Chapter 22: Polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar

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[a]Introduction

If biochar is going to be used as animal feed supplement, as additive for livestock bedding, conditioner for manure or as a soil improver, it has to meet all applicable legislator demands. This includes compliance with limits on pollutant residues such as heavy metals or organics such as polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzo-*p*-dioxins, -furans (PCDD/F), or polychlorinated biphenyls (PCB). Such compounds may either be introduced with feedstock, or produced during pyrolysis. Consequently, the International Biochar Initiative (IBI) set a range of maximum allowed threshold values (varying between different countries) for the sum of the 16 US Environmental Protection Agency's (EPA) PAHs, PCDD/Fs, and PCBs in biochar to 6 – 20mg kg^{-1} dry weight (dw), 9ng kg^{-1} I-TEQ, and 0.2 – 0.5mg kg^{-1} dw, respectively (IBI, 2013). Similarly, the European Biochar Certificate (EBC) requires PAHs to be below 4 and 12mg kg^{-1} dw, in premium and basic grade biochars, respectively, and PCDD/Fs need to be below 20ng kg^{-1} I-TEQ, and 0.2mg kg^{-1} dw, respectively (EBC, 2012).

This chapter provides a systematic overview of organic pollutants in biochar. Since the data is rather scarce to absent for polychlorinated aromatic pollutants, it will largely focus on PAHs, but address other compounds where possible. After the outline of some basic principles of pollutant formation during pyrolysis of biomass, we will compile and synthesize recent biochar literature data primarily of PAHs, and identify pyrolysis parameters that may be

critical with regard to residual pollutant concentrations. Particular attention is paid to current methodological and procedural shortcomings in biochar sampling, sample processing and pollutant quantification. Bioavailable and bioaccessible pollutant fractions are also addressed, and the data discussed in terms of its environmental relevance. The chapter concludes with identifying knowledge gaps and recommendations for future research.

[a]Principles of organic pollutant formation during pyrolysis

Depending on the required product, the thermo(chemical) decomposition of biomass can be conducted at different temperatures in presence or absence of oxygen (O_2), hydrogen (H) or water. At intermediate temperatures typically between 500 and 700ºC and in absence of such reactants, the process is called pyrolysis (Chapter 3). If O_2 is added (with or without other educts) and at higher temperatures (> 800ºC), pyrolysis turns into gasification. With increasing amount of O_2, gasification converts into combustion (at high temperatures). With increasing amount of water, under pressure, but at lower temperature (< 300ºC), pyrolysis ultimately leads into hydrothermal carbonization (under (supercritical) liquid conditions). For details on the pyrolysis process, we refer to the specialized literature, in particular to the corresponding chapter(s) in this book. In pyrolysis, the major biomass components cellulose, hemicellulose and lignin are transformed into gases, liquid or solid products. This process takes place via a multitude of thermochemical reactions in which biomass educts are eventually converted into syngas, bio-oil and pyrogenic carbonaceous material (PCM), depending on parameters such as temperature, heating rates, or the physical setup of the pyrolysis plant. An uncountable number of organic compounds are involved in these reactions, either as precursor, intermediate or terminal products in any of the three physical states. Examples of such compounds include volatile organic compounds such as carboxylic acids, levoglucosan, substituted phenols (e.g., catechol), and alkylated benzenes (e.g., toluene,

xylene) (e.g., Evans and Milne, 1987; Pakdel and Roy, 1991; Britt et al, 2001; Demirbas and Arin, 2002; Morf et al, 2002; Mohan et al, 2006; Cole et al, 2012; Kibet et al, 2012), to name just a few. Those that exert toxicity are perceived as organic pollutants. Among these, PAHs and polychlorinated aromatic compounds are of most concern and will be discussed in further detail in the following.

[b]Polycyclic aromatic hydrocarbons (PAH)

PAHs are among the most widely discussed potential pollutants of biochar, mainly because of their formation during combustion and pyrolysis. While the processes that govern pyrolysis of biomass, including its major components cellulose, hemicellulose, and lignin, have been intensively studied in the past (and will be briefly outlined below), and while the formation of PAH during combustion under controlled laboratory conditions is well understood (for review, see, e.g., Richter and Howard, (2000)), the knowledge of these processes under conditions typical for biochar production, from low tech small scale to high tech industrial scale, is still rather limited, in particular with regard to PAH formation.

During biomass pyrolysis (Garcia-Perez, 2008; Keiluweit et al, 2012), and more generally in any fuel combustion (Mastral and Callen, 2000), two fundamental mechanisms can lead to PAH formation (Figure 22.1): On the one hand, PAHs are formed by pyrosynthesis, i.e., where different gaseous hydrocarbon radicals are generated by cracking of organic material in the feedstock under high temperature conditions (> 500°C). These radicals then undergo a series of bimolecular reactions to form larger (poly-)aromatic ring structures (Evans and Milne, 1987; Mastral and Callen, 2000; Ravindra et al, 2008). Consistent with such a ring buildup mechanism by H-abstraction and C_2H_2-addition reactions, Ledesma et al (2002) found a decreasing yield of PAHs as the ring number increased when pyrolysing catechol, a monoaromatic model compound for solid fuel, at temperatures between 500 and 1000°C.

