Composition of PAHs in biochar and implications for biochar production

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Two additional tables are supplied in excel format
Materials and Methods – details of biochar production

Of the 73 biochars, the production of 55 biochars was described previously which includes (respective references are also indicated in SI Table 1):

- 13 of the 19 marginal biomass-derived biochars described in Buss et al. (2016b)
- all 46 biochars in Buss et al. (Buss et al., 2016a) with 10 of the biochars are already being part of the 13 biochars in Buss et al. (2016b)
- and the six (post-treated) biochars described in Buss et al., 2015, Buss and Mašek (2016) and Buss and Mašek (2014).

In the following paragraphs, the production of the remaining 18 biochars is described:

Two biochars were produced from softwood pellets (SWP I) at 550°C by the Stage II pyrolysis unit but with following modifications to the unit’s discharge chamber: (i) under normal circumstances the discharge chamber, where pyrolysis vapours and solids are separated, was heated up with two heating tapes (HT I at 500 °C and III at 400 °C) and the hot air from the nitrogen streams through the furnace at a rate of 4 L min⁻¹ (Buss et al., 2016b). Here, however, the purge gas flow rate was turned down to 2 L min⁻¹, producing ‘SWP I - 550 - purge 2 L min⁻¹’. (ii) ‘SWP I - 550 - no HT III’ was produced under identical conditions with the exception that, instead of turning down the nitrogen gas flow, HT III was not in use.

Four biochars were produced from sewage sludge (SS I) and anaerobically digested sewage sludge (AD) from Wessex water (Avonmouth, UK) that were both pyrolysed at a HTT of 550 and 700°C in the Stage II pyrolysis unit. During the production of SS I at 700°C the HT I in the discharge chamber was not in use.

Nine biochars were produced, to test the effect of moisture content on PAH content, six of them were already described in Buss et al. (2016a) (untreated samples). Miscanthus chips (MC) were pre-treated to give a range of moisture contents and were subsequently pyrolysed at 450, 550 and 750°C in the Stage II pyrolysis unit. To obtain dry miscanthus chips, the feedstock was oven-dried at 105°C until constant weight. To obtain high-moisture feedstock, tap water was sprayed onto the material. The samples were stored under ambient conditions. On the day the samples were pyrolysed, the moisture contents were: untreated sample 13.4 wt%, dried sample 0.28 wt% and wet sample 23.5 wt% (determined by drying as above).

Nine biochars were produced from miscanthus, to test the effect of ash content on PAH content, six of them were already described in Buss et al. (2016a) (untreated samples). To obtain low-ash biomass, the chips were washed twice in hot tap water and once with cold deionised water over night. To prepare high-ash biomass, K was added in the form of an aqueous solution of potassium acetate, which was evenly sprayed onto the dried miscanthus chips and restored the original moisture content (13.4%). The ash contents on dry weight basis determined by proximate analysis as described in Buss et al. (Buss and Mašek, 2014) (ashing at 900°C for 20 min in air) were: 4.2% for the untreated miscanthus, 3.2% for the washed sample and 7.4% for the potassium-spiked sample. The untreated and two treated samples (all with same moisture content at start of pyrolysis) were pyrolysed at 350, 550 and 750°C with the Stage II pyrolysis unit.
Figure S1: Schematic illustration of contamination of biochars by condensation of high-vapour pressure (here reflected by benzo(a)pyrene) and low-vapour pressure PAHs (here reflected by naphthalene) in the discharge chamber (post-pyrolysis area) of a pyrolysis unit with fixed temperature. In this particular pyrolysis unit, the temperature in the discharge chamber is set through the use of heating tapes that are fixed at the same temperature regardless of the temperature in the pyrolysis zone. PAHs with a higher vapour pressure condense to a higher extent than PAHs with a lower vapour pressure. The content of PAHs in pyrolysis vapours produced at 750°C (B) is much higher than the concentration of PAHs in pyrolysis vapours produced at lower temperatures, here reflected by 650°C (A). The ratio of PAHs in the gas phase vs. PAHs condensed on biochar is the same in (A) and (B) since the temperature in the discharge chamber area is the same. However, there is a higher level of PAHs condensing in (B), because there is a higher content of PAHs in pyrolysis vapours produced at 750°C.
Table S1 and Table S2 are supplied in form of excel files.
Table S3: The ten biochars with the highest non-NAP PAH content and the feature most likely responsible for the high levels.

| biochar                | non-NAP PAH mg kg⁻¹ | PAH total mg kg⁻¹ | NAP mg kg⁻¹ | % | feature most likely responsible for high non-NAP PAHs                                      |
|------------------------|----------------------|-------------------|-------------|---|------------------------------------------------------------------------------------------------|
| SS I - 700 - no HT I   | 207                  | 232               | 25          | 10.8 | Stage II unit - heating tape in discharge chamber not in use                                      |
| MC - 750 - low ash     | 113                  | 168               | 55          | 32.8 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| WC - 750               | 72                   | 100               | 28          | 28.1 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| SWP I - 550 - VC       | 45                   | 53                | 8.2         | 15.4 | Stage III unit - pipe not insulated – backflow of vapours                                        |
| DNX - 750              | 41                   | 67                | 26          | 39.0 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| DW - 750               | 30                   | 48                | 18          | 37.5 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| MC - 750 - high ash    | 23                   | 49                | 26          | 52.9 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| SWP I - 550 - LC       | 18                   | 28                | 9.9         | 35.5 | Stage III unit - discharge chamber not insulated                                                 |
| MC - 750 - wet         | 16                   | 53                | 37          | 70.4 | Stage II unit 750°C - low-temperature discharge chamber                                          |
| WSP II-350-10-0        | 15                   | 52                | 37          | 71.3 | Stage II unit 750°C - low-temperature discharge chamber                                          |
Figure S3: Effect of pyrolysis temperature on TEQ of PAHs (mg kg\(^{-1}\)) in biochars from different feedstocks. The biochars were produced from four feedstocks in the Stage II pyrolysis unit (ADX, *Arundo donax*; DW, demolition wood; MC, miscanthus chips; WC, willow chips) and one feedstock in the Stage III pyrolysis unit (SS, sewage sludge).
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