Effects of biochar and activated carbon amendment on maize growth and the uptake and measured availability of polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements (PTEs)

Aoife Brennan[1]*, Eduardo Moreno Jiménez[2], José A. Alburquerque[3], Charles W. Knapp[1], Christine Switzer[1]

[1]Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, UK

[2] Departamento de Química Agrícola, Universidad Autónoma de Madrid, 28049 Madrid, Spain

[3] Área de Ecología, Departamento de Botánica, Ecología y Fisiología Vegetal, Universidad de Córdoba, 14071 Córdoba, Spain

* Corresponding author: aoife.brennan@strath.ac.uk

Abstract

With the aim of investigating the effects of carbonaceous sorbent amendment on plant health and end point contaminant bioavailability, plant experiments were set up to grow maize (*Zea mays*) in soil contaminated with polycyclic aromatic hydrocarbons (PAHs) and metals. Maize and pine derived biochars, as well as a commercial grade activated carbon, were used as amendments. Plant growth characteristics, such as chlorophyll content and shoot to root biomass, improved with sorbent amendment to varying extents and contaminant uptake to shoots was consistently reduced in amended soils. By further defining the conditions in which sorbent amended soils successfully reduce contaminant bioavailability and improve plant growth, this work will inform field scale remediation efforts.

Capsule

Biochar and activated carbon reduce PAH and PTE uptake to maize plants to varying extents and improve plant growth.

Keywords: Biochar; PAHs; PTEs; bioavailability; POM

1. Introduction

Contamination arising from industrial and other anthropogenic activities has led to widespread contamination of soils with both inorganic and organic contaminants. This situation has the

potential to affect entire ecosystems as well as to pose risk to human health. Recent advances in the understanding of contaminant behaviour in soils have driven a greater focus on bioavailable fractions of contaminants: how to assess contaminant availability and how to reduce the bioavailable fraction.

The use of carbonaceous sorbents as soil amendments has the potential to reduce contaminant bioavailability (Ahmad et al., 2014; Beesley et al., 2011; Denyes et al., 2013; Hale et al., 2012; Karami et al., 2011; Marchal et al., 2014). This trend comes from a greater understanding of sorption dynamics and organic contaminant relationships with carbonaceous fractions in soils and sediments (Cornelissen et al., 2005; Luthy et al., 1997; Pignatello and Xing, 1995). Both activated carbon and biochar amendments have demonstrated positive results. Plant establishment can be enhanced by amendment and contaminant availability can be reduced (Fellet et al., 2014; Jakob et al., 2012), but results vary widely because of the heterogeneous nature of different biochars.

The environmental impact of the sorbents themselves is another important consideration if remediation practices are to be ultimately sustainable. A life cycle assessment (LCA) study on the use of activated carbons (AC) for sediment remediation found that coal derived AC had a higher environmental footprint than biomass derived AC (coconut waste) when energy and resource use were factored into the analysis (Sparrevik et al., 2011). If the activation step is removed from the process (e.g. steam or phosphoric acid activation to increase porosity and surface area), biochars are also of a lower cost than activated carbons, US$51 - 386 per tonne for biochars (Meyer et al., 2011) compared to around US$2200 per tonne for activated carbon (Ghosh et al., 2011), although prices are highly dependent on market fluxes. These LCA and cost factors highlight the potential for biochar use in remediation, if its efficacy can be established.

Carbonaceous sorbent amendment may assist phytostabilisation as part of an integrated *in situ* remediation approach. Biochar research in the agriculture domain has shown that biochar has the capacity to alter soil physical and chemical properties , leading to potentially beneficial effects on plant establishment and growth (Atkinson et al., 2010; Lehmann et al., 2011). Phytomanagement of

degraded soils aims to establish plant cover that primes ecosystem succession and concomitantly reduces soil erosion and contaminant mobility on a degraded site. Biomass crop generation on degraded sites is a proposed solution for deriving commercial benefit from a phytomanagement approach (Houben et al., 2013; Van Slycken et al., 2013). Maize (*Zea mays*) is a potential crop choice due to its quick growth cycle and high biomass production, having previously been used to investigate contaminant impact on plant health and growth (Lin et al., 2008). However, a greater mechanistic understanding of the effects of amendment on contaminant availability and plant establishment, as well as interactions between contaminants, plants and soils is required before full scale field application.