Light PAHs preceded heavy ones in as much as they formed at 700°C, whereas, formation of heavier ones commenced above 800°C. Similarly, Morf et al (2002) reported negligible formation of PAHs in tars produced with pyrolysis of wood chips up to a temperature of 750 to 800°C, then a dramatic increase in their yields was observed. Naphthalene was quantitatively the most important PAH (Morf et al, 2002). Pyrosynthetic formation of PAHs at temperatures between 700 and 920°C was also observed as a result of laboratory pyrolysis of terpenes (Britt et al, 2004), cellulose, pectin, and chlorogenic acid (McGrath et al, 2001), and polyphenolic compounds (Sharma and Hajaligol, 2003). Generally, PAH yields increased with increasing temperature and residence time (in the order of (milli)seconds) (Britt et al, 2001; McGrath et al, 2001).

On the other hand, low temperature formation (< 600°C) of PAHs takes place as a result of condensation, carbonization, and aromatization of the solid material as it transforms from feedstock to PCM (Hajaligol et al, 2001; McGrath et al, 2003) (Figure 22.1). This has been shown in the laboratory specifically for cellulosic materials (at 400 – 600°C; Hajaligol et al, 2001; McGrath et al, 2003), and plant steroids, although at slightly higher temperatures of 600 – 700°C (Britt et al, 2001). Evidence for low temperature formation of PAH in biochar was recently also provided by Kaal et al (2012), who detected increasing amounts of PAHs in wood and rice straw PCM produced at temperatures between 200 and 700°C, and Fagernas et al (2012) who quantified PAHs in gas and tar samples collected at different time points and increasing retort temperatures from 195 to 445°C.

Figure 22.1 *Main products of biomass pyrolysis and presumed major PAH formation processes (gas phase pyrosynthesis and solid phase reactions such as carbonization, aromatization, and reduction) associated with it. Parameters and products related to biomass pyrolysis, and PAH formation, are marked black, and grey, respectively. It is assumed that PAH formation occurs predominantly via gas*

phase pyrosynthesis at higher temperatures. If so, any condensation of gas and tar phases onto biochar should be avoided during biochar production.

The formation of polycyclic aromatic structures during pyrolysis has also been investigated with ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectroscopy. Although such studies characterize primarily the solid phase as a whole, and not necessarily the extractable fraction, they may be indicative of processes that lead to these chemical structures. Measurements indicated that PCM produced at temperatures below 500°C contain aromatic domains no larger than coronene (seven rings). For comparison, the 16 US EPA PAHs consist of two to six rings. At higher temperatures up to 700°C, the number of rings increased to up to 19 (McBeath et al, 2011), indicating that the PCM produced at these temperatures can be regarded as partly macro-PAH. ^{13}C-NMR studies by Brewer et al (2009) showed that PCM produced by slow and fast pyrolysis contained aromatic clusters around seven to eight rings, whereas gasification led to larger structures with up to 17 fused rings. However, the notion that such materials consist primarily of graphitic polyaromatic structures may be oversimplified. At least, chars originating from forest fires may still contain heteroatomic structures as remnants of lignin and cellulose (Knicker et al, 2008).

[b]Polychlorinated aromatic compounds

Ample information regarding the formation of PCDD/F during thermal processing is available for combustion and incineration, primarily of municipal waste products (for review, see e.g., Tuppurainen et al (1998), McKay (2002), Kulkarni et al (2008), and Altarawneh et al (2009)). The high-temperature pyrolysis of chlorinated hydrocarbons was reviewed by Taylor and Dellinger (1999), and the formation of PCDD/F from pyrolysis of chlorinated organic educts such as chlorobenzenes, 2-chlorophenol, or PCBs was studied by Buser et al (1978), Buser

(1979), and Evans and Dellinger (2003). However, the information about the possible formation of polychlorinated aromatic compounds during pyrolysis of biomass is very scarce. One of the few studies was provided by Bjorkman and Stromberg (1997), who investigated the release of chlorine from biomass during pyrolysis and gasification. No chloro-organic compounds were found in tars from pyrolysis of switch grass at temperatures between 300 and 500°C, whereas polychlorinated benzenes, i.e., potential precursors of PCDD/Fs, were quantified during combustion of lucerne. The authors therefore stated that O_2 seemed a vital component for the formation of chlorinated benzenes. From the limited information available, one may conclude that a *de novo* formation of polychlorinated aromatic compounds under fully pyrolytic conditions is not likely, whereas PCDD/Fs may be formed if suitable precursors are present in feedstock.

