

## Quantifying the Total and Bioavailable Polycyclic Aromatic Hydrocarbons and Dioxins in Biochars

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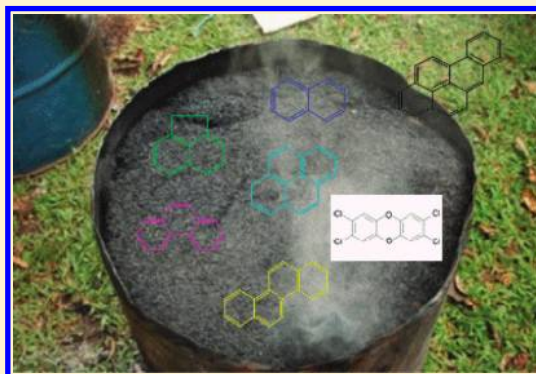
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### Supporting Information

**ABSTRACT:** Biochar soil amendment is advocated to mitigate climate change and improve soil fertility. A concern though, is that during biochar preparation PAHs and dioxins are likely formed. These contaminants can possibly be present in the biochar matrix and even bioavailable to exposed organisms. Here we quantify total and bioavailable PAHs and dioxins in a suite of over 50 biochars produced via slow pyrolysis between 250 and 900 °C, using various methods and biomass from tropical, boreal, and temperate areas. These slow pyrolysis biochars, which can be produced locally on farms with minimum resources, are also compared to biochar produced using the industrial methods of fast pyrolysis and gasification. Total concentrations were measured with a Soxhlet extraction and bioavailable concentrations were measured with polyoxymethylene passive samplers. Total PAH concentrations ranged from 0.07  $\mu\text{g g}^{-1}$  to 3.27  $\mu\text{g g}^{-1}$  for the slow pyrolysis biochars and were dependent on biomass source, pyrolysis temperature, and time. With increasing pyrolysis time and temperature, PAH concentrations generally decreased. These total concentrations were below existing environmental quality standards for concentrations of PAHs in soils. Total PAH concentrations in the fast pyrolysis and gasification biochar were 0.3  $\mu\text{g g}^{-1}$  and 45  $\mu\text{g g}^{-1}$ , respectively, with maximum levels exceeding some quality standards. Concentrations of bioavailable PAHs in slow pyrolysis biochars ranged from 0.17  $\text{ng L}^{-1}$  to 10.0  $\text{ng L}^{-1}$  which is lower than concentrations reported for relatively clean urban sediments. The gasification produced biochar sample had the highest bioavailable concentration ( $162 \pm 71 \text{ ng L}^{-1}$ ). Total dioxin concentrations were low (up to 92  $\text{pg g}^{-1}$ ) and bioavailable concentrations were below the analytical limit of detection. No clear pattern of how strongly PAHs were bound to different biochars was found based on the biochars' physicochemical properties.



### INTRODUCTION

Biochar, the carbonaceous material produced during the pyrolysis of biomass can contribute positively to the mitigation of climate change, in waste management strategies, to energy production, and for soil improvement.<sup>1</sup> When added to soil, biochar can increase pH, increase cation exchange capacity,<sup>2</sup> improve physical properties (such as aggregation, porosity,

aeration and water holding capacity), and adsorb hydrophobic organic pollutants,<sup>3</sup> and therefore ultimately increase soil

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productivity.<sup>4</sup> Biochar is a deliberately generated black carbonaceous material and is not to be confused with atmospheric black carbon particles that have complex effects on the climate,<sup>5,6</sup> (although such particles can be a small byproduct of biochar production). There are also potential complications regarding biochar implementation that remain under investigation. Because of their sorption affinity for organic compounds, biochars can immobilize herbicides in unpredictable ways, which may yield unexpected outcomes when following standard agricultural practices.<sup>3,7,8</sup>

In addition, the inherent nature of the biochar production process makes the formation of polycyclic aromatic hydrocarbons (PAHs)<sup>9–11</sup> likely and the formation of dioxins and furans (PCDD/Fs)<sup>12</sup> possible. During pyrolysis, organic compounds contained in the biomass are partly cracked in to smaller and unstable fragments. These fragments are composed of highly reactive free radicals that combine and lead to more stable PAHs through recombination reactions. Dioxins are mostly formed on solid surfaces when the pyrolysis temperature is 200–400 °C and the pyrolysis times is seconds.<sup>13</sup> Often the presence of chlorine from, for example, salt (NaCl) or polyvinylchloride enhances the observed levels of dioxins.<sup>14</sup> To date there have been no studies to address this important issue in depth.

Both from a regulatory and environmental perspective, using a soil amendment material that contains PAHs and dioxins that pose a threat to the soil is unacceptable. From a regulatory perspective, guideline values of toxin concentrations that should not be exceeded in order to protect the environment exist in many developed countries. For example, benzo(*a*)pyrene, a common toxic PAH has a maximum acceptable soil concentration of 0.6, 3, 2–10, 0.5, 0.15, and 0.1–7.5  $\mu\text{g g}^{-1}$  in Canada,<sup>15</sup> Denmark,<sup>16</sup> Germany,<sup>17</sup> Norway,<sup>18</sup> the UK,<sup>19</sup> and other European Countries.<sup>20</sup> A full list of soil environmental quality standards for PAHs is given in Table S1 in the Supporting Information (SI). A Swedish guideline value for dioxin contamination in nonsensitive land use has been set at 250  $\text{pg g}^{-1}$  soil toxic equivalents (TEQ).<sup>21</sup> Another important legislative point relates to regulation surrounding the reuse of wood ash as a fertilizer as this could be analogous to using some biochars for agricultural improvement. For example, the Finnish Ministry of Agriculture and Forestry stipulates that the highest total PAH content that is permitted in an ash product intended to be spread on forest land is 2  $\mu\text{g g}^{-1}$ . In many Nordic countries large amounts of wood ash is generated annually in forest industry and energy plants and some of this is used as a forest fertilizer. Many of the currently advocated biochars are not from wood but from agricultural waste, therefore it is unclear to what extent these guidelines apply to biochars from wood feedstock.

