Strategies for producing biochars with minimum PAH contamination

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Abstract

With the aim to develop initial recommendations for production of biochars with minimal contamination with polycyclic aromatic hydrocarbons (PAHs), we analysed a systematic set of 46 biochars produced under highly controlled pyrolysis conditions. The effects of the highest treatment temperature (HTT), residence time, carrier gas flow and typical feedstocks (wheat / oilseed rape straw pellets (WSP), softwood pellets (SWP)) on 16 US EPA PAH concentration in biochar were investigated. Overall, the PAH concentrations ranged between 1.2 and 100 mg kg^{-1}. On average, straw-derived biochar contained 5.8 times higher PAH concentrations than softwood-derived biochar. In a batch pyrolysis reactor, increasing carrier gas flow significantly decreased PAH concentrations in biochar; in case of straw, the concentrations dropped from 43.1 mg kg^{-1} in the absence of carrier gas to 3.5 mg kg^{-1} with a carrier gas flow of 0.67 L min^{-1}; for woody biomass PAHs concentrations declined from 7.4 mg kg^{-1} to 1.5 mg kg^{-1} with the same change of carrier gas flow. In the temperature range of 350-650°C the HTT did not have any significant effect on PAH content in biochars, irrespective of feedstock type, however, in biochars produced at 750°C the PAH concentrations were significantly higher. After detailed investigation it was deduced that this intensification in PAH contamination at high temperatures was most likely down to the specifics of the unit design of the continuous pyrolysis reactor used. Overall, it was concluded that besides PAH formation, vaporisation is determining the PAH concentration in biochar. The fact that both of these mechanisms intensify with pyrolysis temperature (one increasing and the other one decreasing the PAH concentration in biochar) could explain why no consistent trend in PAH content in biochar with temperature has been found in the literature.

Abbreviations

HTT, highest treatment temperature; I.D., inner diameter

Keywords

1 Introduction

Biochar is the solid product of thermochemical conversion of biomass under an atmosphere with reduced content of free oxygen or its complete absence, i.e. pyrolysis and gasification [1]. During such conversion, biomass undergoes extensive devolatilisation and develops a solid carbonized matrix [2]. This is accompanied by formation of polycyclic aromatic hydrocarbons (PAHs), an important class of organic contaminants, associated with environmental problems [3]. PAHs can have acute adverse effects on human health, plants and the wider ecosystem with some displaying carcinogenic, mutagenic and teratogenic effects [4].

PAHs are defined as aromatic structures that consist of two or more linked carbon rings and only contain the elements carbon and hydrogen [3]. PAHs are formed during incomplete combustion of any type of biomass and biomass-derived material. Thus, PAHs are present in the environment naturally through forest fires and volcanic eruptions, with UK rural soils containing a mean PAH concentration of 2.2 mg kg^{-1} [5]. However, human actions increase PAH concentrations locally and the average PAH concentrations in UK urban soils were reported to be 14.2 mg kg^{-1} [5]. In soil they are known to accumulate as they are difficult to degrade, associate with organic matter and have low water solubility (half-life of PAHs of more than 3 rings > 20 to hundreds of days) [4].

There are two main pathways by which PAHs are known to form: at lower conversion temperatures Diels-Alder reactions take place which involve dehydrogenation, polymerization, cyclization and aromatization of hydrocarbons to form PAHs [6–8]. At temperatures above 400-500°C, the alternative is a pyrosynthetic pathway consisting of demethylation, demethoxylation and dehydroxylation of lignin, cellulose and hemicellulose to form phenol, alkyl-phenols and BTEX. This is followed by deoxygenation /

dehydrogenation, connecting single compounds and condensing these into larger compounds which end up as polyaromatic networks (PAHs or pyrolytic carbon) [6,7,9,10].

Research effort regarding anthropogenic pollution with PAHs used to focus on reducing PAH emissions from fossil fuel- and biomass combustion [3]. Studies that dealt with PAHs and pyrolysis mostly investigated PAH formation and concentrations in pyrolysis liquids / gases [6,9,11–13]. Recently, attention has shifted to PAH concentrations in pyrolysis solids because of the potential application of biochar to soil for soil improvement, -remediation and carbon sequestration [8,14–19]. In order to avoid possible negative effects on soil ecosystems and to comply with environmental legislation, it is essential to produce biochars with low PAH concentrations. Biochar guideline values have been established which are based on current legislation. For example, the European Biochar Certificate (EBC) allows up to 12 mg kg^{-1} of 16 US EPA PAHs for basic grade and up to 4 mg kg^{-1} for premium grade biochar which was adopted from the Swiss Chemical Risk Reduction Act [20]. The International Biochar Initiative (IBI) guidelines use threshold value of 20 mg kg^{-1} and 6 mg kg^{-1} based on the Austrian Compost Ordinance [21].

