Physico-chemical properties and effects of Biochars from Hydrothermal Carbonization and Pyrolysis of organic residues in agricultural soils

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Abstract

Carbon (C-) rich solids from the incomplete combustion of biomass (termed biochars) produced by pyrolysis (pyrochars) and hydrothermal carbonization (hydrochars), have the potential to improve certain soil properties when applied to agricultural soils. The main hypotheses of this work are (i) to examine if physico-chemical properties of different feedstock are reflected in different C degradation rates of hydrochars. Furthermore, it is assumed that (ii) sorption of the water soluble phenyl-urea pesticide isoproturon (IPU) in soil amended with pyrochar is higher compared to soil amended with hydrochar. In addition, it is suggested that (iii) the bioaccessibility of IPU depends on the degradability of pyrochars and hydrochars. Lastly, it is hypothesized that (iv) the water repellency of biochars inhibits the increase of the plant available water capacity and hydraulic conductivity of the soil amended with biochars. Physico-chemical properties of the biochars, their short-term C degradability, the sorption and mineralization of IPU, and the soil hydraulic properties were examined in four independent laboratory investigations. Therefore, loamy sand soils were amended with different hydrochars (carbonized at 200 and 250°C for 6 h and 2 MPa) and pyrochars (pyrolyzed at 750°C for 0.75 h) in realistic addition amounts (0.5 to 5% by weight). Feedstock materials (digestate, miscanthus and woodchips) of different biological resistance (C/N ratio) were chosen for pyrolysis and carbonization. For evaluation of the short-term C degradability additional hydrochars from digestate, grass, straw and woodchips, carbonized under gentle conditions (180°C for 8 h and 2 MPa) were used.

Pyrochar degradation within 56 days was low (<2% of initial char-C). In contrast, hydrochars revealed a high content of readily available C (up to 14% of the original char-C was degraded within the same period of time). Lower degradation rates were found for biochars from lignitic raw materials, with a high C/N ratio and low O/C and H/C ratios, and for hydrochars carbonized under high temperatures (250°C). Sorption of IPU increased by a factor of 13 after hydrochar application and by a factor of 2283 after pyrochar application. The mineralization of IPU was significantly reduced by up to 56% after hydrochar application and up to 81% after pyrochar application. Presumably, pyrochars will occlude the pesticide in their micro-porous structure resulting in long-term persistence of IPU in soil. In contrast, hydrochars will guarantee the bioaccessibility of IPU, because hydrochars likely degrade within a few years. The retention of plant available water of the soil increased after application of hydrochars (5 to 15%) and pyrochars (3 to 10%). Water repellency of biochars had little counteracting effects on the improvement of soil water retention and saturated conductivity. Thus, other biochar properties (i.e., particle size, intra-particle porosity, shape, and plasticity) are over-compensating possible negative effects of repellency. In conclusion, due to their good pesticide and water retention, hydrochars can be recommended for application to extensively used, agricultural soils, if they are relatively stable in soil, hence, when they are produced at high process temperatures (≥250°C) and from lignitic feedstock. Because of the high diversity of biochar types, standard procedures should be developed to evaluate the suitability of a specific type for a desired use in a certain soil before its application. In addition, to guarantee that there is no risk for human living and the environment, a monitoring program should be installed after biochar application at the agricultural site.

Keywords: biochar, pyrolysis, hydrothermal carbonization, agricultural soil, isoproturon

Zusammenfassung

Kohlenstoff (C-) reiche Feststoffe aus der unvollständigen Verbrennung organischen Materials (Biokohlen), die mittels Pyrolyse (Pyrokohlen) und hydrothermaler Carbonisierung (Hydrokohlen) hergestellt wurden, bieten nach Einarbeitung in landwirtschaftliche Böden die Möglichkeit, bestimmte Bodeneigenschaften nachhaltig zu verbessern. Die dieser Arbeit zugrunde liegenden Hypothesen sind, zu untersuchen, (i) ob sich die physiko-chemischen Eigenschaften verschiedener Ausgangsmaterialien in den daraus produzierten Hydrokohlen wiederspiegeln, z. Bsp. in unterschiedlichen C Abbauraten. Darüber hinaus besteht die Annahme, dass (ii) die Sorption des wasserlöslichen Pestizids Isoproturon (IPU) aus der Klasse der Phenyl-Urea im Boden nach Zugabe von Pyrokohlen höher ist als von Hydrokohlen. Zudem wird angenommen, dass (iii) die Bioverfügbarkeit von IPU von der Abbaubarkeit der Biokohlen abhängt. Abschließend wird vermutet, dass (iv) die wasserabweisenden Eigenschaften von Biokohlen den positiven Auswirkungen nach Biokohlezugabe entgegenwirken, den Pflanzen verfügbaren Wasseranteil und die hydraulische Leitfähigkeit zu erhöhen. Die physiko-chemischen Eigenschaften von Biokohlen, ihr kurzzeitiger C Abbau, die Sorption und Mineralisierung von IPU, und die hydraulischen Bodeneigenschaften wurden in vier unabhängigen Laborexperimenten untersucht. Dazu wurden lehmige Sandböden mit verschiedenen Hydrokohlen (bei 200 und 250°C für 6 h und 2 MPa carbonisiert) und Pyrokohlen (bei 750°C für 0.75 h pyrolysiert) in realistischen Mengen (0.5 bis 5 Gewichts-%) verwendet. Als Ausgangsmaterialien wurden organische Reststoffe (Gärreste, Miscanthus, Holzhackschnitzel) mit unterschiedlicher biologischer Resistenz (C/N Verhältnis) ausgewählt. Für die Bewertung des kurzzeitigen C Abbaus standen zusätzlich Hydrokohlen aus Gärresten, Grünschnitt, Stroh und Holz zur Verfügung, die unter milden Bedingungen (180°C für 8 h und 2 MPa) produziert wurden.

Pyrokohlen wurden innerhalb von 56 Tagen kaum abgebaut (<2% des Biokohle-bürtigen C). Hydrokohlen hingegen wiesen einen hohen Anteil an leicht verfügbarem C auf (bis zu 14% des ursprünglichen Biokohle-bürtigen C abgebaut). Geringere Abbauraten wurden für Kohlen aus Lignin haltigen Ausgangsmaterialien, mit hohem C/N und niedrigem O/C–H/C Verhältnis festgestellt und für Hydrokohlen, die bei hohen Temperaturen carbonisiert wurden. Die Sorption des gut wasserlöslichen Pestizids IPU konnte um das 13-fache nach Hydrokohlezugabe und um das 2283-fache nach Pyrokohlezugabe gesteigert werden. Die Mineralisierung von IPU wurde nach Zugabe von Hydrokohlen um bis zu 56% und von Pyrokohlen um bis zu 81% reduziert. Pyrokohlen binden das Pestizid in ihrer Mikrostruktur wahrscheinlich langfristig. Hingegen gewährleisten Hydrokohlen die Bioverfügbarkeit von IPU, da sie dem C-Abbau sicherlich schon binnen weniger Jahre unterliegen. Die Rückhaltung Pflanzen verfügbaren Wassers im Boden erhöhte sich nach Zugabe von Hydrokohlen (5 bis 15%) und von Pyrokohlen (3 bis 10%) im Vergleich zum reinen Boden. Wasserabweisende Eigenschaften hatten kaum gegenläufige Auswirkung auf die Erhöhung der hydraulischen Bodeneigenschaften. Folglich scheinen andere Biokohleeigenschaften (z. Bsp. Partikelgröße, innere Porosität, Form und Verformbarkeit) mögliche negative Effekte zu kompensieren. Zusammenfassend können auf Grund der guten Schadstoff- und Wasserrückhaltung Hydrokohlen für den Einsatz auf landwirtschaftlichen Flächen empfohlen werden, wenn diese relativ schwer abgebaut werden, also bei hohen

Temperaturen (≥250°C) und aus Lignin reichen Ausgangstoffen hergestellt wurden. Auf Grund der Vielzahl an Biokohle-Typen, sollten Standardtests entwickelt werden, die die Eignung eines Typs für eine vorgesehene Verwendung noch vor Ausbringung prüfen. Zudem sollten Monitoring Programme sicherstellen, dass nach Ausbringung auf landwirtschaftliche Flächen, keine Gefahr für Mensch und Umwelt von der eingesetzten Biokohle ausgeht.

Schlagworte: Biokohle, Pyrolyse, Hydrothermale Carbonisierung, Ackerboden, Isoproturon

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List of publications

The following articles of the dissertation have been published:

Eibisch, N., Helfrich, M., Don, A., Mikutta, R., Kruse, A., Ellerbrock, R., Flessa, H., 2013. Properties and degradability of hydrothermal carbonization products. Journal of Environmental Quality 42, 1565-1573. Doi:10.2134/jeq2013.02.0045

Eibisch, N., Schroll, R., Fuß, R., Mikutta, R., Helfrich, M., Flessa, H., 2015. Pyrochars and hydrochars differently alter the sorption of the herbicide isoproturon in an agricultural soil. Chemosphere 119, 155-162. Doi:10.1016/j.chemosphere.2014.05.059.

Eibisch, N., Schroll, R., Fuß, R., 2015. Effect of pyrochar and hydrochar amendments on the mineralization of the herbicide isoproturon in an agricultural soil. Chemosphere (*in press*). Doi:10.1016/j.chemosphere.2014.11.074

Eibisch, N., Durner, W., Bechtold, M., Fuß, R., Mikutta, R., Woche, S.K., Helfrich, M., 2015. Does water repellency of pyrochars and hydrochars counter their positive effects on soil hydraulic properties? Geoderma 245-246, 31-39. Doi:10.1016/j.geoderma.2015.01.009.

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List of abbreviations

ANOVA	Analysis of variance
APR	Average pore radius
ASE	Accelerated solvent extraction
AWC	(Plant) Available water capacity
CA	Contact angle
DOC	Dissolved organic carbon
FTIR	Furier-transform infrared spectroscopy
HTC	Hydrothermal carbonization
iMDQ	*in-situ* mass distribution quotient
IPU	Isoproturon
LASSO	Least absolute shrinkage and selection operator
NER	Non-extractable (isoproturon) residues
OECD	Organisation for economic co-operation and development
OM	organic matter
PS, PaS	Particle size
PWE	Pore water extraction
SSA	Specific surface area
TPV	Total pore volume
WEOC	Water extractable organic carbon

1 General introduction

1.1 Introduction and definition

Biochars are carbon (C) rich solids from incomplete combustion (e.g., pyrolysis, gasification, combustion, carbonization, vaporization) that are used as soil amendment (Lehmann and Joseph, 2009). After appropriate application (in terms of amount, timing, frequency of application), amendment of agricultural soil with biochars is expected to result in an increase of water and nutrient retention, an improvement of aggregate structure and stability, and, with respect to climate change mitigation, an increase of the C stability in soil. However, so far, no standard procedures for appropriate application of biochars have been established. Similarly, application techniques and practical recommendations for proper utilization are lacking. Most likely, this can be ascribed to the large variety of biochars that originate from the above mentioned different carbonization processes and numerous possible feedstock materials, which in turn result in differences of physico-chemical properties of the chars and their effects on soil quality which are matter of ongoing research.

The term biochar does not define solely products from ecological farming. Therefore, in German language the term "*Pflanzenkohle*" has been introduced as synonym (Schmidt, 2011). But this labeling seems to be misleading and deficient, because biochars are not exclusively produced from vegetable material but also from e.g., animal wastes or municipal sewage sludge. Moreover, since a few years, many scientists refer to biochar when the charred material is produced by pyrolysis (also termed pyrochar) (Cao et al., 2011; Schimmelpfennig and Glaser, 2012). Products from hydrothermal carbonization (HTC) are termed HTC-chars or hydrochars, respectively. Products with carbonaceous properties from other production processes are currently of less ecological and economic interest. Thus, this work focuses on pyrochars and hydrochars. The generic term for chars from different production processes in this work is the most commonly used term biochar.

1.2 Production processes

Currently, biochars are produced either conventionally in pits or brick kilns or in modern, automated reactors, which allow controlled process engineering. Product yield and characteristics are thereby determined by a set of factors: process technology, feedstock material, moisture of the feedstock, way of feeding (continuous, singular batch), highest heating temperature, heating rate, cooling rate, pressure, and process duration (Schimmelpfennig and Glaser, 2012). All organic materials from domestic waste to municipal sewage sludge can be used as feedstock. In Germany, the recycling of digestate from biological treatment plants and waste from landscape management as well as renewable raw materials (e.g., from short rotation coppice) are applied. According to the process technology, pre-drying of the feedstock and chaffing may become necessary.

The production processes are distinguished in thermochemical processes (e.g., pyrolysis, gasification) and hydrothermal techniques (e.g., hydrothermal carbonization, vaporization). According to the process conditions the basic compounds (cellulose, hemi-cellulose, lignin) of the feedstock undergo a sequence of chemical modifications (e.g., dehydration, depolymerization, dehydrogenation, decarboxylation, recondensation, degasification, carbonization), and determine the product yield both quantitatively and qualitatively (Knicker, 2007; Keiluweit et al., 2010; Titirici and Antonietti, 2010).

Pyrolysis is the most frequently used production process. It is performed in a wide temperature range under oxygen limiting conditions that inhibit complete combustion of the biomass (Karaosmanoglu et al., 2000). According to the process duration, slow, conventional and fast (or flash) pyrolysis can be differentiated (Quicker, 2012). According to the process temperature, low (<500°C), medium (500-800°C) and high (>800°C) temperature pyrolysis are distinguished. Besides the solid product biochar (or pyrochar), pyrolysis produces ash, bio-oil, and non-condensable gases (CO_2, CO, CH_4, H_2) (Spokas et al., 2009).

In the year 2006, the article "*Zauberkohle aus dem Dampfkochtopf*" about the research of Dr. M. Antonietti from the Max Planck Institute of Colloids and Interfaces, drew the attention on a technique that had already been developed by Bergius (1913) and had been further investigated by Berl and Schmidt (1932). Today the technique is known as hydrothermal carbonization (HTC). It allows the use of organic residues with a water content between 50 and 80% and is conducted at temperatures between 180 and 250°C and under a pressure of around 2 MPa (Libra et al., 2010). Thus, the HTC process is less energy and cost intensive than e.g., pyrolysis. The products comprise a higher solid yield compared to pyrolysis, a significant amount of dissolved organic compounds and a small quantity of gases (Libra et al., 2010; Cao et al., 2011). Due to the different production conditions of pyrolysis and HTC, the physico-chemical properties of pyrochars and hydrochars vary substantially as specified in the following.

1.3 Physico-chemical properties of pyrochars and hydrochars

The microstructure of pyrochars comprises three main components: first, a principal component, in which aromatic-aliphatic structures are held together amorphously and in which the heteroatoms H, O, N, P and S are imbedded cyclically (Keiluweit et al., 2010; Knicker, 2010); second, a mineral component, and third; a crystalline component of conjugated aromatic compounds (Keiluweit et al., 2010). At higher temperatures, the latter progressively adopts the structure of graphite layers. With increasing age (ageing) the biochar surfaces will undergo partial oxidation creating an aryl-C backbone with substituted carboxyl- and carbonyl groups (Glaser et al., 2002; Cheng et al., 2006). The greater amount of functional groups in aged biochars results in an increased cation exchange capacity, and a stronger formation of soil char complexes that have already been detected for a loamy soil amended with pyrochars from rye grass (Hilscher and Knicker, 2011). Furthermore, ageing reduces the amount of hydrophobic functional groups with unknown effects on the soil hydrologic budget.

Hydrochars are typically produced at temperatures between 180 and 250°C (Funke and Ziegler, 2011). Visually, hydrochars from lignitic materials resemble their raw feedstock (see woodchips in Fig. 1.1) because lignin primarily breaks down when temperatures exceed 300°C (Liu et al., 2013). Like a sponge, these materials are characterized by a continuous amorphous nano-pore system with high amounts of hydrophilic carbonyl, carboxyl and hydroxyl functional groups on their surfaces (Sevilla and Fuertes, 2009; Titirici and Antonietti, 2010). Hydrochars of less lignitic feedstock appear as meso-porous spherical particles of 20 to 200 nm size (Titirici and Antonietti, 2010). The particle size is mainly determined by the temperature, pressure, and duration of the production process and added catalysts (e.g., citric acid). Additionally, the formation of raspberry like structures has been identified (right side in Fig. 1.1) that have been created after impregnation of beech wood with the sulfurous amino acid cysteine, and are probably due to an increase of the surface tension of C droplets (Kruse, 2011).

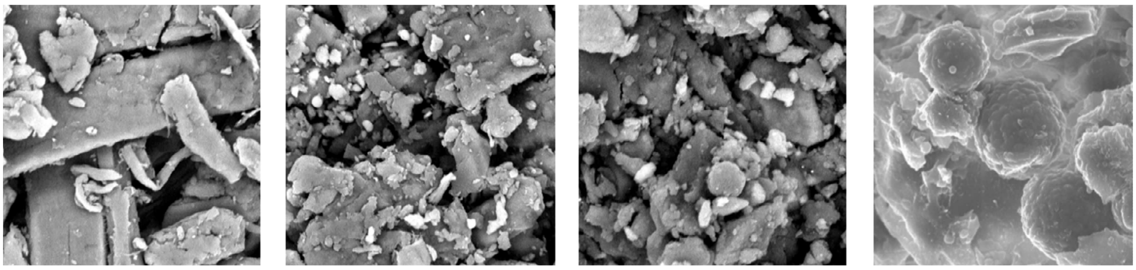

Fig. 1.1 SEM images (3000-fold) from HTC (180°C, 8h) of woodchips, straw, grass cutting (from l. to r.), and from HTC (180°C, 4h) of beech wood impregnated with 10% Cystein, modified after Kruse (2011)

The meso-porous network of hydrochars and the complex turbostratic structure of pyrochars generate a specific surface area (SSA) of different dimensions. For hydrochars, SSA values of around 10 $m^2 g^{-1}$ have been measured (Schimmelpfennig and Glaser, 2012). Pyrochars possess an SSA of up to 1000 $m^2 g^{-1}$ (Uchimiya et al., 2011). Nonetheless, different methods (e.g., feedstock loading with salts and water soluble monomers, post-treatment with hydrogen peroxide) may be helpful in increasing the SSA and reactivity of hydrochars (Titirici and Antonietti, 2010; Xue et al., 2012). According to intended use, the biochar can be optimized in its desired functionality via systematically pre- and post-treatments thereby producing so called designer biochars (Novak et al., 2009).

For evaluation of the short-term C degradability of biochars the atomic O/C ratio of the charred material is plotted against the atomic H/C ratio in a so called Van Krevelen diagram (Fig. 1.2). Generally, the O/C and H/C ratios decrease with increasing degree of carbonization, and are typically lower for pyrochars than for hydrochars and untreated feedstock (Keiluweit et al., 2010; Hoekman et al., 2011). The decrease of the O/C and H/C ratios usually goes along with the formation of stable aromatic structures and an increase of the calorific value (Chun et al., 2004; Cantrell et al., 2012).

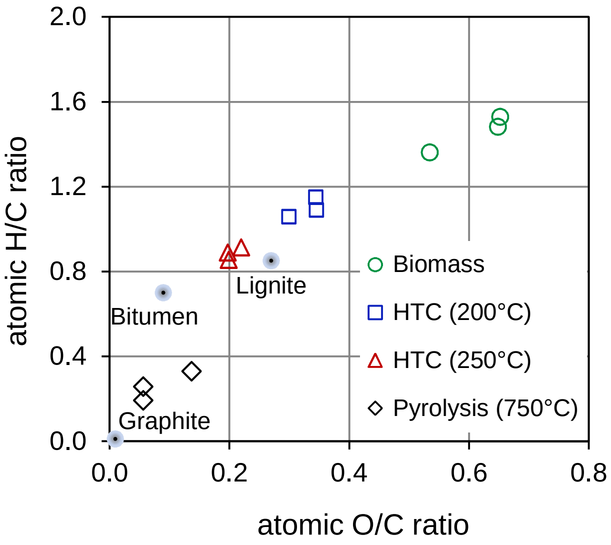

Fig. 1.2 Van Krevelen diagram, values of biomass and biochars from Eibisch et al. (2015), and values of bitumen, graphite, and lignite (grey dots) from Allen-King et al. (2002)

The liquid products of HTC have been subjected to little research so far. However, it is known that HTC liquids are rich in readily available organic compounds (Libra et al., 2010), which in turn cause a high microbial activity at room temperature. This can be observed e.g., from the formation of biofilms on the product surface (i.e., mould spores or fungal growth). It is conceivable that during separation of the solid and liquid phase at the end of the HTC process, these C condensates adhere on the hydrochars. In C mineralization experiments this would cause a high initial CO_2 emission peak leading to an overestimation of the degradability of pure hydrochars. Washing with water or a solvent may be an effective procedure to remove the condensates from the hydrochar surfaces (Cao et al., 2011; Spokas et al., 2011; Gajić et al., 2012). Furthermore, in the HTC process water a set of intermediates from the decomposition of carbohydrates has been detected. Typically these are acetic, glycolic and carboxylic acid, different aldehydes, ethanol, phenol, as well as furfural, methylfurfural and hydroxymethylfurfural, that all contribute to the total C content of the liquid HTC product (Kruse et al., 2003; Berge et al., 2011). The quantitative composition and the enrichment or depletion of specific elements in the solid or liquid phase strongly depend on the feedstock and process conditions and are still matter of research.

1.4 Potential benefits and knowledge gaps of biochar application to soil

Prototypes of biochars are highly aromatic components of the so called Amazonian dark earths (portug. *Terra preta*) that were formed 500 to 7000 years ago throughout the Brazilian Amazon Basin and that are characterized by a high soil fertility (Glaser, 2007). As the name suggests, these dark Anthrosols can be distinguished from adjacent soils by their dark color and by the high amount of ceramic fragments. Presumably, organic residues from pre-Columbian settlements had been collected in clay jugs, which then had been burned and subsequently been ploughed in the soil, for waste disposal on the one hand, and on the other hand to allow cultivation of tropic soils that are otherwise poor in nutrients (Solomon et al., 2007). The procedure that resulted in the accumulation of carbonaceous material and the formation of *Terra preta* soils is not exactly known. But it is widely accepted that carbonaceous components are responsible for the improved water retention, the higher nutrient availability and cation exchange capacity, and the higher amount of stable organic substance in these soils (Glaser et al., 2001; Birk et al., 2011).

Recent positive experimental results on C sequestration and nutrient and water retention by application of pyrochars to soil give rise to expect beneficial effects when biochars are used constantly in agriculture. However, there is a lack of systematic investigations with pyrochars from different feedstock and process conditions that justify repetitive application. Moreover, knowledge about the material and structural characteristics of HTC-biochars, and their impacts on soil hydraulic properties, nutrient and pesticide retention, and the C degradability in soil has just begun to grow in the last few years. In the following this is explained in more detail.

Biochars for carbon sequestration

The high resistance of char particles in the Amazonian dark earths encouraged the scientific and public community to believe in the use of biochars as large and long-term sink of atmospheric

CO_2 by the path of the photosynthesis (Kuzyakov et al., 2009). According to estimations, an amount of 5.5 to 9.5 Gt C could be sequestered per year by the production of biochars (Lehmann et al., 2006). This approach would actively counteract the anthropogenic emissions from fossil fuel combustion and effectively contribute to climate change mitigation. The recalcitrance of different pyrochars has been investigated intensively in the last decade, primarily under laboratory conditions (Sohi, 2009). From $\delta^{13}C$ incubation experiments over 120 days with soil amended with 1 to 4% (w/w) Eucalyptus pyrolyzed at 450 and 550°C for 40 min, mean residence times of biochars were calculated from the reciprocal of the decomposition rate and range between 62 to 248 years (Keith et al., 2011). Higher residence times have also been reported (200 to >3000 years), generally increasing with process temperature (200-600°C) and duration (2-48 h) (Kuzyakov et al., 2009; Major et al., 2010a; Peng et al., 2011). For hydrochars estimated mean residence times lay within a few decades (Steinbeiss et al., 2009; Gajić et al., 2012). However, investigations on the mineralization of hydrochars from different feedstock are rare and labile and stable hydrochar C fractions are usually not differentiated. Hence, residence times are likely underestimated. In addition, estimations of mean residence times are based on short-term incubations and generally do not consider dynamics of mineralization conditions in the field (e.g., biological activity, C stock, and climate) which complicates the evaluation of the C sequestration potential of biochars. Moreover, climate smart indirect impacts, e.g., on the primal soil C content, the demand of fertilizers, and on the greenhouse gases N_2O and CH_4 have to be considered as well. In short-term studies it was shown that N_2O emissions decreased after application of pyrochars and hydrochars to sandy silt, and then increased significantly after a rain event and N fertilization (Kammann et al., 2012). These opposing results demonstrate that different parameters (e.g., climate, soil type, management) have to be taken into account to validate conclusions on the potential reduction of greenhouse gases after application of biochars to agricultural soils.

Biochars for improvement of pesticide sorption

In the recent years, various studies have reported that the yield of diverse crops (e.g., rice, sorghum, maize) could be increased considerably after application of pyrochars to different soil types (Steiner et al., 2007; Major et al., 2010b; Uzoma et al., 2011a; Liang et al., 2014). The increase was attributed to an improved nutrient availability and reduced leaching after rainfall, and highly depended on the process temperature and feedstock of the added biochar. In soil amended with high temperate pyrochars (<750°C) lower concentration of N, P and heavy metals were measured, which has been ascribed to the change of structural product properties after pyrolysis (i.e., break down of micro-porosity, decrease of SSA, formation of aromatic structures) (Gaskin et al., 2008). Additionally, at pyrolysis temperatures above 400°C negatively charged functional groups were lost resulting in a lower cation exchange capacity (Chun et al., 2004).

Most likely, the high SSA, the micro-porosity, and the quality and quantity of functional groups of biochars are also responsible for the retention of organic compounds, such as pesticides in soil. Zheng et al. (2010) have found out that the sorption of triazine pesticides onto pyrochars from green cuttings (pyrolyzed at 450°C for 1h) was higher for finer pyrochar particles (≤0.125 mm) with an overall higher SSA than for coarse particles (≥0.250 mm). Moreover, it took less time to reach the sorption equilibrium in soil amended with fine sized pyrochars compared to coarser particles. This points to the circumstance that pesticide diffusion in the micro-porous structure and occlusion takes longer for coarse char particles. Nonetheless, most sorption studies are based on batch experiments in soil suspension, and therefore, do not reflect natural conditions in the soil very well. Furthermore, different feedstocks have not been considered so far, and the sorption potential of hydrochars as used in this study has been rarely investigated (Sun et al., 2011; Sun et al., 2012).

There are indications that pyrochars reduce pesticide mineralization due to their sorption capacity (Jones et al., 2011). However, most experiments concerning pesticide mineralization were done in soil suspensions (Zhang et al., 2005), or examined insecticides with high hydrophobicity (Yu et al., 2009; Yang et al., 2010). These are considerably different to the relatively water soluble phenyl-urea herbicide isoproturon (IPU) that is frequently applied to agricultural soils and has been used in the present study. Only Si et al. (2011) and Sopeña et al. (2012) investigated the mineralization of IPU. The reported amounts of mineralized IPU were high (i.e., up to 50% of the original IPU amount), probably because IPU had been applied regularly in the past to soils that have been amended with technical charcoal. Thus, the microbial community could already adapt to mineralize IPU metabolically. Soils from organic farming that have not been subjected to pesticide application for at least 15 years have not been used so far and the effects of pyrochars from different feedstocks are not known. The impact of hydrochars on pesticide mineralization as used in this study has not yet been investigated.