As useful as these guideline values are, they only give a very rough approximation of actual environmental quality, as they are based on the total pollutant concentration in the soil, and not on the bioavailable concentrations, which are more closely related to risk.<sup>22,23</sup> It is common practice when assessing environmental risk to use the total pollutant concentration as a proxy for the level of contamination, but evidence has been presented to show that bioavailable pollutant concentrations are more relevant.<sup>22,26,27</sup> A bioavailable compound has been defined as one that is freely available to cross an organisms cellular membrane from the medium at a given time.<sup>24</sup> Once this transfer has occurred, storage, assimilation and degradation processes can take place within the organism. In addition, these

bioavailable compounds are more labile and able to leach to the surrounding areas. Currently only one upper acceptable total PAH concentration in biochar of 16  $\mu\text{g g}^{-1}$  has been recommended if the biochar is to be sold and marketed as having desirable properties.<sup>25</sup>

There are very few studies that have evaluated the total and bioavailable concentration of PAHs and dioxins in biochars. Previous research has focused on PAHs (most often the 16 priority PAHs defined by the U.S. Environmental Protection Agency (USEPA)) in the syn-gas<sup>28–32</sup> and bio-oil,<sup>33–36</sup> products. Those studies that have chemically extracted a limited number of biochars<sup>19,37–43</sup> have reported total PAH concentrations ( $\Sigma 16$  USEPA PAHs) from negligible<sup>41</sup> up to 45  $\mu\text{g g}^{-1}$ .<sup>38</sup> The results of these studies are shown in Table 1. The biomass feedstock, pyrolysis temperature<sup>37,44</sup> and the biochar production method<sup>37,39</sup> were important in determining concentrations and distribution of PAHs by ring size. However, the results from these studies were not always clear and consistent. Brown et al.,<sup>37</sup> observed that low-temperature chars contained higher relative concentrations of low-molecular weight, high-vapor pressure PAHs. However, the opposite was observed by Nakajima et al.,<sup>44</sup> as higher pyrolysis temperatures resulted in a dominance of these PAHs. There has only been one study that attempted to quantify the concentration of bioavailable PAHs.<sup>45</sup> A wood chip biochar produced at 450 °C was extracted with a supercritical water method but did not result in any detectable PAHs. Studies have quantified dioxins in biochars produced via gasification and combustion,<sup>46,47</sup> but not via pyrolysis.

To address this important knowledge gap, we measured total and bioavailable PAHs and dioxins in a vast array of biochars. The 59 biochars were produced from 23 different feedstocks (both tropical, temperate and boreal), through slow pyrolysis using various laboratory and in situ equipment (household stoves, traditional kilns, muffle furnaces, double drum, modern slow pyrolysis units) and via fast pyrolysis and gasification.

## ■ MATERIALS AND METHODS

**Biochars.** Biochars were produced from digested dairy manure (DDM), food waste (FW), paper mill waste (PMW), corn stover (CS), wheat straw (WS), rubberwood sawdust (RWSD *Hevea brasiliensis*), lodgepole pine (LPP), pine wood (PW *Pinus ponderosa*), switch grass (SG *Panicum virgatum*), laurel oak (*O Quercus laurifolia*), loblolly pine (*P Pinus taeda*), eastern gamma grass (*G Tripsacum dactyloides*), hardwood (HW), heartland pine (HP), secondary mixed wood, corn cob, rice husk, maize residues, corn stover, sawdust, empty fruit bunches (EFB), and coconut shell (CCS). Biochars were produced at 250–900 °C, commercially, in the laboratory or in the field via slow pyrolysis, fast pyrolysis and gasification. Gasification is a partial oxidation process that aims to optimize the syngas yield in comparison to pyrolysis which is carried out in the almost complete absence of oxygen. The char used here had a residence time in the fluidized bed and thermal cracker (which comprise gasification) of 12.5 s. Slow and fast pyrolysis can be distinguished based on the length of time of the pyrolysis where fast pyrolysis encompasses those processes of only a few seconds. Biochars were ground and sieved to 300  $\mu\text{m}$ . Biochar physicochemical properties and production methods are given in SI Table S2. SI Table S3 shows the time and conditions the biochars were stored under prior to use. This is important to consider because PAHs sorbed to biochar can show variable stabilities and may degrade even in the absence of