The few systematic studies on dependence of PAH concentrations on pyrolysis conditions that exist provide different perspectives and no overall trend is observed [8,14–19,22]. In Hale *et al.* (2012) [16], the effects of highest treatment temperature (HTT - maximum temperature material is exposed to), residence time and feedstock was investigated by analysing 59 biochars, however, due to the highly variable technologies used for biochar production only limited conclusions could be drawn. This shows the absolute need for a systematic study on the relationship of pyrolysis conditions and feedstock with PAHs in biochars produced from highly controlled, slow pyrolysis units.

Consequently, in this work the effects of two common feedstock types (wood and straw) and typical pyrolysis parameters (residence time, HTT and carrier gas flow rate) were investigated to determine their effect on total concentrations of 16 US EPA PAHs in resulting biochars. The overall objective was to provide recommendations to produce pyrolysis solids (biochar) with minimal PAH contamination based on a data set of biochars produced from highly controlled pyrolysis units.

2 Materials and Methods

2.1 Feedstocks

For production of the 46 biochars, 7 feedstocks were used: 1) straw pellets (WSP) from 50/50 wheat : oilseed rape straw [23]; 2) softwood pellets (SWP) from 5/95 pine : spruce; 3) willow chips (WC) Koolfuel 40, supplied by Strawsons (Retford, UK); 4) miscanthus chips (MC) (*Miscanthus x giganteus*); 5) demolition wood (DW) and 6) *Arundo donax* (ADX) as described in Buss *et al*. (*2016*) [24]; and 7) sewage sludge (SS).

2.2 Biochar production

46 biochars were produced under highly controlled pyrolysis conditions using three different slow pyrolysis units that are located at the UK Biochar Research Centre (UKBRC). The smallest unit ("Stage I") is a fixed bed, batch, quartz tube reactor with an inner diameter (I.D.) of 50 mm and around 200 mm sample bed depth which is heated up by an infrared gold image furnace and can pyrolyse about 15-40 g per batch [25]. The second unit ("Stage II") typically processes 500 g h^{-1} and is a continuous pyrolysis unit with a furnace screw which is heated up by an electric split-tube furnace (Buss *et al*. (*2016*)) [24]. The pilot scale pyrolysis unit ("Stage III") has a rotary kiln and can process up to 50 kg h^{-1} of feedstock [26]. Production parameters, such as HTT (350-750°C), residence time (10, 20, 40 min) and carrier gas flow (0, 0.33, 0.67 L min^{-1}) were varied. The carrier gas flows under standard conditions were 10 L min^{-1} for Stage III (I.D. 244 mm), 1 L min^{-1} for Stage II (I.D. 100 mm) and 0.3 L min^{-1} for Stage I (I.D. 50 mm). When inconsistencies during a pyrolysis run were detected, such as high pressure peaks, the biochars were discarded and the pyrolysis run was repeated ensuring comparative conditions between runs. An overview of all the biochars including production conditions and feedstocks can be found in Table S1.

2.2.1 Highest treatment temperature (HTT)

To be able to find overall trends of the influence of HTT on the total PAH concentration in biochar, different feedstocks were pyrolysed using two pyrolysis units in the typical temperature range used for biochar production (350 - 750°C). Stage II pyrolysis unit was used to pyrolyse demolition wood and *A. donax* at 5 temperatures (350, 450, 550, 650, 750°C), willow chips at 3 temperatures (350, 550, 750°C) and miscanthus chips at 4 temperatures (350, 450, 550, 750°C). Furthermore, sewage sludge was pyrolysed at 5 temperatures (350, 450, 550, 650, 750°C) with the Stage III pyrolysis unit.

2.2.2 Effects of carrier gas flow rate, HTT, feedstock, and residence time at HTT

The Stage I pyrolysis unit was used to pyrolyse straw pellets (WSP) and softwood pellets (SWP) at 2 HTTs (350, 650°C), 2 residence times (10, 40 min) and 3 carrier gas flows (0, 0.33, 0.67 L min^{-1}). In total, 24 biochars were produced. The feedstocks and production conditions were chosen as typical feedstocks and production conditions for biochar production. More details on the production and on the feedstocks, such as elemental content (ultimate analysis) and biomass components, can be found in Crombie & Mašek (2015) [23].

2.3 PAH analysis

2.3.1 Sampling

To gain representative samples, first the container with the biochar was mixed and around 1/10 of the biochar was sampled (~10 g) from all areas of the container. The 10 g sample was ground with mortar and pestle and homogenized, transferred into a sample tube, and mixed again before a 2 g sub-sample was taken. Finally, accurately weighed aliquots (1 g) were used for extraction.

2.3.2 Extraction and analysis

Biochar has a very strong sorption capacity for PAHs and studies have shown that a longer extraction duration results in much higher PAH recovery compared to conventional extraction techniques used for soil (e.g. 6 h Soxhlet extraction) [16,27,28]. Since recovery rates reached maximum values after an extraction for 36 h [27,28], the method recommended in the European Biochar Certificate [20] is a 36 h Soxhlet extraction using toluene [27], followed by GC-MS analysis which was also applied in this study.

