydrochar is currently pursued by many researchers globally and more detailed information about the potential for using hydrochar as an environmental adsorbent will be unraveled in the near future.

8.2.3.2 Energy Source

HTC of waste streams has emerged as a potential alternative strategy to produce a renewable solid fuel source. Pressure to reduce greenhouse gas emissions has prompted the re-evaluation of current approaches and spurred the development of hydrochar production as a source of alternative, renewable energy. Currently, less than 1% of total energy generation in the United States originates from waste sources (including biogenic MSW, landfill gas, sludge waste, agricultural byproducts, and other biomass solids, liquids, and gases [18]), far below its total energy generation capacity. It should be noted that this is not necessarily the case in other countries.

An important advantage of the HTC process is that it produces a homogenized and stabilized char from highly heterogeneous organic waste streams, thus improving the handling, transportation, and storage and increasing its potential as renewable energy source. Ultimately, it is expected that the char may be used as a solid fuel source and be combusted. Muthuraman *et al.* [28] found an additional advantage – the blending of hydrochar produced from MSW and Indian coal resulted in significant reduction in coal ignition temperature.

Many of the experiments evaluating the conversion of waste streams via HTC have focused on evaluating the energy-related properties of the hydrochar (see Table 8.3). Through the hydrothermal reactions, the energy density of the wastes is increased up to 40%. Hydrochar has an energy density equivalent to lignite coals or higher, ranging from 15 to 30 MJ kg^{-1}, and it increases with reaction severity [9, 12, 27, 75]. Berge *et al.* [9] and Ramke *et al.* [12] report that the hydrochar energy content correlates well with carbon content of the solids.

Berge [15] conducted an analysis between the energy potentially generated from the char resulting from the carbonization of paper, food waste, and model mixed MSW and that potentially generated from currently used waste management processes (landfilling and incineration), and reports that there is the potential for waste carbonization to surpass the energy generation from current waste management processes. Note that if using the hydrochar for energy generation, any carbon sequestered will be released.

A further appealing aspect of the HTC process is the ability to influence the size, form, and properties of the char by varying process conditions, opening up new possibilities in energy production. Instead of being restricted to combustion in conventional furnaces, colloidal hydrochar can be used in fuel cells as a fuel [76, 77], or its material properties can be exploited as a solid phase for hydrogen storage [78] or as a catalyst in low-temperature fuel cells to enhance reaction rates [79].

8.3 Soil Application

8.3.1 History of the Idea to Sequester Carbon in Soils Using Chars/Coals

The idea to apply recalcitrant carbonized materials to soils to increase soil fertility was mainly born from research on Amazon dark earth (ADE) soils (also known as "terra preta"), building on the work of Wim Sombroek [80, 81]; it was him and his coworkers' dream to replace current CO_2-emitting slash-and-burn agriculture by slash-and-char practices to create terra preta *nova* sites for sustainable forest farming and forest protection [82–84]. In the face of accelerating rainforest destruction, such approaches for sustainable development (even building on ancient traditions) should urgently be pursued, perhaps via carbon-sequestration- and rainforest-protection-targeted development aid, provided by the industrialized nations. As it happened, the time suddenly seemed to be ripe for this certain idea. Thus, the idea to use charcoal, or "biochar" (which is commonly used to denote pyrochar in soil applications) as a means of sequestering carbon in soils, previously taken from the atmosphere via photosynthesis in soils, was also put forward in the early 1990s by Ogawa [85] and discussed in more detail by Okrimori *et al.* [86]. In the best case, stable-carbon application should be associated with beneficial agricultural effects as exemplified by the terra preta soils [81, 87] as well as in Asian cultures where charcoal has been traditionally used in soil substrate production (e.g., charcoal *bokashi* in Japan [88]).

Until a few decades ago, it was unclear if the darker, nutrient-rich, and fertile ADE soils in Brazil were of natural or anthropogenic origin; now it is clear beyond doubt that they developed due to human activities [89–91]. The exact method or purpose for their creation is, and likely will, largely remain unknown, but more and more places with ADE soils and archeological evidence of urban garden settlements have been found at the shores of the rivers of the Amazon basin [91–93], as well as other signs of ancient geoengineering in central America (e.g., [94]).

It is now recognized that these indigenous populations that (purposefully or unintended) created these soils could not have been hunter-gatherers, but rather settled cultures (e.g., employing pottery [89]), and that they must have been many [91, 95, 96]. Thus, the original testimony, given by the Dominican friar Gaspar de Carvajal who accompanied the expeditions of the Spanish Conquistador Francisco de Orellana, seems to be true. For about 450 years, their expedition reports on densely populated river banks in the Amazon basin were discarded as tell-tale or fairy-tale stories.

The recent frequent findings of ADE sites, rich in human waste such as pot shards, fish bone, and signs for human feces [91], provide a late rehabilitation of part of their reports. They indicate that indeed perhaps a million people or more lived there and that what we see as a "native" jungle might instead be 470-year-old secondary forest [93, 96]. However, it still remains a mystery why these cultures vanished, why missionaries following a few decades after de Orellana did not find people there (giving him the "story-teller" reputation). It is assumed that the first Europeans were also the last to see them, because they probably brought deadly infectious diseases to these ancient cultures [96]. If this is true, it is hardly bearable to imagine what tragedies must have taken place on the shores of the rivers in the Amazon basin.

In essence, the long-term stability of old, aged black carbon or biochar is exemplified in terra preta soils that contain considerable amounts of black carbon, most of which is 500–2000 years old, sometimes up to 7000 years (^{14}C dating [89–91, 97]). Considerable biochar stocks of 50 tons of C ha^{-1} have been found down to 1 m depth in such soils, despite the climatic conditions strongly favoring decomposition and despite the lack of additional biochar additions in the last 450 years [82, 90, 91]. Indeed, the oldest carbon pool in ecosystems prone to natural fire is comprised of black carbon/charcoal [98, 99]. Lehmann *et al.* [99] conservatively assessed mean residence times (MRTs) for naturally generated biochars in Australian woodlands to be 1300–2600 years (range: 718–9259 years). The MRT of charcoal buried in sea sediments or anaerobic places may be even higher [100]. Although the term "long-term stability" clearly needs to be explored experimentally to produce more precise numbers, it is obvious that a wider use of such recalcitrant carbon fractions in soils will increase the carbon pool size, thus providing a sink for atmospheric CO_2. However, there is always a long way from a brilliant idea into frequently applied use in reality – a way that today is still paved with many unknowns.

8.3.2 Consideration of Hydrochar Use in Soils

While knowledge on biochar use in soils slowly starts to accumulate, knowledge on hydrochar use in soils is in its infancy compared to biochar [11]. Before we visit the first available results and draw conclusions, the following points need to be taken into consideration. Any hydrochar (as well as biochar) application to soils aimed at achieving soil carbon sequestration can only claim success if beneficial effects on plant yield, soil water availability, soil fertility, or other positive amelioration effects can be shown. In addition, it must be kept in mind that hydrochar (and also biochar) has a high energetic value: both carbon products were designed for use as fossil fuel substitutes, namely for burning in the first place (even historically, where charcoal was produced for ore smelting); hence they will have a monetary value that will be tied to fuel prices. Thus, as long as "soil carbon sequestration" is not paid for, soil amendment will only take place when the created value associated with soil amendment *is greater than that of the "fuel hydrochar."* If this value only arises in the long-term (several years, decades) or starts to be recognized as a public interest (e.g., restoration of degraded soils, remediation of contaminated soils) then soil application will depend on our societies' (political) will to *give* it the same or even a greater monetary value than it would have as a fuel. Today, no prices tied to agricultural use exist: knowledge on beneficial use (where a certain effect can be guaranteed, with a specific char, for a specific soil problem) is still incomplete. In addition, large suppliers of biochar or hydrochar do not exist in most countries and legal regulations on char use in soils also do not yet exist.