Biochars for improvement of soil hydraulic properties

Due to their high SSA and micro-porosity, biochars are likely able to hold high quantities of water. Hence, the soil water storage capacity increases after application of biochars (Karhu et al., 2011; Kammann et al., 2012). However, generally, the water storage capacity is not well defined. Establishing water retention curves, as conducted in this study, is convenient to assess the plant available water capacity (AWC) that is defined as the fraction of water released between field capacity, pF 1.8, and permanent wilting point, pF 4.2, and an important issue in agriculture. In most cases, the AWC increased between about 30 and 170% after pyrochar additions compared to control treatment. The increase was significantly higher for high char additions (5% compared to 1%, w/w) and higher pyrolysis temperatures (500°C compared to 300°C), and generally higher for sands compared to loamy sands (Uzoma et al., 2011b; Kinney et al., 2012; Peake et al., 2014). Hardie et al. (2014) gives the following explanations for the improvement of water retention by char addition: (i) intra-particle porosity of the added char, (ii) modification of the original soil pore system by the new texture of soil and char particles, and (iii) improved persistence of soil pores due to increased aggregate stability. The impact of the char particle size on the soil porosity and soil hydraulic properties was not clear so far and has been investigated in this study.

It is often assumed that the water repellency of chars is an important factor influencing the water retention of soils. Water repellency is induced by polar aliphatic and aromatic functional groups on the biochar surfaces. When the water content increases, the inner polar ends of amphiphilic groups may change their orientation to the outer water side and allow wettability of the surface (Fig. 1.3) (Doerr et al., 2000). On the other hand, surface hydrophilic groups tend to bind to each other under desiccative conditions and cause increasing water repellency (Diamantopoulos et al., 2013). Both processes imply that the water repellency depends on time and the water content of the soil. Consequently, in laboratory drainage experiments the initial moisture content and the way of sample saturation is assumed to fundamentally determine retention and hydraulic conductivity curve characteristics. To investigate the soil hydraulic properties, in this study biochar amended soils were capillary saturated under the atmosphere of the lab as well as under vacuum conditions.

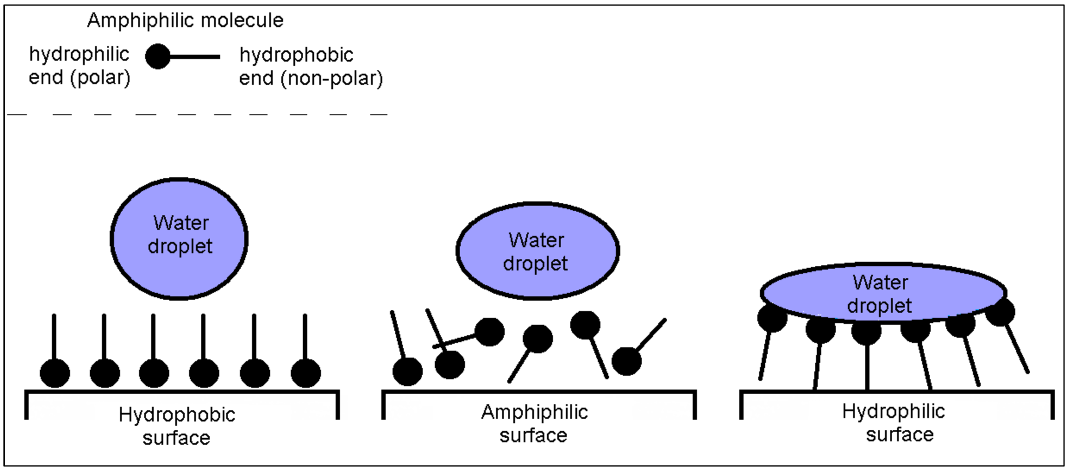

Fig. 1.3 Change in orientation of functional groups while in contact with increasing water content (changed after Doerr et al., 2000)

2 Objectives and working hypotheses of the present study

For the present study biochars were produced from pyrolysis and HTC and different organic residues were selected as feedstock. The main objectives of this research were to

1. investigate physico-chemical properties of biochars resulting from different feedstock and different carbonization processes (pyrolysis, HTC) as well as of HTC process water,
2. examine their short-term C degradability,
3. evaluate the impact on pesticide sorption and mineralization, and
4. assess the effects on soil hydraulic properties in an agricultural soil.

The different issues were realized in four scientific articles with the following working hypotheses:

Article I “*Properties and degradability of hydrothermal carbonization products*” *(Journal of Environmental Quality* 42, 2013) comprises a comprehensive physico-chemical characterization of the solid and liquid phase of the HTC of feedstocks (digestate, green cuttings, straw, woodchips) with different physico-chemical properties, e.g., C/N ratio, pH value, and ash, lignin and dissolved organic C content. In addition, aerobic incubation experiments over 30 days were performed to evaluate the short-term C degradability of different hydrochars which was then related to the HTC product properties. This work comprises two main hypotheses:

Hypothesis I: Differences in physico-chemical properties of different feedstock are reflected in hydrochars, i.e., resulting in different C degradation rates.

Hypothesis II: A significant part of easily degradable C, which may sorb onto hydrochar surfaces during separation of liquid and solid phase after the HTC process, may be removed by washing the hydrochars with water before application to soil in order to decrease hydrochar degradability.

The experimental part of this work was conducted at the Thünen Institute of Climate-Smart Agriculture in Braunschweig.

The laboratory work for articles II and III was performed at the Institute for Soil Ecology of the German Research Center for Environmental Health in Munich. Article II “*Pyrochars and hydrochars differently alter the sorption of the herbicide isoproturon in an agricultural soil*” (*Chemosphere* 119, 2015) describes the impact of different feedstocks, process conditions, and char addition amount on the sorption capacity of the herbicide isoproturon in an agricultural loamy sand.

Hypothesis III: Isoproturon sorption capacity in soil amended with pyrochar is higher compared to soil amended with hydrochar and varies with the used feedstock.

Article III “*Effect of pyrochar and hydrochar amendments on the mineralization of the herbicide isoproturon in an agricultural soil*” (*Chemosphere*, submitted) aims to clarify if pyrochar and hydrochar application to an agricultural soil reduces the mineralization of the herbicide isoproturon.

Hypothesis IV: Isoproturon mineralization is directly related to the sorption of the herbicide.

Hypothesis V: The production process and feedstock have significant effects on the bioaccessibility of isoproturon, and the bioaccessibility depends on the degradability of pyrochars and hydrochars.

The work to article IV “*Does water repellency of pyrochars and hydrochars counter their positive effects on soil hydraulic properties?*” (*Geoderma*, submitted) has been assessed at the Department of Soil Science and Soil Physics of the Institute for Geoecology at the Technische Universität Braunschweig. As there is sparse knowledge about the change in hydraulic properties after application of biochars to soil, the main objective of this work was to comparatively investigate the effects of pyrochars and hydrochars, and to evaluate the impacts of different feedstock and char particle size, as well as saturation under atmospheric and vacuum conditions.

Hypothesis VI: Particle size and type of added char affect water retention characteristics and hydraulic conductivity.

Hypothesis VII: The water repellency of chars inhibits the increase of the plant available water capacity and hydraulic conductivity of the soil amended with chars.

The dissertation is based on an inquiry of the German Federal Ministry of Food and Agriculture, and was financed by means for the reporting on the German national greenhouse gas inventory for the sectors agriculture and land use.

3 Article I. Properties and degradability of hydrothermal carbonization products

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Abstract

Biomass carbonized via hydrothermal carbonization (HTC) yields a liquid and a carbon (C)-rich solid called hydrochar. In soil, hydrochars may act as fertilizers and promote C sequestration. We assumed that the chemical composition of the raw material (woodchips, straw, grass cuttings or digestate) determines the properties of the liquid and solid HTC products including their degradability. Additionally, we investigated whether easily mineralizable organic components adsorbed on the hydrochar surface influence the degradability of the hydrochars and could be removed by repetitive washing. Carbon mineralization was measured as CO_2 production over 30 days in aerobic incubation experiments with loamy sand. Chemical analysis revealed that most nutrients were preferably enriched in the liquid phase. The C mineralization of hydrochars from woodchips (2% of total C added), straw (3%), grass (6%) as well as digestate (14%) were dependent on the raw material carbonized and were significantly lower(by 60-92%; $p < 0.05$) than the mineralization of the corresponding raw materials. Washing of the hydrochars significantly decreased mineralization of digestate-hydrochar (up to 40%), but had no effect on mineralization rates of the other three hydrochars. Variations in C mineralization between different hydrochars could be explained by multiple factors, including differences in the O/C–H/C ratios, C/N ratios, lignin content, amount of oxygen-containing functional groups, and pH. In contrast to the solids, the liquid products were highly degradable with 61 to 89% of their dissolved organic carbon being mineralized within 30 days. The liquids may be treated aerobically e.g., for nutrient recovery.

3.1 Introduction

Incomplete combustion of biomass yields a carbon (C)-rich solid, called biochar, which can be used as soil amendment to increase soil fertility and mitigate climate change (Lehmann et al., 2006; Yu et al., 2009). The debate on biochar as a soil amendment was stimulated by the discovery of the archetype *Terra Preta do Indio* which had been formed by anthropogenic practices (i.e., slash and char) (Glaser et al., 2002). Stable organic material (e.g., from charred food waste) mixed with soil was found to be responsible for long-lasting, high level of soil fertility and greater crop yields compared to the surrounding soils in the tropics (Glaser et al., 2000; Yamato et al., 2006; Woods et al., 2009; Verheijen et al., 2010).

A high potential for long-term C sequestration has been associated with biochars derived from carbonization processes using high processing temperatures (>450°C; e.g., pyrolysis). Under these conditions, the resulting biochars show a high degree of aromaticity (Lehmann et al., 2006; McBeath and Smernik, 2009) which, in turn, increases the resistance to mineralization, compared to the raw materials used for biochar preparation (Glaser et al., 2002). Recently, the production of low-temperature carbonized material via hydrothermal carbonization (HTC), so-called hydrochar, has received increasing attention (Funke and Ziegler, 2010), and the possibility of using hydrochars for C sequestration was indicated by positive experimental results for biochars produced by pyrolysis (Lehmann et al., 2006; Nguyen et al., 2008). Biochars produced by pyrolysis are likely to possess lower C degradability than hydrochars (Kammann et al., 2012); however it is conceivable that hydrochars also possess the ability to stabilize C due to aromaticity in the structure of hydrochars (Titirici et al., 2007; Sevilla et al., 2011).

Hydrothermal carbonization (HTC) is a wet chemical process that transforms biomass at relatively low temperatures between 180 and 250°C and pressures of about 20 bars (Funke and Ziegler, 2010). As energy-intensive pre-drying, such as that required for pyrolysis, is not necessary, organic residues with water contents of 50 to 90 wt% (i.e., sewage sludge, municipal waste, digestate, etc.) can be used directly (Mumme et al., 2011). The succession of different HTC reaction steps (hydrolysis, dehydration, decarboxylation, condensation) generate (i) hydrochars, (ii) liquids and, (iii) small amounts of CO_2 and other trace gases (Sevilla and Fuertes, 2009; Funke and Ziegler, 2010).

Recently, the influence of different process conditions on the physico-chemical properties of solid products was studied by Schimmelpfennig and Glaser (2012). Compared to biochar from pyrolysis or charcoal, HTC led to a lower degree of carbonization, as well as a lower specific surface area (SSA) and lower amounts of aromatic C; however, a higher number of reactive, O-containing functional groups were maintained. Furthermore, physico-chemical properties of products produced under similar process conditions were highly variable, indicating a considerable influence of the raw material undergoing HTC. However, only a few studies have systematically investigated the physico-chemical characteristics or mineralization behavior of hydrochars produced from different raw materials under the same process conditions (Gajić et al., 2012; Kammann et al., 2012; Schimmelpfennig and Glaser, 2012). Furthermore, to our best knowledge, the liquid phase generated during HTC has not yet been examined in existing studies to date.

Therefore, our objective was to determine the effect of different raw materials (woodchips, straw, grass cuttings, digestate) on the physico-chemical properties of hydrochars and liquid phases produced by HTC, and to assess the specific enrichment and depletion of elements as compared to the raw materials. We hypothesized that variation in the structural properties and biochemical composition of the products obtained by HTC from different raw materials have different rates of C mineralization which we tested by short-term incubation experiments. Moreover, we assumed we could remove labile components of the hydrochars that may have sorbed from the liquid phases onto the surface of the hydrochars during phase separation and the drying. This would create a high mineralization pulse and lead to an overestimation of hydrochar C mineralization in short-term incubation experiments. In order to evaluate if the components can be removed by water washing, the incubation was performed with water-washed and unwashed hydrochars.

3.2 Materials and methods

Hydrochar production and analysis of HTC products and raw materials

Hydrochars and liquids were produced under the same HTC conditions (180°C, 8 h, 20 bar) from woodchips (from pine tree woodchips), straw, grass cuttings, or digestate (>80% corn) by Artec Biotechnologies, Bad Königshofen, Germany. The input material was shredded to < 40 mm and carbonized with water (1:10, *w/w*) in a tabular reactor (0.19 m^3) made of structural steel (type ASTM A 36 M). At initiation of digestate HTC, pH was adjusted from 9.0 to pH 4.5 with citric acid to facilitate dehydration processes and increase C yield in the solid product (Wang et al., 2010). After cooling, the hydrochars were separated from the liquid products by coarse filtration with gauze (105 μm diam.). Hydrochar masses were determined gravimetrically after drying at 105°C for 24 h. The oven dry masses were 23.4% (woodchips-hydrochar), 6.9% (straw-hydrochar), 8.5% (grass-hydrochar), and 9.0% (digestate-hydrochar), relative to the masses before drying (100%). The solids were ground using a 1.5-mm rotor mill, except for the woodchips and woodchips-hydrochar, which were ground using a high performance 1-mm Retsch type SK100 (1.1 kW, 2850 rounds min^{-1}). The liquid products were filtered (0.45 μm, Sartorius Stedim Biotech; Göttingen, Germany) and frozen at -18°C until analysis.

For the incubation experiments, a sub-fraction of each hydrochar was washed to evaluate whether a sorptive C fraction could be readily mineralized. The hydrochars were purged with deionized water (1:100, *w/w*) for two minutes and then passed through 7–12-μm filters (black ribbon filter, type MN 640 w). The procedure was repeated up to five times, and the hydrochars were named according to the number of wash cycles, i.e., 0x, 1x, 3x and 5x, respectively.

The pH values of the unwashed hydrochars and raw materials were measured at a solid : solution ratio of 1:20 (w/w) in deionized water. The specific surface area (SSA) and total pore volume were derived from N_2 gas adsorption isotherms recorded at 77 K using an Autosorb analyzer (Quantachrome Corp., USA). SSA values were calculated using the BET equation based on seven adsorption points in the relative pressure range 0.05 to 0.3 P/P_0 (Brunauer et al., 1938). Total pore volume was determined at a relative pressure of 0.995 P/P_0.

Fourier-transform infrared (FT-IR) measurements were performed using a BioRad® FTS 135 (Cambridge, MA, USA) to examine functional groups via the KBr technique (Ellerbrock et al., 2005). Briefly, 1 mg of finely ground unwashed hydrochar or freeze-dried liquid product (-20°C, 40 h, <100 µbar, Jumo IMAGO 500, Fulda, Germany) was mixed with 80 mg KBr and dried over silica gel in a desiccator for 12 h. For each spectrum, 16 scans were collected at a resolution of 1 cm^{-1}. Adsorption bands resonating at 3005 to 2765 cm^{-1} were taken to represent hydrophobic methyl (CH-) groups and were combined to one absorption band (A). The summed intensity of peaks appearing at 1620 cm^{-1} and 1740 cm^{-1}, reflecting hydrophilic, oxygen-containing (CO-) groups was assigned as band B. The ratio of band A relative to B (A/B ratio) serves as an indicator of wettability (Ellerbrock et al., 2005). If the A/B ratio is close to zero, the samples are expected to be potentially wettable. Hydroxyl-groups appearing above 3200 cm^{-1} were not considered as they may reflect differences in water content (Günzler and Böck, 1990).

The dissolved organic C (DOC) content of the liquid products was measured by thermal oxidation using a DIMATOC2000 (DIMATEC, Essen, Germany). Carbon and N contents of the unwashed hydrochars and raw materials were determined via dry combustion (LECO TruSpec, St. Joseph, MI, USA). As no differences between the C concentrations of unwashed and HCl-washed (4 M HCl, Scheibler method; Gajić et al., 2012) samples were observed, total C was considered to be totally organic. The ash content of the solids was determined gravimetrically by loss on ignition in a muffle furnace at 550°C for 5 h.

For elemental analyses, 0.15 g of the unwashed hydrochars or raw materials were digested with 8 mL nitrohydrochloric acid (concentrated nitric acid and hydrochloric acid, 1:3) at 180°C for 30 min using a modular microwave system (Anton Paar Multiwave 3000, Graz, Austria). Digests were adjusted to 25 mL with deionized water and then diluted 1:10. The element contents (e.g., Al, Ca, Fe, K, Mg and Na) of the prepared samples and also of the liquid phases were analyzed using inductively coupled plasma-optical emission spectroscopy (Varian Liberty 150, Palo Alto, CA, USA). In the liquid phases phenol and substituted phenols (sum parameter) were determined photometrically at 280 nm (Hach-Lange LCK 346, Düsseldorf, Germany). Acetic acid, formic acid, glycolic acid and formaldehyde contents of the liquid phases were determined by high performance liquid chromatography coupled to an UV detector at 210 nm and a RI-detector using a Rezex ROA column (Phenomenex, Aschaffenburg, Germany) and 0.1mM H_2SO_4 as the eluent. Furfural, methylfurfural and hydroxymethylfurfural contents in the liquid phases were measured with a UV detector at 290 nm usinf a LiChroCART 250:4 LiChrospher 100RP-18 column (Merck, Darmstadt, Germany) with a 9:1 water/ACN eluent-mixture. Organic acids and furfurals were analyzed as they represent key substances formed by the cleavage of sugars during hydrothermal reaction steps (Schmieder et al., 2000; Kruse et al., 2003). All analyses were performed in triplicate at least, ensuring a maximum deviation ≤ 3% from the mean.

Soil sampling

Soil material was sampled at a depth of 10 to 25 cm from an Alfisol soil at an agricultural cropland site of the Thünen-Institut in Braunschweig, Germany (10°26’ E, 52°17’ N, 80 m a.s.l.). The soil was dried at 40°C and sieved to ≤ 2 mm, and represented a loamy sand with 76% sand, 19% silt, and 5% clay. The pH value measured in deionized water (1:2.5, w/w) was 6.8. The organic C and total N contents determined using an elemental analyzer (LECO Corp., St. Joseph, MI, USA) were 1.09% and 0.09%, respectively. Carbonate C was not detected. The DOC content was measured in $CaCl_2$ (0.01 M) extracts (1:5, *w/w*) by thermal oxidation using a DIMATOC2000, and was 87.1 mg L^{-1}. The gravimetric water holding capacity was 27% (*w/w*). The soil was equilibrated at 10°C for a week to activate microbial activity before use in the incubation experiments.

Incubation experiments

The degradability of the raw materials, hydrochars (washed and unwashed) and liquid phases was tested in quadruplicate in 30-day incubation experiments at 22 ± 1°C using an automated system coupled to an infrared CO_2–gas analyzer (Heinemeyer et al., 1989). Fifty grams of dry soil sample were thoroughly mixed with 1.35 g raw material (27 g kg^{-1} soil) or 1.15 g hydrochar (23 g kg^{-1} soil) in order to double the original soil organic C content. The hydrochar additions were within the range of reasonable field application rates (Busch et al., 2011). The untreated soil (control), soil-raw material and soil-hydrochar mixtures were wetted to 70% of the water holding capacity of the soil and transferred into incubation tubes (240 mm length, 40 mm inner diam.). In order to record the CO_2–C evolution from C mineralization of the liquids, the soil was oxidized at 550°C for 2 h. Preliminary experiments confirmed that the liquids were not sterile and enabled microbial reactivation. The C concentrations of the liquids were 3.7, 3.2, 1.9 and 0.7 g L^{-1} for straw-, woodchips-, digestate- and grass-hydrochar, respectively. For incubation, the soil was adjusted to 60% water holding capacity with each individual liquid product (equates to 8.1 mL 50 g^{-1} soil) and transferred into incubation tubes. Five hundred milliliter gas washing bottles filled with acidified deionized water were installed upstream of the incubation tubes to avoid sample desiccation. The CO_2–C evolution was measured hourly at an air flow rate of 220 mL min^{-1}.

Statistical analysis

To identify significant differences between the treatments and between the materials on cumulative C mineralization, two-way analysis of variance (ANOVA) was used, followed by the post-hoc Tukey test for pairwise comparison of individual means at $p < 0.05$. All statistical tests were performed using SigmaPlot v. 11 (Systat Software Inc, Erkrath, Germany).

3.3 Results

Properties of raw materials and HTC products

Compared to the raw materials, the carbonization process slightly increased the percentage C content in the hydrochars by 3% (woodchips), 4% (straw and grass), and 5% (digestate, Table 3.1). Likewise, the C/N ratio for all carbonized materials increased from 271, 72, 11 and 11 to 304, 115, 21 and 25 for unwashed woodchips-, straw-, grass- and digestate-hydrochar, respectively. The molar H/C ratios of the hydrochars (1.4–1.5) were slightly lower than the molar H/C ratio of the raw materials (1.5–1.6; Table 3.1). Additionally, the molar O/C ratios of the hydrochars were slightly lower than those of the raw materials. The Ca content was high for grass (7.68 g kg^{-1}, Table 3.1) and digestate (24.4 g kg^{-1}) as well as grass-hydrochar (12.8 g kg^{-1}) and digestate-hydrochar (9.8 g kg^{-1}). The K, Mg and Na contents of grass and digestate were also higher than that of woodchips and straw. Congruently, the K, Mg and Na contents were higher for grass- and digestate-hydrochars than for woodchips- and straw-hydrochars (Table 3.1). In consideration of the low Fe contents of woodchips and straw, the Fe contents of the corresponding hydrochars were relatively high. Digestate and digestate-hydrochar had the highest Fe contents. In consideration of the Al contents of the raw materials, the relative content of Al in grass-hydrochar was higher than in the three other hydrochars. As reported above, the DOC of the liquid phases was high (Table 3.2). Other elements (Ca, K, Mg, N, Na and Fe) were detected at considerable concentrations in the liquids (Table 3.2).

Table 3.1 Physico-chemical properties of the different hydrochars and their raw materials

Parameter	Raw material (dry-matter basis)				Hydrochar (dry-matter basis)			
	Digestate	Grass	Straw	Woodchips	Digestate	Grass	Straw	Woodchips
C, g kg^{-1}	392.0†	439.0	452.0	488.0	446.0	474.0	496.0	516.0
N, g kg^{-1}	34.1	38.7	6.3	1.8	18.2	22.8	4.3	1.7
C/N	11.5	11.4	71.8	271.0	24.5	20.8	115.0	304.0
Molar O/C	0.58	0.58	0.62	0.61	0.54	0.50	0.55	0.51
Molar H/C	1.5	1.6	1.6	1.5	1.5	1.4	1.5	1.4
Al, g kg^{-1}	2.4	0.56	< 0.10	< 0.10	2.0	4.3	0.41	0.53
Ca, g kg^{-1}	24.4	7.7	2.2	1.2	9.8	12.8	1.9	0.78
Fe, g kg^{-1}	2.8	2.4	0.1	0.20	19.4	1.1	4.0	5.9
K, g kg^{-1}	42.5	30.1	20.4	0.70	2.5	2.5	0.38	0.40
Mg, g kg^{-1}	0.81	1.6	0.91	0.40	2.0	2.3	0.44	0.36
Na, g kg^{-1}	2.4	0.39	1.7	0.60	0.49	0.43	0.38	0.32
Ash, g kg^{-1}	237.0	122.0	69.0	7.0	148.0	145.0	26.0	19.0
pH (H_2O)	9.9	6.9	7.2	5.6	7.6	5.1	5.7	4.0
SSA, m^2 g^{-1} ‡	-	-	-	-	6.4	5.5	3.7	1.9
TPV,cm^3 g^{-1} §	-	-	-	-	0.06	0.05	0.03	0.01

† Mean values are presented (maximum deviation ≤ 3%), n ≥ 3.
‡ Specific surface area.
§ Total pore volume.

For comparison of nutrient element distribution between hydrochars, liquids and the respective raw materials, the element contents were normalized to their C contents (Table 3.3). Element ratios of the HTC product and the corresponding raw material close to one indicate neither enrichment nor depletion in the liquid or solid phase. The ratios obtained revealed that the carbonization process caused element enrichment of Ca, K, Mg, N and Na in the liquid phase, while the hydrochars were frequently depleted in elements, particularly potassium (Table 3.3).

Table 3.2 Chemical composition of the liquid phases derived from the hydrothermal carbonization of four different raw materials

Parameter	Digestate	Grass	Straw	Woodchips
Dissolved organic carbon, g L^{-1}	3.4†	1.4	5.0	5.7
Ca, mg L^{-1}	654.0	286.0	224.0	214.0
K, mg L^{-1}	916.0	520.0	1490.0	58.0
Mg, mg L^{-1}	304.0	137.0	94.0	63.6
N, mg L^{-1}	725.0	155.0	151.0	26.0
Na, mg L^{-1}	67.0	46.0	136.0	98.0
Al, mg L^{-1}	< 1.0	< 1.0	2.7	1.5
Fe, mg L^{-1}	19.9	18.8	252.0	501.3
Acetic acid, mg L^{-1}	2845.0	51.6	875.7	1259.0
Formic acid, mg L^{-1}	83.6	< 0.01	259.1	670.6
Glycolic acid, mg L^{-1}	< 0.01	117.9	419.5	433.4
Phenol (index), mg L^{-1}	45.7	24.7	106.0	78.4
Formaldehyde, mg L^{-1}	106.0	< 0.01	< 0.01	< 0.01
Furfural, mg L^{-1}	< 0.01	1.1	966.5	647.6
Methylfurfural, mg L^{-1}	< 0.01	< 0.01	16.9	41.8
Hydroxymethylfurfural, mg L^{-1}	< 0.01	3042.0	79.8	708.3
pH	7.1	5.7	4.4	3.9

† Mean values are presented (maximum deviation ≤ 3%), n ≥ 3.

Table 3.3 Ratios indicating the element distribution of different raw material between the liquid phase or hydrochar on the basis of C content.

Element	Liquid phase / Raw material				Hydrochar / Raw material			
	Digestate	Grass	Straw	Woodchips	Digestate	Grass	Straw	Woodchips
Ca	5.6	22.2	12.5	27.4	0.35	1.5	0.80	0.61
K	4.5	10.3	9.0	12.7	0.05	0.08	0.02	0.54
Mg	77.9	52.0	12.7	24.4	2.2	1.3	0.44	0.85
N	4.4	2.4	3.0	2.2	0.47	0.55	0.62	0.89
Na	5.9	70.3	10.2	25.1	0.18	1.0	0.21	0.50

On a dry matter basis, the percentage ash content increased for hydrochars from woodchips and grass, and decreased for hydrochars from straw and digestate (Table 3.1); however, these changes were not statistically significant. The pH values of the hydrochars ranged from 4.0 (woodchips-hydrochar) to 7.6 (digestate-hydrochar), and were one to two units lower than the pH values of the corresponding raw materials (Table 3.1). Overall, the hydrochars had relatively low SSA values of 1.9 to 6.4 m^2 g^{-1} and low total pore volumes of 0.01 to 0.06 cm^3g^{-1} (Table 3.1).