In this paper, we present results from a 21 day pot trial growing maize in an experiment designed to compare the efficacy of two different biochars and a commercial activated carbon in reducing the negative effects of soil contaminants on plant establishment. Based on the hypothesis that the carbonaceous sorbents would reduce contaminant availability to plants and in the soil and improve plant growth overall, polycyclic aromatic hydrocarbon (PAH) and potentially toxic element (PTE) concentrations were assessed in the soil, soil porewater and plants across treatments.

2. Methods

2.1 Experimental set up

Soil was obtained from a former manufactured gas plant site in the UK and from an abandoned mine site in Spain. Both soils were air dried, sieved to 4 mm and mixed together in the ratio 1:1 in order to obtain a soil with both organic and inorganic contaminants. The resulting soil was classified as a loam (43% sand, 47% silt and 10% clay), with a pH of 7.1 and 7.1% organic matter content. The soil was contaminated with As, Cu and Zn (3604, 276 and 2226 mg kg^{-1}, respectively) and moderate levels of 13 USEPA priority PAHs (those with three or more benzene rings, 68.6 mg kg^{-1}).

Two biochars, derived from the slow pyrolysis of pine woodchip (PB) and maize stubble (MB), were used to amend the contaminated soil in order to investigate feedstock differences and were lightly crushed and sieved to 0.5 - 2mm. Biochars were produced in a pilot plant at 450 °C by the University

of León, with a 15 minute residence time in the reactor (Natural Resources Institute, Spain). Biochar properties are summarised in Table 1. Methods used for characterising the biochar properties are fully described in Brennan et al. (2014). The activated carbon (AC) used in the experiments was in granular form and branded as Norit® GAC 1240 (Norit, USA), with the following properties: bulk density 0.49 g cm^{-3}, specific surface area 1175 m^2 g^{-1},pH 10.3, effective particle size 0.65mm (range 0.42mm-1.7mm) (data provided by manufacturer).

Table 1 Characteristics (on a dry weight basis) of the two biochars (PB: pine woodchip biochar, MB: maize stubble biochar).

Parameters	**PB**	**MB**
Bulk density (g cm^{-3})	0.63	0.24
Liming equivalence (g $CaCO_3$ kg^{-1})	7.4	61.6
pH	7.52[a]	9.81[a]
Electrical conductivity (µS cm^{-1})	256[a]	2945[a]
Organic matter (g kg^{-1})	982	794
C (g kg^{-1})	837	686
N (g kg^{-1})	3.6	7.9
P (mg kg^{-1})	148	2981
K (mg kg^{-1})	1708	22331
Zn (mg kg^{-1})	42	99
Cu (mg kg^{-1})	134	41
As (mg kg^{-1})	1.7	n.d.[b]
∑13 EPA PAH (mg kg^{-1})[c]	18.5	14.5
Specific surface area (m^2 g^{-1})	288	240
Germination index (lettuce, %)	92	66
Germination index (cress, %)	117	92
Cation exchange capacity (cmol kg^{-1})	12.6	52.3
Water-soluble fractions		
Water-soluble organic C (WSC, mg kg	920	2919
Water-soluble inorganic C (mg kg^{-1})	122	1817
Water-soluble N (WSN, mg kg^{-1})	10	41
WSC/WSN	90	71
Water-soluble P (mg kg^{-1})	6	489
Water-soluble K (mg kg^{-1})	256	7632

[a] water extract 1:10 (w/v) [b] n.d. not determined [c]PAHs from flourene to benzo (g,h,i) perylene