To consider the agricultural use of hydrochar in particular with regard to carbon sequestration, several open questions must be explored experimentally: (i) Is hydrochar stable (i.e., recalcitrant and resistant to degradation)? Does it make sense to use hydrochar for carbon sequestration if it is less stable than pyrogenic biochar? (ii) Does it have, or can it at least *theoretically* have, positive effects on plant growth and soil fertility or on nutrient retention in soils (beyond waste nutrient recycling)? Are there problems or toxic effects associated with its soil use? (iii) What are the effects of hydrochar application to soils on the greenhouse gas balance of crop production? This requires knowledge on not only direct changes in the emission or consumption of stable greenhouse gases (N_2O and CH_4) from/into agricultural soils after hydrochar application, but also of changes in the initial stock of the soil organic carbon (SOC) pool. These questions are discussed in subsequent sections.

The most important question, however, cannot be answered experimentally but rather by consensual agreement: *What reference system will we use for comparison to obtain a true value for carbon sequestration via hydrochar application?* Any reference system must be chosen carefully, it must be realistic and conservative, and it must be based on well-established scientific evidence, to ensure that real-world soil carbon pools are increased in the end. Otherwise, a useless but costly carbon sequestration trading business might spring up that sequesters money in some pockets, but not stable carbon in real-world soils.

8.3.3 Stability of Hydrochar in Soils

8.3.3.1 Carbon Sequestration by Chars

The suitability of chars for carbon sequestration in soils will depend on several factors that are not well known to date: (i) the overall carbon balance of the production process, (ii) the chars' long-term stability, (iii) secondary carbon turnover effects, such as an increase in the photosynthetic carbon input (e.g., biomass growth increases), or losses of old SOC by priming, and finally (iv) on the chars' effect on the fluxes of other climate-relevant greenhouse gases such as N_2O or CH_4 [101], which should be included as CO_2-equivalents, calculated based on their 100-year global warming potential [102].

The carbon yield (i.e., the amount of biomass carbon that be converted to char) can vary considerably depending on the carbonization technique and its operation, as detailed by others (e.g., [11]). Commonly in dry pyrolysis, 50% or more of the biomass carbon is converted to bio-oils, tars, H_2 and CO (syngas), or CO_2 [87, 103], while in the HTC process 75–90% of the biomass carbon may remain in the end-product hydrochar [11, 104]. Thus, the "carbon-yield" of hydrochar is usually larger than that of dry pyrolysis. However, this will only be an advantage if hydrochar is as stable as biochar or, at least, not considerably less stable. In addition, the time horizon used for consideration is crucial. So far, no clear, common definition exists: Do we consider the carbon to be "sequestered" (i.e., withdrawn from the atmosphere) when it remains in a given soil or at a given storage location for 50 years, for 100 years, for 1000 years – or "forever" (what ever that means)? If carbon is considered to be "sequestered" in wooden furniture such as a wardrobe we are surely considering a time horizon that is completely different from the situation where carbon is sequestered in charcoal and buried anaerobically in sea sediments [100]. Three orders of magnitude or more may lie between these two forms of sequestration (e.g., MRTs of 10 versus 10 000 years); but the former, "carbon sequestration in woody structures," figures far more prominently in public discussion than the latter.

For char application to soils to be included in carbon-trading schemes, reliable factors are needed that enable the assessment of sequestered CO_2 equivalents with reliable (at least centennial) mean residence times. Biochar or hydrochar properties, soil, climatic, and management conditions may vary widely, but all will influence the chars' recalcitrance. A systematic analytical characterization of biochar/hydrochar properties is urgently demanded, but has not yet been established [105]. Some general deductions can be made from chemical and physical char properties towards its long-term stability, such as aromaticity or the H/C versus O/C atomic ratios of a char (i.e., its place within the van Krevelen diagram) [106, 107].

8.3.3.2 Decomposition, Mineralization, and Fate of Chars in Soils

Although biochar is often considered to be "inert," it will finally be decomposed and mineralized over sufficiently long time scales; otherwise the worlds' carbon stocks would finally end up in biochar [101, 106]. Nevertheless, as discussed above, biochar contributes the longest-living organic carbon pool in soils [108–110].

Hydrochars are comparable to lignite (or brown) coal with less aromatic structures when sorted into a van Krevelen diagram (see Figure 8.4). The process water of hydrochar production contains high fractions of labile dissolved organic carbon (i.e., see BOD and COD values Table 8.3) [9, 11]. Even when the hydrochar slurry is pressed or otherwise dried after production, the solids will contain large labile fractions, either because of some process water dried onto the char or because the char itself contains labile fractions. In a study where hydrochar/soil mixtures were incubated, they produced substantially higher CO_2 emissions than the control soil without amendment or than soil/biochar mixtures [111]. In another study with plants, the HTC-amended soil showed nearly the same CO_2 emissions than the

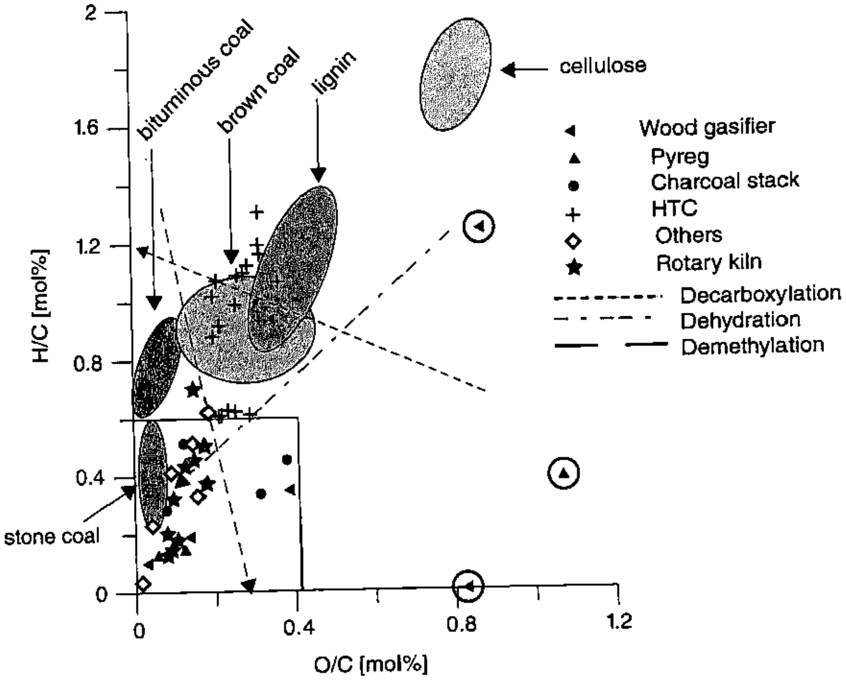

Figure 8.4 van Krevelen diagram comparing atomic ratios of biochar and hydrochar in comparison to other carbonaceous organic materials such as cellulose, lignin, and brown, bituminous, and stone coal. The square indicates the range of desirable char properties with regard to carbon stability as a soil amendment. The lines for decarboxylation, dehydration, and demethylation are given according to van Krevelen and Schuyer [114]. (Reprinted with permission from [107]. © 2012 Journal of Environmental Quality.)

feedstock-amended soil (feedstock: *Miscanthus x giganteus* chips), while the CO_2 emissions from *Miscanthus*-biochar-amended soil did not differ from a control without amendment [112]. It is thus reasonable to assume (as long as the experimental evidence is limited) that hydrochar, and here in particular the initial available labile carbon, will decompose quicker than a biochar produced from the same material. However, hydrochar will likely decompose slower than uncarbonized material, as found in a 12-month incubation study using wheat straw, bark-HTC, charcoal and a low-temperature conversion char [113]; in this study, Qayyum *et al.* [113] used three different soils and employed compensation fertilization with mineral nitrogen to obtain the same total nitrogen supply to each soil at the start.