All hydrochars showed a pronounced resonance at 1620 cm^{-1} in the FT-IR spectra, suggesting a high amount of hydrophilic (hydroxyl, carbonyl and carboxyl) groups. These groups were assigned to band B and were most pronounced for digestate- and grass-hydrochar. As a consequence, these two hydrochars had low A/B ratios (digestate-hydrochar: 0.41; grass-hydrochar: 0.42). The hydrochars of woodchips and straw were characterized by comparatively higher A/B ratios (0.73 and 0.93, respectively). The A/B ratios of the liquids were low (woodchips-hydrochar: 0.17; straw-hydrochar: 0.11; grass-hydrochar: 0.24; digestate-hydrochar: 0.09). The pH values ranged from 3.9 for the woodchips-hydrochar liquid to 7.1 for the digestate-hydrochar liquid (Table 3.1). Large amounts of acetic acid, formic acid, glycolic acid and phenols were released into the liquid phase during the carbonization of all four raw materials (Table 3.2). Intermediates of the HTC process, such as furfural, methylfurfural and hydroxymethylfurfural, were detected in the liquid phases of woodchips- and straw-hydrochar, e.g., up to 5.9 g furfural kg^{-1} straw-hydrochar.

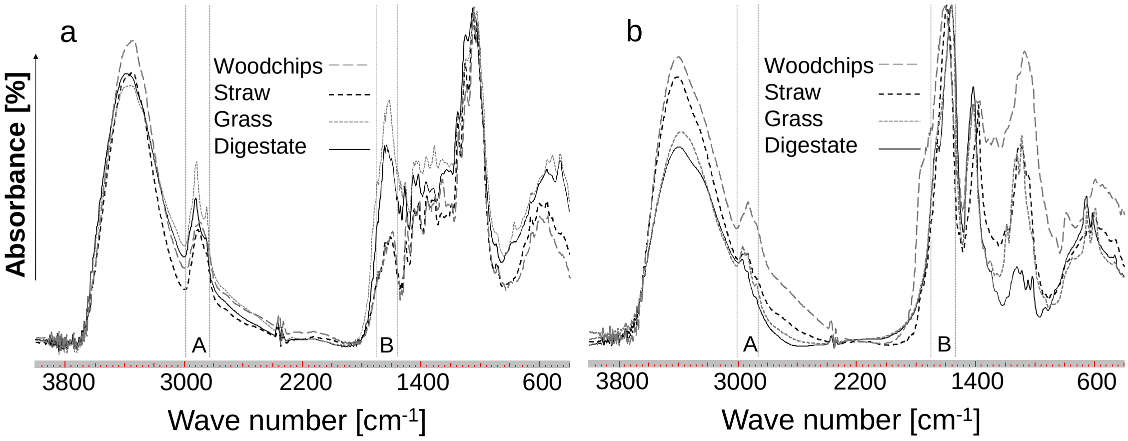

Fig. 3.1 FT-IR spectra of the hydrochars (a) and the respective liquid products (b)

Mineralization of raw materials and HTC products

After 30 days of incubation the lowest cumulative C mineralization of total C added was observed for woodchips-hydrochar (2%, Table 3.4), followed by straw-hydrochar (3%), grass-hydrochar (6%), and digestate-hydrochar (14%) with statistically significant differences observed between the materials (Table 3.4). Furthermore, cumulative C mineralization differed significantly between the hydrochars and the corresponding raw materials (Table 3.4), and reduced by up to 92, 90, 70 and 59% for grass, straw, digestate and woodchips, respectively. The C mineralization of total C added varied significantly between the raw materials. Grass was most rapidly mineralized, followed by digestate and straw (Fig. 3.2). Woodchips were barely degraded throughout the incubation time, with a total C mineralization of 4%.

Table 3.4 Total C mineralization (% CO_2–C loss of total C added) derived from unwashed (0x), one (1x), three (3x) and five times (5x) washed hydrochars, or the liquid products (LP) or raw materials after 30 days of incubation. Values are mean and standard error of the mean, n=4.

Treatment	Material			
	Digestate	Grass	Straw	Woodchips
	% mineralized of total C added			
Hydrochar 0x	13.96 (1.31) ^{aA†}	6.10 (0.35) ^{aB}	3.38 (0.17) ^{aC}	1.67 (0.07) ^{aD}
Hydrochar 1x	8.84 (0.56) ^{bA}	5.88 (0.33) ^{aB}	3.89 (0.07) ^{aC}	1.57 (0.05) ^{aD}
Hydrochar 3x	8.37 (0.16) ^{bA}	5.65 (0.08) ^{aB}	3.50 (0.05) ^{aC}	1.42 (0.09) ^{aD}
Hydrochar 5x	8.75 (0.50) ^{bA}	5.85 (0.13) ^{aB}	3.40 (0.20) ^{aC}	1.59 (0.05) ^{aD}
Liquid	76.14 (1.93) ^{cA}	89.29 (5.62) ^{bB}	58.13 (10.26) ^{bC}	60.78 (4.89) ^{bD}
Raw material	46.38 (1.52) ^{dA}	75.37 (1.33) ^{cB}	33.52 (1.47) ^{cC}	4.04 (0.15) ^{cD}

† Significant differences between treatments are indicated by lower case letters and between different materials by upper case letters; $p \leq 0.05$; two-way ANOVA followed by Tukey post-hoc tests.

The temporal dynamics of hydrochar-C mineralization were similar for the four materials (Fig. 3.3). The highest C mineralization rate for digestate- and straw-hydrochar occurred after three and two days, respectively. The highest C mineralization rates for woodchips- and grass-hydrochar were observed on the first day of incubation. The major proportion of total hydrochar-C mineralization occurred within the first half of the incubation (woodchips-hydrochar: 59%, straw-hydrochar: 64%, grass-hydrochar: 58%, digestate-hydrochar: 68%) before altering to relatively constant, low mineralization rates in the last ten days (25.2 ± 1.5, 31.5 ± 2.7, 52.3 ± 5.5, 70.1 ± 5.9 μg CO_2–C g C_0^{-1} h^{-1}, respectively). The amount of hydrochar-C mineralized during the last ten days was up to three times lower than that released during the first ten days (data not shown).

The DOC of the liquid products was easily mineralized (Fig. 3.4). During 30 days of incubation, the grass-, digestate-, woodchips-, and straw-hydrochar liquids lost 89, 76, 61, and 58%, respectively, of the total C added (Table 3.4). As observed for mineralization of the hydrochars and raw materials, the major part of the total CO_2–C released from the liquid products was also generated during the first half of incubation (Fig. 3.4).

Effect of washing

Washing the hydrochars once, three or five times did not significantly change the C concentration or C/N ratio, compared to unwashed hydrochars (data not shown). Washing had no significant effect on the total amount of C mineralized, except for digestate-hydrochar (Table 3.4). Unwashed digestate-hydrochar showed higher C mineralization (14%) than the washed hydrochars (8–9%). The temporal dynamics of hydrochar-C mineralization were not affected by washing, and are only presented for hydrochars washed once (Fig. 3.3).

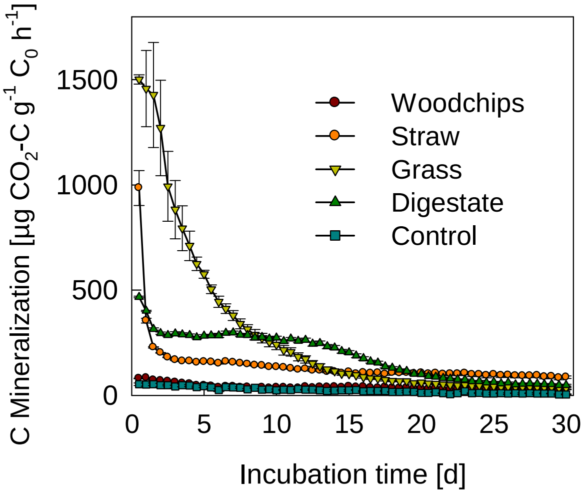

Fig. 3.2 Carbon mineralization of raw woodchips, straw, grass or digestate and the soil alone (control) over 30 days; values are mean and standard error of the mean, n = 4.

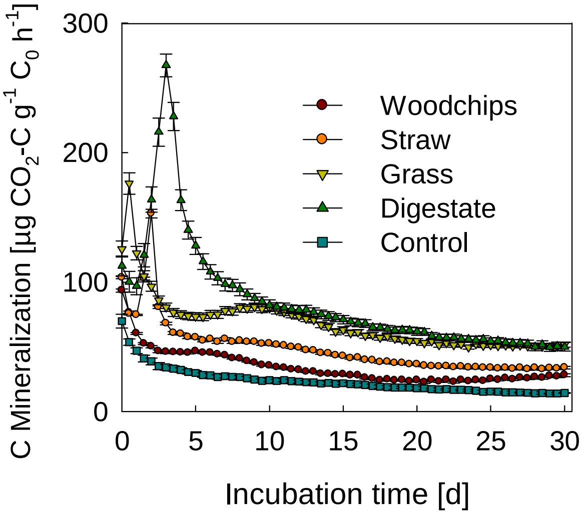

Fig. 3.3 Carbon mineralization of single washed hydrochars derived from woodchips, straw, grass or digestate and the soil alone (control) over 30 days; values are mean and standard error of the mean, n = 4.

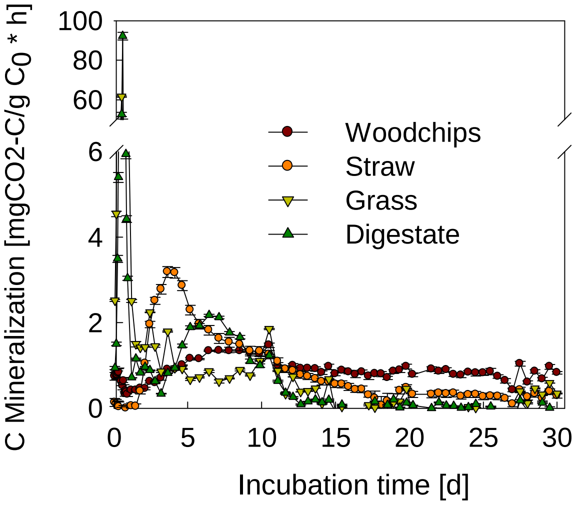

Fig. 3.4 Carbon mineralization of the liquid products derived from woodchips-,straw-, grass- or digestate-hydrochars over 30 days; values are mean and standard error of the mean, n = 4.

3.4 Discussion

Chemical enrichment and depletion of elements

The distribution of elements between the liquid and solid phases during HTC was element specific. The content of the heavy metal Fe was high for digestate–hydrochar and relatively high for woodchips- and straw-hydrochar in consideration of the low Fe content of the corresponding raw materials. This suggests that Fe is enriched in hydrochars and that this enrichment may be promoted by the amount of relatively heat-resistant components (i.e., lignin) in the raw material (Kang et al., 2012; Liu et al., 2013). However, the conclusion could not be completely verified, as the Fe content of the lignitic raw materials was very low and the liquids also contained Fe. The high Fe concentrations of the liquids may depend on pH and may originate from corrosion of the steel reactor (Haiduc et al., 2009). Other elements, e.g., the alkaline or alkaline earth metals (e.g., K, Na, Ca, Mg) are dissoluble under the moderate process conditions applied in this study (e.g., low carbonization temperature) (Valdez et al., 2012). The nutrient concentration of the liquids varied highly, and most likely depends on the initial nutrient concentration of the raw material and the pH of the liquid product (Fuertes et al., 2010). The relatively high nutrient concentration of the liquids is consistent with the low nutrient content of the solids, e.g., of hydrochars from sugar beet chips or draff (Gajić et al., 2011). We assume that the low concentration of N in the liquid phase of grass-hydrochar, compared to the liquid of digestate hydrochar, was the result of nitrification processes. This is in agreement with the rapid formation of fungal hyphae on the liquid surface shortly before filtration and the low DOC. The availability of hydrochar-N is generally low as observed in pot and field trials with sugar beet plants; however the effects are not yet totally clear (Gajić and Koch, 2012). The content of water-soluble nutrients indicates that these factors are available to plants, so the liquids can be used as growth media, e.g., for algal cultivation (Biller et al., 2012).

Degradability of the hydrochars and liquids from different raw materials

The short-term incubation experiments demonstrated that hydrochars produced from different raw materials exhibited significantly different degradability. Studies reporting hydrochar-C mineralization from different raw materials are rare. Gajić et al. (2012) reported significant differences in the C mineralization of hydrochars from draff and sugar beet pulp when carbonized at 180, 200, and 250°C (about 0.3-1.5% of total C lost within 30 days); however, no significant differences were noticed between draff- and sugar beet-hydrochars carbonized at the same process temperature. Furthermore, the C degradability of the hydrochars tested in this study was higher than that observed for hydrochars in other studies. The total C mineralization of bark-hydrochars (carbonized at 200°C), mixed with different soils (23 g kg^{-1} soil) were 0.2-0.3% after 30 days of incubation (Qayyum et al., 2012). Hydrochars from bark or beet root chips (carbonized at 203°C and 16 bars) demonstrated similarly low C mineralization (0.5% and 0.4%) for the same incubation time (Kammann et al., 2012). The amount of C mineralized in these previous reports was nearly two orders of magnitude smaller compared to the amount of C mineralized in digestate-hydrochar, and was one order of magnitude smaller compared to the amount of C mineralized in woodchips-, straw- and grass-hydrochar in this study. This may be due to the influence of different process conditions (temperature, pressure, duration), incubation conditions (amount of soil and hydrochar, soil moisture, temperature), the soils used (texture, microbial community composition) (Steinbeiss et al., 2009; Lehmann et al., 2011), as well specific hydrochar properties, as discussed below.

Analysis of temporal dynamics revealed that a major proportion of hydrochar-C was mineralized within the first 15 days, which agrees well with the findings of other studies (Steinbeiss et al., 2009; Gajić et al., 2012; Kammann et al., 2012; Qayyum et al., 2012). The raw material had no significant influence on temporal dynamics. These results indicate the existence of both a rapid and a more slowly mineralizable C fraction in hydrochars from different raw materials, and also implies that short-term incubation may underestimate the overall C degradability (Libra et al., 2010). However, results of a 365 day incubation revealed no considerable changes in the mineralization rate of bark-hydrochar after initially intense CO_2–C release during the first week (Qayyum et al., 2012). Therefore, we expect that - in a given soil - relative degradability of hydrochars from different raw materials carbonized under the same process conditions will remain the same as observed during our incubation experiment. Yet, we are aware that no conclusions can be drawn on long-term hydrochar degradation in soil environments. It should be noted that a well-developed microbial activity in an environment with degradable organic matter such as hydrochar, fosters a healthy soil biodiversity and aggregate stability (Bronick and Lal, 2005). In turn, this would support C sequestration and improve soil fertility; however, these factors were not examined in this study.

The DOC of the liquids was quantified relative to the DOC of the soil. The major proportion was mineralized within 30 days of incubation; therefore, we assume that the bioavailability and degradability of liquid-C is good. Carbon was mineralized at similar percentage intensities, as the highest percentage C mineralization was observed for the liquid with the lowest C concentration (liquids of grass- and digestate-hydrochar). The low pH and N concentration, and high concentrations of acid and hydroxymethylfurfural (e.g., in the liquid of woodchips-hydrochar) had no effects on the intensity of C mineralization, compared to the other liquids. From this, we conclude that the bioavailability and degradability of C in the liquids derived from HTC of any raw material are generally good, and that the liquid phase can be treated aerobically (e.g., for nutrient recovery) (Funke and Ziegler, 2011). This also implies that pH, nutrients and furfurals do not have a considerable impact on the degradability of liquid-C.

Relationship between degradability of the hydrochars and product characteristics

The molar O/C and H/C ratios for all hydrochars (O/C: 0.5–0.6; H/C: 1.4–1.5) were slightly lower than the ratios for the raw materials, but still higher than the ratios reported for hydrochars in other studies (O/C = 0.3; H/C = 1.0) (Fuertes et al., 2010; Berge et al., 2011; Mumme et al., 2011). For C sequestration of biochars, desirable O/C and H/C ratios are ≤ 0.4 and ≤ 0.6, respectively (Schimmelpfennig and Glaser, 2012). High H/C and O/C ratios are indicative of a low degree of carbonization and may explain the good degradability of the hydrochars used in this study. This conclusion is confirmed by a previous study reporting that the O/C ratio correlated positively with hydrochar-C mineralization and negatively correlated with the stable C content (Gajić et al., 2012).

Furthermore, the high O/C and H/C ratios indicate a relatively low degree of aromaticity and high amount of oxygen-containing functional groups (e.g., hydroxyl, carbonyl, and carboxyl groups) (Chen et al., 2011). The high amount of oxygen-containing functional groups may be responsible for the higher reactivity of hydrochars in soil compared to chars produced at higher temperatures (Gajić et al., 2012; Schimmelpfennig and Glaser, 2012). A better wettability due to increased surface hydrophilicity may facilitate direct access of microbial decomposers or extracellular enzymes to the hydrochar surfaces. In this study, FT-IR analyses showed that the amount of hydrophilic functional groups was higher for digestate- and grass-hydrochar and lower for woodchips- and straw-hydrochar (Fig. 3.1, band B). Accordingly, the highest C mineralization was observed for digestate-hydrochar.

The SSA values measured in this study are in the range of SSA values for hydrochars reported in other studies (4 to 12 $m^2 g^{-1}$) (Mumme et al., 2011; Sevilla et al., 2011). Mineralization of hydrochar-C correlated positively with the SSA ($R^2 = 0.8$, $p < 0.05$) as, e.g., digestate-hydrochar was characterized by the highest C mineralization and also well by the highest SSA. A higher surface area generally promotes the availability of residue-C to decomposing microorganisms (Angers and Recous, 1997). However, since the hydrochars in this study and the bark-hydrochar in the study by Qayyum et al. (2012) had comparable SSAs but different C mineralization rates, this causal relationship might be perturbed by other factors such as particle size and morphology, as well as the structure of the decomposer community (Garnier et al., 2008).

Carbon mineralization was also in good accordance with the C/N values, with low C/N ratios correlating with high mineralization. Generally, biomass with a low N content or a high C/N ratio is more stable than biomass with a high N content or low C/N ratio (Nicolardot et al., 2001; Korsaeth et al., 2002). Comparison of the C/N ratio and C mineralization, e.g., for woodchips-hydrochar (304 and 1.7%, respectively), to the results of other incubation studies under similar conditions, e.g., bark-hydrochar (55 and 0.5%) (Kammann et al., 2012) makes it clear that the C/N ratio alone cannot explain the degree of hydrochar-C mineralization.

As mentioned above, lignin is more resistant to hydrothermal conversion under moderate process conditions than carbohydrates (Wang and Low, 1990; Funke and Ziegler, 2011). Mineralization of ligneous substances is primarily performed by white-rot fungi through co-metabolic pathways (Jastrow et al., 2007). A lack of easily available substrate for co-metabolic degradation may, thus, explain the low mineralization of woodchips and woodchips-hydrochar. In our study, low C mineralization corresponded with a low pH (Table 3.1). This is in line with the fact that microbial degradation primarily takes place under circum-neutral conditions (Geller, 1991). However, to provide clear evidence of the influence of pH, mineralization should be studied under varying soil pH values.

Effects of washing

We hypothesized that readily mineralizable components of the liquid phase attached onto the surfaces of the hydrochar could be removed by washing. Most studies related to the macromolecular core of hydrochars recommend washing with deionized water after phase separation to remove soluble intermediates (Fuertes et al., 2010; Rillig et al., 2010; Kumar et al., 2011; Sevilla et al., 2011). We confirmed our hypothesis for digestate-hydrochar, since washing with deionized water decreased C mineralization by up to 40% compared to unwashed hydrochar. However, washing had no effect on C mineralization for the other hydrochars, due to their small fraction of water-soluble compounds. To date, few studies have investigated the effect of washing on the degradability of hydrochars. Cao et al. (2011) found that washing swine-manure-hydrochars (carbonized at 250°C for 20 h) with acetone led to a decrease of O-alkyl C and an increase of aromatic C compared to unwashed hydrochars, indicating that washing increased stable C content. They ascribed these alkyl components to long-chain fatty acids and wax-like materials, which are most likely to be derived as soluble intermediates from peptides, hemicelluloses and cellulose oligomers. Washing agents may increase the percentage content of stable C, but may also partially elutriate and destroy the hydrochar surface and exert undesirable effects on C availability and degradability. Nevertheless, for certain hydrochars, gentle, and short washing with water could be a useful means of removing labile C components for investigation of C degradability. However, this needs to be investigated further using a larger set of hydrochar types.

3.5 Conclusions

Non-standardized carbonization protocols and the different raw materials used in HTC processes often complicate mechanistic conclusions on the properties and degradability of hydrochars. For hydrochars carbonized under the same process conditions, this study provides the first evidence that the structural properties inherited from different raw materials play an important role in limiting the extent of microbial hydrochar utilization. The short-term C degradability of hydrochars decreased significantly in the order digestate > grass > straw > woodchips. A high degradability of hydrochars in soil coincides with a high amount of hydrophilic functional groups, high molar O/C and H/C ratios, low C/N ratio, and a low lignin content of the raw material. Water-washing may be an effective pre-treatment to remove easily degradable C, which otherwise creates a high mineralization pulse shortly after application to soil; this effect seems to be specific to each hydrochar and needs to be considered in short-term incubation experiments. More than 50% of the DOC in the liquids was easily mineralized, which may limit the use of fresh HTC liquids in field applications.

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4 Article II. Pyrochars and hydrochars differently alter the sorption of the herbicide isoproturon in soil

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Abstract

Carbonaceous material from pyrolysis (pyrochars) and hydrothermal carbonization (hydrochars) are applied to soil to improve soil fertility and carbon sequestration. As a positive side effect, the mobility of pesticides and the risk of groundwater contamination can be minimized. However, the impact of various raw materials on the sorption capacity of different pyrochars and hydrochars is poorly understood. Thus, sorption experiments were performed with ^{14}C-labeled isoproturon (IPU, 0.75 kg ha^{-1}) in a loamy sand soil amended with either pyrochar or hydrochar (0.5% and 5% dry weight, respectively). Carbonaceous materials were produced from three different raw materials: corn digestate, miscanthus, woodchips of willow and poplar. After 72 h of incubation, a sequential extraction procedure was conducted to quantify in situ IPU bioavailability, total amount of extractable IPU, and non-extractable pesticide residues (NER).

Added char amount, carbonization type, and raw materials had statistically significant effects on the sorption of IPU. The amount of in situ available IPU was reduced by a factor of 10–2283 in treatments with pyrochar and by a factor of 3–13 in hydrochar treatments. The surface area of the charred material was the most predictive variable of IPU sorption to char amended soil. Some physical and chemical char properties tend to correlate with pore water-, methanol- or non-extractable IPU amounts. Due to a low micro-porosity and ash content, high water extractable carbon contents and O-functional groups of hydrochars, the proportion of NER in hydrochar amended soils was considerably lower than in soil amended with pyrochars.

4.1 Introduction

Groundwater contamination by leaching of pesticides from agricultural soils is a severe problem in modern food production worldwide (Lehr et al. 1996). The phenyl urea herbicide isoproturon [3-(4-isopropylphenyl)-1,1-dimethyl-urea; IPU] is intensively used in European cereal production (Umweltbundesamt, 2006). The pesticide has a high water-solubility (70 mg L^{-1}), which frequently results in surface- and groundwater concentrations exceeding the maximum tolerable concentration of the European directive for drinking water ($\geq 0.1\ \mu g\ L^{-1}$) (Umweltbundesamt, 2006).

The mobility of pesticides in soils depends highly on the sorption potential of soil organic matter (OM) (Ertli et al. 2004). Therefore, the development of approaches to minimize the mobility of critical pesticides is a promising step towards sustainable groundwater protection. In recent years, the addition of carbon (C)-rich solids from the incomplete combustion of biomass via pyrolysis (termed pyrochars or biochars; Wiedner et al. 2013) to agricultural soils has gained considerable interest in order to improve soil C sequestration and crop yield by better retention of nutrients and water (Glaser et al., 2002; Kammann et al., 2012). As a positive, desirable side effect, these materials have been shown to increase the sorption potential of soils for several pesticides (Yang et al., 2006; Yu et al., 2009; Martin et al., 2012). The high sorption potential of pyrochars is the result of their physico-chemical properties, e.g., a large specific surface area (SSA), and micro-porosity, as well as a high aromaticity coupled to the presence of oxygen-containing functional groups (Chun et al., 2004; Cao and Harris, 2010; Liu and Zhang, 2011). These properties may entail different sorption mechanisms of variable strength (Sobek et al., 2009; Tian et al., 2010). Furthermore, sorption of organic chemicals in pyrochar amended soils may be enhanced indirectly, e.g., by increasing the cation exchange capacity and reduction of the dissolved organic C content (Gomez-Eyles et al., 2011). Nonetheless, it remains poorly understood to which extent the sorption potential of pyrochars is affected by the type of raw material used (Chen et al., 2008; Uchimiya et al., 2010; Zhang et al., 2011).

Promising experimental results regarding the impact of pyrochar amendment on C sequestration and nutrient retention encouraged the scientific community to seek for less energy-intensive processes yielding carbonization products with similar capabilities (Titirici et al., 2007; Steinbeiss et al., 2009; Cao et al., 2011). During hydrothermal carbonization (HTC), residues of OM are converted into C-rich solids, called hydrochars, at relatively low temperatures (180-250 °C) and under high pressure (about 2MPa) in the presence of water. In contrast to pyrolysis, this process does not require an energy-intensive pre-drying step (Mumme et al., 2011). While high-temperature pyrochars are considered the most promising additives for agricultural soils concerning climate change mitigation due to their high microbial resistance (Kammann et al., 2012), HTC products have been reported to have beneficial effects on the plant available water capacity in sandy soils (Abel et al., 2013). Their effects on selected soil functions will likely differ as result of their varying physico-chemical properties arising from the specific production conditions (Libra et al., 2010). For example, the SSA of pyrochars varies considerably and reaches values up to 1000 m^2 g^{-1} (Qiu et al., 2009; Uchimiya et al., 2011). For hydrochars, average SSA values of 8 m^2 g^{-1} have been reported (Schimmelpfennig and Glaser, 2012). The molar H/C and O/C ratios, which describe the carbonization degree of chars and char-like material, are generally lower for pyrochars than for hydrochars (Gajić et al., 2012). However, the sorption potential of hydrochars for organic agrochemicals in soil has been rarely investigated (Sun et al., 2012).

Most studies concerning sorption of pesticides examined the adsorption distribution coefficient (K_d) from standard batch experiments in solution (Yang and Sheng, 2003; Sobek et al., 2009; Yu et al., 2011; Martin et al., 2012), and thus under conditions that hardly resemble soil environmental conditions. Alternatively, Folberth et al. (2009) used an approach that mimics *in-situ* pesticide availability in soils and allows pesticide quantification in the soil pore water following centrifugation of soil samples. Using a field equivalent soil water potential and bulk density during incubation, they introduced the *in-situ* mass distribution quotient (iMDQ), which is calculated as the quotient of the adsorbed and dissolved pesticide concentrations. Thus, the iMDQ reflects more natural conditions because it takes the soil to pore water ratio into account and has been proven to adequately describe the bioavailability of IPU in soils (Folberth et al., 2009).

The main objective of this study was to comparatively investigate the pesticide sorption capacity of pyrochar versus hydrochar amended soil using the iMDQ approach. We hypothesized that (i) the IPU sorption capacity in soil amended with pyrochar is higher compared to soil amended with hydrochar and (ii) different sorption mechanisms account for the differences in sorption behavior. To test this, soil was incubated for three days with pyrochars carbonized at 750°C and hydrochars carbonized at 200°C and 250°C, and the underlying sorption mechanisms were derived from applying a sequential extraction procedure involving extraction with water and methanol, followed by combustion of the extracted samples. Finally, we (iii) expected that the IPU sorption within each material group varies with the raw material used. Therefore, different raw materials (corn digestate, miscanthus, woodchips of willow and poplar) were used as precursor materials in the production of pyro- and hydrochars.