**Table 1. Reported Concentrations of USEPA PAHs in Biochars from Different Source Materials, Produced under Different Conditions and Quantified Using Different Methods**

biochar source material	biochar production method	PAH extraction method	PAH concentration ( $\mu\text{g g}^{-1}$ )	reference
wood chips ( <i>Eucalyptus camaldulensis</i> )	wood chips and pea straw were heated at 450 °C for 1 h in a muffle furnace.	extraction for 1 h in an ultrasonic bath with 70 mL heptane. Extracts were filtered through a 0.5 $\mu\text{m}$ pore size PTFE millipore fiber	0.07 0.12 <0.01 (PHEN to B(ghi)P)	39
pea straw ( <i>Pisum sativum</i> ) vegetation fire residues (predominantly leaves and branches of eucalyptus trees)	vegetation fire residues were collected 4 days after the controlled burning of native vegetation along the boundary of a nature reserve in Australia			
Japanese Hinoki cypress ( <i>Chamaecyparis obtuse</i> )	furnace with carbonization temperatures of 400, 600, 800, and 1000 °C held at the final temperature for 1 h	soxhlet extraction with toluene:ethanol 3:7 for 16 h	0.08 – 0.11 0.06 – 0.12 0.08 – 0.15 (all PAHs except NAP)	44
Japanese chestnut ( <i>Castanea crenata</i> )				
Moso bamboo ( <i>Phyllostachys pubescens</i> ) xylem from a freshly cut pitch pine log ( <i>Pinus rigida</i> ) and naturally charred branches of pitch pine	pyrolysis at 450 – 1000 °C at various ramp rates and held at the final temperature for 30 min. Natural charring was via prescribed burning	analysis carried out by the National Institute of Standards and Technology	1.01 – 3.68	37
birch	slow pyrolysis under a heating rate of 1.5 – 2 °C/minute to a final temperature of 600 °C	toluene extraction with sample preparation according to Amtliche Sammlung § 35 LMVG Method L07,00–40	0.005 0.013	40
pine		soxhlet extraction with dichloromethane for 12 h	Negligible	41
<i>Eucalyptus saligna</i> wood, <i>Eucalyptus saligna</i> leaves, paper sludge, cow manure and poultry litter	slow pyrolysis at 400 or 550 °C with and without steam activation. Chars were pyrolyzed at 5 – 10 °C/minute heating rate and a 40 min residence time			
charcoal from the "combustion of bark", particles <150 $\mu\text{m}$	data not given	soxhlet extraction with 70 mL of toluene for 16 h	45	38

light.<sup>48</sup> It is outside the scope of the present paper to investigate this fully, and we chose to deploy biochars as they would be used in practice.

**Total PAH and Dioxin Concentrations in Biochar.** Total PAH and dioxin concentrations were measured via triplicate Soxhlet extractions (0.5 g biochar, 90 mL of toluene, 6 h, 160 °C). Toluene was selected as the extraction solvent as it has previously been identified to give optimal recovery of PAHs from a biochar produced from the combustion of bark.<sup>38</sup> A small scale test was carried out before undertaking the extractions where toluene and toluene:methanol were compared. The highest PAH concentration (1.6  $\mu\text{g g}^{-1}$  for toluene and 1.0  $\mu\text{g g}^{-1}$  for toluene:methanol) and largest recovery of deuterated standard (average of 73% compared to 65% for toluene:methanol) was obtained when toluene was used as the extraction solvent. Prior to extraction, a mixture of deuterated PAHs ( $d_{10}$  phenanthrene,  $d_{10}$  pyrene,  $d_{12}$  benzo(a)anthracene,  $d_{12}$  benzo(a)pyrene and  $d_{12}$  benzo(ghi)perylene) were added to the extraction thimble to monitor the recovery of PAHs or 17 <sup>13</sup>C-labeled dioxins and furans were added prior to clean up to monitor the recovery of dioxins. The recovery of PAHs ranged from 56 to 79% across 178 extractions. Individual PAH compounds were not corrected based on the recovery of just five standards. In some cases recovery was the lowest for the biochars produced at the highest temperatures, although clear trends across all of the biochar types were difficult to observe. The recovery of dioxins ranged from 80 to 97%. Following the Soxhlet extraction, the toluene was reduced to 1 mL, cleaned up with dimethylformamide:water 95:5<sup>49</sup> and then eluted with 10 mL heptane over a precleaned (6 mL heptane) silica gel column (3 cm, 10% deactivated silica gel) topped with sodium sulfate. The solvent was reduced to less than 1 mL and each sample was spiked with polychlorinated biphenyl 77 as an internal standard before gas chromatography mass spectroscopy (GCMS) analysis.<sup>50</sup> Total dioxins were quantified via GCMS following a multilayer silica column cleaning and fractionation on carbon/Celite and a clean up on a miniaturized multilayer silica column.<sup>51</sup>

**Bioavailable PAH and Dioxin Concentration in Biochar.** Polyoxymethylene (POM) passive samplers were precleaned with methanol (1 day), heptane (1 day), Millipore water (1 day) and rinsed with Millipore water prior to use. POM (0.4 g), either 55  $\mu\text{m}$  thick (PAHs) or 17  $\mu\text{m}$  thick (dioxins) were exposed to a mixture of biochar (0.2 g) and water (40 mL spiked at 1% volume  $\text{NaN}_3$  from a 20 g/L stock) for 2 (PAHs) and 6 (dioxins) months, respectively (all carried out in triplicate). During this time, an equilibrium between the sampler and the water is reached and the bioavailable pollutant concentration can be obtained.<sup>52</sup> Equilibrium is achieved more slowly for dioxins<sup>53,54</sup> (4 months for POM-17) than PAHs<sup>55</sup> (10 days for POM-55), hence a thinner membrane was used. After this time, POM samplers were removed, cleaned, extracted with a 20:80 mixture of acetone:heptane for 2 days and the solvent cleaned up using a silica gel column before GCMS analysis. Prior to extraction, the deuterated PAHs were spiked to the solvent to monitor process recovery and the same 17 <sup>13</sup>C-labeled dioxins and furans were used prior to clean up. Extraction recovery was within an acceptable 70–130% range for PAHs and from 87 to 107% for dioxins and furans. In addition, sample blanks were treated in the same way as biochar and POM samples and gave comparable recovery standard results. Bioavailable concentrations were calculated using predetermined POM-water partitioning coefficients specific to each