A perception of the overall carbon loss during production versus char stability compared to uncarbonized biogenic residues is provided in Figure 8.5. A two-component decay model was used where a labile carbon fraction with a MRT of 10 years was assumed, as well as a recalcitrant fraction with a MRT of 1000 years. The MRT is the average time that an initial carbon addition is present in soil and is the inverse of the decay rate coefficient k. The decay rate of SOC to CO_2 is frequently modeled by assuming an exponential decay.

$$C_{\text{left}} = C_{\text{lab}} * e^{(-1/k-\text{lab}*t)} + C_{\text{rec}} * e^{(-1/k-\text{lab}*t)} \tag{8.1}$$

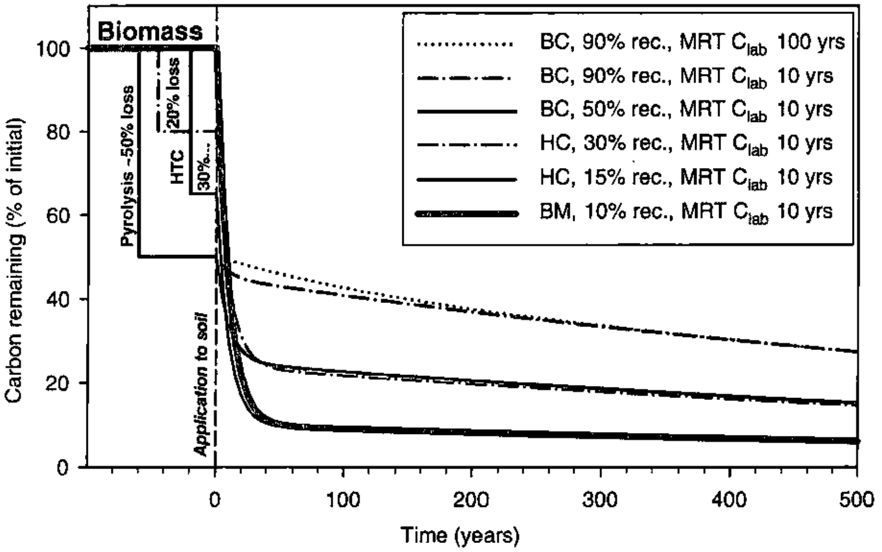

Figure 8.5 Conceptual model of carbon from biomass (= 100%) remaining after direct application, or carbonization and subsequent application, assuming 50% remaining carbon in biochar after pyrolysis or 65–80% remaining carbon after HTC. BC = biochar; HC = hydrochar; BM = biomass; rec. = recalcitrant; for further explanations see text. (Modified from and reprinted with permission from [101]. © 2009 Taylor & Francis.)

where C_{left} is the proportion of initial carbon left in soil after a certain time has elapsed, C_{lab} is the labile carbon pool with a MRT of 10 years (only dotted line in Figure 8.5: 100 years), C_{rec} is the recalcitrant carbon pool with a MRT of 1000 years, k is the decay constant of the labile (k-lab) or recalcitrant (k-rec) carbon pool, and t is the time after soil application.

Although the assumptions behind this approach (Eq. 8.1) will likely be correct for biochar (which consists mainly of recalcitrant material) and for biomass (consisting mostly of labile carbon materials) this may not be entirely true for hydrochar where we do not yet have a good perception of the decay behavior of its different fractions. Nevertheless, for the purpose of comparison with biochar or with direct application of uncharred biomass we assumed, as an upper boundary ("best case"), a carbon recovery of 80% and a recalcitrant fraction of 30% (which may be rather high, given the low average black carbon content of 21 hydrochars of around 5% in the study of Schimmelpfennig and Glaser [107]). As a lower boundary ("worst case"), we choose a low recalcitrant fraction only slightly above that of biomass and a larger carbon loss during the production process with only 65% carbon recovery.

Figure 8.5 reveals several points. (i) More carbon remains in soil if a char possesses a sufficiently large fraction of long-term stable, recalcitrant carbon; here biochar with its greater proportion will likely result in the larger amount of carbon sequestered over centennial time scales. (ii) Given that a hydrochar has a notable recalcitrant fraction it may result in the same carbon sequestered after about 50 years have passed due to the trade-off between its larger labile proportion, but higher initial carbon recovery. (iii) A hydrochar with a lower carbon recovery and low proportion of recalcitrant carbon will not be much different from uncarbonized biomass in its long-term carbon sequestration proportions. As already pointed out by Lehmann *et al.* [101], it becomes obvious here that it is the recalcitrant fraction that really matters. Modifying the MRT of the labile pool (e.g., for the most stable biochar in Figure 8.5) did not make much of a difference for the long-term carbon sequestration function.

Also, the incubation time in a given study will matter. While Kuzyakov *et al.* [108] calculated MRTs of about 2000 years from their 3.2-year incubation study in the lab with ^{14}C-labeled biochar, Steinbeiss *et al.* [115] reported MRTs between 4 and 29 years for two ^{13}C-labeled hydrochars made from glucose (without nitrogen) and yeast (5% nitrogen) in a 4-month incubation study. However, studies with durations of less than 100–500 years (which means essentially all experimental studies) will very likely underestimate the "true" MRT. The shorter the study, the stronger the underestimation will be. This is illustrated in Figure 8.6 for hypothetical data, where the decay of a char is again approximated with a double-exponential decay curve. Using only the first 2 years of a 100-year dataset, Lehmann *et al.* [101] calculated the MRT of the recalcitrant fraction to be 57 years. In contrast, using the entire 100-year dataset resulted in a MRT of 2307 years. Overestimation of char degradability may therefore occur when evaluating data from shorter incubation times (e.g., smaller datasets). For the reliable estimation of MRTs, long-term incubation studies and knowledge on the decay kinetics of the various carbonaceous fractions (e.g., labile, recalcitrant) are required for hydrochars. Furthermore, effects on other properties need to be considered as well. For example, with biochar, decomposition of the labile carbon substances on the surfaces of the chars and surface oxidation lead to increases in the cation exchange capacity [116, 117].

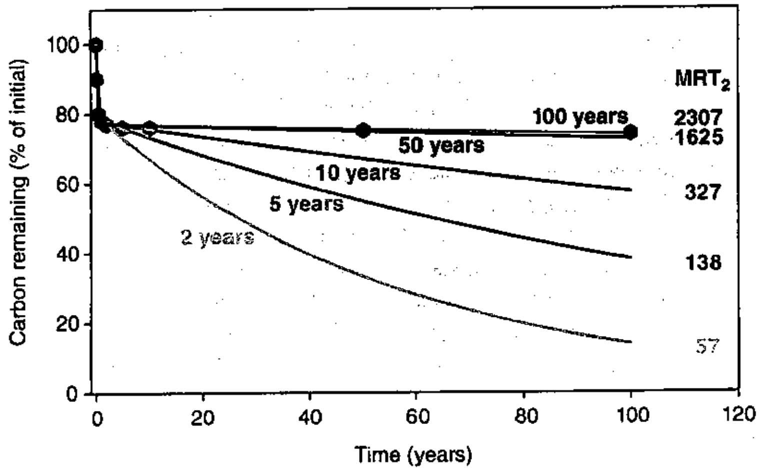

Figure 8.6 Double-exponential decay model (see Figure 8.5 and text) fitted to hypothetical data of char decay after 0.1, 0.5, 2, 5, 10, 50, or 100 years, assuming data availability for either the first 2, 5, 10, 50, or 100 years. MRT_2 = mean residence time of the recalcitrant carbon pool of the char, derived from k-rec (see text) and given in years. (Reprinted with permission from [101]. © 2009 Taylor & Francis.)