4.2 Material and Methods

Soil material

Soil material was taken from 5 to 25 cm depth of a Cambisol at the organic farming section of the research station Scheyern in southern Germany (11°26'21" E and 48°29'51" N, 477 m a.s.l.). The soil was air-dried and sieved to ≤ 2 mm. The soil is a loamy sand with 68% sand, 15% silt, and 17% clay. Selected soil properties are given in Table 4.1. The air-dry soil was stored at -20 °C. Prior to laboratory experiments it was equilibrated at a soil water content of 10% (w/w) for 2 days at 4 °C and a further day at 20 °C.

Pyrochars and hydrochars

Pyrochars (pyro750) were produced from pyrolysis at the standard operating temperature of the Pyreg technology of 750°C for 45 min (Pyreg GmbH, Dörth, Germany). Hydrochars (hydro200 and hydro250) were generated from HTC at 200 or 250°C and 2 MPa for 6 hours (SmartCarbon AG, Jettingen, Germany). Raw materials in each case were corn digestate, miscanthus, and woodchips (willow and poplar), respectively. After cooling overnight, hydrochars were separated from the liquid phases with a 105-μm gauze filter. The pyrochars and hydrochars were oven-dried at 105 °C and sieved to <1 mm. Selected properties of the raw and carbonized materials are given in Table 4.1. The C and N contents were determined via dry combustion (LECO TruSpec, St. Joseph, USA). Total C is considered to equal organic C as no differences between C concentrations of unwashed and HCl-washed (4 M HCl) samples were observed (Scheibler method; Gajić et al., 2012). Water-extractable organic carbon (WEOC) contents of the solid materials were quantified after extraction with deionized water (1:10, w/v) and 0.45 μm-filtration by thermal oxidation with a TOC analyzer (DIMATOC2000, DIMATEC Essen, Germany). Hydrogen and oxygen contents of pyrochars, hydrochars, and the raw materials were determined with an elementary analyzer (Vario EL3, Elementar, Hanau, Germany). The pH of the solids was measured in 0.01 M $CaCl_2$ (1:10, w/v). The specific surface area (SSA), total pore volume (PV; pores <~200 nm), and average pore size (PS) were derived from 40-point N_2 gas adsorption isotherms recorded at 77 K with an Autosorb analyzer (Quantachrome Corp., USA). The SSA was calculated using the Brunauer-Emmett-Teller equation based on seven adsorption points in the relative pressure range of 0.05-0.3 P/P_0 (Brunauer et al., 1938). Total PV was determined at a relative pressure of 0.995 P/P_0 and the average PS was calculated as $r_p = 2V_{liq}/SSA$, where V_{liq} is the volume of liquid N_2 contained in the pores.

Fourier-transform infrared (FTIR) measurements for quantification of oxygen-containing surface functional groups were performed with a Tensor 27 (Bruker Optics, Billerica, USA) using the KBr technique (Ellerbrock et al., 2005). Briefly, 1 mg oven-dry solid sample was mixed with 200 mg KBr. For each spectrum 128 scans were collected with a resolution of 4 cm^{-1}. For quantitative comparison, normalization to the maximum absorbance of one and base line correction were performed for all spectra (OPUS 5.5 software). Summed intensities of oxygen-containing functional groups (O-functional groups) were assigned according to literature (Nguyen et al., 2008; Chen and Chen, 2009; Cantrell et al., 2012). Adsorption bands resonating at 1740 to 1700 cm^{-1}, 1630, and 1600 cm^{-1} were taken to represent aromatic carboxyl and carbonyl groups. Peaks appearing at 1160, 1100, 1059, and 1035 cm^{-1} were considered to represent aliphatic C-O groups. Hydroxyl-groups appearing above 3200 cm^{-1} were not considered as they may reflect differences in water content (Günzler and Böck, 1990).

Table 4.1 Properties of pyrochars (Pyro750) and hydrochars (Hydro250/200) from digestate (D), Miscanthus (M), Woodchips (W), of the raw materials and of the soil; standard deviations were < 3% if not explicitly mentioned.

Property	Pyro750-			Hydro250-			Hydro200-			Raw material			Soil
	D	M	W	D	M	W	D	M	W	D	M	W	
C (%)	52	77	68	62	69	68	54	58	60	42	46	49	0.87
N (%)	0.90	0.87	0.89	2.98	1.18	1.22	2.59	0.67	1.07	1.57	0.52	0.78	0.10
C/N	57.7	88.4	76.1	20.7	58.5	56.1	20.8	86.6	55.8	26.7	87.7	62.3	8.8
Molar O/C	0.14	0.06	0.06	0.22	0.20	0.20	0.34	0.35	0.30	0.65	0.65	0.53	n.d.
Molar H/C	0.33	0.19	0.26	0.91	0.86	0.89	1.15	1.09	1.06	1.53	1.48	1.36	n.d.
WEOC[a] (mg L^{-1})	12 ±0.01	7 ±0.2	3 ±0.1	231 ±1.5	165 ±2.7	181 ±0.5	247 ±2.5	210 ±0.3	244 ±0.3	177 ±2.5	124 ±0.3	44 ±0.3	7 ±0.1
Ash content (%)	46	15	25	13	4.5	5.4	10.3	3.9	5.0	12	2.9	4.2	n.d.
pH (0.01M $CaCl_2$)	10.5	10.0	8.7	6.4	4.9	5.3	6.3	4.7	5.0	7.6	5.6	4.8	5.3
SSA[b] (m^2 g^{-1})	448	279	210	2.8	5.8	3.5	13	5.2	10	8.6	1.0	1.6	8
Pore volume (cm^3 g^{-1})	0.28	0.19	0.17	0.02	0.05	0.04	0.09	0.05	0.09	0.03	0.01	0.02	0.02
Average pore size (Å)	12	14	17	167	179	207	192	180	180	61	154	206	51
O-groups[c]	0.15 ±0.01	0.17 ±0.03	0.15 ±0.02	0.37 ±0.03	0.35 ±0.02	0.36 ±0.00	0.37 ±0.00	0.39 ±0.01	0.38 0.01±	0.34 ±0.02	0.31 ±0.01	0.31 ±0.03	n.d.

[a] WEOC = water extractable organic carbon; [b] SSA = specific surface area; [c] O-groups = summed band intensities of O-containing functional groups; n.d. = not determined

Isoproturon

Uniformly ^{14}C-ring labeled isoproturon (^{14}C-IPU, GE Healthcare, Little Chalfont, UK; purity >98%, specific radioactivity 10 kBq μg^{-1}) was mixed with non-labeled IPU (Dr. Ehrensdorfer Augsburg, Germany; purity >98%) and diluted in methanol resulting in a final specific radioactivity of 148 Bq μg^{-1}.

Isoproturon sorption experiments

The sorption capacity was evaluated in triplicates using 30 g of dry soil or mixtures composed of 30 g soil with either 0.5 or 5% (w:w, referred to as low or high char addition) pyrochar or hydrochar. These additions are equivalent to 19.5 and 195 t ha^{-1}, respectively, under the assumption that pyrochars and hydrochars are uniformly distributed over a soil depth of 30 cm during ploughing. Experiments were conducted at 1.3 g cm^{-3} bulk soil density and a matrix potential of -15 kPa. The soil water content at a matrix potential of -15 kPa (Fig. 4.1) was determined specifically for each treatment in five-fold repetition using a sand/kaolinbox (08.02 Eijkelkamp, Netherlands; Schroll et al., 2006). Samples were pre-incubated in 100 mL opaque glass incubation vessels at 20 ± 1 °C for one week. Subsequently, for microbial inhibition, 1 μg NaN_3 g^{-1} soil was applied to 2.5 g soil (dry weight; dw), thoroughly mixed with a metal spatula for one minute, transferred into incubation vessels and mixed with 27.5 g pre-incubated samples (dw) by stirring for two minutes (Folberth et al., 2009). After 3 days pre-incubation, 5 μg ^{14}C-IPU g^{-1} soil, corresponding to common field amounts of 0.75 kg ha^{-1} (Schroll and Kühn, 2004), were applied following the identical protocol. Samples were then incubated for 72 h in order to achieve sorption equilibrium (Folberth et al., 2009). Thereafter, samples were sequentially subjected to a soil pore water extraction (PWE) followed by an accelerated solvent extraction (ASE). For PWE, sample aliquots were centrifuged for 90 min at 9170 × *g* and 21°C (Thermo Scientific Sorvall RC 6 Plus, Osterode, Germany) according to the method described by (Folberth et al. (2009). The volume of the soil pore water was measured and subsequently the amount of dissolved ^{14}C-IPU was quantified in duplicates in 100 μL aliquots mixed with 5 mL scintillation cocktail (Ultima Gold XR, Perkin Elmer, USA) by using a scintillation counter (TriCarb 2800 TR, Canberra-Packard GmbH, Dreieich, Germany). The final ^{14}C-content in the soil pore water was calculated accounting for the total water content of the respective soil samples. For ASE, pore water extracted samples were transferred into stainless steel columns and extracted with methanol at 90 °C and 10 MPa with an ASE 200 instrument (Dionex, Idstein, Germany). The extract volumes were quantified and ^{14}C content of duplicate were measured as described above. The ^{14}C content of the residual pore water was discounted from the ^{14}C content of the methanol extracts. The iMDQ was calculated according to Eq. 1 (Folberth et al., 2009):

$$iMDQ = \frac{m_{MeOH}^{IPU} - m_{EQ}^{IPU}}{m_{EQ}^{IPU}}, \qquad \text{Eq. 4.1}$$

where m_{MeOH}^{IPU} represents the methanol extractable IPU amount and m_{EQ}^{IPU} the pore water extractable amount at sorption equilibrium. In case the iMDQ was close to zero, IPU was expected to be completely extractable, and, hence, remaining primarily in bioavailable form. To quantify the amount of non-extractable IPU residues (NER) and to establish a ^{14}C-mass balance of the sorption experiments, ASE extracted samples were combusted with an automatic sample-oxidizer (307, Perkin Elmer, Waltham, USA) in triplicates as described in Folberth et al. (2009).

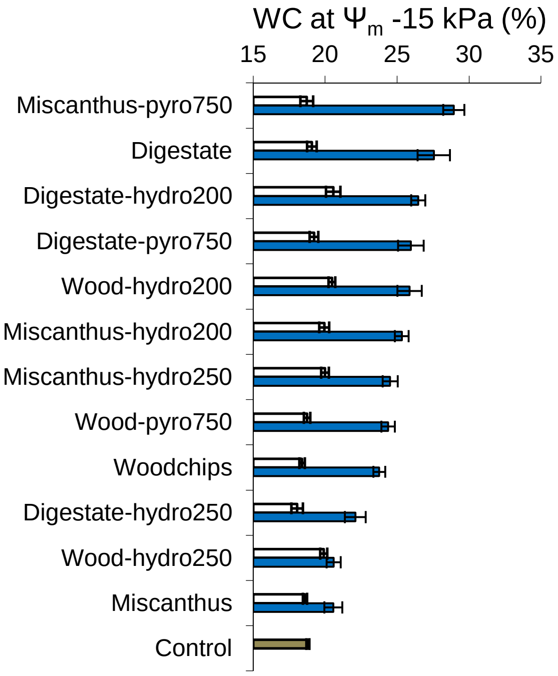

Fig. 4.1 Water content (WC) at matrix potential (Ψ_m) of -15 kPa of 0.5% (white bars) and 5% (blue bars) pyrochar (pyro750) or hydrochar (hydro250/ 200) soil additions and soil alone (= control, brown bar), means ± standard deviation, n = 5.

Statistics

To test for significant differences between treatments, three way analysis of variance (ANOVA) was used and Tukey's HSD test employed for pairwise comparison of individual means (Spokas et al., 2009). To achieve normality and variance homogeneity, data were log transformed if necessary. Correlations were tested using Pearson's correlation coefficient. Because of a high degree of multicollinearity in the dataset, penalized linear regression using the least absolute shrinkage and selection operator (LASSO; Tibshirani, 1996) was conducted to identify the properties which produce the best prediction of the sorption capacity (Friedman et al., 2010). Cross validation was applied to evaluate the appropriate number of predictors. The significance limit was set to 0.05. Statistical tests were carried out in SigmaPlot 11 (Systat Software Inc.) and R 2.15.3 (R.Core-Team, 2013).

4.3 Results and Discussion

Basic material properties

Pyrochars featured a high SSA (210 to 448 m^2 g^{-1}) and high micro-porosity (PS of 12 to 17 Å) whereas hydrochars had much lower SSA and wider PS (Table 4.1). Hydro200 and hydro250 had similar SSA (5.2 to 13 m^2 g^{-1} and 2.8 to 5.8 m^2 g^{-1}, respectively) and PS (180 to 192 Å and 167 to 207 Å, respectively). Furthermore, molar O/C and H/C ratios of pyrochars (0.06 to 0.14 and 0.19 to 0.33, respectively) were small compared to those of hydrochars (0.20 to 0.35 and 0.86 to 1.15, respectively), and, consequently, C/N ratios of pyrochars (58 to 88) were higher than of hydrochars (21 to 87). The amounts of WEOC were highest for digestate (Table 4.1) and decreased in the order hydro200 (210 to 247 mg g^{-1}), hydro250 (165 to 231 mg g^{-1}), raw materials (44 to 177 mg g^{-1}), and pyrochars (3 to 12 mg g^{-1}). These differences in physico-chemical properties between pyrochars and hydrochars are in line with findings of previous studies (Busch et al., 2011; Schimmelpfennig and Glaser, 2012; Wiedner et al., 2013). Figure 2 shows the FTIR spectra of the charred and raw materials. Summed intensities of FTIR bands revealed that moieties of O-functional groups increased by HTC (Table 4.1). In contrast, pyrolysis caused a decrease of O-functional groups resulting in a more hydrophobic surface composition (Zhang et al., 2011; Cantrell et al., 2012). Nevertheless, absolute absorbance intensities in the spectra of pyrochars should be considered with care because many bands overlapped and thus, complicate interpretation. The results of the FTIR analysis were, however, similar to those obtained by Chen et al. (2011) for pyrochars carbonized at different temperatures and the proportion of O-functional groups has been reported to be lower in pyrochars than in hydrochars due to dehydration at high carbonization temperatures (Liu et al., 2010).

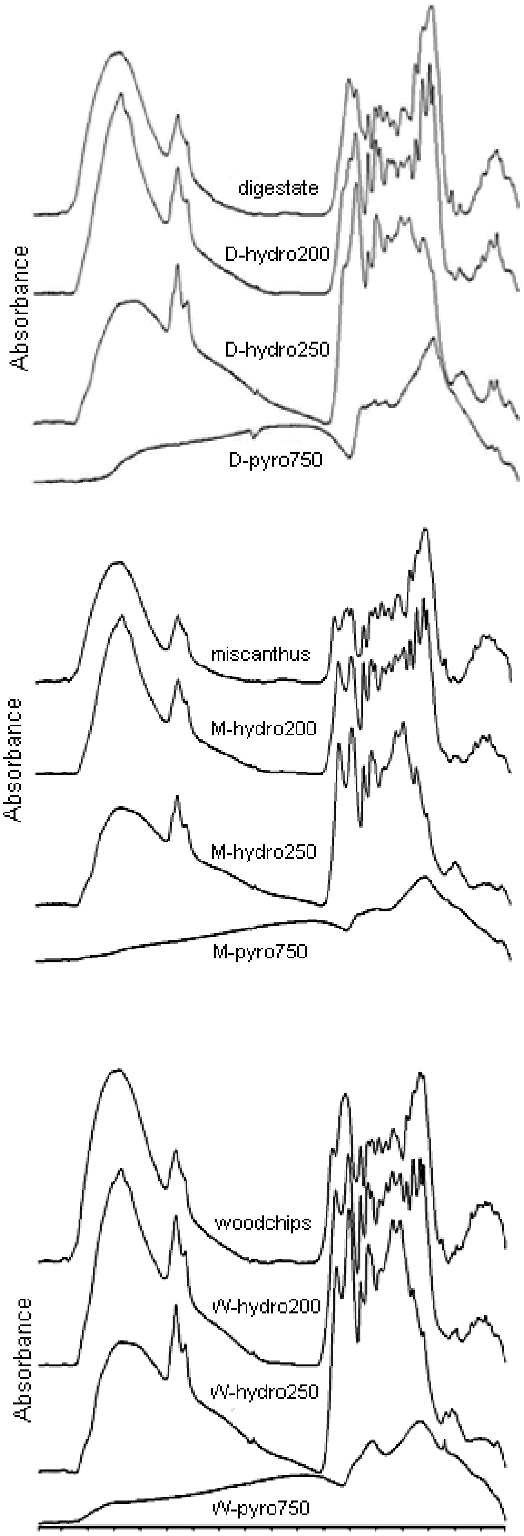

Fig. 4.2 FTIR spectra of pyrochars (carbonized at 750°C), hydrochars (carbonized at 200 and 250°C) and the corresponding raw materials (D, digestate; M, miscanthus; W, woodchips).

Sorption of isoproturon

Mass balances in the sorption experiments were calculated based on the total added ^{14}C-IPU amount and the ^{14}C activities recovered in pore water, methanol, and after combustion of the extracted samples. In all experiments ^{14}C balances averaged 100 ± 10% (median = 99%, n = 3) and recoveries matched the limits recommended by OECD (2000).

The char addition, carbonization type, and respective raw material had a statistically significant effect on the sorption of IPU ($p < 0.001$). At sorption equilibrium, the amount of pore water extractable IPU was reduced by a factor of 10 to 2283 in pyrochar treatments and by a factor of 3 to 13 in treatments with hydrochar compared to the soil without amendment (Fig. 4.3A). Consequently, treatments with pyrochar or hydrochar amendment had higher iMDQs (Fig. 4.3B) with the iMDQs being significantly higher for pyrochars than for hydrochars ($p < 0.05$). This suggests a lower IPU bioavailability in pyrochar amended soils than in those amended with hydrochars, which agrees well with the larger amount of NER for both, low and high pyrochar additions (pyrochar: 18.6 to 29.6% vs. 24.2 to 32.4%; hydrochar: 4.9 to 7.7% vs. 2.7 to 3.6%; $p < 0.05$; Fig. 4.3C). These significant differences likely arise from the physico-chemical properties of each char material.

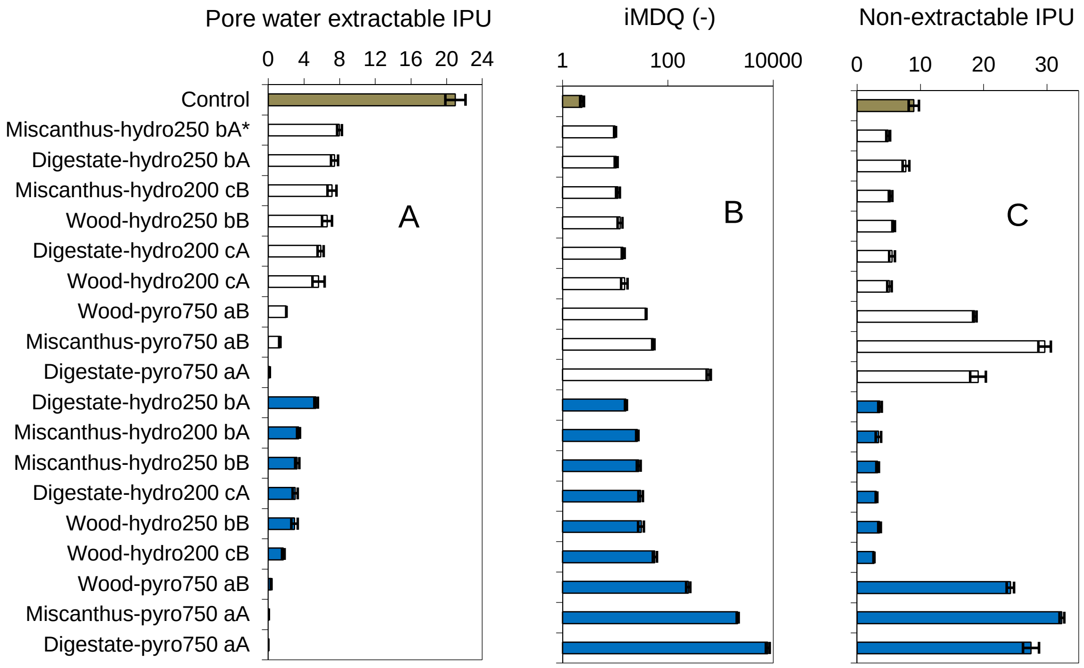

Fig. 4.3 A, Pore water extractable isoproturon (IPU, % of added IPU) at sorption equilibrium, B, *in-situ* mass distribution quotient (iMDQ), and C, non-extractable IPU (% of added IPU) in soil amended with 0.5% (white bars) and 5% (blue bars) pyrochars (-pyro750) and hydrochars (-hydro250/ 200) from three different raw materials, and soil alone (= control, brown bars), means ± standard deviation, n = 3.

* significant differences of pore water extractable IPU within the same raw material at 0.5 or 5% char addition is indicated by different lower case letters, and within the same carbonization process at 0.5 or 5% char addition by different upper case letters ($p < 0.05$).

Previously, it has been shown in batch experiments that the sorption capacity for IPU correlates positively with the addition of technical charcoal (particle size 0.08 and 0.8 mm) in soils with relatively low OM content (<3 %) and that even low charcoal amendments (1 wt%) govern the IPU sorption capacity of soils (Tian et al., 2010; Si et al., 2011). Such a behavior has been attributed to the high SSA and small particle size of charcoals (Tian et al., 2010). In line with these observations, Fig. 4.4 shows tendencies towards decreasing amounts of pore water extractable IPU and higher SSAs at both, low and high char addition (R = 0.94 and 0.81, respectively, $p < 0.001$). Likewise, penalized regression revealed that the SSA was the main factor influencing the sorption capacity ($p < 0.001$). There was strong multicollinearity between the different properties as indicated by high variance inflation factors. For high char additions, the effect of the SSA was more pronounced ($p < 0.001$) and the C/N ratio was an additional significant factor ($p < 0.05$).

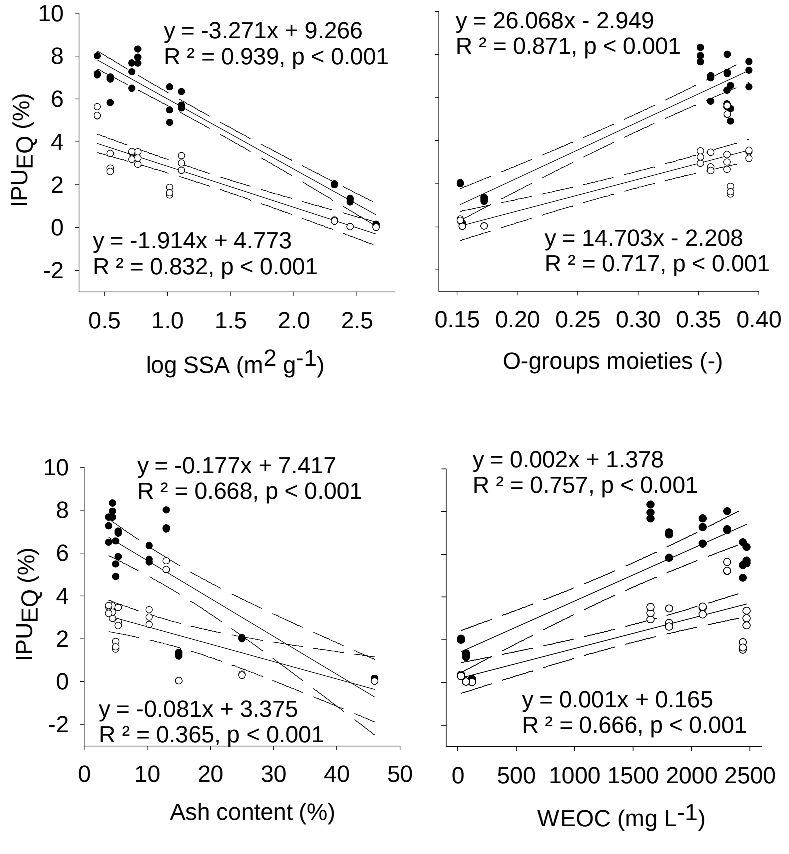

Fig. 4.4 Trends between amount of pore water extractable isoproturon at sorption equilibrium (IPU_{EQ}) and char properties (logarithmic specific surface area, SSA, summed intensities of O-containing functional groups, O-groups, ash content, and water extractable organic C, WEOC) in soil amended with 0.5% (black dots) and 5% (white dots) pyrochar and hydrochar, dashed lines indicate 95% confidence interval.

The same statistically significant relationship (between the pore water extractable IPU amount and the char addition, SSA, and C/N ratios) was observed for the iMDQs (R = 0.98, p <0.001). Treatments with pyrochars from digestate had the highest iMDQs that coincided with the highest SSA. For hydrochar treatments, iMDQs were lower for digestate than for woodchip hydrochar, except for treatments with low additions of hydro200. In the latter case, iMDQs from digestate and woodchips were similar. The differences may be explained partially by the SSA and C/N ratio but also by other hydrochar properties. In accordance with the observed multicollinearity in the dataset, there were strong correlations among all properties except for C/N ratios (Table 4.2). In particular, there were strong negative correlations between SSA and PS, O-functional groups, WEOC, and molar H/C ratios, and positive correlations to the pH and ash content (Table 4.2). Although the effect of these properties on pesticide sorption could not be clearly separated from the effect of SSA due to collinearity and the small sample number, it is nevertheless reasonable to presume that they directly and indirectly contribute to the observed IPU sorption patterns.

Table 4.2. Pearson correlation coefficients (*R*) for properties from pyrochars and hydrochars

R	SSA[a]	PS[b]	WEOC[c]	O-groups[d]	Molar O/C	Molar H/C	pH	C/N
PS	-0.924	-	-	-	-	-	-	-
WEOC	-0.887	0.950	-	-	-	-	-	-
O-groups	-0.925	0.981	0.978	-	-	-	-	-
Molar O/C	-0.694	0.822	0.899	0.868	-	-	-	-
Molar H/C	-0.866	0.955	0.981	0.972	0.948	-	-	-
pH	0.945	-0.943	-0.876	-0.936	-0.762	-0.898	-	-
C/N	0.365	-0.477	-0.580	-0.459	-0.419	-0.506	0.245	-
Ash	0.908	-0.795	-0.725	-0.802	-0.550	-0.706	0.852	0.051

[a] SSA = specific surface area; [b] PS = average pore size; [c] WEOC = water extractable organic C; [d] O-groups = summed band intensities of O-containing functional groups

Isoproturon sorption mechanisms

The large abundance of O-functional groups together with relatively low pH values of hydrochars (Table 4.1) indicate a substantial surface acidity (Chun et al., 2004). This suggests that the slightly polar herbicide IPU primarily reacts with the hydrochar surfaces as H-bond acceptor (-N, -H, -O, -C=O) (Ertli et al., 2004; Tian et al., 2010), and to a lesser extent as H-donor (-NH_2). In pyrochar amended soil the additionally sorbed IPU with respect to the control may have arisen from hydrophobic interactions as well as H-bonding involving aromatic and aliphatic groups (Sun et al., 2011; Zhang et al., 2011) that have frequently been reported to be more abundant in pyrochars (Sun et al., 2011; Lin et al., 2012). Quantitatively, the higher sorption of two herbicides (fluridone and norflurazon) in hydrochar amended soil than in pyrochar amended one has been attributed to their higher affinity towards O-functional groups compared to aromatic and aliphatic groups (Sun et al., 2012). Predominant hydrophobic interactions and H-bonding in combination with a high SSA of technical charcoal might have caused the tight IPU sorption observed by Tian et al. (2010) and slow IPU desorption in soil amended with wood charcoal (Sopeña et al., 2012).