Each homogenised biochar sample was subjected to a 36 h Soxhlet extraction using approximately 100 mL of toluene. The resulting extract was rotary evaporated to 1 mL and analysed without clean-up for the 16 PAHs on the US EPA priority pollutants list by GC–MS (Agilent 6890 GC plus 5975c MS). Full details including validation of the method can be found in Hilber *et al.* (2012) [27]. Naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene d-12 were used as internal standards. RSD of the GC-MS analysis for all individual PAHs measuring high and low standards can be found in supplementary information in Buss *et al.* (2015) [29]. The limit of detection for the individual PAHs was 0.10 mg kg^{-1}. The analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), accredited by United Kingdom Accreditation Service (UKAS). The sum of 16 US EPA priority PAHs is reported for 46 biochars. Several of these were extracted and analysed in triplicate (separate vials on separate occasions) and RSD values were typically $< 20\%$.

2.4 Statistics

Results were evaluated statistically using two-sample, two-tailed t-tests and Analysis of Variance (ANOVA) followed by Student-Newman-Keuls post hoc tests performed with SigmaPlot 12 (Systat Software Inc., Chicago, IL). Significant differences are stated with a p-value < 0.05.

3 Results

Production conditions and total PAH concentrations for all 46 biochars used in this work are shown in Table S1. The PAH concentrations measured in the biochar sample set covered a wide range, from ~1.2 to ~100 mg kg^{-1}. Comparison of the measured values against guideline values for acceptable PAHs concentrations in biochar for soil application showed that out of the 46 biochars tested 59% exceeded the EBC premium grade PAH limit (4 mg kg^{-1}), 46% were above the EBC basic grade limit (12 mg kg^{-1}) and 43% were higher than the IBI threshold (20 mg kg^{-1}) (Table 1).

Table 1: Biochars exceeding PAH guideline values. The values depicted are for biochar soil application according to European Biochar Certificate (EBC) and International Biochar Initiative (IBI), and number and percentage of biochars out of the set of 46, exceeding these guideline values.

		EBC premium	EBC basic	IBI
threshold	mg kg^{-1}	4	12	20
exceedance	biochars	27	21	20
	%	59	46	43

3.1 Highest treatment temperature (HTT)

Four different feedstocks were pyrolysed with Stage II pyrolysis unit and one with Stage III pyrolysis unit in the temperature range 350-750°C (Figure 1). For production temperatures of up to 650°C, biochars from both pyrolysis units showed some variations in the PAH concentrations, but, taking all feedstocks and both pyrolysis units into account, there was no significant change in the range 350-650°C (one-way ANOVA).

However, on average, the biochars produced at 750°C showed significantly higher PAH concentrations than biochars produced at any of the lower temperatures (one-way ANOVA). Yet, the PAH concentrations of the biochar produced at 750°C with the Stage III pyrolysis unit was only 1.2 fold higher than the biochar from the same feedstock produced at 350°C, while the PAH concentrations in the biochars produced at 750°C with the Stage II pyrolysis unit were 1.9 fold to 23.3 fold higher than the 350°C-biochars (DW 21.8 fold, ADX 23.3 fold, MC 1.9 fold and WC 5.0 fold).
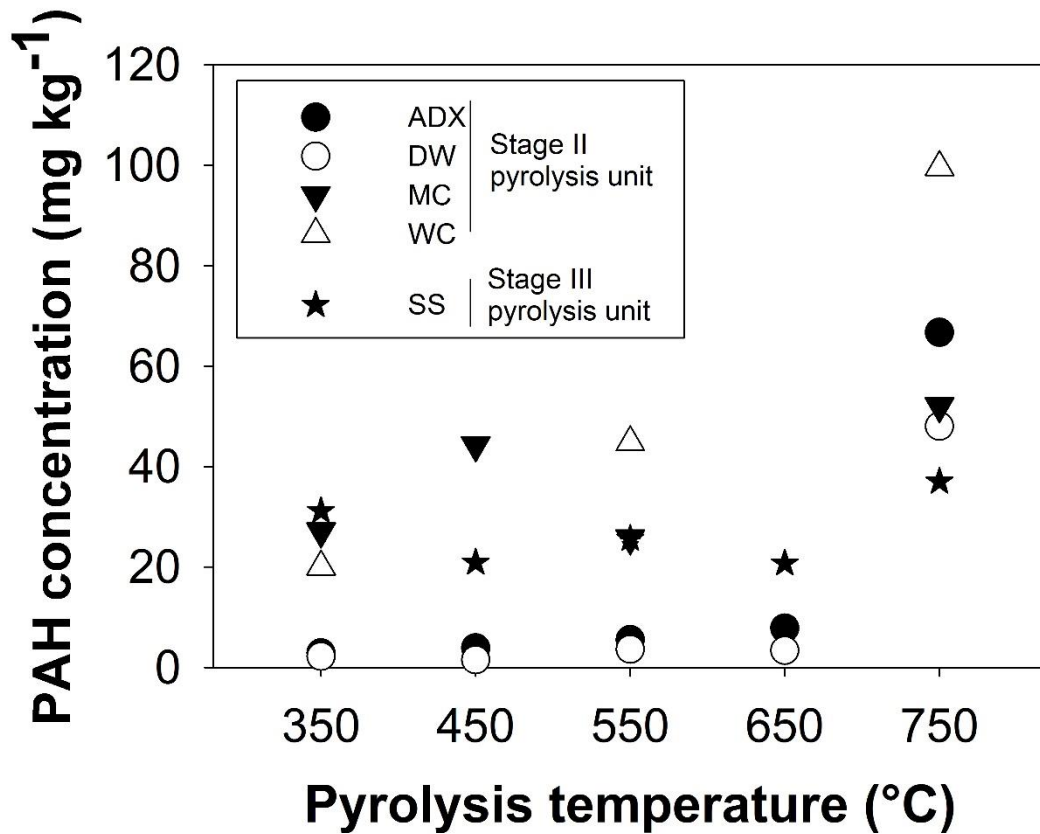
Figure 1: Effect of pyrolysis temperature on 16 US EPA PAH concentration in biochar (mg kg^{-1}). The biochars were produced from 4 different feedstocks in Stage II pyrolysis unit (ADX, *Arundo donax*; DW, demolition wood; MC, miscanthus chips; WC, willow chips) and 1 feedstock in Stage III pyrolysis unit (SS, sewage sludge). For all the feedstocks combined, the PAH concentration in the biochars produced at 750°C is significantly different to all the other HTTs (one-way ANOVA).