Since it will be hard to carry out studies with durations of at least a decade or more, we propose the following, probably more feasible approach, which may be combined with functional group and structure analyses. Incubations should be performed over 1 year where every "ingredient" for fast biological degradation of any degradable carbon in the hydrochar is provided or imposed upon the char. Mixing with the most fertile soils, incubation at high temperatures and optimum soil moistures, application of, for example, wood-rotting, lignin-degrading fungi (see below), "priming" (comineralization) by application of easily degradable carbon substrates, optimal nutrient supply, planting of mycorrhizal fast-growing plants, and drying/rewetting as well as freezing/thawing cycles; several such treatments should be combined to obtain the highest possible degradation rate in the shortest time feasible. Those combined treatments that produce the highest char carbon loss in the same char may be used later in standardized incubations to characterize various chars for the biological recalcitrance of the labile to moderately stable carbon fraction. Subsequently, maximum decomposition rates should be compared to the chemical characteristics of the chars to obtain a "biological stability" regression with the associated char characteristics (related to feedstock and hydrochar production parameters). Measuring decomposition rates in such a manner on hydrochars may serve as a first proxy to obtain the MRTs of several hydrochar carbon fractions with different stability, characterizing their size and MRT. Chemical characterization of the remaining char carbon fractions before and after rigorous biological attack may provide further insights into the magnitude and structure of its long-term recalcitrant fraction. Even now, without a wealth of data, it can be assumed from the chemical characteristics that hydrochars produced at higher temperatures and pressures will be more stable than weakly carbonized hydrochars made from the same material [107].

However, decomposition of char is not the only pathway of "loss" when one aims at determining the amount of remaining char in a given soil horizon over time. Char may be lost from soils due to surface erosion, run-off, and transport to the subsoil (via rain water as small particles or as dissolved organic carbon). Other potential mechanisms of char intrusion to deeper subsurface layers include bioturbation (e.g., earthworms), kryoturbation (i.e., mixture and movement by frost/thaw cycles), or anthropogenic management [106, 118, 119]. Carbon losses due to erosion or transport to deeper soil layers can be significant and occur over relatively short periods of time. Major *et al.* [118] reported a migration rate of 379 kg carbon ha^{-1} year^{-1} from the biochar application of 116 ton ha^{-1} to the top 10 cm of a grassland soil. The char migrated downward 5–20 cm over a 2-year study in Columbia. Respiratory or dissolution-related carbon losses were reported to be small in comparison (2.2% and 1%, respectively [118]). Due to the above-mentioned characteristics of hydrochar, and its less-particulate nature, the proportions might be reversed: we hypothesize that a larger fraction might be lost by mineralization in the first years, but that the downward migration may be considerably lower.

Char particles may shatter or fractionate into smaller particles via different physical or biological forces, such as freeze/thaw or swelling/shrinking of clay minerals, or in-growth of plant roots and fungal hyphae. Changes in particle size expose additional surface area that may increase char oxidization and/or degradation. In old charcoal-containing soils, biochar particles are very small (e.g., terra preta or chernozems); most of the biochar is included within microaggregates where it seems to be protected from further decomposition [98, 120]. Addition of labile carbon substrates has been reported to increase biochar decomposition; however, the extent was small [101, 106, 108]. White-rot fungi (usually decomposing lignin) or other basidiomycetes are able to slowly decompose lignite, sub-bituminous coal, or biochar via excretion of exoenzymes, such as laccase, mangane peroxidase, or phenol oxidase [100, 121]. A nitrogen-rich hydrochar was preferentially decomposed by fungi [115]. Rillig *et al.* [122] recently reported a considerably stimulated root colonization of arbuscular mycorrhizal fungi in mixtures of up to 20 vol% beet-root hydrochar chips. We observed in incubation studies that various fungi grew quickly on a mixture of brown earth with 8% (weight) hydrochar (sugar beet or bark) until they formed a dense, hydrophobic white layer on the top after 3–4 weeks at 22 °C [111]. It is unknown if fungal decomposition will continue in the field when the labile fraction of the hydrochar has been mineralized. The dense fungal mycelia and fruiting bodies were gone after 150 days of incubation [111]; the same was observed in other experiments with another hydrochar in the presence of plants [112, 123]. In the field it will likely depend on the presence of easily degradable carbon if a hydrochar (in particular, one that is nutrient-rich) will be quickly mineralized. Thus, degradation may be more pronounced over the years in the presence of (mycorrhizal) plants.

8.3.3.3 Carbon Sequestration Potential: Soil Carbon Priming or Buildup?

An intriguing find in terra preta soils is that the SOC stocks are higher than in adjacent Ferralsols, even disregarding the black carbon [90]. In contrast, Wardle *et al.* [124] reported an increased loss of organic matter over 10 years from mesh bags that contained charcoal compared to those without charcoal. Such a finding in a boreal forest soil may be explained by the promotion of nitrification, which has been frequently observed in boreal forest soils when charcoal is added (after forest fire or burnings, e.g., [125, 126]). Thus, addition of biochar or hydrochar to soils or litter layers must be carefully investigated with regard to possible priming effects that endanger the existing old soil carbon pool. However, so far there is not much evidence, at least for biochar, that it will promote old SOC decomposition. An exception may be forest soils where inhibitory phenolic compounds are adsorbed and hence the microbial activity is stimulated (such as the above-mentioned needle-litter dominated boreal forest soils). Moreover, in terra preta soils the increased SOC contents (*in addition to biochar*) do not indicate a long-term SOC loss due to biochar application [90, 98, 120].

Biochar and hydrochar seem to promote fungal growth (e.g., that of arbuscular mycorrhiza) [122, 127]. These fungi produce the protein glomalin which, as a binding agent, significantly promotes soil aggregation [128, 129]. Hence, both chars may in the long-term increase the protection of nonbiochar SOC by increasing soil aggregation through fungal promotion [122] or by formation of organomineral complexes and aggregates [101]. On the other hand, the labile, easily degradable carbon in hydrochar may present a risk if it leads to a priming effect on the old SOC. This aspect needs to be investigated.

Another possible way to cause an indirect positive effect on the soil carbon pool by char application is to increase the net primary productivity. If the net primary productivity increases the root biomass and turnover will increase, the litter carbon input will also rise and result in a SOC buildup in addition to the char carbon input. The annually repeated inputs of organic material (residues, litter, i.e., plant growth) will subsequently be mineralized and transferred into stable humus fractions. Alternatively, the presence of the char particles may provide "condensation nuclei" for the buildup of *a larger proportion* of more stable humus fractions. This would also promote the increase of the total SOC pool besides char-applied carbon. However, both mechanisms may also be working in the opposite direction. With biochar, it is likely that it may have positive effects on the soil carbon buildup besides the applied char carbon (see above [90]). With hydrochar, however, there is simply not enough knowledge available to make predictions.

8.3.4 Influence of Hydrochar on Soil Fertility and Crop Yields

8.3.4.1 Change of Soil Characteristics with Hydrochar

As mentioned before, the use of hydrochar in soils has seldom been investigated so far; the idea of using hydrochar as a soil amendment has its origin in biochar research and in the nanoscale properties of the hydrochar product [13, 11, 130–134].

Biochar application to soils has been shown to have a beneficial effect on soil physicochemical properties. Biochar presence may (i) enhance the water-holding capacity (WHC) [111, 135–137]), aeration, and hydraulic conductivity of soils [82, 135, 138], (ii) reduce the tensile strength of hard-setting soils [139, 140], (iii) increase the cation-exchange capacity of soils [82, 117, 141], resulting in an improved nutrient retention or higher nutrient use efficiency [142–144], (iv) in combination with increases in pH values [90, 140], and (v) stimulate growth, activity, and the metabolic efficiency of the microbial biomass [145, 146], including (vi) arbuscular mycorrhiza [122, 127, 147] and (vii) nitrogen-fixing rhizobiota [148], and it could also (viii) attract beneficial earthworm activity [140, 149–152].