Isoproturon sorption and char porosity

The micro-porous structure of pyrochars and hydrochars may be an important parameter in explaining the significant differences in NER between soil and pyrochar or hydrochar amended soil. The small PS of 12 to 17 Å of pyrochars (Table 4.1) probably facilitated diffusion and binding of IPU in nanopores (so called occlusion sites) (Cornelissen et al., 2005), resulting in large amounts of inaccessible IPU in pyrochar amended soils. For example, the large proportion of NER of miscanthus-pyrochar coincides with a small PS. In comparison to pyrochars, the minor amounts of NER in hydrochar amended soil may be attributed to a larger IPU accessibility caused by larger PS (167 to 207 Å; Table 4.1). The differences in the amount of NER among hydrochars from different raw materials at low or high addition were negligible, although hydro250 from digestate at low addition had a slightly higher amount of NER (7.7%), again coinciding with the lowest PS among the hydrochars (167 Å). Based on our findings, we suggest that in comparison to pyrochar amended soil, only minor IPU residues will form in hydrochar amended soil, irrespective of the raw material, thus rendering a larger portion of IPU bioaccessible. Occlusion and thus less reversible immobilization in micro-pores of biochars has also been considered for other pesticides such as pyrimethanil (Yu et al., 2010). In batch experiments with IPU, Tian et al. (2010) observed a pronounced adsorption-desorption hysteresis, which has been attributed to a strong physical adsorption of IPU within the micro-porous network of technical charcoal. A positive relationship between the extent of IPU desorption and the total PV of woodchips-pyrochars (carbonized at 850 °C) has also been observed for diuron, which belongs to the same pesticide family as IPU (Yu et al., 2006).

Isoproturon sorption and WEOC

In contrast to the sorptive nature of soil-inherent OM, readily dissolvable organic C may cause a decrease in the IPU sorption capacity due to associations with the pesticide (Ertli et al., 2004). The trend between higher amounts of WEOC and IPU in the pore water at sorption equilibrium at low and high char additions corroborates this suggestion ($R = 0.87$ and 0.82, respectively, $p < 0.001$; Fig. 4.4). Hydrochars contained a large WEOC fraction, and treatments with hydrochars from digestate had a particularly low sorption capacity coinciding with the highest WEOC content (Table 4.1). Earlier work showed that the sorption capacity for IPU decreased with an increasing amount of dissolved humic substances due to partitioning processes (Ertli et al., 2004). The extent of sorption or mobility of IPU strongly depended on the type of the dissolved C fraction and soil pH. Ding et al. (2011) likewise showed a low IPU sorption in soil due to the formation of stable complexes with dissolved OM as well as the competition between IPU and dissolved organic OM for sorption sites, with high proportion of WEOC also promoting the sorption reversibility of IPU. In addition to the high micro-porosity of pyrochars, this may further explain the high amount of NER of miscanthus-pyrochar, which had the lowest WEOC content among pyrochars.

Isoproturon sorption and ash content

Generally, higher carbonization temperatures lead to a higher ash content, higher pH values and higher total surface charge compared to low-temperature pyrochars and hydrochars (Novak et al., 2009; Kang et al., 2012). In this study lower ash contents tend to reduce the amount of pore water extractable IPU at sorption equilibrium at low and high char addition ($R = 0.82$ and 0.61, respectively, Fig. 4.4). Similar to the competition of IPU with dissolved OM, inorganic components like ash and silicates partly covering the surface of char particles through electrostatic interaction, complexation or non-specific adsorption may likewise reduce the accessibility of pesticides to biochars (Ji et al., 2011). On the other hand, increased adsorption through additional electron and H-bonding and hydrophobic interactions with the charged mineral surface of ash-rich pyrochars is conceivable as well (Lehmann et al., 2011; Zhang et al., 2013). Zhang et al. (2013) reported increased sorption of carbaryl and atrazine on pyrochars from pig manure (carbonized at 350 and 700°C) after de-ashing compared to the original pyrochars. They attributed the lower sorption capacity of the original pyrochars to ash covers which impaired the access to sorption sites. The contribution of ash in promoting pesticide adsorption has been described as being weak or even negative for the high-temperature pyrochar (Zhang et al., 2013). However, in this study due to the multicollinearity with the other char properties (Table 4.2) and the strong sorption effect of the SSA, the contribution of the ash content to increase or reduce the extractable IPU amount was not quantifiable.

Isoproturon sorption and carbonization degree

There was a high correlation between the amount of WEOC and the molar O/C and H/C ratios ($R = 0.90$ and 0.98, respectively, $p < 0.001$; Table 4.2), indicating a strong relationship to the degree of carbonization. This result is in accordance with previous studies showing that the amount and composition of WEOC of chars decreases with process temperature due to the more effective breakdown of the main biopolymers (cellulose, hemicellulose, lignin) during carbonization (Lin et al., 2012). For the herbicide simazine, Zhang et al. (2011) demonstrated that the sorption was positively linked to the carbonization degree of biochars produced from corn straw at different temperatures. They proposed that a high degree of carbonization (low O/C ratios and low amount of O-functional groups) increases the surface hydrophobicity of pyrochars, thus promoting hydrophobic interactions with non-polar compounds similar to simazine. At the same time, hydrophobic surfaces may cause larger sorption reversibility for polar and slightly polar pesticides like IPU.

4.4 Conclusions

This study shows that even low additions of pyrochar and hydrochar to an agricultural soil significantly increase their sorption capacity for IPU. The results in this study are restricted to chars of only two ranges of process conditions (temperatures of 200 to 250°C with a pressure of 2 MPa and temperature of around 750°C in the absence of oxygen). Nevertheless, the high correlations between char properties (SSA, O-containing functional groups, WEOC, ash content) and the carbonization degree (molar O/C and H/C ratio) which altogether reflect the impact of process conditions, lead to the suggestion that there exists a close relation between the amount of sorbed IPU and respective char properties. The most relevant sorption parameter identified was the SSA of the carbonized material. Unlike for hydrochars, high SSA of pyrochars located primarily in micro-pores, facilitated the sorption of IPU therein, and thus constrains IPU bioavailability. IPU availability in hydrochar amended soil was higher as revealed by the minor proportion of NER due to the low micro-porosity and ash contents, high WEOC contents and O-functional groups of hydrochars. A sustained IPU bioavailability in case of hydrochar amendments is also guaranteed due to their more favorable decomposability. Efforts should be taken to optimize carbonization conditions and pre- and post-treatments for hydrochars, aiming at enlarging their sorption capacity (e.g., by increasing pore volumes and, hence, the SSA) by ensuring an appropriate compound degradability under natural conditions. In comparison, IPU sorption in nanometer-scale micro-environments in pyrochar amended soils would facilitate the formation of bound residues and thus contribute to a larger ecosystem persistence of applied pesticides. For evaluation of the sorption capacity the raw material should also be considered as contrary sorption effects can arise. For example, digestate promoted a high WEOC content when carbonized hydrothermally, thus reducing IPU immobilization, but supported a high SSA and IPU retention when pyrolyzed. Nevertheless, this study suggests that application of hydrochars from various raw materials to agricultural soils may present an effective management practice to ensure availability of the polar soil pesticide IPU while coevally reducing the risk of drinking water contamination.

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5 Article III. Effect of pyrochar and hydrochar amendments on the mineralization of the herbicide isoproturon in an agricultural soil

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Abstract

Carbon (C)-rich, solid products from pyrolysis (pyrochars) and hydrothermal carbonization (HTC, hydrochars) are expected to reduce the bioavailability and bioaccessibility of pesticides as side effect of soil addition. To compare effects of different feedstocks (digestate, miscanthus, woodchips) and production processes (pyrolysis at 750°C, HTC at 200 and 250°C), ^{14}C-labeled isoproturon (IPU) was applied at 0.75 kg ha^{-1} to loamy sand amended either with 0.5 or 5% pyrochars or hydrochars, which was then incubated for 50 days. Mineralization of IPU was measured as ^{14}C-CO$_2$ released from soil-char composites. Pore-water and methanol extractable ^{14}C-IPU was quantified as well as non-extractable ^{14}C-residues (NER). Furthermore, C mineralization of pyrochars, hydrochars and feedstocks was studied to assess the relationship between IPU bioaccessibility and char decomposability.

In pure soil, 8.1% of applied IPU was mineralized after 50 days. This was reduced more strongly in pyrochar treatments (81±6% reduction) than in hydrochar treatments (56±25% reduction). Different feedstocks had no significantly different effect when 5% char was added, but their effect was significant and dependent on the production process in 0.5 % amendments. Pesticide binding can occur by surface sorption as well as by diffusion and subsequent occlusion in micropores. The latter can be expected to result in high amounts of NER, as it was observed in the pyrochar treatments. Hydrochars were less stable than pyrochars and contained lower amounts of NER. Thus, in hydrochar amended soils, better accessibility of IPU to microbial degradation may be a result of full char decomposition within decades ensuring controlled pesticide degradation.

5.1 Introduction

In recent years, the idea of adding carbon (C)-rich solids from pyrolysis of biomass (referred to as pyrochars) to soil with the aim of increasing crop yield and soil C sequestration has gained considerable interest (Lal, 2011; Vaccari et al., 2011). There are wide agro-environmental benefits of char addition to soils. For instance, it has been reported that the addition results in an increase of the nutrient (Uzoma et al., 2011) and water retention (Abel et al., 2013), the soil pH (Cao and Harris, 2010) and cation exchange capacity (Liang et al., 2006), and changes the aggregate stability and bulk density of soils (Laird et al., 2010). The improvements are likely due to physic-chemical properties of the chars such as their specific surface area (SSA), porosity, pH value, and oxygen-containing functional groups.

Apart from the potential to improve soil fertility and sequester C, as a side effect, pyrochar addition presumably reduces the bioavailability and bioaccessibility of polar and non-polar organic chemicals in soils and sediments (Beesley et al., 2011; Gomez-Eyles et al., 2011; Zhang et al., 2011). Bioaccessibility of a certain compound is understood as the proportion of the compound that is available immediately and potentially over time to organisms for further processes (e.g., mineralization) (Semple et al., 2004). In soils, bioaccessibility of organic chemicals such as pesticides is mainly controlled by the sorption potential of organic matter as well as pyrochars (Bending and Rodriguez-Cruz, 2007). Furthermore, pyrochar induced indirect effects such as pH shift, change in cation exchange capacity and dissolved organic carbon content may also affect the bioaccessibility of organic chemicals (Gomez-Eyles et al., 2011). Previous studies that investigated the effects of char addition on the bioavailability or bioaccessibility largely examined the effects on hydrophobic organic compounds (e.g., polycyclic aromatic hydrocarbons) (Yang et al., 2010; Rhodes et al., 2012). But information on the bioaccessibility especially of relatively good water soluble and mobile pesticides is scarce (Sopeña et al., 2012).

In this study we tested the effect of carbonization products on the bioaccessibility of the water soluble phenylurea herbicide isoproturon [3-(4-isopropylphenyl)-1,1-dimethyl-urea] in soil (water solubility = 70 mg L^{-1}; partition coefficient, log K_{OW}, at 25°C = 2.5; half-life in water = 20-61 days and in soil = 6-23 days) (Umweltbundesamt, 2006). Use of this pesticide is widespread in European cereal production. As a consequence, it frequently exceeds the maximum allowable concentration of the European directive for drinking water (≥ 0.1 µg L^{-1}) (Umweltbundesamt, 2006) in surface water and groundwater. To our best knowledge only two studies investigated mineralization of isoproturon (IPU) in a soil amended with charred material, i.e., with technical charcoal (Si et al., 2011) and charcoal produced from wood in a brick kiln (Sopeña et al., 2012). Overall, there is potential to significantly reduce mineralization of mobile organics like IPU in soil through pyrochar amendment. Nevertheless, the effects of pyrochars from different feedstocks carbonized under similar conditions on the bioaccessibility of organic substances are not clear. Furthermore, the decomposability of pyrochars has not been considered in pesticide mineralization experiments so far.

In contrast to pyrolysis, hydrothermal carbonization (HTC) is an energy-saving carbonization process that converts organic residues with water contents of 50 to 90 wt% at relatively low temperatures (180-250°C) and high pressure (around 2 MPa) (Libra et al., 2010; Mumme et al., 2011). The physico-chemical properties (e.g., SSA, H/C and O/C ratios) of hydrochars and pyrochars differ considerably due to specific production conditions (e.g., temperature, time, pressure) (Libra et al., 2010). For instance, results from short-term incubation studies indicate that hydrochars are relatively well decomposable in contrast to pyrochars (Kammann et al., 2012). This study investigated for the first time the mineralization of a pesticide in a soil amended with various types of hydrochar.

The main objective of this study was to comparatively assess IPU mineralization in pyrochar versus hydrochar amended soil. We assumed that (i) pyrochars as well as hydrochars significantly reduce IPU mineralization in soil and that (ii) production process and feedstock material type have significant effects on the bioaccessibility of IPU. Further, we expected that (iii) IPU mineralization is directly related to the sorption of IPU. Lastly, we hypothesized that (iv) the bioaccessibility of IPU depends on the degradability of pyrochars and hydrochars.

5.2 Material and Methods

Soil material

A soil with slow and constant co-metabolic IPU mineralization dynamics was selected for the experiments to avoid intensive microbial growth reactions after herbicide application, which would occur when already adapted catabolic organisms proliferate (Bending et al., 2006). Under co-metabolic degradation conditions a linear correlation between IPU bioavailability and IPU mineralization in soils can be expected (Folberth et al., 2009). The selected soil is a Cambisol and was sampled at the organic farming section of the research station Scheyern in southern Germany. Soil texture is loamy sand with 68% sand, 15% silt and 17% clay. The same soil material has been used in Eibisch et al. (2015) for IPU sorption experiments. Soil properties are given in Table 5.1. The air-dry soil was stored at -20 °C and was equilibrated at a soil water content of 10% (w/w) for 2 days at 4 °C and a further day at 20 °C prior to laboratory experiments.

Pyrochars and hydrochars

For the carbonization three different feedstock materials (corn digestate, miscanthus, and woodchips of poplar and willow) had been used. Pyrochars (pyro750) were produced by pyrolysis at the standard operating temperature of the Pyreg technology of 750°C for 45 min (by pyrolysis (Pyreg GmbH, Dörth, Germany). HTC was conducted at 200 as well as 250°C and 2 MPa for 6 h (hydrochars referred to as hydro200 and hydro250) by SmartCarbon AG, Jettingen, Germany. The carbonization products were oven-dried at 105°C and sieved to < 1 mm. Physico-chemical properties of feedstock and carbonized material are taken from Eibisch et al. (2015) and selected properties are given in Table 5.1.

Table 5.1 Physico-chemical properties of pyrochars (pyro750) and hydrochars (hydro250/200) from digestate (D), miscanthus (M), and woodchips (W), the feedstock materials, and the soil; standard deviations were <3% if not explicitly mentioned (data from Eibisch et al., 2015).

Property	Pyro750-			Hydro250-			Hydro200-			Feedstock material			Soil
	D	M	W	D	M	W	D	M	W	D	M	W	
C (%)	52	77	68	62	69	68	54	58	60	42	46	49	0.87
N (%)	0.90	0.87	0.89	2.98	1.18	1.22	2.59	0.67	1.07	1.57	0.52	0.78	0.10
C/N	57.7	88.4	76.1	20.7	58.5	56.1	20.8	86.6	55.8	26.7	87.7	62.3	8.8
Molar O/C	0.14	0.06	0.06	0.22	0.20	0.20	0.34	0.35	0.30	0.65	0.65	0.53	n.d.
Molar H/C	0.33	0.19	0.26	0.91	0.86	0.89	1.15	1.09	1.06	1.53	1.48	1.36	n.d.
WEOC[a] (g kg^{-1})	1.2 ±0.01	0.7 ±0.02	0.3 ±0.01	23.1 ±0.15	16.5 ±0.27	18.1 ±0.05	24.7 ±0.25	21.0 ±0.03	24.4 ±0.03	17.7 ±0.15	12.4 ±0.1	4.3 ±0.02	6.7 ±0.01
pH (0.01M $CaCl_2$)	10.5	10.0	8.7	6.4	4.9	5.3	6.3	4.7	5.0	7.6	5.6	4.8	5.3
SSA[b] (m^2 g^{-1})	448	279	210	2.8	5.8	3.5	13	5.2	10	8.6	1.0	1.6	8
Average pore size (Å)	12	14	17	167	179	207	192	180	180	61	154	206	51
Sum FTIR[c] O-groups[d]	0.15 ±0.01	0.17 ±0.03	0.15 ±0.02	0.37 ±0.03	0.35 ±0.02	0.36 ±0.00	0.37 ±0.00	0.39 ±0.01	0.38 0.01±	0.34 ±0.02	0.31 ±0.01	0.31 ±0.03	n.d.

[a] WEOC = water extractable organic carbon; [b] SSA = specific surface area; [c] FTIR = Fourier transform infrared analysis; [d] O-groups = band intensities of O-containing functional groups; n.d. = not determined

Chemicals

For pesticide mineralization experiments uniformly ^{14}C-ring labeled isoproturon (^{14}C-IPU, GE Healthcare, Little Chalfont, UK; purity > 98%, specific radioactivity 10 kBq µg^{-1}) mixed with non-labeled IPU (Dr. Ehrensdorfer Augsburg, Germany; purity > 98%) was diluted in methanol to achieve a final specific radioactivity of 375 Bq µg^{-1}. Pyrochar-, hydrochar- and feedstock material-C mineralization experiments were performed with non-labeled IPU.

Experiments with pyrochar-, hydrochar- and feedstock-soil composites

Pesticide mineralization experiments were carried out in quadruplicates with pure soil (= control) and soil amended either with 0.5 or 5% (dry weight, dw) hydrochar or pyrochar addition. For C mineralization experiments, treatments with pyrochars, hydrochars, and feedstocks at 0.5 or 5% addition were used in triplicates. Under the assumption that materials are distributed over a soil depth of 30 cm in soils, these additions are equivalent to 19.5 and 195 t material ha^{-1} and correspond to reasonable and large field application rates, respectively (Novak et al., 2009; Jones et al., 2012).

All pesticide and C mineralization experiments were conducted under identical test conditions at 20±1°C over a period of 50 days. Experiments were performed with 50 g (dw) of equilibrated soil either without or with 0.5 or 5% material addition in 250 mL incubation vessels. All treatments were compacted to a bulk density of 1.3 g cm^{-3} and the matric potential adjusted to -15 kPa. The soil water content at a matric potential of -15 kPa was determined specifically for each treatment (Eibisch et al., 2015) and has been reported to be optimal for microbial activity in agricultural soils (Schroll et al., 2006). To all treatments a solution of NH_4NO_3 was added to achieve sufficient N supply and equal N concentrations corresponding to the treatment with the highest N content (Table 5.1). Digestate-hydro250 had the highest N content and N of all materials was assumed to be fully available for mineralization processes. E.g., to 50 g soil (= control) 27.2 mg NH_4NO_3 were applied (Table 5.2).

IPU mineralization experiments

After amending chars to soil and rewetting, subsequent CO_2 emissions were expected to be very high due to labile C compounds of young chars. These emissions would most likely hamper the effectiveness of CO_2 traps used for quantification of ^{14}C-CO_2 emissions. For this reason, soil-char composites were pre-incubated for 12 days to achieve relatively stable CO_2-emissions prior to IPU application. Pesticide application was conducted with a concentration of 5 µg g^{-1}soil that corresponds to common field amounts of 0.75 kg ha^{-1} (Schroll and Kühn, 2004). IPU was applied drop-wise with a Hamilton syringe to 3.5 g oven-dried (105°C) soil aliquots, thoroughly mixed with a metal spatula for one minute, transferred into incubation vessels and mixed with 46.5 g (dw) pre-incubated samples by stirring for two minutes (Folberth et al., 2009). During incubation, emitted ^{14}C-CO_2 was trapped in 9 mL NaOH (0.1 M) using beakers, which were fixed to the bottom side of the lid of the incubation vessels. The NaOH solution was sampled and replaced three times a week. To quantify IPU mineralization, the ^{14}C content of the NaOH-solution was mixed with a scintillation cocktail (Ultima Flo AF, Perkin Elmer, USA) and measured with a scintillation counter (TriCarb 2800 TR, Canberra-Packard GmbH, Dreieich, Germany). The cumulative amount of mineralized IPU, IPU_{min}, after 50 days of incubation was calculated as follows:

$$IPU_{min} = \sum_{1}^{50} \left(\frac{IPU_t * 100}{IPU_{t=0}}\right), \qquad \text{Eq. 5.1}$$

where IPU_t is the amount of ^{14}C-CO_2 measured in NaOH solution at time t, and $IPU_{t=0}$ is the total amount of ^{14}C applied to the treatment as ^{14}C-IPU at the beginning of the experiment.

Table 5.2 Addition of NH_4NO_3 to treatments of 50 g soil amended either without (=control) or with 0.5 or 5% hydrochar (-hydro200/-250) and pyrochar (-pyro750) from different materials to ensure sufficient N supply and equal N concentrations in all treatments

Material	Process	NH_4NO_3 [mg]	
		0.5%	5%
Digestate	-pyro750	20.7	207.4
	-hydro250	0.0	0.0
	-hydro200	8.2	81.6
Miscanthus	-pyro750	21.0	210.1
	-hydro250	21.3	212.7
	-hydro200	22.4	224.2
Woodchips	-pyro750	20.8	208.1
	-hydro250	18.8	187.57
	-hydro200	20.5	205.0

At the end of the experiments, soil char composites underwent a pore-water extraction (PWE) followed by an accelerated solvent extraction (ASE). For PWE, sample aliquots were centrifuged at 21°C for 90 min with a centrifugal force of 9170 × *g* (Thermo Scientific Sorvall RC 6 Plus, Osterode, Germany) according to the method described by Folberth et al. (2009). The amount of dissolved ^{14}C-IPU in soil pore-water was determined in duplicates in 100 µL aliquots which were mixed with a scintillation cocktail (Ultima Gold XR, Perkin Elmer, USA) and measured in a scintillation counter. The final ^{14}C-content in the soil pore-water was calculated accounting for the total water content of the respective soil sample. Pore-water extracted samples were transferred into ASE columns and extracted with methanol at 90°C and 10 MPa (Dionex ASE 200, Idstein, Germany). The extract volumes were quantified and ^{14}C

content of duplicate 100 µL aliquots was measured by scintillation counting. Residual pore-water ^{14}C was deducted from ^{14}C content of the methanol extracts. After ASE, sample aliquots were combusted in triplicates of 0.3 g in an automatic sample-oxidizer (307, Perkin Elmer, Waltham, USA) to quantify the amount of non-extractable pesticide residues and to establish a ^{14}C-mass balance (Folberth et al., 2009). The mass balance averaged to 101±6% (median=100%, n=76) of the added ^{14}C-IPU amount.

IPU mineralization might be affected indirectly by the soil pH. A low pH can support H-bond formations between the char as sorbent and the pesticide molecule (Ertli et al., 2004). Near-neutral pH conditions foster high bacterial activity (Fogarty and Tuovinen, 1991). For identification of a possible pH effect, experiments were carried out under the same incubation conditions of soil but with different pH values. As buffer, three different amounts of $CaCO_3$ (0.01, 0.05 and 0.1%, w/w) were used shifting the pH in the pore-water of the soil samples from 5.4 to 5.8, 6.2, and 6.4, respectively.

Mineralization of pyrochars, hydrochars and feedstocks

Carbon mineralization of hydrochars, pyrochars, and feedstocks in soil was measured by quantifying the CO_2 production with a respirometer which quantifies CO_2 emission by measurement of conductivity in CO_2 traps filled with KOH (Respicond) (Nordgren, 1988). KOH (0.06 M) was replaced by fresh KOH regularly throughout the incubation time. For representation and evaluation of the C degradability the total mineralization of soil organic C (C_{soil}) and material-C was used. Priming was not considered. The pH of sample replicates was measured in extracted pore-water at the beginning (pH_{0d}) and the end of incubation (pH_{50d}).

Statistics

Three-way analysis of variance (ANOVA) with the factors added char amount, production process and feedstock material was used to test for the significance of differences between the treatments and Tukey’s HSD test was used for pairwise comparison of individual means. To achieve normality and variance homogeneity, the arc sine transformation was applied. Correlations were tested using Pearson’s correlation (r) and Spearman correlation (ρ) in case of non-constant residuals. To test if the char addition had a significant influence on the relation between the amount of mineralized IPU and the amount of pore-water extractable IPU a multiple regression followed by a Wald test (F-test) was performed. The significance limit was set to 0.05. Statistical tests were carried out in SigmaPlot v. 11, Systat Software Inc..

5.3 Results and Discussion

Mineralization of isoproturon

The amount of added char, the production process, as well as the feedstock material type of the chars had significant effects on IPU mineralization ($p<0.001$). Cumulative IPU mineralization after 50 days was reduced by 81±6% in treatments with pyrochar and by 56±25% in treatments with hydrochar ($p<0.001$) compared to the control where 8±0.2% of applied IPU was mineralized (Fig. 5.1). IPU mineralization in treatments with 0.5% char addition differed between feedstocks carbonized under the same conditions. For example, IPU mineralization in soil amended with hydro250 from digestate (7.1%) was significantly higher compared to soil amended with hydro250 from miscanthus and woodchips ($p<0.05$). In contrast, IPU mineralization in soil amended with pyro750 from digestate (1.3%) was significantly lower compared to the corresponding treatments ($p<0.05$). Anyhow, the feedstock material effect was less pronounced than the effect of production process and char concentration. It should be noted that IPU metabolites were not considered and total IPU degradation was probably higher than just IPU mineralization. For instance, monodemethyl-IPU that is at the beginning of the IPU degradation path, made up to 50% of acetone extracted metabolites in a mineralization experiment with 1.25 kg ha^{-1} IPU in sandy loam originating from organic farming and conventional management (Lehr et al., 1996). However, mineralization of IPU in this study was much lower than reported in other soils. Si et al. (2011) observed about 50, 30 and 30% mineralization of total IPU within 50 days in a Paddy soil, an Alfisol, and a Vertisol, respectively, amended with 5% charcoal. In a study by Sopeña et al. (2012) only 10 and 30% of initially added IPU remained in soil after 50 d of incubation for 0.1 and 2% (w/w) char addition, respectively. Nevertheless, the reported dissipation of IPU was still much lower for soil amended with 2% char compared to their control. The high dissipation of IPU in these studies was likely due to different physico-chemical properties of the carbonized material but primarily indicates the predominance of specific, growth-linked degradation processes (Bending et al., 2006). Mineralization of IPU in agricultural soils that had been exposed to IPU application over years is generally high (>30% of IPU being metabolized within one to three months) (Priha and Smolander, 1999; Schroll et al., 2006). Low cumulative IPU mineralization (3-18% of applied IPU within 46 days), which indicates co-metabolic degradation, has been found for nine agricultural soils in a previous study and was likely given for the soil used in this study (Folberth et al., 2009). According to its long-term organic farming history, present soil microorganisms had not adapted on the use of IPU as primary energy source resulting in slow and co-metabolic IPU degradation.