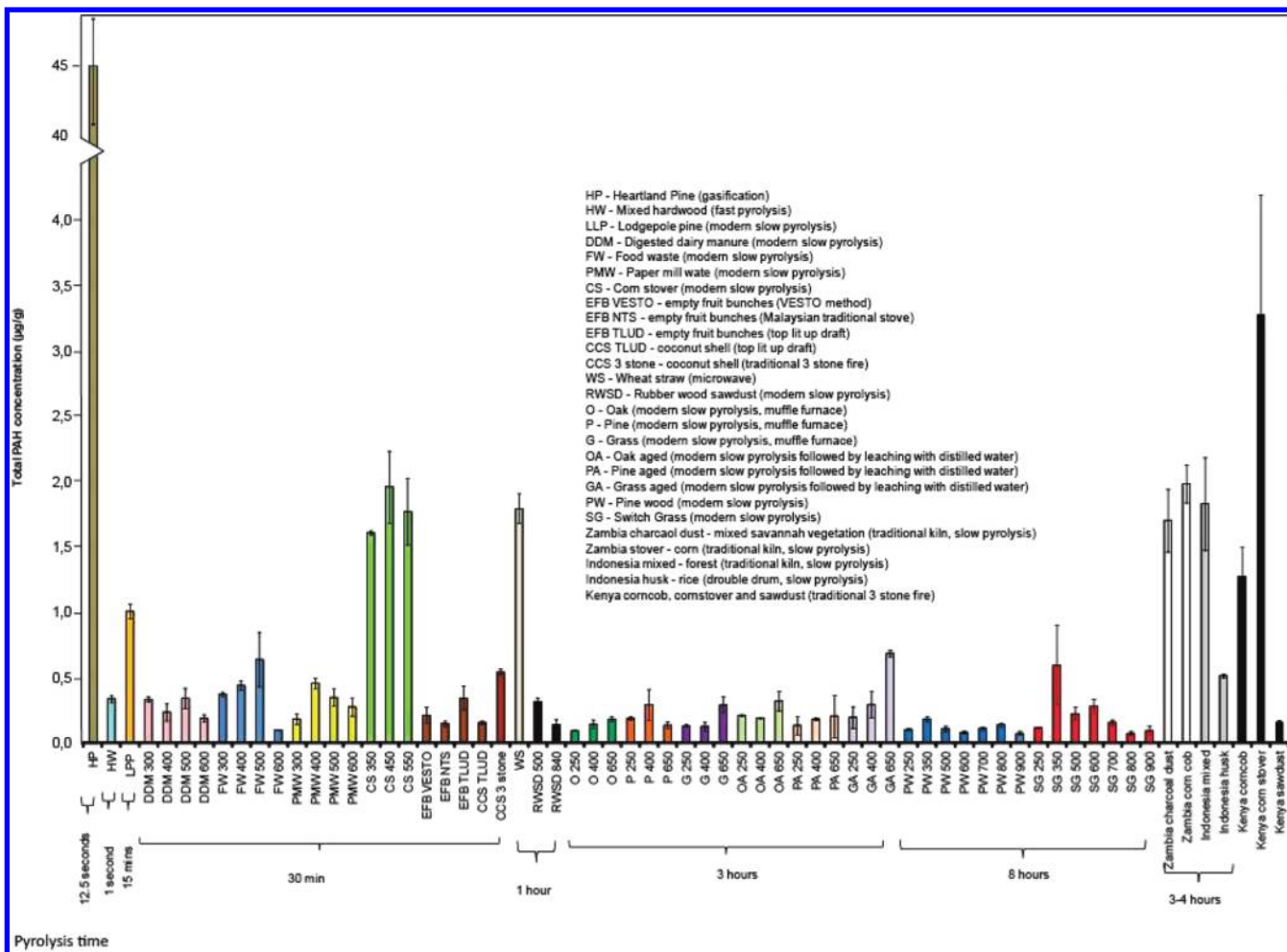


Figure 1. Total PAH concentration ( $\mu\text{g g}^{-1}$ ) in biochars. Bars are grouped by color according to the biochar source material and country of production.