Hydrochar will affect soil properties based on the same principles. It will very likely reduce the tensile strength, increase the hydraulic conductivity at least in some soils, and enhance the soil WHC due to its microstructure [130–133]. Hydrochars will likely not have the very large, internal surfaces that biochars have when produced at temperatures above 450 °C since hydrochars are produced at lower temperatures [153, 154]. Usually, typical surface areas measured via the Brunauer, Emmett, and Teller (BET) method range between 3 and 30 $m^2\ g^{-1}$. Pyrolyzing the same feedstock at temperatures above 420–430 °C can result in much higher surfaces ranging from 100 to 800 $m^2\ g^{-1}$ (or even up to 1700 $m^2\ g^{-1}$ with activated charcoal), depending on the maximum pyrolysis temperature, production process, and feedstock [107]. Therefore, water retention curves of hydrochar/soil mixtures may be different to biochar/soil mixtures so that the effect of hydrochar on plant growth (via the "water supply" pathway) will probably resemble that of peat or compost additions to soils.

Measurements of the WHC of hydrochar after production and after two types of post-processing (pressing and drying) showed that drying considerably reduced the WHC, but not pressing the hydrochar out [11]. Some hydrochars become hydrophobic when oven- or completely air-dried; we observed this in particular in planting experiments when dry soil/hydrochar mixtures were wetted for the first time. Theoretically, the presence of a greater number of carboxyl groups in production-fresh hydrochars than in biochars should result in hydrophilic behavior and give hydrochar a larger cation-exchange capacity directly after production [107, 130, 132, 133]. It is unknown to date but likely that hydrochars will undergo ageing processes similar to biochars, where the number of functional groups on the biochar surfaces increases over time [116, 117].

Since the pH of production-fresh hydrochars is rather acidic [9, 107, 131, 155] this may have beneficial effects, in particular in alkaline soil where certain micronutrients are immobilized due to the high pH, while it may have less beneficial effects in acidic soils.

8.3.4.2 Hydrochar, Soil Fertility, and Crop Yield

Biochar can lose some of the initial feedstock nutrients during pyrolysis (e.g., nitrogen via volatilization as NO_x) or the nutrients may become unavailable to plants by inclusion into aromatic stable structures [156, 157]. In contrast, hydrochar, with its lower production temperature, will retain more nutrients in a plant-available form (depending on the feedstock), either in the hydrochar itself or in the aqueous phase. The conservation of nutrients from waste materials and sludge for agricultural use thus may, in the face of problems such as the declining phosphate deposits worldwide, become one of the most interesting features of hydrochar. Sustainable nutrient recycling may in the end govern hydrochar use in agriculture. However, the current experimental evidence is very limited. In the following, we thus give a brief comparison to biochar with theoretical considerations for hydrochar, followed by the available (sparse) evidence.

It is well documented that biochar application can improve crop yields (reviewed in [158]). However, yield increases depend on the combined biochar/soil properties, absolute amounts of biochar and on the concomitant nitrogen application (nitrogen form as well as amount [150, 157, 159, 160]). Analysis of recent literature [11] has shown that biochar application can increase yields (i) in degraded or low-fertility soils, rather than at already-fertile sites [137, 139, 160, 161], (ii) in weathered tropical rather than in temperate soils ([83, 160] versus [149, 157]), (iii) in combination with NPK fertilizers or nutrient-releasing substances (composts, manures) [83, 139, 150, 161], or (iv) when the chars themselves were sources of nutrients (e.g., biochar from poultry litter [140]). It should be noted, however, that nutrient supply, pH, and other soil parameter changes are not always sufficient to fully explain observed biochar effects [157, 160].

In the first hydrochar field study undertaken in Germany [162, 163], labile carbon in the hydrochar was found to initially induce nitrogen deficiency by nitrogen immobilization. The authors conducted a full factorial field study where they applied 10 ton ha^{-1} of two different hydrochars (from beer draff/spent grain and sugar beet pulp, with C/N ratios of 16 and 38, respectively), combined with four levels of nitrogen fertilization (0, 50, 100, and 150 kg N ha^{-1}). The soil was a fertile Haplic/Stagnic Luvisol near Göttingen, Germany. The authors reported that at this hydrochar application level, no significant effect on the soil physicochemical properties such as field capacity, pneumatic conductivity, bulk density, or water-stable aggregation was found. (A concomitantly included compost treatment with 10 ton ha^{-1} also did not have any effect on these parameters.) The results of Gajic and Koch [163] with regard to sugar beet yield confirmed the above-mentioned hypothesis of nitrogen immobilization by the hydrochar: they did not observe germination reduction, but a significant growth reduction, in particular in the young seedlings. This was more pronounced with the hydrochar that had the larger C/N ratio (made from sugar beet pulp). Also, the relative sugar yield per hectare was reduced by hydrochar application. Moreover, the growth limitation was somewhat overcome by higher rates of nitrogen fertilization [163]. The authors reported a quick initial mineralization of both applied hydrochars: in the plots fertilized with 100 kg N ha^{-1} they assessed the CO_2 efflux via closed chambers and acidic traps. They detected a loss of more than 10% of the applied carbon within 2 months; the carbon loss was even significantly larger than that of the applied compost [162]. However, after about 3 months the CO_2 release from the hydrochar-amended plots slowed down to rates not different to the unamended control or the compost treatment

[162]. Thus, their results agree well with the available incubation studies reporting high initial mineralization rates [111, 113, 115]. Those initial high CO_2 efflux rates are the most likely reason for the observed nitrogen deficiency in growing seedlings (see below) due to a burst of microbial growth with the labile fraction in the hydrochar. It should be considered that during composting, a considerable fraction of such a labile initial biomass carbon fraction is also mineralized while in the HTC process, a higher proportion of the initial biomass carbon is retained in the solid HTC product. We therefore propose to use in future studies hydrochars that have been washed free of labile carbon compounds; it is plausible to assume that the strong nitrogen immobilization will be alleviated or absent without the labile carbon fraction.

However, there have been first reports of (phyto)toxic behavior of some hydrochars. Busch *et al.* [151] observed significantly negative effects in the cress germination test for phytotoxic gases (none of the seeds germinated), in the salad germination test (ISO-17126) with increasing amounts of char mixed into fine sand, and also in the barley germination and growth test where a sugar beet hydrochar was mixed in growing volumes with unfertilized standard peat substrate. However, in a subsequent regrowth of the harvested barley seedlings, the hydrochar-amended plants developed significantly larger biomasses than the control plants although there were less germinated plants present for regrowth [151]. In the earthworm avoidance test (ISO-17512), however, the animals significantly avoided the hydrochar-amended vessel side while they actively preferred the biochar-amended side in a concomitantly running test [151]. Rillig *et al.* [134] observed significant growth-reducing effects of hydrochar on *Taraxacum officinalis* plants. These initial problems with some hydrochars (all carbonized at temperatures and pressures around 200 °C and 2 MPa) have also been observed in other biotoxicity tests with different kinds of hydrochar, but not with all hydrochars that were ever tested [164]. In addition, the "nitrogen block" (likely microbial nitrogen immobilization) that is ameliorated by nitrogen fertilization has repeatedly been observed. Gajic and Koch [163] not only observed this in their field study, but also in a greenhouse experiment where the fine-ground hydrochar was more homogenously mixed into the soil. We observed the same [112] where the same feedstock was applied either as uncarbonized feedstock, as hydrochar, or as biochar: the growth of the radish plants in a fertile clayey loam was greatly retarded in the presence of feedstock or hydrochar (Figure 8.7).