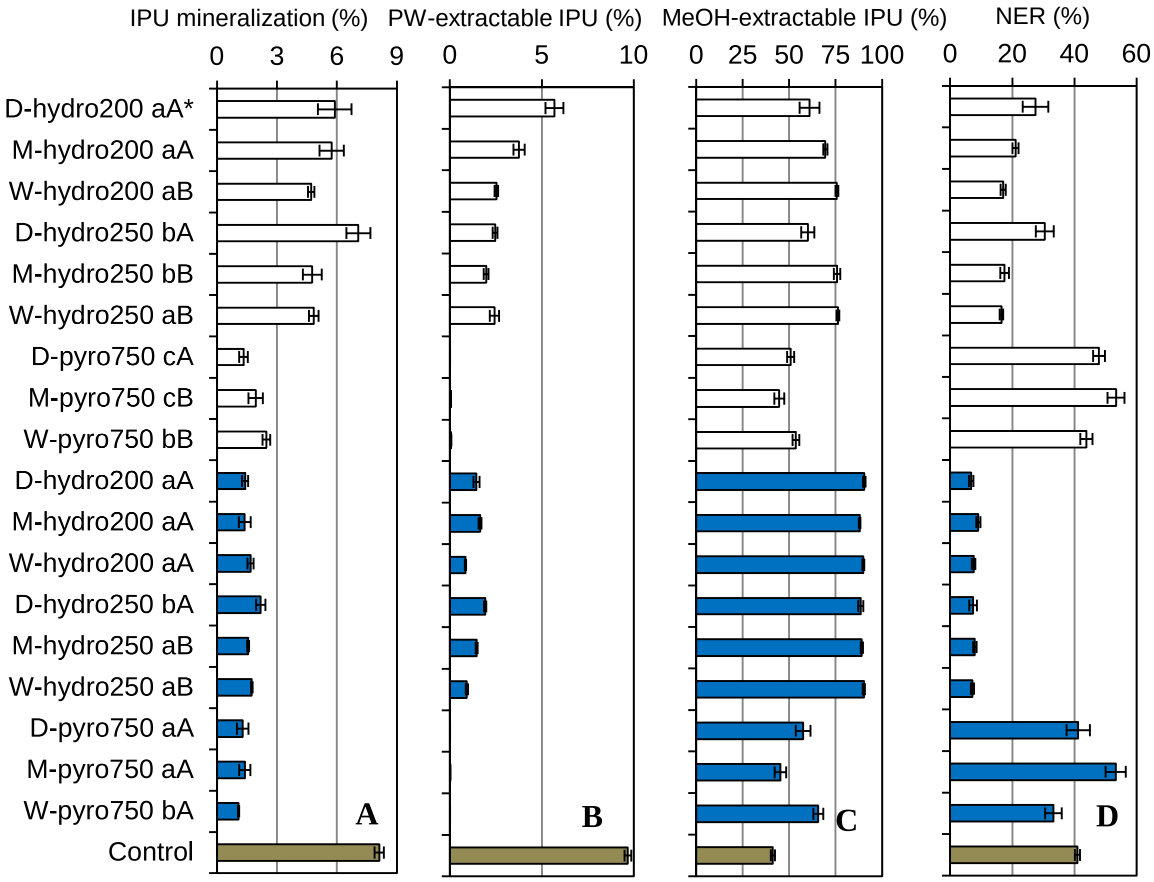

Fig. 5.1 Amounts of isoproturon (IPU, % of added IPU) mineralized, pore-water (PW) and methanol (MeOH)-extractable IPU, and non-extractable residues (NER) in soil amended either with pyrochar (pyro750) or hydrochar (hydro250/ 200) from different feedstock materials (digestate: D, miscanthus: M, woodchips: W) at 0.5% (white bars) or 5% (blue bars) addition, means ± standard deviation, n = 4.
* significant differences of the IPU mineralization within the same feedstock material at 0.5 or 5% char addition are indicated by different lower case letters, and within the same production process at 0.5 or 5% char addition is indicated by different upper case letters (p<0.05).

Mineralization and sorption of isoproturon

A high sorption capacity of chars likely explains the reduced availability of IPU for mineralization compared to the soil without char addition (Si et al., 2011). The amount of mineralized IPU correlated positively with the amount of pore-water extractable IPU (Fig. 5.2A), with significant influence of the added char amount ($p<0.001$). Soil amended with 0.5% digestate-hydrochar and miscanthus-hydro200 exhibited the highest IPU mineralization as well as the highest amount of pore-water extractable IPU (Fig. 5.1A and 5.1B). In 5% char treatments IPU mineralization and amounts of pore-water extractable IPU were lower for all treatments. Furthermore, the amount of pore-water extractable IPU that was measured at the end of the pesticide mineralization experiments correlated strongly with the amount of pore-water extractable IPU at equilibrium in sterilized sorption experiments that were performed in a previous study (Fig. 5.2B, see Eibisch et al., 2015, for sorption experiment). The positive correlations between IPU mineralization and pore-water extractable IPU, and between the latter and IPU at sorption equilibrium corroborates the suggestion that IPU mineralization is directly linked to the sorption capacity of soils amended with chars (Sopeña et al., 2012). Consequently, in soil amended with 5% char, IPU mineralization was low because all of these treatments exhibit high sorption capacities (Eibisch et al., 2015).

Bioaccessibility of isoproturon

To draw conclusions on the bioaccessibility of IPU from the sorption capacity of chars and IPU mineralization results, the type of bonding has to be considered. It is likely that IPU reacted with oxygen-containing functional groups on the surfaces of hydrochars through reversible H-bonding (Eibisch et al., 2015). In contrast, diffusion and occlusion (Yang et al., 2010) of IPU in micro-pores likely occurred in soil amended with pyrochars that generally have a high surface area and micro-porosity (Schimmelpfennig and Glaser, 2012). Consequently, IPU bioaccessibility in hydrochar amended soil will be higher than in pyrochar amended soil.

This is in accordance with high amounts of NER in 0.5 and 5% pyrochar amended soil (average of 45±7% of applied IPU in 0.5 and 5% pyrochar amended soil) that were in the order of miscanthus > digestate > wood (Fig. 5.1C). High amounts of NER in pyrochar amended soils and occlusion by micro-pores has been proposed previously for other pesticides (e.g. diuron, pyrimethanil) (Yu et al., 2006; Yu et al., 2010). Also the soil without char addition had a high amount of NER (41%). In accordance with high IPU mineralization in soil, the high amount of NER may be attributed to high amounts of IPU metabolites that have been sorbed effectively by the soil organic substance as it has been suggested previously for i.e., isopropyl-aniline (Lehr et al., 1996). In charcoal amended soil, the amount of isopropyl-aniline was much lower than in pure soil (Sopeña et al., 2012). This supports the assumption of a low bioaccessibility of IPU in pyrochar amended soil. In contrast, soil amended with 0.5% hydrochar additions had lower amounts of NER (average of 22±5% of applied IPU in 0.5% hydrochar amended soil). Furthermore, in soil amended with 5% hydrochar the highest amount of NER was 9% (hydro200 from miscanthus). It is unclear why addition of hydrochars reduces NER formation compared to the pure soil. We suggest that compounds from the hydrochars could compete with IPU metabolites for sorption sites of soil organic matter or even react with enzymes involved in co-metabolic IPU degradation steps. Modification of hydrochars (e.g., by treatment with hydrogen peroxide) could increase the proportion of oxygen-containing functional groups, hence increase their sorption capacity as it was shown for the sorption of heavy metals onto peanut hull hydrochars (Xue et al., 2012). If this post-treatment of the HTC would have an impact on the bioaccessibility of pesticides needs to be clarified by sorption-desorption experiments.

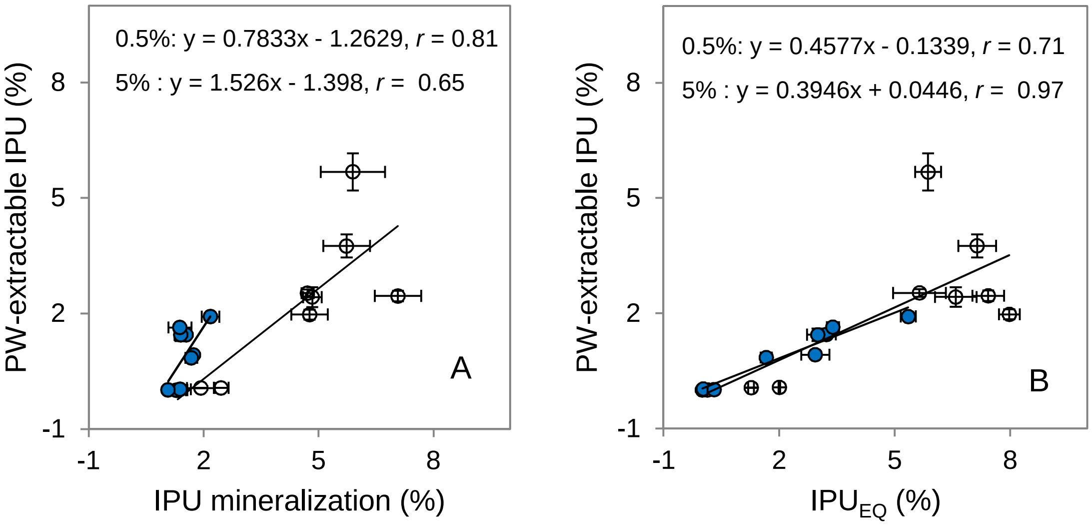

Fig. 5.2 Correlation of the amount of pore-water (PW) extractable isoproturon (IPU, % of added IPU) after incubation and (A) mineralized IPU, and (B) the extractable IPU amount at sorption equilibrium (IPU_{EQ}, data from Eibisch et al. 2015) in 0.5% (white dots) and 5% (blue dots) pyrochar and hydrochar amended soil, means ± standard deviation, n=3, linear regression equations and Pearson correlation coefficients, *r* ($p<0.05$).

It is conceivable that the efficacy of IPU is associated with its bioaccessibility. In pyrochar amended soils the efficacy may be largely constrained because IPU will probably be occluded in micro-pores in the long-term. It was shown previously for other pesticides (i.e., diuron, atrazine, trifluralin, chlorpyrifos, and carbofuran) that the efficacy was reduced in soil amended with different pyrochars in dependence of the pesticide concentration, the char addition, and the pyrolysis temperature (Yang et al., 2006; Yu et al., 2009; Nag et al., 2011). However, the effectiveness of isoproturon on weed control was not investigated in this study and has to be considered when chars are applied to soil.

Mineralization of isoproturon and pH

From the literature it is known that in acidic soils the sorption of IPU can increase causing its degradation to decrease due to intensive H-bond formation between the sorbent and pesticide molecule (Ertli et al., 2004). A test with pH-adjusted soil confirmed a positive correlation between pH and IPU mineralization ($y = 2.4795x – 5.7319$, $\rho = 0.78$). However, the pH does not fully explain differences in IPU mineralization between char treatments, since pH was highest in pyrochar treatments (Table 5.3) which exhibited lowest IPU mineralization. The pH of pyrochars and hydrochars ranged from highly alkaline to slightly acidic (Table 5.1), and the shift of the pH in the pore-water of the treatments from beginning to the end of incubation (pH_0 and pH_{50d}) were small for 0.5% char additions (Table 5.3). For 5% additions, the pH decreased in soil amended with chars from digestate during incubation. Digestate contains high ammonium concentrations. Hence, acidification may be explained by nitrification (Libra et al., 2010; Kammann et al., 2012). Treatments with digestate-hydro250 exhibited the highest IPU mineralization and pore-water extractable IPU amount (Fig. 5.1). IPU mineralization of digestate-hydro200 and -pyro750 did not differ from the corresponding treatments. Apparently, there was no influence of the pH on the capacity to sorb IPU that was applied in small amounts (Larsbo et al., 2013). However, an acidic pH constrains the growth of microbial communities that generally prefer neutral conditions for IPU (co-)metabolism (Bending et al., 2006).

Degradability of pyrochars, hydrochars and feedstocks

Interactions between amount of added char, production process, and feedstock material type were found to have significant effects on total C degradability (mineralization of C_{soil} and material-C, $p<0.001$). Carbon degradability increased in the order pyro750 < hydro250 < hydro200 < untreated feedstock ($p<0.001$, Fig. 5.3). Furthermore, degradability was significantly lower for woodchips and woodchips-hydro200 compared to the other corresponding treatments. Differences of C degradability between pyro750 and hydro250 were smaller than of hydro200 to the other char types. Low degradability of pyrochars (Spokas et al., 2009; Bruun et al., 2011) and high degradability of hydrochars (Gajić et al., 2012; Kammann et al., 2012) were already observed by other authors. The impact of the feedstock material on C degradability of pyrochars (van Zwieten et al., 2010) and hydrochars (Eibisch et al., 2013) has also been described. Carbon degradability of 0.5% char additions correlated significantly with atomic O/C ratios ($r = 0.87$, $p<0.001$) and atomic H/C ratios ($r = 0.82$, $p<0.001$). This indicated a dependence on the degree of carbonization as it has been previously reported (Gajić et al., 2012; Schimmelpfennig and Glaser, 2012). For example, the O/C and H/C ratios of pyrochars from miscanthus (0.06 and 0.19, respectively) increased to 0.2 and 0.86, 0.35 and 1.09, and 0.65 and 1.48 for hydro250 and hydro200 from miscanthus, and the feedstock material, respectively. Congruently, the 4% C degradability in soil amended with 0.5% pyro900 from miscanthus increased to 6, 15 and 24% for hydro250, hydro200, and raw miscanthus.

Table 5.3 pH-values in pore-water extracts of soil amended either with 0.5 or 5% pyrochar (-pyro750) or hydrochar (-hydro200/-hydro250) from different materials at the beginning (pH_{0d}) and end of incubation (pH_{50d}).

Material	Process	pH_{0d}	pH_{50d}	pH_{0d}	pH_{50d}
		0.5%		5%	
Digestate	-pyro750	6.4	6.9	7.5	6.8
	-hydro250	6.1	6.1	7.4	6.5
	-hydro200	5.8	6.5	6.9	5.8
	feedstock	7.0	6.2	7.1	5.8
Miscanthus	-pyro750	6.5	6.7	6.8	6.1
	-hydro250	6.1	6.1	5.3	5.1
	-hydro200	6.5	6.2	5.1	4.9
	feedstock	5.8	5.7	5.1	5.1
Woodchips	-pyro750	6.9	6.6	7.1	6.9
	-hydro250	6.6	6.5	5.4	5.9
	-hydro200	6.3	6.4	5.8	5.5
	feedstock	5.5	5.9	5.2	4.8

Mineralization of isoproturon and C degradability

In addition to the relationship between the degree of carbonization and C degradability, a positive correlation between the degree of carbonization and sorption capacity has been documented (Eibisch et al., 2015). Consequently, IPU mineralization in the long-term can be expected to depend on the decomposability and environmental fate of pyrochars and hydrochars in soil. Thus, amounts of mineralized IPU and IPU in the pore water will be high in soils amended with chars that are relatively good degradable. This was the case for all hydrochars, especially for soil amended with 0.5% digestate- and miscanthus-hydro200, where the highest amounts of pore-water extractable IPU and highest CO_2 emissions of 0.5% char amended soil were measured (Fig. 5.1B and 5.3).

In 5% hydrochar amended soil where also a high C degradation was measured, a higher release of IPU into the pore water may have been compensated by high sorption capacities at 5% char addition (Eibisch et al., 2015). Mean residence times of hydrochars in soils range from 4 to 29 years (Kammann et al., 2012). Hence, in hydrochar amended soils, adsorbed IPU will be accessible in the time scale of years to decades in contrast to pyrochars with estimated residence times of hundred to thousand years (Kammann et al., 2012).

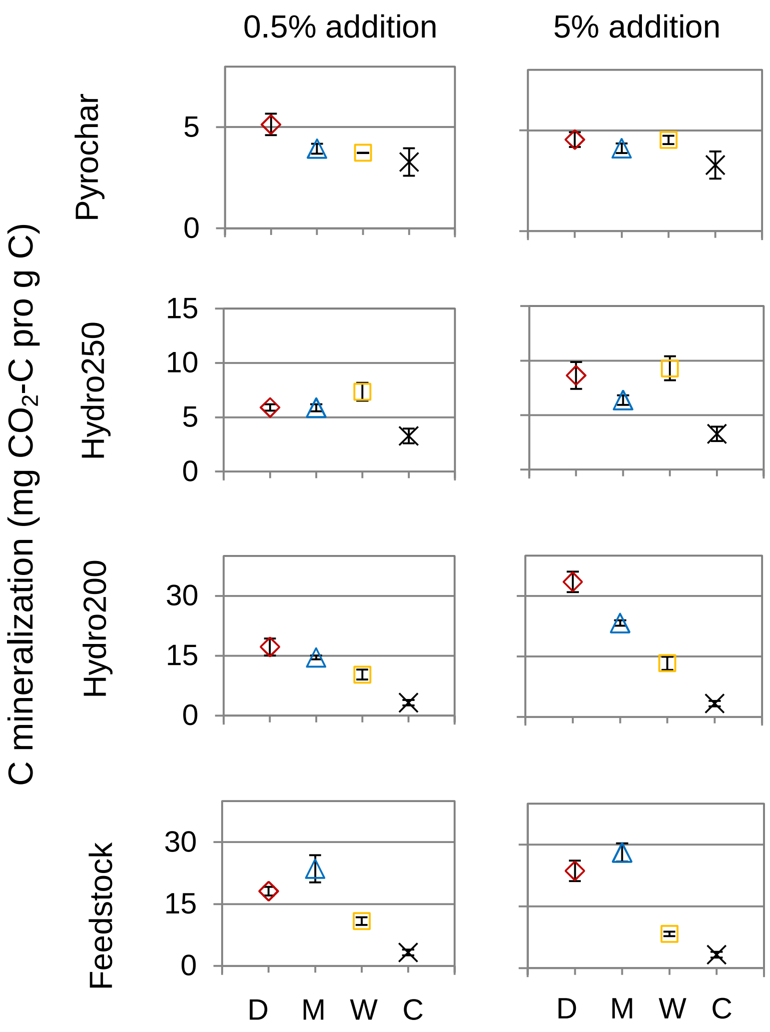

Fig. 5.3 Total C mineralization in soil amended either with 0.5% or 5% feedstock material, hydrochar (hydro250/ 200), or pyrochar (pyro750) of different materials (digestate: D, miscanthus: M, and woodchips: W) and the control, C, means ± standard deviation, n = 3.

Agro-environmental implications

There is a knowledge gap concerning the mineralization and bioaccessibility of relatively good water soluble pesticides in soil amended with chars that are subjected to surface oxidation (ageing). However, in order to evaluate the long-term impact of char addition on the bioaccessibility of IPU, not only the degradability of chars but also the effects of ageing have to be considered. It has been reported previously that the sorption capacity of pyrochars decreased upon ageing with probably direct consequences on pesticide mineralization (Yang and Sheng, 2003; Zhang et al., 2010). Martin et al. (2012) showed that ageing of pyrochars (at 550°C) from poultry litter in soil (10 t ha^{-1}) for 32 months decreased the sorption for diuron by 68% and for atrazine by 82% compared to soil amended with fresh pyrochar. However, the sorption of diuron was still higher compared to the pure soil and significantly higher for high pyrochar addition rates (50 t ha^{-1}). Moreover, the char surface may become blocked or fouled by mineral and organic matter in soil that masks the true sorption capability of chars for organic and inorganic contaminants (Cornelissen et al., 2005; Cui et al., 2013). Nonetheless, ageing and fouling did not change remarkably the sorption capacity for pyrene (Hale et al., 2011) and simazine (Jones et al., 2011). These aspects may entail agronomic consequences. As outlined above the efficacy may be reduced after soil amendment with chars and higher pesticide doses may become necessary to obtain the desired effects on plant growth control. When chars are subjected to ageing and fouling, the pesticide doses that have to be applied could be reduced and should be adjusted with each cropping cycle according to the changing sorption capability of chars. However, evaluation of IPU sorption and mineralization upon ageing and fouling would only be speculative and was beyond the scope of our study.

5.4 Conclusions

This study has shown that IPU mineralization is significantly reduced after application of pyrochars and hydrochars to soil at reasonable (0.5%) and high (5%) char additions due to the high sorption capacities of chars. However, the impact of the feedstock material on char properties, and hydrochar properties in particular, is quite relevant for IPU mineralization rates if the added amount of biochar is not higher than realistic for field applications.

The low IPU bioaccessibility in pyrochar amended soils can be expected to last for long time periods due to low IPU mineralization, high amounts of NER and high recalcitrance of pyrochars. In contrast, in hydrochar amended soils, all applied IPU will be bioaccessible within years to decades due to the degradation of hydrochars. This allows for controlled pesticide mineralization meanwhile reducing the risk of leaching and pesticide accumulation in hydrochar amended soil.

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6 Article IV. Does water repellency of pyrochars and hydrochars counter their positive effects on soil hydraulic properties?

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Abstract

Several studies showed that adding carbon-rich solids from pyrolysis (pyrochars) and hydrothermal carbonization (hydrochars) to soils can improve their hydraulic properties, in particular increase the plant available soil water capacity (AWC). However, the effects of the specific char characteristics on soil hydraulic properties are still little understood and thus, difficult to optimize for soil amendment. It is often assumed that the water repellency of chars is an important factor influencing the water retention of soils. In using the evaporation method and saturated conductivity measurements, we investigated how changes of hydraulic properties of a loamy sand with 2% (w/w) char addition depend on (i) production processes, (ii) feedstocks, (iii) particle size, and (iv) wetting properties of added chars. Applied chars comprised pyrochars carbonized at 750°C and hydrochars carbonized at 200°C and 250°C from two different feedstocks (digestate and woodchips) and two particle sizes (<0.5 mm and 0.5-1.0 mm). The wetting properties of the pure chars and soil-char composites were determined by the sessile drop method. To investigate the impact of the water repellency of chars, treatments were saturated by capillary water uptake under atmospheric conditions and by saturation from the bottom under vacuum conditions.

The chars showed highly variable wetting properties with the contact angles being strongly correlated to the specific surface area of the chars. The saturated hydraulic conductivity was significantly increased after char addition for both vacuum and capillary saturated samples, while being independent of wettability characteristics. The effects for the unsaturated conductivity were negligible. In contrast to expectation, soil amendments with more water repellent chars caused higher increases of AWC (up to 15%), both after vacuum and capillary saturated conditions. Highest increase of AWC occurred for chars from digestate material, particle size fractions <0.5 mm, and chars hydrothermally carbonized at 200°C. The increase of AWC only occurred in the low pressure range (pF 1.8 to 2.5), whereas it was decreased in the high pressure range (pF 2.5 to 4.2). Our study indicates that water repellency of pyro- and hydrochars have little counteracting effect on the overall improvement of soil water retention and saturated conductivity, and other factors that also depend on production process and feedstock, such as particle size, intra-particle porosity, shape, and plasticity are more important.

6.1 Introduction

Adding biomass combustion products derived from pyrolysis (termed pyrochar) and hydrothermal carbonization (HTC, termed hydrochar) to soil for increasing carbon (C) sequestration and soil fertility has gained considerable interest in recent years (Glaser et al., 2001; Jones et al., 2011b; Kammann et al., 2012). In contrast, the comparative impact of pyro- and hydrochars on soil physical and hydraulic properties has been rarely investigated despite these properties largely influence the plant availability of water particularly in arid regions and dry seasons (Ulyett et al., 2014), the infiltration capacity after extreme rainfall events (Moody et al., 2009), and the solute transport dynamics in the unsaturated zone (Feyen et al., 1998).

Previous studies, primarily relying on pyrochars, have shown that char application modifies the hydraulic properties of soils. The reported effects on the saturated hydraulic conductivity, K_s, are not consistent but seem to depend on soil texture. The increase of the K_s of a sandy clay loam by amendment with 1.6% (w/w) wood-pyrochar was attributed to a reduced dry bulk density after char addition (Major et al., 2010b). In contrast, the K_s of a sand was reduced after addition of wood-pyrochar (0.5 and 0.9%, w/w, Uzoma et al., 2011), and no significant effects of wood-pyrochar addition (0.5, 1 and 2%, w/w) were found on the K_s of loamy soil (Laird et al., 2010).

Furthermore, other studies reported that the addition of pyrochars to soils increased the saturated water content (e.g., Karhu et al., 2011; Kammann et al., 2012) and the plant available water capacity (AWC) of soils. Here, AWC is defined as the fraction of water released between field capacity, pF 1.8, and permanent wilting point, pF 4.2. The increase of the AWC was attributed to soil properties and physico-chemical properties of the carbonized material such as specific surface area (SSA), intra-particle porosity, or dry bulk density (Crabbe, 2009; Uzoma et al., 2011), which vary substantially according to the production conditions (Libra et al., 2010). In most cases, the AWC increased between about 30 and 170% after pyrochar additions compared to control treatment. The increase was significantly higher for high char additions (5% compared to 1%, w/w) and higher pyrolysis temperatures (500°C compared to 300°C), and generally higher for sands compared to loamy sands (Uzoma et al., 2011; Kinney et al., 2012; Peake et al., 2014). Abel et al. (2013) recently observed for sandy soils that the increase of the AWC due to char addition primarily occurred in the drier range of the AWC (pF 2.5 to 4.2) and with stronger effects for maize-hydrochar than for maize-pyrochar. They attributed their findings to the deformability of hydrochars and the possibility to impress them into wider pores which causes an increase of medium pores (0.2-10 µm) and a decrease of wide pores (>10 µm). As stated by Hardie et al. (2014), the proposed explanations for the improvement of water retention by char addition can be summarized as follows: (i) intra-particle porosity of the added char, (ii) modification of the original soil pore system by the new texture of soil and char particles, and (iii) improved persistence of soil pores due to increased aggregate stability.

Findings about the effect of soil amendment with pyro- and hydrochar on hydraulic properties were commonly based on data obtained from hydrostatic column experiments. However, this method has to face at least two difficulties. First, reaching the hydrostatic equilibrium at which the water content of a sample is measured often takes several weeks and is associated with uncertainties in the high pressure range. Consequently, the water content may be overestimated for a specific matric potential when assuming hydrostatic equilibrium too early (Abel et al. 2013). Secondly, the compromise to use small sample volumes (generally 100 cm^3) for reducing the equilibration time may result in the loss of the connectivity between sample and ceramic tension plate (Kameyama et al., 2014), and reproducibility of the method decreases. To overcome these discrepancies, in this study water retention data were collected by the simplified evaporation method (Schindler and Müller, 2006) and using sample volumes of 250 cm^3. In most standard laboratory systems the method includes continuous measurements of the matric potential in two column heights from saturation to pF 3 (Peters and Durner, 2008), and a potential extension to pF 3.7 (Schindler et al., 2010; Zhang et al., 2014). Additionally, the hydraulic gradient and the evaporation rate can be used to derive the unsaturated hydraulic conductivity curve (Peters and Durner, 2008). In comparison to common equilibrium methods, no systematic deviations have been found which suggests good reproducibility and reliability of the evaporation method (Kameyama et al., 2014; Zhang et al., 2014).

The impact of soil water repellency on hydraulic properties including infiltration capacity, surface runoff and erosion has been studied intensively during the last two decades (e.g., Bachmann et al., 2013). The hydraulic system becomes more complex when pyro- or hydrochars are added to soil because functional surface groups of chars create hydrophobic hot-spots thereby increasing spatial heterogeneity of the water repellency of the soil (Kinney et al., 2012). It has been reported that water repellency is linked to the abundance of non-polar aliphatic and aromatic groups of organic compounds (Ellerbrock et al., 2005). These structures may also change their steric orientation upon contact with water, thus, increasing surface wettability (Doerr et al., 2000; Diamantopoulos et al., 2013). Binding of hydrophilic, oxygen-containing functional groups or polar ends of amphiphilic molecules to each other can induce repellency under drying conditions (Doerr et al., 2000). As such, water repellency depends on the initial moisture content and time. Consequently, in laboratory drainage experiments the initial moisture content and the way of sample saturation is assumed to essentially determine retention and hydraulic conductivity curve characteristics. In most of the studies, water retention characteristics have been determined after capillary, atmospheric saturation over a time of 2 to 24 h (Karhu et al., 2011; Kammann et al., 2012). This may exclude hydrophobic zones and micropores (≤0.2 µm) from complete saturation and, therefore, published values of the saturated water content and AWC and heir modification by soil amendment of chars may only partially reflect the total available pore space. In contrast, saturation under vacuum conditions leads to complete wetting of even water repellent spots within the pore system, and therefore, indicates total porosity of the sample (Diamantopoulos et al., 2013).