3.2 Carrier gas flow, HTT and residence time

The effects of carrier gas flow rate, HTT, and residence time at HTT on PAH concentrations were tested by pyrolysing 2 feedstocks (straw, wood) at 12 different conditions in a batch pyrolysis reactor (Stage I), respectively (Figure 2). Straw pyrolysis yielded biochar with much higher PAH concentrations than wood (further discussed in 3.2). The biochars that only differed in residence time show very similar PAH concentrations (Figure 2), confirming previous observations that in these samples residence time at HTT in the range investigated had negligible effect on resulting biochars (energy content of pyrolysis products and carbon sequestration potential tested in Crombie & Mašek (2015) [23]).

It is also apparent that the concentration of PAHs in biochar decreased with increasing carrier gas flow rate irrespective of HTT and residence time from 43.1 mg kg^{-1} to 17.3 mg kg^{-1} and 3.5 mg kg^{-1} for biochars produced from WSP and 7.4 mg kg^{-1} to 2.0 mg kg^{-1} and 1.5 mg kg^{-1} for biochars produced from SWP (Figure 2, averages in Table S2). For biochars from both feedstocks this meant a significant reduction of PAHs due to increased carrier gas flow rates from 0 to 0.33 L min^{-1} (two-sample, two-tailed t-test; WSP: p-value = 0.046, SWP: p-value = 0.048) and from 0 to 0.67 L min^{-1} (WSP: p-value = 0.0003, SWP: p-value = 0.035).