In another experiment with radish, five plants were grown in 500-ml pots in a sandy loam. In this study, four biochars (from peanut hull, maize, wood chip sievings, and barbeque charcoal) or two hydrochars (bark and sugar beet) were mixed into the soil at 8% (w/w). The soil and the chars are the same as those described for experiment II in Kammann *et al.* [111]. The pots with the mixtures were brought to equal water holding capacities (60%) and were kept in the greenhouse at 22 °C and 12/12-h day/night cycles. Regular (every 2 days) weighing and watering was performed to keep the soils at optimal water-holding capacities (50–60% of the respective maximum of the mixture). While seeds germinated and grew normally in the control and biochar-amended soils, germination and growth was greatly retarded in the hydrochar-amended treatments; the radish plants remained small and yellow-leafed. Instead, we noticed the growth of several reddish small fruiting bodies of unknown fungi on the pot surfaces (hydrochar treatments only). Three weeks after seedling emergence the pots were fertilized (100 kg N ha^{-1}) with a full-compound fertilizer solution (same as in Kammann *et al.* [137]). From the fertilization date onwards, the young radish

Figure 8.7 Growth of radish plants in a clay loam soil (SOC 3.5%, pH 6) amended with 5% (w/w; from left to right): nothing (control); feedstock, hydrochar, biochar, or a 1 : 1 hydrochar/biochar mixture. The retarded growth with the pure feedstock, pure hydrochar, and the 1 : 1 soil-mix containing hydrochar is easily visible.

plants growing on the hydrochar-amended soils became green and showed a completely normal growth, confirming the observations of Gajic and Koch [163]. At harvest, the radish plants reached the same leaf chlorophyll content as the controls (an indication for the nitrogen supply; Figure 8.8b). However, they were not able to completely compensate the initial deficiency-caused delay until the final harvest (Figure 8.8a). The biochar treatments as well as one of the hydrochar treatments all significantly increased the water use efficiency (WUE) over the growth period of 6 weeks compared to the control (Figure 8.8b). It is reasonable to assume that the discrepancy between the biochar- and hydrochar-amended plants in their WHC is due to the initial "nitrogen block" observed with the hydrochar plants, similar to the observations of Gajic and Koch [163]. A higher initial application of nitrogen in the hydrochar treatments might have resulted in the same significantly higher water use efficiency with hydrochar than observed here with four different biochars (Figure 8.8b).

All hydrochar growth experiments described here used hydrochars with relatively high C/N ratios; hydrochars were moderately carbonized (around 200 °C) either in water or steam and did not contain large amounts of plant-available nutrients [162]. It must be urgently identified if the initial negative effects that seem to vanish or were alleviated after some time of char ageing are simply due to a kind of "nitrogen blocking" (which is also frequently observed when carbon-rich organic materials such as harvest residue or immature compost are incorporated into the soil) or if some toxic compounds may be present [151]. So far, we have not been able to identify such substances in analyses for polyaromatic hydrocarbons, heavy metals, polychlorinated biphenyls, or other potentially harmful persistent organic pollutants in any of the hydrochars that caused reduced germination in tests [164]. A more nutrient-rich hydrochar from manure or sludge waste streams might have entirely different effects. Theoretically, the chemical structure (carboxyl groups) and the greater nutrient

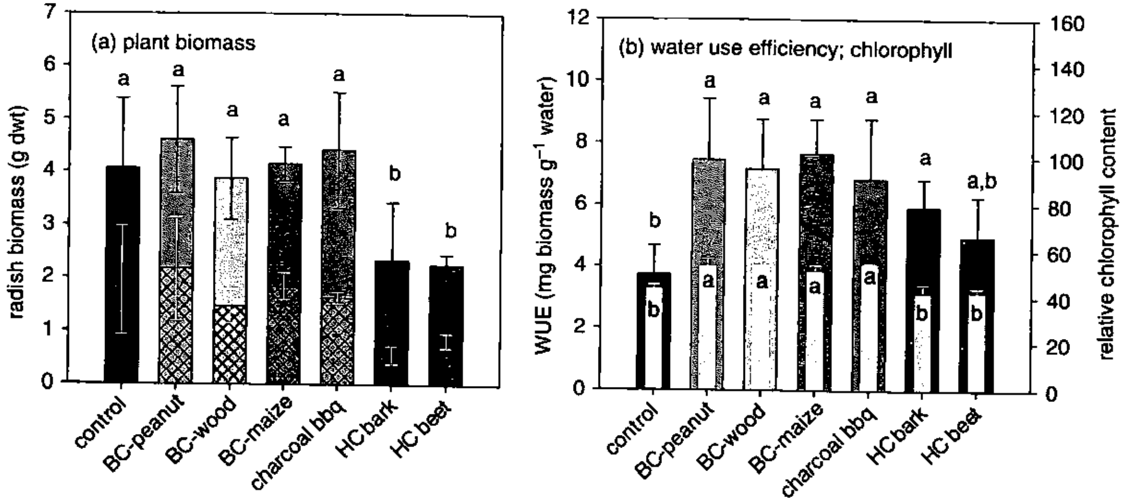

Figure 8.8 *(a) Radish biomass yield of hypocotyl (cross-hatched) and leaves (open) in soil/char mixtures. (b) Water use efficiency (mg yield produced g^{-1} water consumed) and relative leaf chlorophyll content at the harvest (method description in [137]). Means ± standard deviation, n = 5 pots per treatment with n = 5 plants per pot. Different letters indicate significant differences between treatments (analysis of variance + Student–Newman–Keuls* post-hoc *test, $p < 0.05$). BC = biochar, HC = hydrochar; biochars/hydrochars used here are equal to those used in Experiment II in [111]. Peanut = peanut hull residue; wood = wood chip sievings (dominated by needles); maize = maize silage; bark = bark and wood residue; beet = beet-root chip residue.*

(in particular, nitrogen) retention with HTC still make it a highly interesting option for closing nutrient cycles, hygienization of wet wastes, and conversion of waste streams into fertilizers. Hydrochar may not come as a ready-made tool, but demand that some effort is put into its development into a suitable agricultural management strategy. There is simply not enough known on the effects of hydrochar on plant growth to draw any general conclusions so far – more research is urgently required to identify risks, as well as benefits.

8.3.5 Greenhouse Gas Emissions from Char-Amended Soils

Quantification of greenhouse gas emissions (CO_2, N_2O, and CH_4) following char application to soils is crucial because any positive carbon sequestration effect could become negligible if the emissions of other potent greenhouse gases increase after char application. For CO_2 emissions from soils, the possibility of "priming" of old SOC as been discussed earlier. Hence, this section mainly focuses on N_2O and CH_4 fluxes.

8.3.5.1 Sources of N_2O Emissions from Soils

N_2O is a potent greenhouse gas with a global warming potential of 298 [165]. It is predominantly produced during heterotrophic denitrification of NO_3^- to N_2 as a gaseous intermediate and usually to a lesser extent by nitrification of NH_4^+ to NO_3^- as a byproduct (for reviews, see, e.g., [166, 167]). N_2O emissions from agricultural soils are particularly high after application of nitrogen-rich fertilizer (particular in the presence of labile carbon, e.g., manures, slurries), during the conversion of aerobic soils to anaerobicity, during freeze/thaw cycles in spring, and/or in the presence of urine patches [168].

Neglecting N_2O emissions may cause considerable misinterpretation of the real carbon (i.e., CO_2-equivalent) sink capacity of agricultural [169] or seminatural [170] ecosystems. Reductions of N_2O emissions as a result of char application would considerably improve the greenhouse gas balance of biochar-grown agricultural products.

8.3.5.2 Effects of Char Application to Soils on N_2O Emissions

Rondon *et al.* (cited in [154]) reported reduced N_2O emissions after biochar application. Since then, several more reports of reduced N_2O emissions in the presence of biochar have followed [11]. Others have also observed significant reductions of N_2O emissions with biochar, either without plants or in the presence of plants [111]. In addition we observed reductions in a low-SOC as well as high-SOC soil with two different biochars applied at 4% (w/w) in the presence of earthworms, which are known for their high N_2O production [152]. The effects of hydrochar on N_2O formation in soils have to our knowledge not been investigated so far except for our study [111]. In an incubation study of soil mixed with 8% (w/w) of a bark and beet-root hydrochar, we observed significant reductions of the N_2O emissions in unfertilized soil directly after application up to 3 weeks. However, after stirring (to mimic ploughing) and, in particular, after nitrogen fertilization the N_2O emissions rose considerably and exceeded those of the control soil without amendment; the N_2O emissions with 8% (w/w) additions of four different biochars were significantly reduced (see Experiment II in [111]). However, the effect depends on the chosen comparison system. In two other studies where feedstock, hydrochar, and biochar (made from the same feedstock) were applied at equal rates we always observed the highest N_2O emissions from the feedstock mixtures, followed by the hydrochar mixtures while the N_2O emissions from the biochar mixtures were lower (sometimes significantly) compared to the untreated control. The feedstock and hydrochar N_2O emissions, however, were larger than those from the unamended control [112, 123]. It is essential to compare measured N_2O emissions after hydrochar application to a meaningful reference system and to provide information on the chosen reference system.