It is reasonable to assume that hydrophobic characteristics of pyro- and hydrochars counteract the positive effect of char addition on AWC and hydraulic conductivity. Water repellency and delayed wetting are commonly causing higher fractions of entrapped air and thus decrease the fraction of saturated pores, which should reduce both, at least partly the AWC and hydraulic conductivity. Therefore, the development of chars with low water repellency has been proposed for optimizing the improvement of soil hydraulic properties (Kinney et al., 2012).

The objective of this study was to investigate how the modifications of the soil hydraulic properties due to char addition depend on the char properties (carbonization type, feedstock, particle size), and whether dependencies to the wetting properties of the chars and char-soil composites can be identified. We assume that (i) the amendment of pyro- and hydrochars to a loamy sand leads to an increase of the amount of medium soil pores between 0.2 and 50 µm, hence to a higher AWC, and to a modification of the hydraulic conductivity. We hypothesize that (ii) particle size (PaS) and type of added char affect water retention characteristics and hydraulic conductivity. Therefore, columns were prepared in different treatments with soil amended with pyrochars carbonized at 750°C and hydrochars carbonized at 200°C and 250°C from two different feedstocks (digestate, woodchips) and two particle sizes (<0.5 mm and 0.5-1.0 mm). Lastly, we hypothesize that (iii) water repellency of pyro- and hydrochars counteracts the positive effects on AWC and hydraulic conductivity. We assume effects of water repellency being highest near full saturation. Samples were capillary saturated as well as saturated under vacuum conditions to test whether more hydrophobic chars lead to larger fractions of air entrapment.

6.2 Material and Methods

Soil material

Soil was sampled at a depth of 10 to 25 cm from an Alfisol at the agricultural cropland site of the Julius Kühn-Institute in Braunschweig, Germany (10°26’ E, 52°17’ N, 80 m a.s.l.). The soil was dried at 40°C and sieved to ≤2 mm. Texture is a loamy sand with 76% sand, 19% silt, and 5% clay. Organic C content, which was determined using an elemental analyzer (LECO Corp.), was 1.09%. The soil was oven dried (105°C) and stored in the dark at 15 °C prior to experimental work.

Pyrochars and hydrochars

The experiments were performed with pyrochars (pyro750) from pyrolysis (750°C, 0.75 h, Pyreg GmbH, Dörth, Germany.) and hydrochars (hydro200/250) from hydrothermal carbonization (200 and 250 °C, 6 h, 2 MPa, SmartCarbon AG, Jettingen, Germany) of digestate (99% corn) and woodchips (willow and poplar, Table 6.1). The carbonized material was from the same batch as used in Eibisch et al. (2015) for pesticide sorption and mineralization experiments. All materials were oven-dried at 105 °C and sieved to obtain two PaS fractions, <0.5 mm and 0.5 to 1 mm. The SSA, total pore volume (TPV) and average pore radius (APR) were derived from N_2 gas adsorption isotherms recorded at 77 K with an Autosorb analyzer (Quantachrome Corp., USA). With the N_2 method, it is only possible to describe micro-pores with diameters in the range of approximately 2 to 50 nm (Kinney et al. 2012). As SSA is dominated by mirco-pores, SSA values can be considered representative for the total pore system of the chars. The SSA was calculated using the Brunauer–Emmett–Teller (BET) equation based on seven adsorption points in the relative pressure range of 0.05–0.3 P/P_0 (Brunauer et al., 1938). The TPV was determined at a relative pressure of 0.995 P/P_0 and the APR was calculated as $r_p = 2V_{liq}/SSA$, where V_{liq} is the volume of liquid N_2 contained in the pores.

Wetting properties

To assess the wetting properties of pyrochars, hydrochars, soil, and soil-char composites with 2% (w/w) pyro- and hydrochars, the sessile drop method (Bachmann et al., 2000; Bruun et al., 2014) was applied using a CCD-equipped contact angle microscope (OCA 15, DataPhysics, Filderstadt, Germany). The method allows simple, direct and reproducible contact angle (CA) measurements of rough surfaces within a wide sensitivity range (Bachmann et al., 2000;

Leelamanie et al., 2008). A one-grain-layer of the sample was fixed on a glass slide with double sided adhesive tape by sprinkling and gentle pressing. The placement of a drop of deionized water and its subsequent behavior was recorded with a video camera and CA then calculated with the software SCA20 (DataPhysics, Filderstadt, Germany). Beside the initial CA (after 0.03 s; termed CA0.03s), CA was evaluated additionally after 1 s (CA1s) and 5 s (CA5s) as an estimate of CA stability. The drop volume was 1 µL and the recording frequency was 33 frames per second. A zero degree CA (*cos*CA=1) indicates a wettable (hydrophilic) surface, a CA >0° and <90° (0< *cos*CA <1) a subcritically water repellant surface, and a CA ≥90° (*cos*CA ≤0) a hydrophobic surface. The surface free energy of a solid, which is the force that is necessary to expand its surface, is strongly related to its wettability characteristics and according to Youngs' equation, it is linearly related to the cosine of the CA (*cos*CA) (Zisman, 1964). In the following, *cos*CA is used as measure of material wettability.

Hydraulic properties

Hydraulic properties of disturbed soil samples were studied either without (= control) or with 2% (w/w) pyrochar or hydrochar. The 2% amendment was chosen as it corresponds to a reasonable field application rate of 46.8 Mg ha^{-1} assuming soil depth and bulk density values of 15 cm and 1.56 g cm^{-3}, respectively (Novak et al., 2009). Either the soil-char-composites or the pure soil were filled in 250 cm^{3} (8 cm in diameter) soil columns in four steps and pressed at each filling step with a falling weight (2000 g) from 10 cm height three times resulting in individual dry bulk densities for the different treatments (Table 6.2). Saturation of the soil columns was performed from the bottom under vacuum as well as capillary under atmospheric conditions at 20 ± 1°C for seven days. The saturated hydraulic conductivity, K_s, was determined by falling water head according to DIN ISO 18130-1 with a KSAT (UMS GmbH Munich, Germany).

Water retention was investigated with the evaporation method (Akhtar et al., 2014) using a HYPROP device (UMS GmbH Munich, Germany). For this, saturated soil columns were exposed in triplicates to evaporation at 20 ± 1°C. Matric potential was automatically recorded every minute for the first three hours and each ten minutes afterwards. The gravimetric water content of the samples was recorded twice a day throughout the experiment. Measurements were stopped when the tensiometers reached their suction limits (around pF 3.0). Based on the matric potential and water contents, discrete data points of the retention and unsaturated hydraulic conductivity curves were calculated with the HYPROP 2011 software (UMS GmbH Munich, Germany) using spatial and temporal linearization (Peters and Durner, 2008).

The water content at higher pressures was evaluated with a WP4C potentiometer (Decagon Devices, Inc., Pullman WA, USA) based on the chilled-mirror dewpoint technique (Kameyama et al., 2014). For this, six different amounts of water were added to two replicates of 5 mg dry weight samples in plastic cups, with the aim to obtain after equilibration water tensions between pF 3.8 and 5.1. The cups were closed tightly and samples allowed equilibrating for at least seven days. During WP4C measurements water tension was recorded when the water potential of the sample was in equilibrium with the vapour pressure of the measurement chamber. Sample weight was determined immediately after measurement and related to the weight after oven drying at 105°C yielding the corresponding water content. The bimodal function of Durner (1994) coupled with the hydraulic conductivity function of Mualem (Priesack and Durner, 2006) was fitted to the results from the evaporation method and WP4C measurements.

To evaluate hydraulic characteristics, water contents at selected pressure heads (pF 0, 1.8, 2.5, 4.2) were compared among the treatments. We assumed full saturation (S = 1) for the vacuum saturated samples at pF 0, with the corresponding water content defining the porosity of the samples (Table 6.2). The AWC_C (capillary) and AWC_V (vacuum) were calculated from the water content between pF 1.8 and pF 4.2 after capillary (C) and vacuum (V) saturation. We further differentiated a low pressure range (pF 1.8 to 2.5) and a high pressure range (pF 2.5 to 4.2) for the AWC. Delta θ [Δθ(pF)] or delta AWC (ΔAWC) refers to the difference of the water content at a specific pF or of the AWC between the amended soil and the pure soil, i.e., it points at the change of these values with the soil as reference.

Statistics

Hydraulic characteristics, char properties (SSA, TPV, APR), and soil-char composites (bulk density, BD) were analyzed for Pearson correlation (r). Correlations with hydrophobicity or *cos*CA and K_s values of chars and composites were investigated using Spearman (ρ). Significance of the PaS on selected points was tested with a two-way analysis of variance (ANOVA) and the Holm-Sidak method for multiple pairwise comparisons. ANOVA was also used to evaluate significant effects of the carbonization type, feedstock, saturation conditions, PaS, and *cos*CA0.03s on ΔAWC of the total as well as of the low and high pressure range. The significance limit was set to 0.05. Statistical tests were carried out with SigmaPlot 11 (Systat Software Inc.) and R 2.15.3 (R.Core-Team, 2013).

6.3 Results

Properties of chars and soil-char composites

The properties of the different char types varied considerably (Table 6.1). The SSA of pyrochars (178 to 346 m^{2}g^{-1}) was significantly higher than that of hydro200 (11 to 15 m^{2}g^{-1}) and of hydro250 (2 to 5 m^{2}g^{-1}). Consequently, the TPV of pyrochars (0.17 to 0.26 cm^{3}g^{-1}) was significantly higher and the APR (1.3 to 1.9 nm) was significantly lower than the TPV and APR of hydrochars (TPV: 0.01 to 0.10 cm^{3}g^{-1}; APR: 10.8 to 16.8 nm). Differences of the SSA, TPV and APR were related to the feedstock and PaS. The differences were less pronounced for hydrochars than for pyrochars. For example, SSA and TPV of chars from digestate were higher, and their APR was lower than for the corresponding char types from woodchips. Further, SSA of pyrochars was higher for smaller PaS, but SSA of hydrochars was positively correlated with PaS (Table 6.1).

Table 6.1 Properties of soil and chars from pyrolysis and hydrothermal carbonization (HTC) and of soil; coefficients of variation of given means were <3% (n = 3).

Process	Feedstock material	Particle size (mm)	SSA (m^{2}g^{-1})	TPV (cm^{3}g^{-1})	APR (nm)	C (%)*	Molar O/C*	Molar H/C*
-	Soil	<2	1.9	0.01	9.5	0.87	n.d.	n.d.
Pyrolysis (750°C)	Digestate	0 – 0.5	271	0.18	1.3	51.9	0.14	0.33
		0.5 – 1.0	346	0.26	1.5			
	Woodchips	0 – 0.5	178	0.17	1.9	67.7	0.06	0.26
		0.5 – 1.0	201	0.18	1.7			
HTC (250°C)	Digestate	0 – 0.5	4.5	0.03	11.8	61.8	0.22	0.91
		0.5 – 1.0	2.3	0.01	10.8			
	Woodchips	0 – 0.5	3.4	0.02	13.2	68.4	0.20	0.89
		0.5 – 1.0	5.1	0.04	16.8			
HTC (200°C)	Digestate	0 – 0.5	15.2	0.10	12.7	53.8	0.34	1.15
		0.5 – 1.0	13.8	0.09	12.6			
	Woodchips	0 – 0.5	11.2	0.09	15.7	59.7	0.30	1.06
		0.5 – 1.0	11.0	0.07	13.2			

SSA = specific surface area, TPV = total pore volume, APR = average pore radius, n.d. = not determined
* taken from Eibisch et al. (2015)

The wetting properties of the chars and soil-char-composites showed some characteristic differences with respect to production conditions, PaS, and feedstock (Fig. 6.1). All pure hydrochars were at least initially (0.03 s) hydrophobic (*cos*CA <0) and *cos*CA increased with PaS for hydro200. All hydro250 had *cos*CA <0 even after 5 s (Fig. 6.1a). The pyrochars showed initially subcritical water repellency (0< *cos*CA <1) with no defined difference for PaS due to a considerable standard deviation, especially for the small sized pyro750 from woodchips (Fig. 6.1a). Addition of hydrochars to soil generally resulted in reduced wettability, in particular initially (CA0.03s, Fig. 6.1b). The PaS effect observed for pure hydrochars was only indicated for hydrochars from digestate, and in contrast to the pure chars, no influence of production temperature could be observed on initial *cos*CA and *cos*CA stability. Soil amended with pyro750 showed *cos*CA comparable to the pure char and had distinctly greater initial *cos*CA than soil amended with hydrochars (Fig. 6.1b). There was a positive correlation between *cos*CA and the SSA of both, the pure materials (p <0.05, $\rho = 0.84$, Fig. 6.2) and the composites ($\rho = 0.60$, data not shown). The *cos*CA of pure chars correlated negatively with the APR ($\rho = -0.82$), and correlations were lower with the *cos*CA of soil-char composites ($\rho = 0.56$).

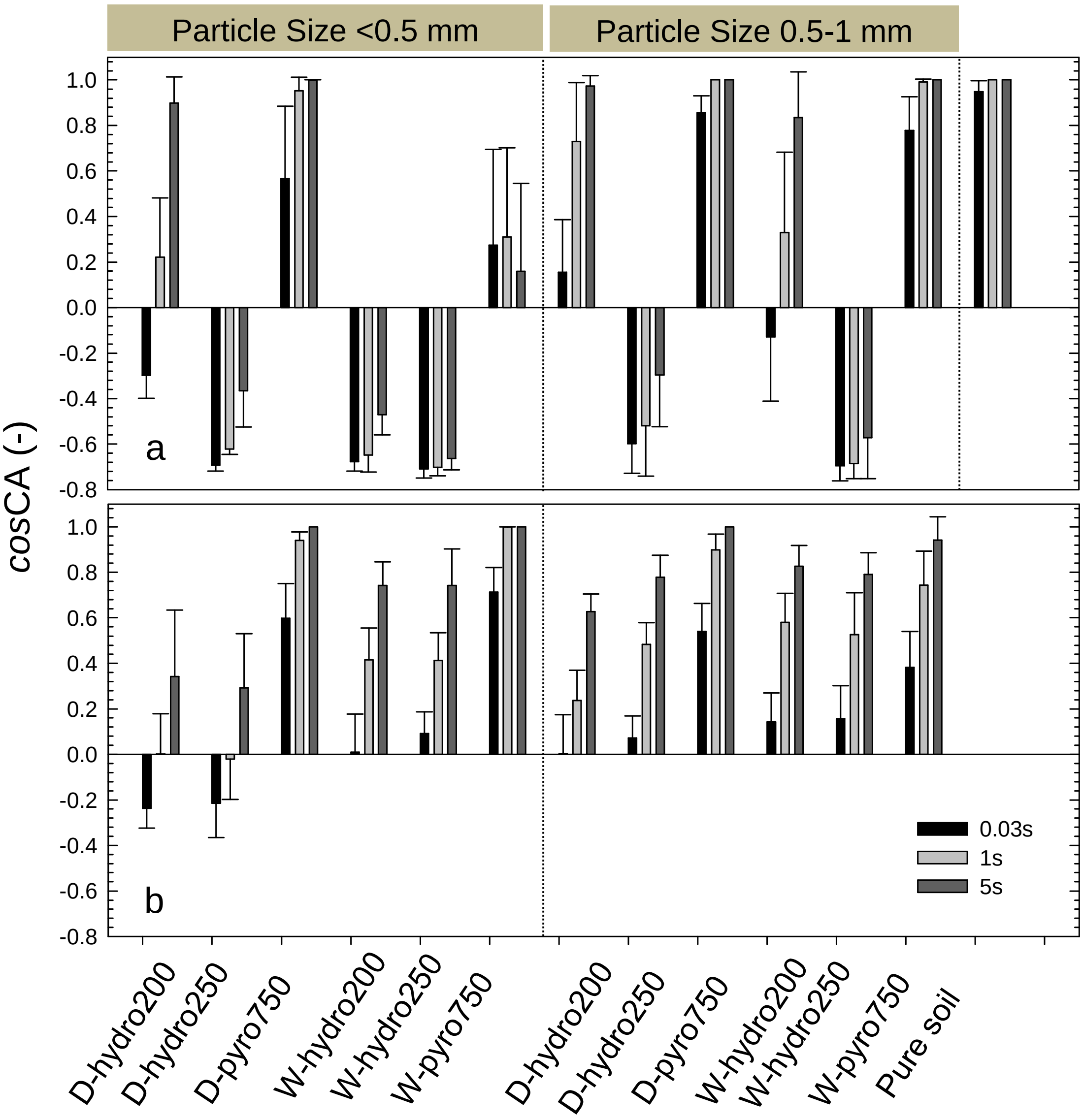

Fig. 6.1 Cosine of the contact angle (*cos*CA) taken after 0.03, 1 and 5 s of (a) pure soil and pure chars from hydrothermal carbonization at 200°C (hydro200) and 250°C (hydro250), and pyrolysis (pyro750) of digestate (D) and woodchips (W), and of (b) soil amended with 2% chars, means and standard deviations, n = 6.

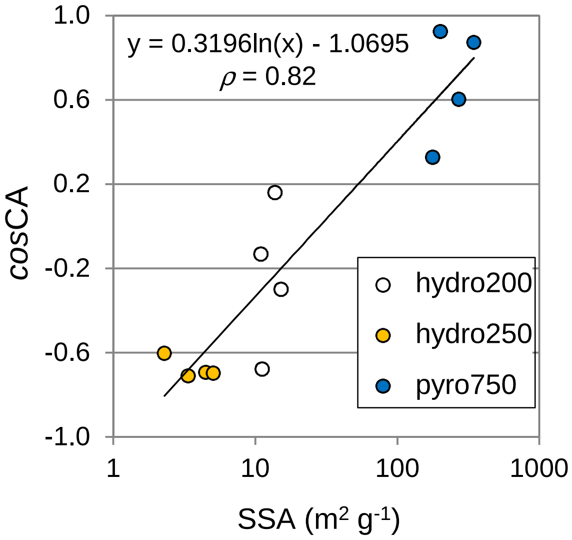

Fig. 6.2 Regression curve of the cosine of the contact angle (*cos*CA) taken after 0.03s, and the specific surface area (SSA) of chars from hydrothermal carbonization at 200°C (hydro200) and 250°C (hydro250), and pyrolysis (pyro750), n >3.

Effect of char addition on soil hydraulic properties

Bulk density and porosity

Char addition to the soil decreased the BD on average by 0.1± 0.0 g cm-3 and increased the porosity (here assumed to correspond to the water content after vacuum saturation) by 3.4 ± 1.0% (p <0.05; Table 6.2). The consistent differences to the pure soil properties and the low standard deviations demonstrate a good reproducibility of the packing procedure. The degree of the increase of the porosity depended significantly on production process and PaS. The increase was lower for hydro250 than for hydro200 and pyro750, and significantly higher for the larger PaS fraction than for the fine sized chars.

Saturation in the open lab atmosphere

Saturation values after capillary saturation under atmospheric pressure conditions (S_C) indicates the fraction of the porosity that is air filled (1-S). The S_C values of soil (0.90 ± 0.03) were not significantly different from the S_C values of soil-char composites (0.91 ± 0.03). Among the soil-char composites, only the PaS effect was significant with lower S_C values for the coarser PaS fraction. Linear models utilizing *cos*CA obtained after 0.03 s, 1 s, and 5 s of the pure chars and the soil-char composites revealed no significant influence of *cos*CA on S_C.

Table 6.2 Bulk density (BD, n=6) and porosity (n=3) assessed from the water content at pF 0 after vacuum saturation of soil amended with 2% (w/w) chars from pyrolysis and hydrothermal carbonization (HTC) in two different particle sizes (PaS), mean and standard deviations.

Process	Feedstock	PaS (mm)	BD (g cm^{-3})	Porosity (%)
Pyrolysis	Digestate	0 – 0.5	1.46±0.02	45.7±0.4
(750°C)		0.5 – 1.0	1.43±0.02	47.2±0.1
	Woodchips	0 – 0.5	1.46±0.03	45.0±0.5
		0.5 – 1.0	1.47±0.06	45.5±1.0
HTC (250°C)	Digestate	0 – 0.5	1.49±0.04	44.3±0.2
		0.5 – 1.0	1.50±0.03	43.5±0.4
	Woodchips	0 – 0.5	1.45±0.03	45.3±0.8
		0.5 – 1.0	1.46±0.03	45.1±0.7
HTC (200°C)	Digestate	0 – 0.5	1.43±0.02	45.8±0.8
		0.5 – 1.0	1.44±0.02	45.8±1.1
	Woodchips	0 – 0.5	1.46±0.01	45.0±0.3
		0.5 – 1.0	1.45±0.03	45.5±0.9
Control		<2	1.56±0.01	41.7±0.2

Water retention characteristics

Water retention characteristics are exemplarily presented for hydrochars from woodchips carbonized at 250°C in Fig. 6.3a. Reproducibility and data resolution were good.

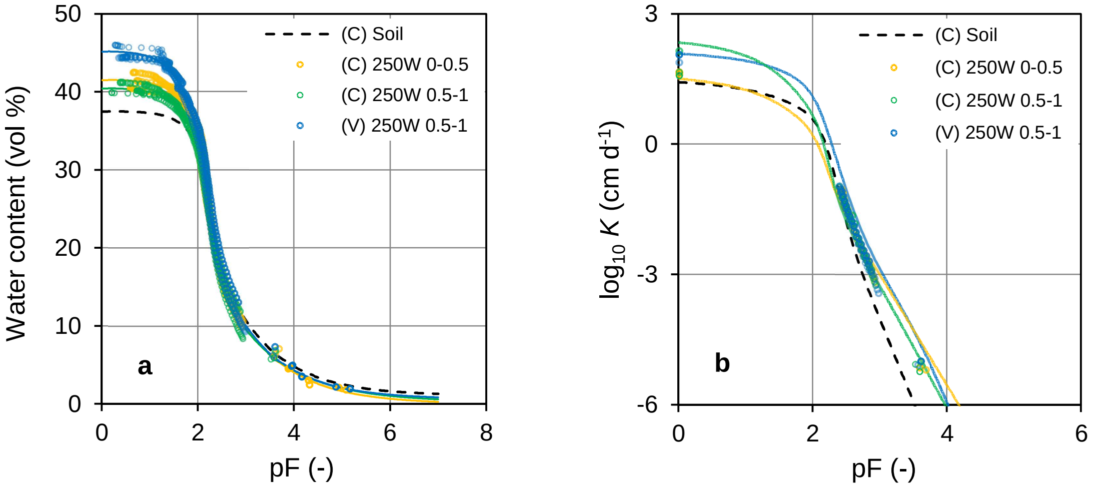

Fig. 6.3 Raw data with (a) fitted water retention curves, and (b) unsaturated hydraulic conductivity curves from results of the evaporation method and WP4C measurements, exemplarily of hydrochars (250°C) from woodchips (W) of two different particle sizes (0-0.5 and 0.5-1 mm) after capillary (C) and vacuum (V) saturation, n = 3.

The retention curves appear similar when comparing the different treatments. However, differences among the treatments and to the pure soil ($\Delta\theta = \theta_{treatment} - \theta_{soil}$) can be observed for the water contents at selected pressure heads (Fig. 6.4). Compared to the pure soil, the water contents were significantly higher for all treatments after capillary saturation (given by the positive values at x-axis in Fig. 6.4a) as well as after vacuum saturation (positive values at y-axis in Fig. 6.4a). The difference to the water content of the pure soil decreased with increasing matric potential (Fig. 6.4b and 6.4c) and approximated zero at Δθ(pF4.2) (Fig. 6.4d). At pF 1.8, production process, feedstock, PaS, saturation conditions, and the interaction between process and feedstock had significant effects on the water content ($p < 0.05$, Fig. 6.4b). The difference to the pure soil was higher for chars from digestate, for finer char particles and hydrochars carbonized at 200°C. As well, the Δθ(pF1.8) values were higher for vacuum saturation.

At pF 2.5, primarily the effect of saturation conditions was significant (Fig. 6.4c). Vacuum saturation caused a higher difference to the water content of the pure soil than capillary saturation for most of the treatments. At pF 4.2, production process, feedstock and the interaction of production process and feedstock had significant effects (Fig. 6.4d). Higher Δθ(pF4.2) occurred for pyro750 as well as for chars from digestate. The large PaS fraction led to lower Δθ(pF4.2) values for woodchips feedstocks.

The results of the ΔAWC were very similar to the ones for Δθ(pF1.8) and depended on production process, feedstock, PaS, process, saturation conditions and the interaction between process and feedstock ($p < 0.05$, Fig. 6.4e). The direction of the dependencies equals the one as for Δθ(pF1.8). For capillary saturation, the AWC of the soil (30.8±0.7 vol%) increased by 15% after amendment with <0.5 mm sized digestate-hydro200. For all chars, the increase of ΔAWC_C in the low pressure range (pF 1.8 to pF 2.5) was mainly due to additional water-filled pore space, while for the high pressure range (pF 2.5 to pF 4.2) the water-filled pore space even decreased upon addition with most of the chars (compare Fig. 6.4c, d). For *cos*CA, strongest differences between the chars were observed for the initial CA taken at 0.03 s. While the ΔAWC_C values did not significantly depend on the *cos*CA0.03s values of the pure chars, ΔAWC_C was significantly related to *cos*CA0.03s of the soil-char composites (Fig. 6.5). This relation suggests an increasing ΔAWC_C with decreasing *cos*CA values, i.e., with increasing water repellency.