At 650°C the effect was more pronounced, with a sharp decline with increase of carrier gas flow rate from 0 to 0.33 L min^{-1} for both feedstocks. At 350°C the decrease with flow rate was more gradual, ultimately reaching concentrations similar to those obtained for the 650 °C biochar when the carrier flow rate was increased to 0.67 L min^{-1}. Most importantly both feedstocks resulted in biochars with PAH concentrations of less than 6 mg kg^{-1} (IBI lower guideline value) at higher carrier gas flow rate, and wood pellets biochars even stayed below the premium grade biochar limit (4 mg kg^{-1}) at low carrier gas flow rate.
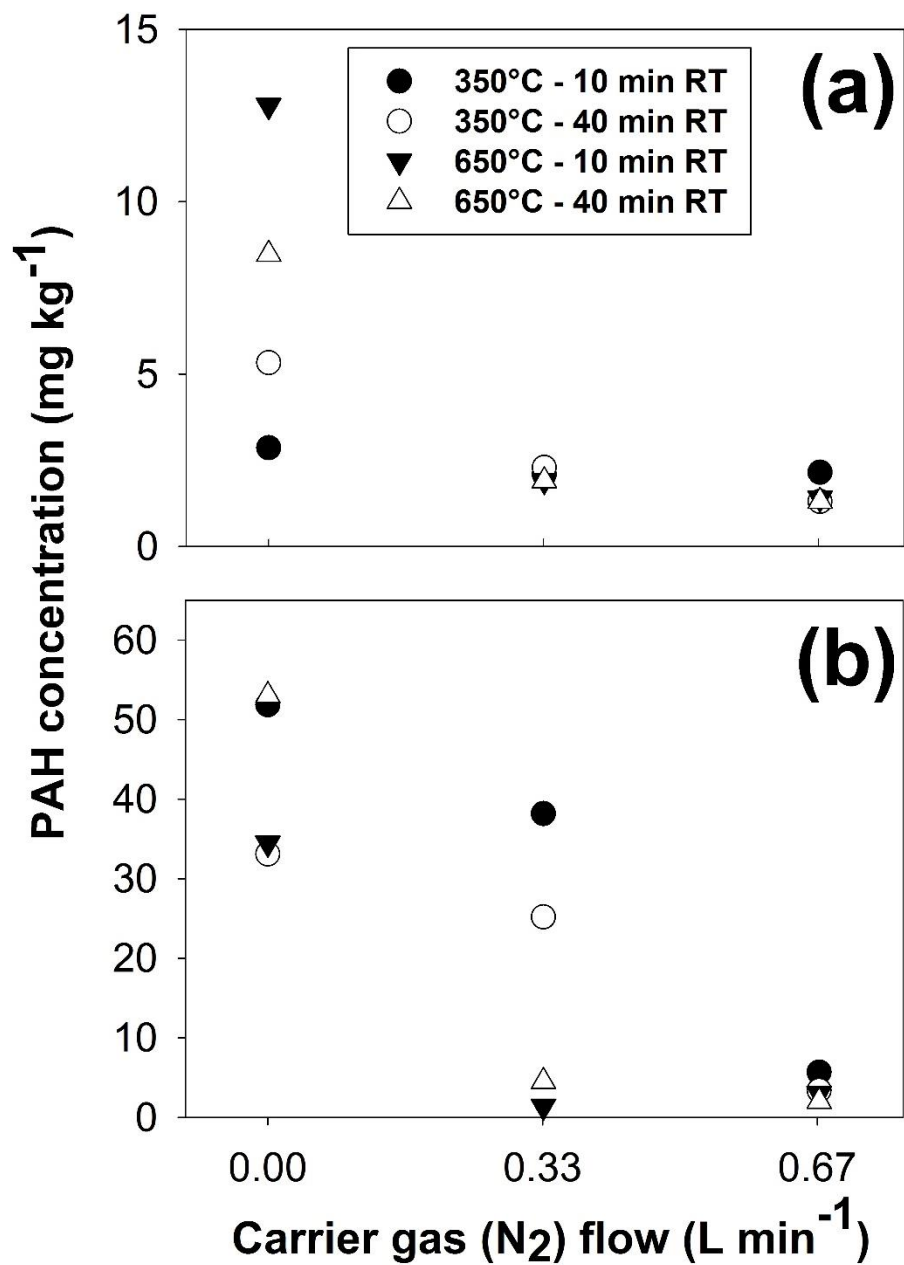
Figure 2: Effects of HTT, residence time (RT) and carrier gas flow rate on 16 US EPA PAH concentration in biochar (mg kg^{-1}). Biochars were produced from (a) softwood pellets (SWP) and (b) wheat straw pellets (WSP) in Stage I pyrolysis unit.