Four soil treatments were prepared: contaminated soil only (C), soil plus 3% PB (PB), soil plus 3% MB (MB) and soil plus 3% AC (AC). Each pot was prepared with 500 g (+/- 0.5 g) of soil plus 15 g (+/- 0.01 g) biochar or AC in the relevant treatments and mixed thoroughly manually together and then with 100 g (+/-0.1 g) of pre-cleaned pebbles (size range 20-25mm). The pebbles were added in order to give the soil structure and minimise compaction and anoxic conditions during the experiment. Each mixture was then added to a plant pot containing 100 g of pebbles at the base, watered to 60% of its water holding capacity (WHC), weighed and left to equilibrate for one week before planting.

Eight replicates for each soil treatment were prepared, resulting in a total of 32 plant pots. Within the eight replicates for each soil treatment, four were planted with maize germinants (+P), and four left unplanted (-P) to in order to compare differences between planted and unplanted soil treatment scenarios. As such, results are discussed according to the following treatment groups: C-P, C+P, PB-P, PB+P, MB-P, MB+P, AC-P, AC+P.

Maize seeds were washed and pre-germinated before planting to ensure only viable seeds were used. They were washed by sonicating in 10% sodium hypochlorite for 30 minutes and then in deionised water for 30 minutes. They were then placed on tissue paper moistened with deionised water and several drops of calcium sulphate (1.5 mM) and incubated at 28°C for 72 hours for germination.

After one week, four pots from each of the treatment scenarios were planted with two maize germinants per pot and all pots were moved to a controlled growth chamber for a 21 day period (with a day/night cycle of 13/11 hours, temperature/relative humidity 25°C/40% by day and 20°C/60% by night and light intensity 520µmol m^{-2} s^{-1}). 60% WHC was maintained in the pots throughout the experiment.

2.2 Sampling regime and methods

2.2.1 Plant extraction and analysis

Shoots were cut 1cm above the soil surface. Roots were carefully removed from the soil, shaken gently to remove excess soil and then cleaned by rinsing and then sonicating in deionised water and

gently patting dry with tissue. Plant shoots and roots were weighed for fresh and dry biomass before and after freeze drying. Freeze dried samples were extracted and analysed for PTEs and PAHs according to the methods described in sections 2.2.2 and 2.2.3.

Fresh shoot material was analysed for chlorophyll content. A 5mL solution of 80% acetone was added to 0.1g shoot tissue and ground with a mortar and pestle, which was then filtered into a 15mL centrifuge tube and the process repeated twice more. Chlorophyll *a*, chlorophyll *b* and total carotenoids were then determined by UV spectrophotometry at 663nm, 645nm and 480nm. (Wellburn, 1994)

2.2.2 Polycyclic aromatic hydrocarbons (PAHs)

At the end of the experiment all soil and amended soil samples were sieved to < 2 mm prior to extraction and analysis. Total and freely dissolved PAH concentrations were determined at the end of the experiment for all samples. Total were determined by hexane-acetone extraction (Gomez-Eyles et al., 2011) while freely dissolved concentrations were determined by aqueous equilibrium experiments using polyoxymethylene (POM) samplers (Jonker and Koelmans, 2001).

For total extractions, 4g of soil or soil + amendment with surrogate solution added (fluorene-D10, phenanthrene-D10, fluoranthene-D10, chrysene-D12) was extracted twice with 10mL 1:1 hexane-acetone for 2 hours per extraction on an orbital shaker at 20°C (Gomez-Eyles et al., 2011). The extractant was filtered with Whatman filter paper grade GF/F. Each vial was then rinsed twice with 10mL solvent, the resulting 40 mL was evaporated to 2mL, exchanged to cyclohexane and cleaned up with a silica gel column topped with sodium sulphate (after EPA method 3630C). A 1mL aliquot of the resulting eluate was analysed by GC-MS following addition of internal standards (1-fluoronaphthalene, p-terphenyl-D14, benzo(a)pyrene-D12). GC-MS conditions were as follows: Trace Ultra GC coupled with DSQ II (Thermo Scientific); splitless mode; column DB-5MS 30m x 0.25mm x 0.25µm; initial temperature 45°C, hold 2 min, ramp 2°C per min to 80°C, then ramp 4°C per min to 320°C, hold 5 min.