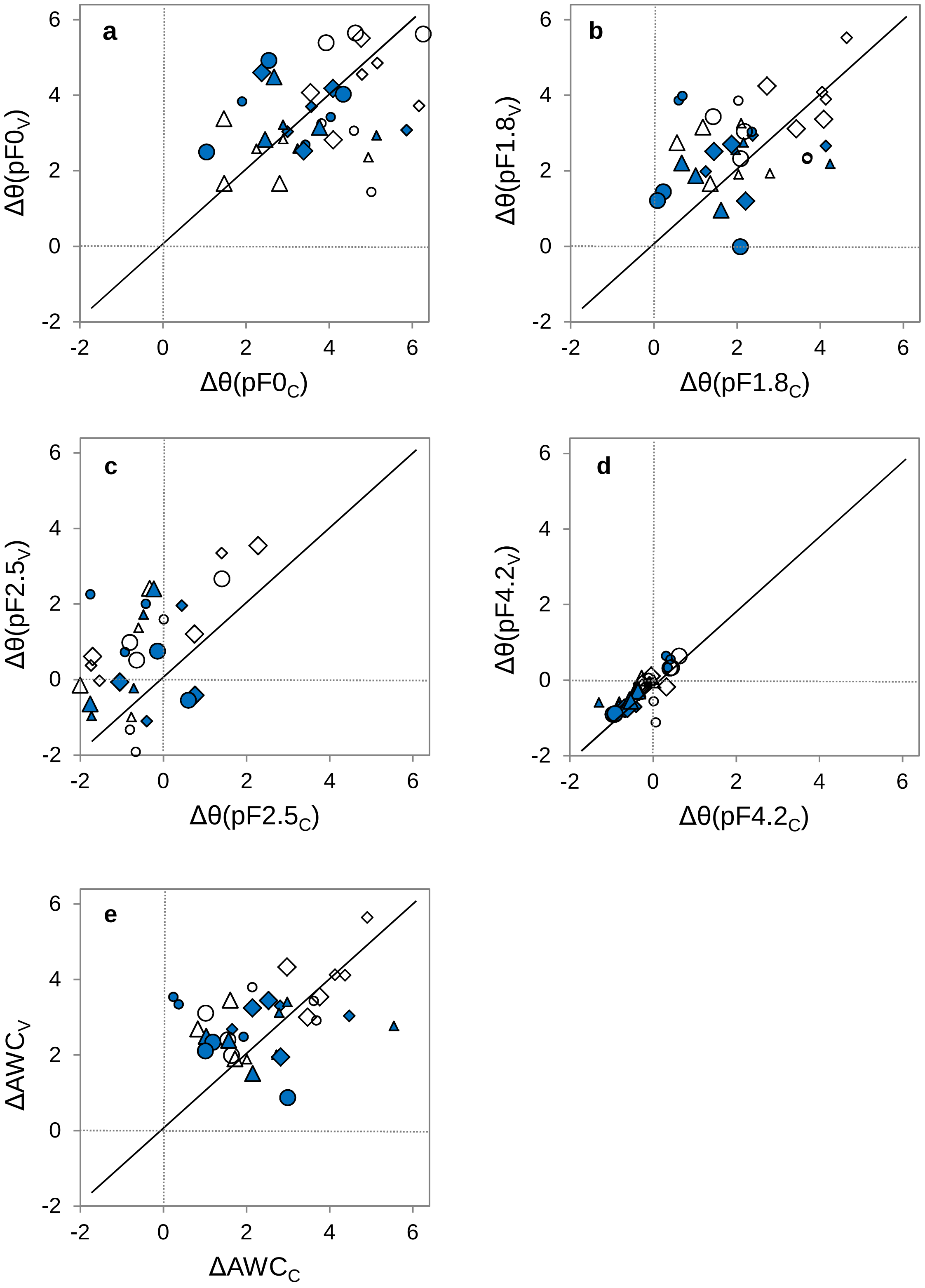

Fig. 6.4 Water content (in vol%) at (a) full saturation (pF 0), and at (b) pF 1.8, (c) 2.5, and (d) 4.2, and (e) the plant available water capacity (AWC) after vacuum (V) and capillary (C) saturation of soil amended with chars either from pyrolysis (dots), HTC at 250°C (triangles) or 200°C (squares) of digestate (white) or woodchips (blue), and particle size of 0-0.5 mm (small symbols) or 0.5-1 mm (large symbols). Delta (Δ) refers to the difference of the water content, θ, at a specific pF value or of the AWC between the amended soil and the pure soil.

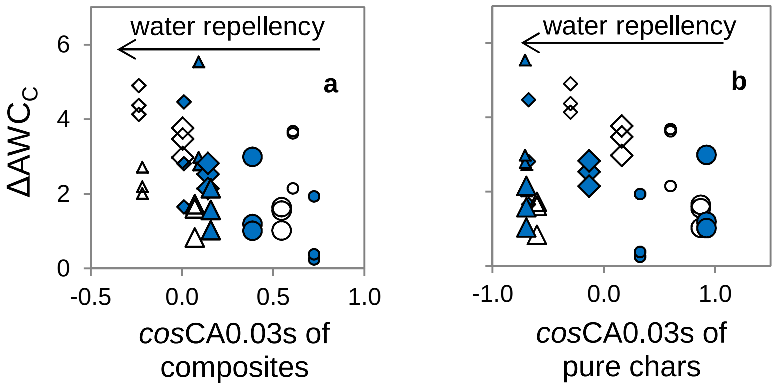

Fig. 6.5 Dependency of the plant available water capacity (AWC) after capillary (C) saturation from the cosine of the contact angle (*cos*CA) of (a) soil amended with 2% chars or (b) pure chars either from pyrolysis (dots), HTC at 250°C (triangles) or 200°C (squares) of digestate (white) or woodchips (blue), and particle size of 0-0.5 mm (small symbols) or 0.5-1 mm (large symbols). Delta (Δ) AWC refers to the difference of the AWC between the amended soil and the pure soil.

Hydraulic conductivity function

Saturated hydraulic conductivity (K_s) was consistently increased by char addition. Relative to the corresponding pure soil treatment, the increase ranged from 30 to 180 % for the capillary saturated treatments and from 10 to 130 % for the vacuum saturated treatments. Generally, K_s values were significantly higher for the vacuum saturated samples ($K_{s,V}$) than for the capillary saturated ones ($K_{s,C}$) (Fig. 6.6, p <0.05). The only significant treatment effect occurred for the feedstock and the vacuum saturated samples with higher K_s values for soils amended with chars from woodchips (p <0.05). The same tendency was observed for the capillary saturated samples, but significance was not observed. Differences among the treatments were too low and scattering of replicates was too high to infer other treatment effects. Furthermore, no correlations were found between the K_s and wetting properties.

The results of the unsaturated hydraulic conductivity (K_u) from the evaporation method are exemplarily given for hydrochars from woodchips carbonized at 250°C (Fig. 6.3b). The data were similar among all treatment as well as for the pure soil but there seemed to be differences in the low pressure range. However, K_u could be measured accurately for only a narrow range of the pressure head between pF 2.5 and pF 4. Consequently, there is a high uncertainty of the fitted conductivity curve in the low pressures range. On base of the true data no significant differences were observed among the treatments and between the treatments and the pure soil except for hydraulic conductivities under saturated conditions as stated above.

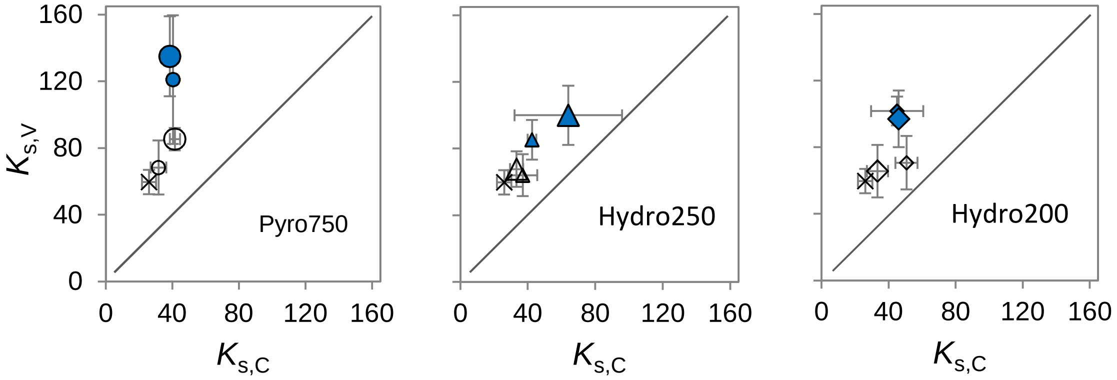

Fig. 6.6 Saturated hydraulic conductivity, K_s after capillary (C) and vacuum (V) saturation (in cm d^{-1}) of pure soil (cross) and soil amended with chars either from pyrolysis (pyro750), HTC at 250°C (Hydro250) or 200°C (Hydro200) of digestate (white) or woodchips (blue) and particle size of 0-0.5 mm (small symbols) or 0.5-1 mm (large symbols), mean and standard deviation, n = 3.

6.4 Discussion

Impact of wetting properties of chars on soil hydraulic properties

Production process and feedstock essentially determine char properties like SSA and type and amount of functional groups that control wetting properties (Eibisch et al., 2015). Oxygen-containing functional groups on the char surface are known to increase wettability by hydrogen-bonding propensity (Pastor-Villegas et al., 2010). Here, the tendency towards increased wettability was more induced by the SSA (structural effect) than by functional surface groups (chemical effect). Thus, chars with less oxygen-containing functional groups but high SSA (e.g., pyrochars) revealed good wettability (high *cos*CA values). The fact that pyrolysis temperature and feedstock alter the water retention of char amended soils was shown previously and has been primarily ascribed to polar surface groups, and high SSA and microporosity of the chars (Novak et al., 2009; Uzoma et al., 2011; Kinney et al., 2012). It is conceivable that oxygen-containing functional groups of hydrochars merge or bind together under dry and drying conditions (Doerr et al., 2000). Only some of the chars of our study were strictly 'hydrophobic' (*cos*CA values around 0 or less for more than 5 s, Fig. 6.1), but all treatments, except the pyrochar composites which only initially had *cos*CA <1, showed subcritical water repellency (*cos*CA values between 0 and 1) up to 5 s.

Significant differences between the various treatments were identified regarding their values of capillary saturation (S_C), AWC_C and $K_{s,C}$. For the two most relevant hydraulic properties of soil amendment, AWC_C and $K_{s,C}$, positive effects were achieved when chars was added to loamy sand. The wetting properties of the added chars, which in contrast to the pure soil were at least initially hydrophobic, did obviously not show negative effect on the water retention behaviour in the pressure range of pF 1.8 to pF 4.2. In contrast to our expectation, results do not even indicate that hydrophobicity reduces the positive effects of char addition. There were no significant relationships between the wetting properties (in terms of *cos*CA) and S_C, AWC_C and $K_{s,C}$. For the *cos*CA of the soil-char composites, we even observed the opposite. The more water repellent soil-char composites even caused a higher increase of AWC_C. Furthermore, the small differences between ΔAWC_C and ΔAWC_V indicate that the additional pore space of the AWC pressure range is not significantly affected by the reduced wettability of the amended soil. This is a further indication that char surfaces in the soil-char composites are largely wetted after capillary saturation which already was indicated by the distinct increase of the *cos*CA within 5 s. We emphasize that our analysis cannot exclude that water repellency of chars diminishes the positive effects on hydraulic properties (here: AWC_C and $K_{s,C}$) of other soils. But our analysis demonstrates that other char characteristics seem to be more important and are over-compensating potential negative effects of water repellent char surfaces.

Only few studies investigated the particular role of char water repellency on hydraulic properties of amended soils (Kinney et al., 2012; Abel et al., 2013; Githinji, 2014). In soil water infiltration experiments the observed reduction of the infiltration rate was attributed to hydrophobic properties of pyrochars (Githinji, 2014). In another study, the water repellency of pyrochars decreased with increasing pyrolysis temperature resulting in higher field capacities (Kinney et al., 2012). In contrast, Baronti et al. (2014) did not find any effects on wettability in a two-year field experiment when sandy-clay-loam was amended with orchard pruning-pyrochar (pyrolyzed at 500°C and sieved <5 mm) at two addition amounts (0.5 and 1.1% w/w). Also Abel et al. 2013 could not detect water repellency in samples amended with pyrochar (at 1, 2.5 and 5% addition rate) when using the water drop penetration time test. They observed local water repellency for soils amended with hydrochars that may have been induced by fungal colonization. We also observed slight fungal growth on the top of some soil-hydrochar composite samples during capillary saturation under the atmosphere of the lab for seven days and cannot exclude that the mycelium had penetrated deeper parts of the sample. However, the SDM used for measuring the CA was performed with samples that had been dried directly after production and fungal growth could not have induced water repellency measured for hydrochars in this study.

Our findings are restricted to the conditions of the laboratory soil columns where a rather long contact time between water and soil of seven days existed due to the slow capillary water uptake for the samples saturated in the open lab atmosphere. Furthermore, effects of water repellency may be stronger when evaluating hydraulic properties for wetting and not for drainage conditions. For the latter, retention dynamics are controlled by a receding, generally higher *cos*CA (Hassan et al., 2014). Thus, further validation of hydraulic properties of char amended soil is required for a broader range of field conditions such as after strong rain-fall events following complete soil dryness. Although water repellency may persist for only a short time, enhanced run-off after dry periods are most likely (Diamantopoulos and Durner, 2012). Thus, charred materials with more persistent hydrophobic characteristics may still be less beneficial as soil amendment in semi-arid regions (Moody et al., 2009).

Impact of particle size and char type on water retention

A factor that over-compensates potential negative effects as induced by water repellency is the beneficial modification of the soil pore space, i.e., pore size distribution by char addition. The influence on the pore space within the AWC range may strongly depend on the PaS of the added chars as well as their shape and plasticity. Shape and plasticity is mainly related to the production process and feedstock. The larger PaS fraction (0.5-1.0 mm) resulted in a lower increase of ΔAWC, both after capillary and vacuum saturation. This may be explained by the PaS that is similar to that of the sand fraction of the soil, and thus no filling of soil pore space may have occurred. In contrast, the finer PaS fraction (<0.5 mm) resulted in a higher ΔAWC, which might possibly be linked to the fact that the small char particles partly filled the pore space of the soil. Very small char particles may have occluded fine soil pores which therefore could no longer contribute to an AWC in the dry range resulting in negative delta values for some samples (Fig. 6.4c and 6.4d).

Recently, Githinji (2014) reported that the total porosity of a loamy sand increased after amendment with chars (0.18 mm sized pyrochars from peanut hulls carbonized at 500°C for 1 h) causing higher volumetric water contents at all matric heads (Githinji, 2014). The increase came along with a decrease in the silt fraction and an increase in the sand and clay fraction of the soil-char composites. However, used pyrochar amounts were much higher than in our study (25 and 75%, v/v, and pure pyrochars). Also for a dune sand an increase of the AWC and water retention was observed up to pF 2.7 after 0.5 and 0.9% (w/w) amendment of wood-pyrochars (pyrolyzed at 300, 400 and 500°C for 16 h) (Uzoma et al., 2011). The increase was higher for high-temperature pyrochars and for the high char application rate. The differences of the hydraulic properties between dune sand and the composites were more pronounced (the highest increase of the AWC after char addition was 97%) than we observed for a loamy sand. They attributed the increase to the porosity of the soil-char composites and the high SSA of pyrochars. In contrast, we did not find such a distinct SSA effect on hydraulic characteristics. There were even indications for an opposite trend: Although hydrochars generally have a lower SSA than pyrochars, in our study they exhibited a stronger increase in ΔAWC than pyrochars.

High SSA values of pyrochars are typically related to a high fraction of micropores (<2 mm), which might be outside the pressure range of AWC and thus cannot contribute to the increase of AWC (Kinney et al., 2012). Also in the study of Abel et al. (2013) the increase of the AWC of loamy sand soil was similar or higher when amended (1 and 2.5%, w/w) with maize-hydrochars (carbonized at 200°C and 2 MPa for 10 h) than with maize-pyrochars (pyrolyzed at 750°C for 0.33 h). Hydrochar particles are deformable and less rigid than pyrochars and can effectively take part in medium pore formation (Abel et al., 2013). Plasticity may explain the highest ΔAWC_C that we observed for the hydro200 chars (Fig. 6.4e).

In contrast to our results, Abel et al. (2013) further observed an increase in water retention at pF >3. The increase was higher for amendments with hydrochars than for amendments with pyrochars and higher for sandy than for loamy sand soils. They proposed that during artificial compaction the hydrochars had been pressed into pores leading to an augmentation of small soil pores in which the water is hold by capillary and adsorptive forces. It is worth mentioning that in the study from Abel et al. (2013) probably the time had been too short to reach the hydrostatic equilibrium by using ceramic tension plates for hydraulic measurements. This may have led to an overestimation of the water content of soil-hydrochar composites especially at high matric potential (Abel et al., 2013).

Impact of char addition on hydraulic conductivity

The observed increase of $K_{s,C}$ by char addition up to a factor of 3 is in agreement with several previous studies that reported a two- to fivefold increase of the $K_{s,C}$ after soil amendment of pyrochars from different feedstock and temperature (Oguntunde et al., 2008; Asai et al., 2009; Major et al., 2010a). Variations of the increase of $K_{s,C}$ values may arise from the use of different chars having variable structural properties, char addition rate, and different soils. Laird et al. (2010) did not find any differences, and only Githinji (2014) found a significant decrease of $K_{s,C}$ after soil amendment with pyrochars. This decrease was ascribed to wetting properties of the chars.

As expected, in our study, the K_s values were significantly higher after vacuum than after capillary saturation. This is explained by entrapped air and lower water contents in the capillary saturated samples which leads to lower cross sectional areas for conducting water. However, we could not observe that this effect is related to the wetting properties of the chars, i.e., $K_{s,C}$ variation did not depend on wetting properties. Previously it has been reported that water repellency depends on time and soil moisture (Doerr et al., 2000). In our study, measurements of $K_{s,C}$ were done after the water flow through the columns remained constant, which took at least twice the time to reach constant flow for samples after capillary saturation. This indicates that probably a part of the entrapped air was rearranged and partly released during the $K_{s,C}$ measurements. However, data still showed significant lower $K_{s,C}$ than $K_{s,V}$ as mentioned above.

No significant correlations were found for the unsaturated conductivity (K_u) among the treatments and the pure soil. However, the evaporation method still lacks information about the conductivity function in the very moist range (Peters and Durner, 2008). Studies on K_u after soil amendment of pyrochars are rare and no studies exist for hydrochars. Uzoma et al. (2011) found a significant decrease of K_u compared to the control with increasing char addition rate and increasing pyrolysis temperature. They observed significant effects probably because of the use of sandy soils and char having a PaS <0.2 mm.

6.5 Conclusions

Our results indicate that small sized hydrochars carbonized at low temperatures are most suitable in enhancing the capacity of loamy sand to retain plant available water. The increase in AWC was higher in the low pressure range, which is of great benefit in agriculture as crop moisture stress often naturally occurs at lower matric potential than at the permanent wilting point (pF 4.2).

It has been postulated that pyro- and hydrochar production should be optimized for minimum water repellency to obtain the best effects on hydraulic properties during soil amendment. Our study showed that for the water retention in the AWC range and the saturated hydraulic conductivity the possible counteracting water repellency characteristics of chars were over-compensated by other char characteristics, like PaS, and probably char plasticity dominated the improvement of the soil hydraulic properties. Thus, the effects of feedstock, production process and conditions on PaS, intra-particle porosity, shape, and plasticity and not only water repellency need to be considered carefully when optimizing the improvement of water retention and hydraulic conductivity by char addition. However, special consideration of wetting properties may be required for semi-arid regions when rare but strong rainfall events occur on dry bare soil surfaces.

6.6 References

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7 Synthesis and general conclusions

Due to their physico-chemical properties, pyrochars and hydrochars have the potential to increase the soil quality in the long-term. Presumably, feedstock and process conditions essentially determine the effectiveness of the potential functionalities. In the framework of four independent investigations, it was shown for agricultural loamy sand soils, which biochar types (pyrochar, hydrochar, and from which feedstocks) have the lowest short-term degradability (article I and III), increase pesticide sorption (article II), and improve the plant available water capacity (article IV). The results were related to biochar properties and discussed in the context of current research.

Loamy sand was selected as soil type because biochars are supposed to have significant positive effects on the physical properties of sandy soils in particular. Because the same soil type has been used in all of the four investigations, their results are comparable and conclusions can be drawn towards the main objective of the present study. The objective was to comparatively investigate the short-term C degradability, the sorption capacity for the herbicide IPU, and the hydraulic effects of different biochar types (pyrochars and hydrochars derived from different feedstock), and to refer the results to selected biochar properties (see chapter 2).

7.1 Impact of process conditions and feedstock on product properties

For the investigations, feedstocks (digestate, miscanthus, woodchips) with different physico-chemical properties were selected for pyrolysis at 750°C for 0.75 h and HTC at 200°C and 250°C, 2MPa for 6 h. To evaluate the short-term C degradability, digestate, grass cuttings, straw, and woodchips that were hydrothermally carbonized under gentle conditions (180°C, 8 h, 2 MPa) were additionally used. Hence, ten hydrochars and three pyrochars were available for laboratory studies. According to selected product characteristics, there was a decrease of O/C – H/C ratios, the oxygen containing functional groups, and the water extractable organic C with increasing process temperature (article I and II). Simultaneously, the C and ash content, the SSA and the pore volume of the charred materials increased for higher process temperatures. The degree by which biochar properties modified with increasing temperature also depended on the feedstock. The ash content decreased for non-lignitic materials when produced at low temperatures (180-200°C), and increased for lignitic materials and high temperate chars in comparison to the raw feedstock (article I and II). The pH values increased for all pyrochars. In contrast, the pH decreased especially for fibrous materials (digestate) that were hydrothermally carbonized at low temperatures as consequence of cellulose degradation. In addition, the HTC-process water of these hydrochars was enriched with acids (e.g., acetic and glycolic acid, article

I), and several specific elements (Ca, K, Mg, N, and Na). Thus, the **hypothesis I** that physico-chemical properties of different feedstock are reflected in the hydrochars was confirmed. Besides feedstock, the production process of the chars influences the properties of the chars. Hence, the variety of applicable materials and control elements during processing complicate mechanistic conclusions. For this reason, it is recommended to subject the carbonization products to a comprehensive physico-chemical standard analysis to evaluate the utility of the intended application.

7.2 Effects of pyrochars and hydrochars in soil

Biochar degradability and pesticide sorption and mineralization

Addition of biochars to soil causes different physical and chemical effects that vary according to the feedstock and production technology. Here, the short-term biochar degradability, and sorption and mineralization of the pesticide IPU after amendment of different biochars (both hydrochars and pyrochars) to an agricultural soil (loamy sand) were investigated.

The amount of C that outgases during the HTC process is little. Consequently, the C efficiency of the process is high. However, the possibility of a high C input after soil amendment with hydrochars encounters a high short-term C degradability that has been measured for the hydrochars selected in this study (article I and III) and the HTC process water (article I). The **hypothesis I** that differences in physico-chemical properties of the used feedstock materials are reflected in the short-term degradability of the hydrochars could be confirmed. Lower degradation rates were found for hydrochars from feedstocks with a high lignin content and high C/N ratio. The short-term C degradation was also lower for biochars that were produced at high temperatures (≥250°C), especially pyrochars (article III). Washing the biochars with water before application to soil decreased the C degradability in the short-term for hydrochars from digestate (confirming **hypothesis II**) but had no effect on degradation of hydrochars from other feedstocks (green cuttings, straw, and woodchips). Thus, water washing seems to be specific to each hydrochar and needs to be considered in short-term incubation experiments.

The capacity of agricultural soils to adsorb organic contaminants could be enhanced by amendment of pyrochars as well as hydrochars. This was shown for the relatively water soluble herbicide IPU in loamy sand that was amended with different biochars from different feedstock in realistic amounts (<50 Mg ha^{-1}, article II). Sorption for IPU in the soil increased by a factor of 13 after hydrochar application and by a factor of 2283 after pyrochar application, thus **hypothesis III** could be confirmed. When digestate was used as feedstock for HTC it promoted a high content of water extractable C to which IPU was bound, and consequently IPU immobilization was reduced. When digestate was pyrolyzed it supported a high micro-porosity leading to occlusion of the pesticide. Hence, for evaluation of the sorption capacity the raw material should also be considered as contrary sorption effects can arise.

Confirming **hypothesis IV**, there was a negative correlation between the sorption capacity of biochars and pesticide mineralization (article II and III), and a positive correlation between pesticide mineralization and biochar C degradability or degree of carbonization (article I and III). Hence, conclusions can be drawn on the accumulation potential of pesticides in loamy sand amended with biochars, e.g., when the degree of carbonization and the sorption potential is known. Exemplarily, pyrochars and high temperate chars have a high sorption capacity if they possess a high SSA that is related to a high micro-porosity which occludes pesticide almost irreversible. If chars are relatively resistant to C degradation it is likely that pesticide mineralization is hampered for long periods of time. Thus, **hypothesis V** that the production process (pyrolysis, HTC) and the biochar degradability have an impact on IPU bioaccessibility could be confirmed. In comparison to pyrochars, hydrochars have a higher content of water extractable C and oxygen containing functional groups, to which the pesticide is bound reversibly (article I and II). Furthermore, hydrochars carbonized under gentle temperature conditions (around 180°C) and with a low C/N ratio, are degraded within a few weeks (article I). Consequently, mineralization and bioaccessibility of pesticides are not restricted by amendment of such hydrochars to soil. In contrast to expectations (**hypothesis V**), the feedstock material is of less importance because a high SSA that essentially determines the sorption capacity, and as consequence IPU mineralization, is a result of high process temperatures.

Soil hydraulic properties

In previous studies the SSA has been addressed to be a crucial factor for the increase of the water retention in soil after biochar amendment. In contrast, we found out that hydrochars that possess a significantly lower SSA compared to pyrochars (article II) are also capable to effectively increase the AWC in soil (article IV). Confirming **hypothesis VI**, the difference of the AWC of biochar amended soil to the pure soil differed among the biochars and was higher for finer biochar particles, for biochars from digestate, and hydrochars carbonized at low process temperatures (200°C). The reason for the higher available water content was rather due to the formation of medium soil pores and an increased total porosity than due to micro-pores of biochars which are responsible for a high SSA and are too small (<2 nm) to significantly contribute to a higher water content.

Furthermore, it could be shown in article IV by measurement of the contact angle that hydrochars are water repellent under dry conditions. So far, it has been assumed that oxygen containing functional groups of hydrochars are responsible for wettability in contrast to aromatic groups that cause water repellency (article II). In contrast to expectations that water repellency of pyrochars and hydrochars counteracts the improvement of AWC and hydraulic conductivity (**hypothesis VII**), other factors that also depend on production process and feedstock, such as particle size, intra-particle porosity, shape, and plasticity are more important and over-compensated possible negative effects. Thus, the effects of feedstock, production process and conditions on these properties and not only water repellency need to be considered carefully when optimizing the improvement of water retention and hydraulic conductivity by biochar addition. Additionally, chemical interactions between functional groups and water molecules are less trivial and have to be related to time and current soil water content. The evaporation method, which was conducted to establish water retention and hydraulic conductivity curves in article IV, is methodically still under development. The article provided an important contribution to the reliability of the evaporation method.

7.3 Conclusions for the use of biochars in agriculture

The results of the investigations show that pyrochars as well as hydrochars can improve certain properties of agricultural sands. However, improved soil properties cannot be ascribed exclusively to one biochar type. In fact, the application of one char type causes several, probably undesired effects. Exemplarily, on the one hand, hydrochars can reduce the mobility of contaminants in soil through sorption and coevally guarantee their bioaccessibility due to hydrochar degradation. On the other hand, the degradation of hydrochars is responsible for high CO_2 emissions. Thus, such chars that are less stable are likely not appropriate for C sequestration.

Biochar effects in soil naturally occur simultaneously and likely influence each other. For example, the soil porosity that increases after application of biochars has an impact on the water budget as well as on the C turnover and pesticide mineralization. The increased soil porosity will probably improve soil aeration, and consequently the aerobic microbial activity. The increased porosity may also accelerate chemical exchange processes through the liquid phase because of enhanced water permeability after rainfall, which creates transport paths for C and N, and contaminant leaching. Water repellency that was measured for hydrochars under drying conditions, in turn, can impede microorganisms to degrade hydrochar C directly, or require specific microbial skills (e.g., capability to biofilm formation on the biochar surface).

From the results of the four investigations in the framework of this work it can be concluded that hydrochars from high carbonization temperatures (250°C) and from woodchips can be recommended for amendment to sandy soils. These hydrochars effectively retain pesticides and plant available water, and are more resistant to C degradation than hydrochars carbonized at lower temperatures or from digestate. Highly stable biochars such as pyrochars may be selected for C sequestration in extensively used agricultural soils. Irrespective of the feedstock material, in conventional, intensive agriculture pyrochars may provoke unforeseeable, negative effects (e.g., pesticide accumulation) that are difficult to control in the future or have to be remediated with high efforts. However, as a matter of course, a comprehensive physico-chemical analysis of the charred material should precede an application to agricultural soils. Thus, intended effects on soil quality can be estimated and in the case of undesired effects be balanced. Due to growing demand for agricultural products as well as progressing climatic change, biochars could provide an important contribution to adapt to these changing situations in the future. For this reason, the optimization of biochar production technologies should be promoted, and the effects and analysis of biochars should be matter of further practical research.

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