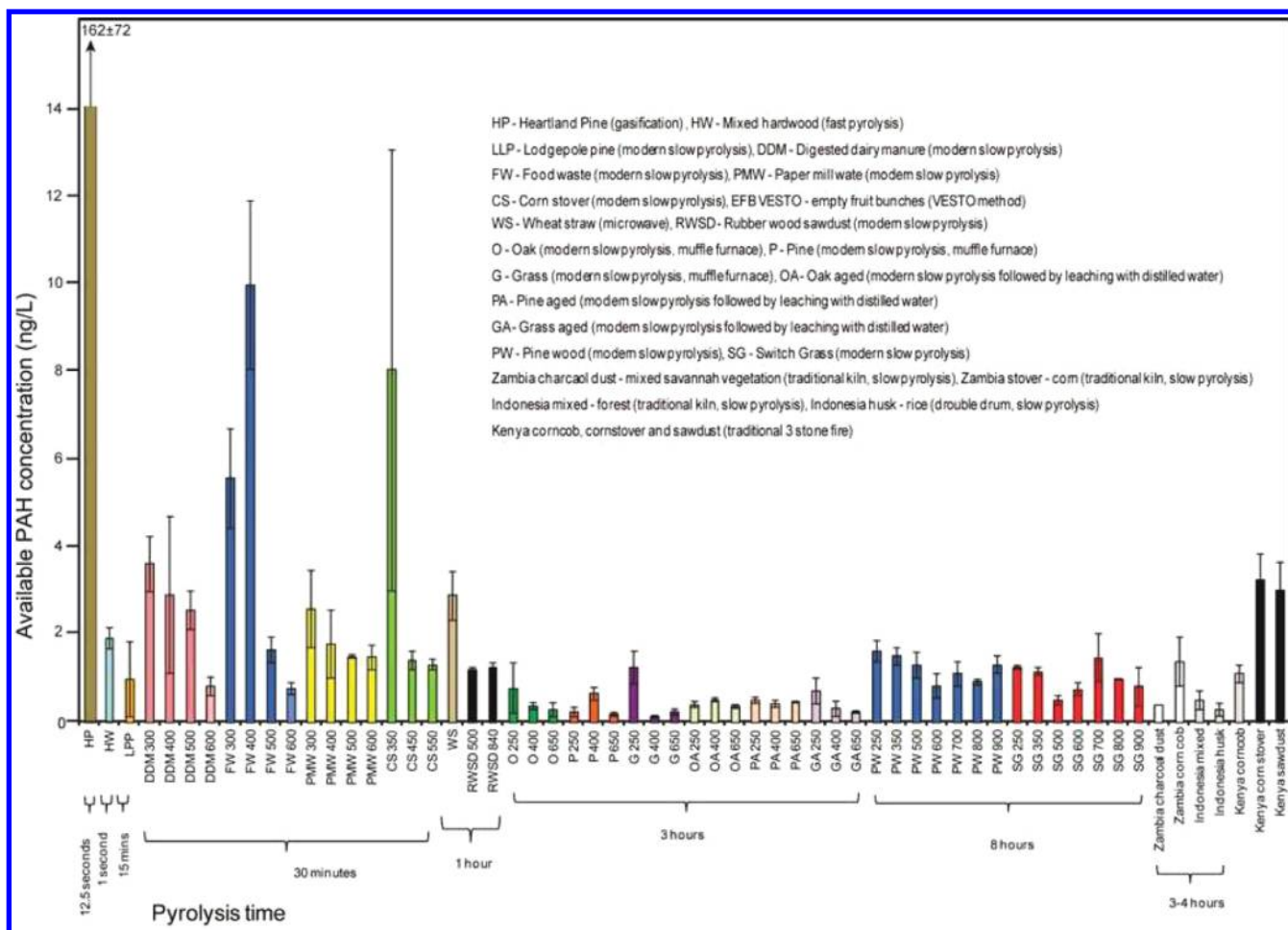
PAH<sup>55</sup> and dioxin<sup>54</sup> compound and the measured POM concentration according to  $C_w = K_{POM}/C_{POM}$ , where  $C_w$  ( $\mu\text{g mL}^{-1}$ ) is the aqueous phase concentration (and is the pollutant concentration that is bioavailable),  $K_{POM}$  ( $\text{mL g}^{-1}$ ) is the POM-water partitioning coefficient and  $C_{POM}$  ( $\mu\text{g g}^{-1}$ ) is the measured POM concentration.

RESULTS AND DISCUSSION

**Total PAH Concentrations.** Figure 1 shows the total PAH concentration (16 USEPA compounds) in the biochars tested, with the commercial and lab samples grouped together and the field samples grouped together. SI Table S4 contains the concentration of individual PAHs in all of the biochars extracted. For the slow pyrolysis biochars, total PAH concentrations ranged from  $0.07 \mu\text{g g}^{-1}$  (switch grass 800 and pine wood 900) to  $3.27 \mu\text{g g}^{-1}$  (Kenya corn stover) and varied with biomass source. These total concentrations we measured fall within the range of concentrations in other biochars reported previously,<sup>19,37–41,43</sup> with the exception of a much higher concentration in a charcoal obtained from the “combustion of bark”<sup>38</sup> (however details are not provided regarding the production and process conditions of this material). Adding biochar at 0.5 to 135 t/ha has been shown to produce positive soil enhancement responses.<sup>4</sup> Even at doses greater than this, with the dose equaling the mass of soil, the levels of introduced PAHs and dioxins from these biochars

would not pose a concern. In general, the biochars with the highest PAH concentrations were those produced in uncontrolled field conditions (Zambia, Indonesia, and Kenya) in traditional kiln, drum, and stove setups. However, Corn Stover 350, 450, and 550 produced under more controlled high-tech pyrolysis conditions contained  $1.5\text{--}2 \mu\text{g g}^{-1}$  total PAHs.

PAH concentrations were affected by pyrolysis time and temperature. Across the suite of biochars produced in more controlled conditions, PAH concentrations are generally higher in biochars pyrolyzed for shorter times. Concentrations decreased in the order: lodge pole pine > digested dairy manure  $\approx$  food waste  $\approx$  paper mill waste > VESTO  $\approx$  TLUD  $\approx$  CCS  $\approx$  rubber wood saw dust > oak  $\approx$  pine  $\approx$  grass > pine wood  $\approx$  switch grass, as the pyrolysis times increased from 30 min to 1, 3, and 8 h. With respect to pyrolysis temperature, in general, the higher pyrolysis temperatures resulted in the lowest total PAH concentrations. The PAH concentration in pine wood 900 was statistically significantly lower (*t* test,  $P = 0.05$ ) than the concentration at all other production temperatures (except 600 °C) and the PAH concentration in switch grass 900 was significantly lower than concentrations at all production temperatures except 800 °C. The greatest PAH concentrations were generally observed among biochars produced in the 350–550 °C range. This observation is in contrast to what has been observed previously (as PAH formation has been observed to increase at higher temperatures<sup>57</sup>).