[a]PAHs in pyrolysis products

As far as we are aware of, the study by Fagernas et al (2012) is currently the only one that conducted a mass balance of PAH in all pyrolysis products, in this case from the slow pyrolysis of birch wood. Of the total of 4kg of PAHs (sum of 33 different compounds) produced in a batch carbonization retort with 3200kg of wood, the overwhelming majority was found in tar (62%) or gas (37%), and only 0.6% resided in the PCM. In another experiment, the pyrolysis process was also run under different conditions, with temperatures varying from 195 to 440°C. Unfortunately, in this experiment PAHs were not quantified in the so produced PCM, but only in the gas fraction, where they reached a maximum at 415°C. This dominance of PAHs in tar and gas over the solid phase is qualitatively in line with the principles of PAH formation outlined above, and probably of direct relevance for optimizing the pyrolysis processes with the goal that residual PAH concentrations in biochar are minimized.

[b]Tars and bio-oils

While the interest in possible residues of PAHs in biochar itself has not been very pronounced until recently, analyses of these compounds in related materials and pyrolysis products have already been ongoing for several decades. In particular, tars originating as unwanted side products of wood gasification and bio-oils have been analysed for PAHs. For instance, Pakdel and Roy (1991) quantified aromatic hydrocarbons between 0.06 and 0.24% of the oil phase obtained from vacuum pyrolysis of aspen poplar wood chips, and a tar sample from a wood gasifier consisted of over 50% of PAHs. Fast pyrolysis at 500°C of different agricultural wastes yielded bio-crudes that contained mean concentrations of PAHs of 3.3 to 12.7mg L^{-1} (sum of 21 individual compounds), with light compounds dominating (Pakdel and Roy, 1991). More recently, Cordella et al (2012) reported concentrations of 28 to 183mg kg^{-1} wet weight of PAHs (sum of 16 US EPA PAH) in bio-oils produced from corn stalks, poplar and switchgrass in a laboratory fixed bed pyrolyser operated at 650°C for 30min. Tar produced by gasification of dealcoholized marc of grape contained roughly 10 – 20% w/w of PAHs, with the light compounds dominating (Hernandez et al, 2013).

[b] Gas phase and air particles

Re-Poppi and Santiago-Silva (2002) reported PAHs to be abundantly present in wood smoke emitted during charcoal production, and Barbosa et al (2006) quantified PAHs in smoke emitting from a traditional charcoal furnace. Average total concentrations were 26 ± 8μg m^{-3}. In accordance with gas-particle distribution theory (Pankow, 1987; Bidleman, 1988), the light PAHs (naphthalene to anthracene) were predominantly emitted in the gas phase, whereas heavier PAHs were overwhelmingly particle bound. Naphthalene contributed about 40% of

the quantified emissions, and dominated at the beginning of the carbonization process, in particular.

[b]Total concentrations of PAH in biochar

The general formation principles of PAHs during pyrolysis presented above have largely been derived from results obtained under controlled laboratory experimental conditions, mostly with fast or flash pyrolysis, with parameters that may not be representative for biochar production in practice, and not primarily with a focus on solid residues. Also, the above discussed general findings are largely conceptual with regard to PAH formation, and it is not clear yet whether they are applicable or helpful to understand PAH residues in biochars. Therefore, we searched for literature that reported PAH concentrations in biochar and related material and identified roughly 20 papers listed in Table 22.1. Most of the literature is very recent, but there are some earlier works that investigated PAHs in biochar-related materials, in particular charcoals. Table 22.1 also contains some of the general aspects of interest, in particular process parameters such as feedstock, and pyrolysis type, and some information about sample preparation and analysis. Again, most of the work was conducted under controlled laboratory conditions, with the aim to investigate the influence of various pyrolysis parameters on PAH formation.

Early reports on PAHs in charcoals date back some 30 years. However, at that time, the methods for reliable trace analysis of PAHs by gas chromatography and mass spectrometry were just about to be developed. We therefore refrain from a systematic review of such pioneering work. As an illustration of such an early paper, we list the paper by Kushwaha et al (1985) (Table 1). They reported wood charcoal briquettes to contain PAHs in the low mg kg^{-1} concentration range. In the first decade of this millennium, black C in its various forms increasingly attracted the attention of environmental chemists, because of its importance as a

strong sorbent of organic pollutants (e.g., Cornelissen et al, 2005). While most of the literature dealt with soot and soot-like materials, this interest is also reflected by several papers that investigated PAH formation and content in biochar and charcoal (Table 22.1). To the best of our knowledge, Singh et al (2010) were the first to analyse PAHs in, what they called, biochar; unfortunately, with concentrations below the quantification limit. Overall, however, the total PAH content in some 220 biochar samples varied widely over largely three orders of magnitude (0.1 to 100mg kg^{-1}; $-1 \leq \log conc \leq 2$), with some outliers up to 10,000mg kg^{-1} (log conc = 4; Table 22.1, Figure 22.2). In the following, we will discuss the reported data and try to identify general trends and determining parameters. Before we do this, we focus on methodological aspects of PAH determination in biochar, because these are essential for the correct interpretation of the data, in particular with regards to comparisons of individual papers.