Specific mechanisms of changes in N_2O fluxes are not currently well-understood and is a rather under studied phenomenon. Libra *et al.* [11] reviewed several potential mechanisms, including: (i) the reduction in anaerobic microsites in soil, (ii) a change in soil pH, (iii) nitrogen immobilization in soil, (iv) stimulation of plant growth, (v) change in nitrogen transformation pathways in soil, and (vi) chemical reduction of N_2O. Many open questions remain and are detailed by Libra *et al.* [11].

8.3.5.3 *Effect of Biochar Soil Application on CH_4 Emission and Uptake Rates*

As organic matter anaerobically decays, CH_4 production will result. CH_4 oxidation by aerobic methanotrophic bacteria (i.e., CH_4 uptake into the soil) is also an ubiquitous process that has been reported to occur under oxic conditions [171]. Char application to soils may increase the CH_4 sink activity, which would be of global significance (see [11] for additional details). The effect that biochar or hydrochar application may impart on CH_4 production or CH_4 oxidation is unknown. Van Zwieten *et al.* [172] suggests that biochar may have a positive influence on CH_4 emissions. They reported that CH_4 production declined to zero in the presence of biochar in a grass stand and in a soybean field [172]. Zhang *et al.* [173] reported that the CH_4 emissions in rice paddies in China increased by 34% and 41% with 40 ton ha^{-1} biochar addition and with/without nitrogen fertilization; however, in this study the N_2O emissions decreased substantially, while rice yields increased by about 10%. Thus, the overall greenhouse gas emission/yield ratio was improved by biochar use in this south-eastern Chinese rice paddy study, despite the increase in CH_4 emissions, which the authors attributed to labile substances that might have been present initially in the biochar [173], but otherwise they did not have an explanation for the increase.

CH_4 uptake in a poor acidic tropical soil increased by 200 mg CH_4 m^{-2} $year^{-1}$ compared to the controls [172], which is quite a large reduction. Priem and Christensen [174] reported that CH_4 uptake rates declined in a savannah that had recently been burned, but it was not clear if noteworthy amounts of black carbon had formed during burning. Spokas *et al.* [175, 176] reported reductions in the CH_4 uptake rates with some biochars and unaltered rates with others. Karhu *et al.* [136], on the other hand, observed significantly increased (more than 100%) CH_4 uptake rates in a northern Europe agricultural soil where the WHC and also aeration were increased by biochar addition. In a greenhouse study with *Lolium perenne*, we found no negative effects (only in tendency positive) of pure biochar addition to an agricultural soil with low native CH_4 uptake rates [111]. In contrast, in a clayey loam high-SOC grassland soil we observed strong stimulations of the endogenous CH_4 uptake rates – not only with biochar, but also with a hydrochar, compared to an unamended control [112, 123]. Changes in the CH_4 fluxes due to char amendment (such as those outlined above) will depend on gas transport in soil. Libra *et al.* [11] provide a detailed discussion on this topic. Briefly, reduced soil compaction and improved soil aeration may stimulate

CH_4 consumption, since O_2 and CH_4 diffusion are regulated by soil water content [177], which has been defined as a key factor.

8.3.6 Best-Practice Considerations for Biochar/Hydrochar Soil Application

Recommendations on how to apply char to agricultural fields are first emerging from the initial field trials. Pyrochars are mostly dry and their application without wetting can result in considerable losses to the air during the transport, spreading, and incorporation into the soil [158]. This can cause dust clouds, which carry the risk of dust explosions, ignited by a spark. Furthermore, fine biochar dust particles in the air may cause health problems [158]. Major and Husk [149] estimated in a commercial biochar field trial in Canada that about 30% of the char was lost by dust erosion during transport and incorporation into the soil. Another concern is that black carbon fine particles and soot have a considerable greenhouse potential [165] so that dust and aerosols must be avoided.

Therefore, appropriate strategies for dry chars would be to mix them with wetter materials such as compost, liquid manures or slurries, or with water. Subsequently the char must be incorporated into the soil by ploughing, disking, or deep-banded application.

However, hydrochar is wet when it leaves the production process, thus no dust losses should take place when it is used directly out of the production process. Gaijć *et al.* reported that they manually spread two different wet hydrochars (from sugar beet and from beer draff) onto the soil surface; the material had to stay there and dry for 10 days, because the wet hydrochar adhered in clods to the tires of the machinery. Our own observations at the start of a field experiment also showed this "clodding" of *Miscanthus* hydrochar [123], only in this case the material had been dried and ground with a 10-mm mesh to a finer particle size. On the other hand, if a wet hydrochar is not dried we frequently observed fungal growth. It may, therefore, be necessary to find a "water content window" (probably 10–15%) where the hydrochar is neither at risk of aerosol formation nor at risk of quick fungal colonization and degradation. So far, the experience with hydrochar storage, handling, and field application is very limited.

Strategies of mixing the biochar (respectively, hydrochar) with a nutrient-rich substance such as green waste compost, slurry, or manure, or of cocomposting or even animal feeding before field application [178] will have the positive side-effect of "loading" the char with nutrients from the start; such techniques may even be comparable to the strategies that the former inhabitants of Amazonia used when creating terra preta [82, 90].

8.4 HTC Technology: Commercial Status and Research Needs

Recently, HTC units for processing thousands of tons biomass residuals per year have been built or are planned (e.g., in the United States, Germany, and Spain), although the research on the details and dependencies of HTC reactions is still very much in its infancy. This of course is not unusual in most fields searching for pragmatic solutions; in the field of waste solids and liquids, processes for treating wet biomass residuals are continually being sought. These wet organic materials can vary widely in chemical composition, volatile and noncombustible fraction, moisture content, particle size, and energy content. In general, multistep process combinations are required to achieve the desired treatment goals, which range from destruction to resource recovery. Currently, many combinations of thermal, chemical, biological, and mechanical processes are already available for treating wet organic wastes. Most often all four types of processes are combined to reach the required level of treatment, using large amounts of energy and equipment. System complexity has grown over the years as treatment limits are lowered and new target compounds are added. Multiple steps for each target compound are often necessary since they can partition between the solid/liquid/gas phases. For example, process chains in municipal wastewater treatment plants usually consist of more than 15 process steps, requiring large expenditures for personnel, capital costs as well as for energy. The chemical conversion of wet organic material to hydrochar through HTC could substantially change the energy balance in many waste treatment plants as well as produce value-added products.

Conceptually, in the process design, pre- and postprocessing steps surround a central reaction process. A HTC process for treating industrial wastes in an urban setting can take advantage of the pre- and postprocessing steps that are part of an existing municipal infrastructure for the collection and disposal of waste streams. For instance, liquids can be discharged to efficient municipal wastewater treatment plants. However, pre-existing infrastructure can be a disadvantage when its inertia to change hinders the introduction of new collection systems for segregated concentrated waste streams (e.g., ecosanitation, biowaste). In a rural setting without such infrastructure, all necessary pre- and postprocessing steps must be accounted for in the process design and operation. Treatment goals for agricultural residues may also differ – resource recovery or pathogen destruction may be the central treatment goals.