3.3 Biomass type: wood – straw

As already indicated above, in Figure 2 there is a notable difference in scale for total PAH concentrations for (a) wood and (b) straw – derived biochars produced at 12 different pyrolysis conditions, respectively. The results showed that straw pyrolysis yielded biochars with significantly higher PAH concentrations compared to softwood pellets (two-sample, two-tailed t-test, p-value = 0.007), on average the PAH concentration in straw biochar was 5.8 fold higher than in wood biochar (Table S3). The difference in PAH concentrations between straw and wood biochar was most apparent at low carrier gas flow rates, but were almost undetectable at the highest carrier gas flow rate in the range investigated.
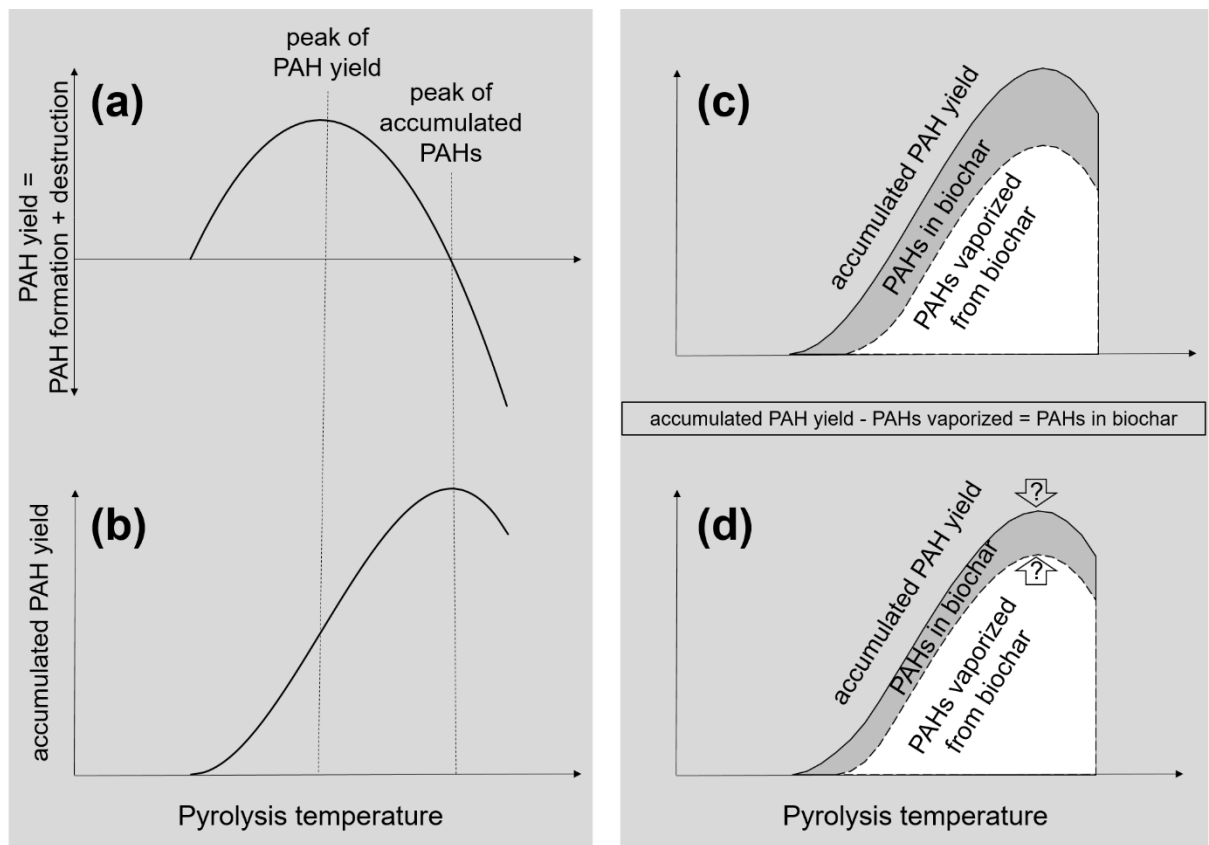
Figure 3: Schematic illustration of conceptual relationship of PAHs and pyrolysis temperature. (a) shows PAH yield consisting of PAH formation and destruction at each individual pyrolysis temperature. (b) is the integral of (a) and shows the total yield accumulated over the whole temperature range up to the highest treatment temperature. (c) shows the concentration of PAHs in biochar as the difference between accumulated PAH yield and PAHs vaporized (released). (d) shows which effect increased carrier gas flow has on PAHs in biochar and what might have caused this effect.

4 Discussion

Studies published to date that employed Soxhlet extraction (various solvents and durations) reported concentrations of the 16 US EPA PAHs in biochars in the range 0.07-355 mg kg^{-1} [16,18,27,28,30–32]. The PAH concentrations detected in the 46 biochars analysed in this study, 1.2 to 100 mg kg^{-1}, fall within the range in published studies. However, according to proposed biochar guidelines (IBI and EBC) only 40-60% of these would satisfy the PAH concentration criteria for safe application to soils.

4.1 Effect of highest treatment temperature (HTT) on PAHs in biochar

So far, no satisfactory explanation has been given in the literature regarding the relationship of PAH concentrations in biochar and pyrolysis HTT [33]. Brown *et al.* (2006) [22] (450 - 1000°C) and Freddo *et al.* (2012) [19] (300, 600°C) reported decreasing PAH concentrations with increasing temperature. Kloss *et al.* (2012) [18] (400 - 525°C) didn't observe any temperature dependence, while Rogovska *et al.* (2012) [17] (450 - 850°C) and Zielińska & Oleszczuk (2015) [34] (500 - 700°C) found that PAH concentrations increased with increasing pyrolysis temperature. In our study, the PAH concentrations were not significantly different in biochars produced in the temperature range 350 - 650°C. At 750°C, however, a significant increase in PAH concentration was observed. Although most published studies did not investigate biochar produced at temperatures $\geq$ 700°C, those that did, did not report any marked increase in PAH concentrations at temperatures $\geq$ 700°C [8,14–16,22]. Several studies observed peak PAH concentrations in biochars produced at lower pyrolysis temperatures than 750°C, e.g. Hale *et al.* (2012) [16] using various feedstocks over the range 350 - 550°C; Devi & Saroha (2015) [15] at 500°C with sewage sludge; Keiluweit *et al.* (2012) [8] at 500°C with wood and grass and Dai *et al.* (2014) [14] at 600°C with sewage sludge.