**Figure 2.** Concentration of bioavailable PAHs ( $\text{ng L}^{-1}$ ) in biochars. Bars are grouped by color according to the biochar source material and country of production.

Artificially aged biochars obtained by successive batch leaching of oak, pine and grass with distilled deionized, UV oxidized water with DOC completely removed, for a period of 100 days in the lab (therefore not exposed to the atmosphere) were also examined. The concentrations of PAHs were greater in the aged materials than the unaged materials (except pine age 250 and pine age 400), and were statistically significant ( $t$  test,  $P = 0.1$ ) for oak 250 and oak age 250, oak 650 and oak age 650 and grass 400 and grass age 400. Leaching likely removed the hydrophilic portion of the biochar source material and possibly ash minerals, but not the PAHs, leaving a PAH-enriched hydrophobic portion. The chemical changes that take place with such aging is the subject of a publication in preparation by Zimmerman et al.

The biochars produced via fast pyrolysis (hard wood) and via gasification (heartland pine) gave different results than for slow pyrolysis. The slow pyrolysis sample had a low total PAH concentration ( $0.3 \mu\text{g g}^{-1}$ ), while the gasification sample had the highest total PAH concentration of any sample, at  $45 \mu\text{g g}^{-1}$ . We speculate that slow pyrolysis results in any PAHs that are produced during the process escaping to the gaseous phase while during gasification and fast pyrolysis, any PAHs that are produced may condense on the biochar material itself. This observation also supports the notion that with greater access to oxygen (gasification is carried out in the presence of some oxygen), the concentration of PAHs is higher.<sup>58</sup> It could also be possible that fast pyrolysis simply allows a higher frequency of

PAH forming reactions. This area requires further investigation, especially if a gasification biochar is being considered in a remediation context, as the level of  $45 \mu\text{g g}^{-1}$  measured here exceeds soil quality guidelines. Clear trends with regards to temperature affecting the concentration of PAHs by ring size were not observed, however over the temperature range of 250–900 °C a comparison of grass (grass and switch grass) and wood (pine wood, oak and pine) biomass sources demonstrated that grass biochars contained five and six ring PAHs around the production temperature range of 350–650 °C while wood biochars were mostly devoid of these larger PAHs (see Figure S1 and discussion in the SI).

To give some additional context to these total PAH concentrations they are compared to the concentration of PAHs in other soil amendments. For example cattle manure slurries can contain  $87\text{--}309 \mu\text{g kg}^{-1}$ , pig slurries  $66\text{--}339 \mu\text{g kg}^{-1}$ , sewage sludge  $1.7\text{--}126 \mu\text{g g}^{-1}$ , and compost  $0.8\text{--}2.7 \mu\text{g g}^{-1}$ .<sup>59–61</sup> The presently studied biochars contain lower total PAH concentrations than these materials.

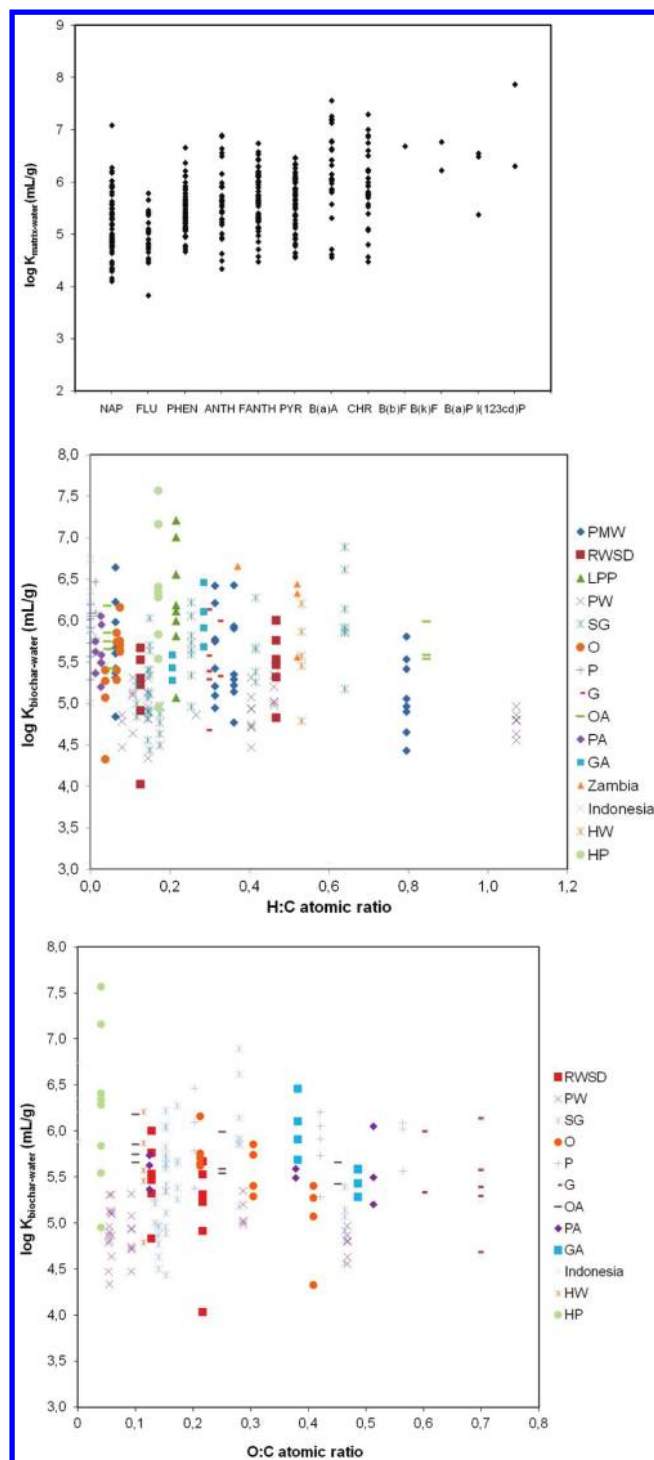
**Bioavailable PAHs.** Concentration of bioavailable PAHs ranged from  $0.17 \pm 0.04 \text{ ng L}^{-1}$  for Pine 650 to  $10.0 \pm 1.1 \text{ ng L}^{-1}$  for Food Waste 400 (Figure 2 and full list in Table S5). The concentration of bioavailable PAHs in the gasification biochar was  $162 \pm 71 \text{ ng L}^{-1}$  with the large standard deviation likely being the result of variable naphthalene concentrations. Concentrations were dependent on the biochar source material, pyrolysis production temperature and pyrolysis time.