8.4.1 Commercial Status

There has been a high level of research activity and commercial development on HTC over the last decade driven in part by the rediscovery of HTC by some researchers for the production of functional carbonaceous materials [5, 6] and the recognition of its potential as a method for carbon sequestration [13]. Its subsequent popularization [179, 180], combined with research funding programs, has resulted in the formation of several spin-off companies in Europe (e.g., in Germany, Spain, and Switzerland). Legislation propagating sustainable resource-efficient materials flow management and renewable sources for energy production set the stage for the recent R&D activity. For example, in Germany, the Closed Substance Cycle and Waste Management Act (KrW-/AbfG 1994) with its tiered management hierarchy (from prevention, reuse, recycling, material, and energy recovery to disposal) paved the way by requiring waste separation with the goal to make full use of substances and materials bound in wastes [181]. In addition, disposal of wastes with an organic content over 5% TOC in landfills was banned in 2005, requiring the development of alternative treatment methods.

A further boost to HTC development was the passage of renewable energy source legislation (e.g., California's Renewable Energy Program [182], Germany's Renewable Energy Sources Act (Erneuerbare-Energien-Gesetz) [183]). The Renewable Energy Sources Act from 2000 and its subsequent amendments, with its guaranteed feed-in tariffs and connection requirement for electricity produced from renewable sources; has been a strong driving force behind the significant growth in renewable energies in the German electricity sector. Electricity produced from hydrochar from certain feedstocks also qualifies for the guaranteed 20-year payment for produced electricity. An additional driving force for the production of hydrochar in Germany is the Renewable Energy Heat Act (Erneuerbare-Energien-Wärmegesetz) from 2008 [184], which stipulates that owners of new buildings must cover part of their heat supply with renewable energies.

Of the over eight German companies active in HTC process development, most are planning systems to produce hydrochar for energy recovery with throughputs ranging from a few thousand to 50 000 metric ton year^{-1} of biomass (http://www.topagrar.com/news/Neue-Energie-News-Erste-Biokohle-ab-2012-am-Markt-100132.html). The first full-scale HTC reactor system in Germany was built in 2010 by a Swiss company (reactor volume of 14.4 m^3, throughput of 8400 metric ton year^{-1}) to convert wet organic waste from beer production to hydrochar and then electricity (http://www.ava-co2.com/web/media/downloads_EN/medienmitteilungen/Press_Release_EN.pdf). In Spain, up to 2000 metric ton year^{-1} of landscape, yard, and forest cuttings are converted to hydrochar (http://www.ingeliahtc.com/English/plantaHTC.html), while in the United States a roughly 100-fold larger HTC unit (capacity 245 000 metric ton year^{-1}) is processing wastewater sludge from five Californian municipalities in the Los Angeles region as a renewable fuel for a cement kiln (http://www.enertech.com/facilities/sitedevelopments/rcrf.html).

Thus, current economic viability is mainly based on renewable energy source regulations and subsidies. Most companies, however, keep an eye on research in the soil application area or actively supply hydrochar to researchers in order to support evaluation of hydrochar potential for increasing soil fertility and/or carbon sequestration. Reactor types vary from batch or continuous-flow mixed tanks to plug flow tubular reactors. Most are modular in design; some are built for mobility in containers.

8.4.2 General Research Needs

Thus, we see that process development as well as the evaluation of the economic and environmental feasibility of a HTC process is very context- and site-specific. Nevertheless, fundamental and systematic investigations still need to be undertaken to determine the general suitability of pyrolysis and char-based concepts for the various environmental applications discussed in this chapter. In particular, investigations on how process conditions affect the physicochemical characteristics of the conversion products and byproducts as well as their ecotoxicity and fates are required. Parallel research on understanding the effects of hydrochar application on soils must continue to determine which properties are responsible for what interactions. With this systematic knowledge, appropriate process combinations can be designed to produce the desired hydrochar and treat any byproducts.

In addition, scenarios for technical implementation need to be evaluated, which include a comprehensive management concept for the feedstock production and collection, treatment of byproducts and recovery of nutrients, and distribution and use of the char. A comparative life cycle analysis should consider the substantial costs and environmental impacts of the current collection and treatment processes in use today for wet organic wastes.

8.4.2.1 *Knowledge Gaps in Process Design and Operation*

Research has just begun to determine the effects of feedstock and process parameters on process energetics, product distribution between phases, and product quality, qualitatively and quantitatively. For some parameters, qualitative trends of their effect on char yield, characteristics, and product distribution are relatively clear (e.g., reaction temperature), while others cannot be generalized yet, owing to the high variation in reported results (e.g., residence time, concentration of feedstock, and the ratio of liquid/gas volumes). Due to the heterogeneity of biomass residuals as feedstock (in composition and form), the complexity of the reaction mechanisms, and the numerous parameters, a broad data basis is required in order to be able to generalize results and develop process models. Some important questions to be investigated on a wide range of systems (in no particular order) are:

- What is the fate of emerging contaminants (personal care products, pharmaceuticals, nanomaterials, and endocrine-disrupting compounds) found in these waste streams? Are they thermally destroyed during carbonization?
- What is the fate of other, potentially toxic compounds (e.g., polychlorinated biphenyls) sometimes found in these waste streams?
- What is the fate of inorganics during HTC? Of particular importance is the fate of chloride.
- How degradable is the process water? Can it be recycled and reused? Can heat be recovered from it?
- Can a catalyst be added to allow for the controlled manipulation of char properties?
- What are the optimal reaction temperatures and times for different waste streams?

The answers to these questions may not only be very dependent on the feedstock and process parameters, but also on the scale of the reaction system since heat and mass transfer may play important roles in the reaction rates. Unfortunately, the cost and safety precautions required for pressurized HTC reaction systems hamper the ability of researchers to experiment at different scales. Most investigations are made at very small scale in batch reactors ranging from 4 ml to 2 l with particulate feedstock. The rates of heat and mass transfer may change substantially in larger-scale reactors with different geometries and mixing patterns, resulting in different product properties. This should be kept in mind when planning experiments and analyzing results.

Most effects still need to be quantified and physical/mathematical models developed for them. Most effects are relevant for environmental as well as energetic applications, indeed, sometimes inversely. For example, higher reaction temperatures produce chars with a higher carbon content and, therefore, with a HHV. This energetic improvement is usually accompanied by a decrease in char yield, resulting in lower carbon efficiencies that reduce the carbon capture potential of the HTC process. Changes in process parameters may also have further consequences downstream – increasing reaction temperature usually results in an increasing amount of colloidal carbon particles and loss of structural features of the original feedstock [185], affecting further processing steps (e.g., solids separation). Moreover, many questions remain on temperature effects, especially with regard to the fate of organic contaminants in the feed such as pharmaceutically active compounds or production of byproducts.

8.4.2.2 *Knowledge Gaps in Char Characterization*

In order to advance our understanding of processes, products, and applications, comprehensive characterization of the chars produced under the various conditions needs to be carried out and reported. This is an essential step in the search to relate char properties to effects in environmental applications, and requires a concerted effort of key players across disciplines, producers, and users to choose the relevant characteristics that need to be measured and develop testing methods for them. There are several important questions that need to be addressed to begin to understand how to most effectively take advantage of the benefits of HTC-derived char:

- Is the process environmentally friendly (e.g., implications associated with liquid-, solid-, and gas-phase parameters, emerging contaminant fate)?
- Can the resulting char be used for environmental remediation, energy generation, and/or soil augmentation? Do harmful contaminants leach from the hydrochar? What is the chemical stability of the hydrochar?
- From a life cycle assessment perspective, when does it make sense to use HTC within a waste management system?

Communication between char producers and users must be developed in order to exploit the ability to influence char properties in the production process and ensure the quality of products. It is important to note that this is an iterative process, particularly at the current stage of development where much is still to be learned about how feedstock and process conditions determine the product chemical composition and efficiencies of conversion. This is especially critical in biochar applications where short-term process developments can substantially change material properties, while long-term research is required to study char–soil–plant interactions and which properties are responsible for the interactions.

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