Although there appears to be no clear trend in biochar PAH concentrations with temperature, PAH yield in all pyrolysis products, i.e. solids, liquids and gases, has been shown to increase with temperature (at least in the temperature range suitable for biochar production) [6,9,11–13,35,36]. PAH yield at a particular temperature consists of PAH formation and destruction (conversion of PAHs into lighter hydrocarbons / gases [12,14] and condensation to form high molecular weight PAHs / pyrolytic carbon [8,9,13]). This concept is illustrated in Figure 3. However, during fast/slow pyrolysis the particle that is heated up goes through all the different temperature phases in rapid/slow succession until the highest treatment temperature (target) is reached, e.g. as shown in Huang *et al.* (2013) [37]. Consequently, what is actually determined when the total PAH concentration in pyrolysis solids, liquids and gases is measured is the PAH yield integrated over temperature which is the accumulation of all PAHs produced from starting- to highest treatment temperature. Consequently, the peak of PAH yield (Figure 3a) indicates the temperature where the highest accumulated yield increase is reached (slope change Figure 3b). At even higher temperatures, the PAH yield decreases until PAH destruction equals PAH formation (PAH yield is zero) and the maximum accumulated PAH yield is reached (Figure 3a, b) which is between 750-900°C [13,14,35,36].

However, neither PAH formation, nor accumulated PAH yield alone are the key for elucidating the relationship between pyrolysis temperature and PAH concentrations in biochar; the distribution of PAHs into the pyrolysis fractions is a highly important contributing factor. Since PAHs are reported to be mostly formed at the gas-solid interphase [6,8,10,13,33], most PAHs created are easily vaporised at typical pyrolysis temperatures (>99% end up in pyrolysis liquids / gases) [14,38]. Naturally, increasing pyrolysis temperature leads to higher PAH vaporisation from pyrolysis solids which counteracts the increasing amount of PAH yield at higher temperatures. The difference between PAHs

formed and -vaporised is the actual concentration of PAHs in biochar, which is illustrated in Figure 3c. It is hypothesised that simultaneous increase in PAH formation and -vaporisation with temperature is the reason why no general trend of PAHs in biochar with pyrolysis temperature has been reported in literature as the effects are counteracting, one resulting in increased and one in decreased PAHs in biochar (Figure 3c).

This explanation is supported by the PAH concentrations in biochars produced in the temperature range 350-650°C (Table 1) where no significant changes were seen. Yet, the significantly higher PAH concentrations observed in biochars produced at 750°C (with the Stage II pyrolysis unit) in our study could be seen as contradictory. However, a plausible explanation of this unit-specific effect, is that it is caused by the pyrolysis unit design and operation, resulting in distribution of temperatures that allowed cooling of volatiles at the discharge end of the unit. Due to the pyrolysis unit design, where pyrolysis vapours (containing >99% of the produced PAHs [14,38]) travel concurrently through the pyrolysis chamber and into a discharge chamber where biochar is separated, extensive contact between biochar and vapours is possible. Therefore, if at any point the reactor or material temperature drops below dew point of the tars, including PAHs in the pyrolysis vapours, these would condense onto the biochar. This effect has been described in Buss *et al.* (2014), (2015) [26,29]. The discharge chamber of the Stage II pyrolysis unit is actively heated up with heating tapes which are fixed at a certain temperature irrespective of the pyrolysis temperature, while the discharge chamber of the Stage III pyrolysis unit is heated by the furnace and released vapours / gases. Consequently, in the Stage III unit the temperature of the discharge chamber depends on the pyrolysis temperature used. The difference in set-up of the discharge chamber may be the reason for the difference in PAH concentration observed for the biochars produced at 750°C with the Stage II and III pyrolysis unit.

4.2 Effect of carrier gas flow and residence time on PAHs in biochar

It was shown that increasing carrier gas flow through the bed of biomass undergoing pyrolysis in a fixed bed reactor decreased the PAH concentrations in biochar. On the other hand, residence time of biomass at HTT in the fixed bed did not have any discernible effect on PAH concentrations.

PAHs are mainly formed through secondary reactions of vapours, and similar reaction pathways also form biochar through combining PAHs to higher molecular weight PAHs and further combine these to build pyrolytic carbon [9,10,12]. It is reported that the magnitude of secondary (char) reactions is mainly influenced by the intensity and duration of contact of vapours with feedstock / biochar [37,39] as longer vapour residence times increase biochar yields [40]. This means that reduced hot vapour residence time, besides reducing biochar formation [23], should also reduce PAH formation as already speculated in McGrath *et al.* (2003) [6] and shown in Dai *et al.* (2014a) [35].

Residence time of feedstock in the heated zone, however, must be clearly differentiated from hot vapour residence time. During fast pyrolysis, vapour residence time indeed is influenced by residence time of the feedstock in the heated zone and has a major effect on PAH yield [12]. Residence time during slow pyrolysis, on the other hand, is in the range of minutes (10 and 40 min tested here) to hours and hot vapour residence time in the range of seconds to tens of seconds, which is much longer than during fast pyrolysis [41]. Consequently, during slow pyrolysis in a batch reactor, variation of the residence time of the feedstock in the heated zone has much less effect on hot vapour residence time. This could explain why no effect of residence time on PAH concentration has been observed in this study. However, it needs to be stressed that this has only been investigated in a batch reactor and in a continuous pyrolysis reactor the system is quite different. In a continuous unit, pyrolysis vapours can interact with pyrolysis solids further down-stream within the pyrolysis unit on their way to

the gas outlet (e.g. after-burner) [37]. Therefore, in a continuous unit a change of residence time could also have an effect on secondary char reaction and on PAH concentration in biochar.