Concentrations decreased as production temperature increased. In concurrence with total concentrations, bioavailable concentrations generally decreased with increasing pyrolysis time, with the exception of the pine wood and the switch grass biochars. The concentrations for all of the biochars except the one produced via gasification are in line with the previously mentioned report for wood chip biochar.<sup>45</sup> To add some context to these results they can be compared to the concentration of bioavailable PAHs found in various sediment pore waters.<sup>62</sup> Urban sediments have concentrations of 0.08–342  $\mu\text{g L}^{-1}$  and those impacted by aluminum smelters and manufactured gas plants have concentrations of 0.02–401  $\mu\text{g L}^{-1}$  and 0.1–10867  $\mu\text{g L}^{-1}$  respectively (when considering all 34 EPA PAHs). As biochars have substantially lower concentrations than the lowest of such values, biochar bioavailable concentration can be considered background or trace. One reason why PAHs have a very low bioavailability lies in their mechanism of binding to biochar. Biochar consists of condensed, aromatic sheets that show highly favorable  $\pi$ - $\pi$  interactions with the planar, aromatic PAHs. In addition, part of the PAHs are formed simultaneously with the biochar, and can become occluded and completely locked up within the biochar structure, rendering them completely unavailable. Some of the occluded PAHs maybe nonextractable, even with the exhaustive solvent extraction, and therefore total PAH could be somewhat higher than analyzed.<sup>56</sup>

The correlation of bioavailable concentrations with pyrolysis temperature resulted in significantly negative slopes for the digested dairy manure ( $P = 0.05$ ), paper mill waste ( $P = 0.1$ ), pine wood ( $P = 0.2$ ), and the correlation of all chars was significant at the 0.1 confidence level. A full statistical analysis for the bioavailable concentration versus biochar production temperature is shown in SI Table S6. The concentration of bioavailable PAHs were affected by artificial aging in the opposite direction to the total concentrations, that is, concentrations decrease following aging (statistically significant differences observed following a  $t$  test  $P = 0.05$  for pine 250 compared to pine age 250 and pine 650 compared to pine age 650). There was no clear correlation between PAH distribution by ring size with pyrolysis temperature, pyrolysis time or artificial aging.

**Biochar-Water Partitioning Coefficients.** Biochar-water partitioning coefficients ( $\log K_{\text{biochar-water}} \text{ mL g}^{-1}$ ) were calculated for each PAH by dividing the average biochar PAH concentration for a specific biochar ( $C_{\text{biochar}} \mu\text{g g}^{-1}$ ) by its average concentration of bioavailable PAHs ( $C_{\text{water}} \mu\text{g mL}^{-1}$ ). It should be noted the method used to obtain these values is subject to errors; in  $K_{\text{POM-water}}$  values (maximally 0.2 log units for chrysene), total PAH concentrations (likely 30–40% given the 56–79% recovery) and the GCMS analyses (around 30% given the 70–130% recovery). In total, the errors in  $K_{\text{biochar-water}}$  values can amount to up to around 0.3 log units (factor of 2). However, this error is encountered in the vast majority of  $K_{\text{passive sampler-water}}$  concentrations published to date.<sup>63</sup>

Figure 3 shows the range of values for each PAH compound (Figure 3a) and the relationship between the  $\log K_{\text{biochar-water}}$  values and the H:C and O:C atomic ratios for the biochars (Figure 3b and 3c grouped according to biochar type). The  $K_{\text{biochar-water}}$  values are high which indicates strong PAH sorption to the biochar matrix and thus a low bioavailable concentration. The large range of  $\log K_{\text{biochar-water}}$  values for each PAH, covering 3 orders of magnitude, is indicative of the range of biochar sorption affinities due to the different biomass sources



**Figure 3.** correlation between experimental  $K_{\text{biochar-water}}$  ( $\text{mL g}^{-1}$ ) values (a) for each PAH, (b) with biochar H:C ratio and (c) with biochar O:C ratio.

and production methods. The sorption properties of individual biochars are likely heterogeneous, and different levels of PAH occlusion in the biochar matrix likely also contributed to this large scatter. No meaningful mechanism or parameter could be identified that reduced this distribution.

Extrapolation of these partitioning coefficients to other biochars should therefore be done with great caution. This point is also illustrated in previous studies where  $K_{\text{biochar-water}}$  values for naphthalene and phenanthrene ranged by up to

10 orders of magnitude (e.g., naphthalene  $\log K_{\text{biochar-water}}$  was between  $1.0^{64}$  and  $10.4^{65}$   $\text{mL g}^{-1}$  calculated at an aqueous concentration of  $1 \text{ ng L}^{-1}$ ). SI Table S7 shows the median and range of experimental  $\log K_{\text{biochar-water}}$  values with a comparison to literature data. The  $\log K_{\text{biochar-water}}$  values are larger than  $\log K_{\text{d}}$  values for sediment<sup>62,66</sup> and soil,<sup>67</sup> but smaller than  $\log K_{\text{AC-water}}$  values<sup>68</sup> implying that for biochars the ratio of bioavailable PAHs to total PAHs is lower than for sediments but higher than for AC. The smallest  $\log K_{\text{biochar-water}}$  value measured was 4 (i.e., 0.01% of total PAHs was bioavailable) and the largest was 7.6 (i.e., 0.000001% was bioavailable), with most values being around 5.5. In line with Rey-Salgueiro et al.,<sup>58</sup> and Jonker and Hawthorne,<sup>69</sup> who carried out long-term leaching studies of black carbon materials, these results indicate the biochar could be a long-term stable PAH reservoir. However, this cannot be said with certainty as no long-term or harsh leaching/desorption studies were performed.

Figure 3b and c also illustrate the variability of  $K_{\text{biochar-water}}$  values when related to biochar physicochemical properties (H:C and O:C biochar atomic ratio). These H:C and O:C ratios provide an indication of the chemical differences between the biochars, with higher H:C and O:C indicating a more condensed residue.<sup>70</sup> The sorption capacity of the biochars does not clearly increase for the PAH compounds when H:C and O:C ratios decrease as may be expected as the number of strong sorption sites are expected to increase with increased carbon content.<sup>56</sup>

**Dioxin Concentrations.** The total dioxin concentrations in 14 biochars are shown in Table 2. These values represent the

**Table 2. Dioxin Concentrations in Biochars**

biochar	total tetra-octa chlorinated dioxin concentration (pg/g) <sup>a</sup>	total 2,3,7,8-substituted dioxin concentration (pg/g)	toxic dioxin concentration (pg/g TEQ)
FW 400	92.0	12.2	0.15
FW 600	84.0	7.5	0.16
DDM 600	85.8	8.0	0.13
PW 900	91.5	10.7	0.15
LPP	86.0	10.5	0.18
FW 300		13.3	1.20
FW 500		0.39	0.008
O 650		1.5	0.02
G 650		2.4	0.02
PW 800		0.5	0.005
SG 800		0.8	0.008
SG 900		2.2	0.22
PMW 600		0.6	0.06

<sup>a</sup>Total of 130 toxic and nontoxic congeners.

analysis of only the 2,3,7,8-substituted “toxic” congeners (17 congeners) for eight biochars and a complete analysis of a total of 130 nontoxic and toxic congeners (2,3,7,8 substituted congeners and the 4–8 substituted congeners) for five biochars. SI Table S8 shows the concentration of toxic and nontoxic congeners found in the biochars. In all cases the concentrations of toxic congeners are lower than the Swedish guideline values for dioxin contamination for nonsensitive land use ( $250 \text{ pg g}^{-1}$  TEQ). Food waste, which often has a high salt content, has been shown to contain significant amounts of dioxins.<sup>71</sup> The food waste biochars used here generally contained higher levels of dioxins than the other biochars possibly because the chlorine content was higher (food waste 300 contained 2.9% chlorine,

food waste 600 had 3.4% chlorine and switch grass 800 had just 0.44%).

The concentration of bioavailable dioxins measured with POM passive samplers were below the analytical limit of detection for all of the biochars analyzed, even though the state-of-the-art passive sampling method is capable of measuring dioxin concentrations down to  $1 \text{ pg m}^{-3}$ ,<sup>53</sup> and the analysis of the 130 congeners was carried out at a leading dioxin laboratory. SI Table S9 shows the analytical LOD for the 130 congeners analyzed and SI Table S10 reports minimum biochar-water distribution ratios.

#### Further Use of Biochar in Environmental Management.

Potential negative side effects associated with the use of biochar in agricultural improvement must be addressed before such a practice will become acceptable from a social, environmental and legislative standpoint. Based on the presently reported screening of a large number of mainly slow pyrolysis biochars, some recommendations can be made regarding the production of a biochar that minimizes the risk of exposure to organic toxins contained within the biochar. Biochar source, production temperature, pyrolysis time and aging all affected the level of toxins in the resulting biochars. Producing biochars from woody feedstocks, using higher production temperatures (between 500 and 600 °C) and longer pyrolysis times resulted in lower toxin concentrations. This is encouraging in those cases where a slow pyrolysis method of making biochar can be incorporated into traditional farming practices in order to produce biochar for soil amendment. All of the total and bioavailable PAHs and dioxins in the slow-pyrolysis biochars were below environmental guidelines for the levels of toxins in soils; however the concentrations for the gasification biochar were above these safe levels. Further investigation is needed to determine whether generalizations can be made regarding the production of a safe gasification biochar and slow pyrolysis biochars using feedstocks and production conditions not tested here.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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