Carrier gas flow rate also affects the vapour-solid interaction. In a batch-reactor with no carrier gas flow, the gas-solid residence time for secondary reactions to take place is maximized [23,40]. Higher carrier gas flow decreases the hot vapour residence time which results in decreased PAH formation [35]. In addition, carrier gas flow rate increases the driving force for physical removal of PAHs from the solids (biochar). Thus, carrier gas flow increases PAH vaporisation from biochar and decreases PAH formation which is illustrated in Figure 3d, however, it is unclear which is the dominant factor. Considering the small proportion of PAHs that attached to pyrolysis solids without carrier gas flow in the Fagernäs *et al.* (2012) study (0.6% = 24 mg kg^{-1}) [38], a small change in the distribution of PAHs in solids and liquids/gases could have a large effect on total PAH concentrations in biochar. The phenomenon that carrier gas flow has a major effect on PAH concentrations in biochar could explain parts of the high fluctuations of PAH concentrations reported in literature and increased PAH concentrations in biochars produced under field conditions (no carrier gas flow) [16]. Again, this has only been investigated in a batch reactor and needs to be tested for continuous units.

4.3 Effect of biomass type on PAHs in biochar: wood – straw

Our findings that straw-derived biochar contained 5.8 times more PAHs than wood-derived biochar are similar to those obtained by Keiluweit *et al.* (2012) [8] who reported four times higher concentrations of PAHs in grass-derived biochar produced at 500°C, compared to wood biochar. Similarly, Kloss *et al.* (2012) [18] observed considerably higher PAH concentrations in straw-derived biochar compared to spruce-derived biochar and Fabbri *et al.*

(2013) [28] reported that slow pyrolysis of woody biomass resulted in the lowest PAH concentrations compared to various other feedstocks.

In general, lignin-rich feedstocks have been observed to produce biochars with less PAHs than those which are comprised mainly of pectin and cellulose [9,42]. The opposite was, observed by Zhou *et al.* (2014b) [43]. As the lignin content of straw pellets and wood pellets used in the current study was very similar (~22%, analysed in Crombie and Mašek (2014) [44]), the content of lignin cannot explain the trends observed in our study. Besides lignin content, the composition of lignin, which is very different between straw and woody biomass [45,46] could be at least partly responsible for differences in PAH content, however, insufficient studies on this are available. In addition, the C, H, N, O-elemental contents and cellulose and hemicellulose content of the feedstocks varied greatly [44] which could explain the different PAH contents after pyrolysis. Zhou *et al.* (2014b) [43] observed non-additive, synergistic effects of biomass components, i.e. of cellulose, hemicellulose and lignin, on the formation of PAHs during pyrolysis, making prediction of PAH concentrations in biomass based on feedstock composition very challenging.

4.4 Conclusions

From data collected on the 46 biochars investigated in this study, it is concluded that residence time at peak temperature (slow pyrolysis, batch reactor) did not influence PAH concentration in biochar. On the other hand, it was observed that pyrolysis of woody biomass yielded biochar with considerably lower PAH contents than straw biomass, at least in the units and operating conditions deployed in this study. Overall, this work showed how complex the matter of effects of feedstock characteristics on PAH concentrations in biochar is and how many factors could have an influence. This study presents a significant contribution to the limited body of knowledge on feedstock effects on PAHs in biochar, and shows that: (i) feedstock selection is a critical parameter and (ii) careful matching with

conversion technology is necessary to ensure production of clean biochar, satisfying proposed biochar guideline values [20,21].

Regarding pyrolysis temperature, based on the extensive data set collected in this study, it is not possible to recommend particular pyrolysis temperature/-range for production of biochar with low PAH content. This research showed that pyrolysis temperature alone did not seem to be the main influencing factor of PAH concentration in biochar. The HTT should be considered in conjunction with the specific design of the pyrolysis unit used, as this study indicates that it is the combined effect that affects the PAH concentrations in resulting biochar. Besides HTT, the flow of carrier gas in the pyrolysis reactor has an important effect, and in general, higher carrier gas flow rate resulted in biochars with lower PAH concentrations (independent of temperature, residence time and feedstock). However, even low carrier gas flow rates can be sufficient for production of biochar with PAH concentrations below guideline values, for certain feedstock, HTT and unit design. Overall, it may not be possible to completely eliminate formation of PAHs during biomass pyrolysis, but it is possible to minimize contamination of produced biochar by suitably combining feedstock with conversion unit and operating parameters. In this study, it was shown that "clean" biochar, i.e., with low PAH content, can be produced from a range of feedstock and in different units. Furthermore, this study provides critical information for bringing us one step closer to production of biochar with low PAH contamination from diverse biomass using different production processes.

Acknowledgements

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