Aqueous equilibrium experiments were used to measure freely dissolved fractions of PAHs in the soil at the end of the experiment. Polyoxymethylene (POM) passive samplers in strips 76 µm thick (POM-76) (CS Hyde, IL, USA) were shaken with soil aliquots slurried with 40 mg L^{-1} sodium azide solution for 30 days (Gomez-Eyles et al., 2011; Jonker and Koelmans, 2001). After 30 days, POM samplers were cleaned with damp tissue, phenanthrene-D10 surrogate standard was added and the POM was extracted three times with 20mL 1:1 hexane-acetone solution for 24:2:2 hours. The resulting 60mL solution was concentrated to 2mL under nitrogen and cleaned (after EPA method 3630C). The resulting eluate was concentrated to 1mL, at which point internal standard for GC-MS analysis was added as for totals extractions. K_{POM} values used for calculating C_w (where $C_w = C_{POM}/K_{POM}$) were taken from literature derived values for POM-76 (Endo et al., 2011).

Root and shoot samples were extracted three times by sonicating approximately 0.1g of tissue with surrogate solution added (as for total soil extractions) in 20mL 1:1 hexane: acetone for 2, 0.5 and 0.5 hours. Samples were then cleaned and analysed as for totals in soil and POM extractions.

Pure biochar (PB, MB) samples were extracted in triplicate by accelerated solvent extraction (Dionex ASE 350) at 100°C by sequential extraction. 1 g biochar sample was ground to a fine powder, mixed with diatomaceous earth into a 5 mL cell and extracted twice with toluene. Toluene has previously been shown to be a suitable extraction solvent for these materials (Hilber et al., 2012). Surrogate recovery was monitored by the addition of phenanthrene-D10, anthracene-D10, and chrysene-D12. In-cell clean-up was performed using 2g activated silica gel (Sigma Aldrich) at the bottom of the ASE extraction cell in addition to a glass fibre filter (Dionex). Extracts were evaporated under a gentle stream of nitrogen to 1 mL, filtered to 0.2 µm with glass syringes using PTFE syringe filters and analysed by GC-MS as described above.

Surrogate recovery exceeded 62% for all total soil extractions data presented (median 98%, mean 91%, rsd 18%). For POM-76 extractions, surrogate recovery exceeded 73% (median 100%, mean 99%, rsd 7%). For plant extractions, recovery exceeded 64% (median 88%, mean 92%, rsd 27%). Biochar recovery exceeded 72% (median 89 %, mean 84 %, rsd 12 %)

166 *2.2.3 Potentially toxic elements (PTEs)*

167 Following autoclaving (Lozano-Rodriguez et al., 1995) and ammonium sulphate extraction (Vázquez
168 et al., 2008), pseudo-total and extractable As in the treatments were determined by atomic
169 fluorescence spectroscopy (Millennium Excalibur, PS Analytical). Pseudo-total and extractable Cu
170 and Zn were determined by atomic absorption spectroscopy (AA800, Perkin Elmer).

171 For pseudo-total soil concentrations, 0.5 g of soil was transferred into 50 ml autoclave bottles to
172 which 6 ml of MilliQ water, 6 ml of 65% HNO_3 and 4 ml of 33% H_2O_2 were added. The autoclave was
173 set at pressure 1.5 kg cm^{-2} (147kPa) and at temperature 125°C for 30 minutes, samples were left to
174 cool, then filtered and made up to 50 mL (Lozano-Rodriguez et al., 1995).

175 Total plant concentrations were determined by weighing 0.1 g dried plant tissue into 20 ml
176 autoclave bottles to which 2 ml of MilliQ water, 1.5 ml of 65% HNO_3 and 1 ml of 33% H_2O_2 were
177 added. The samples were then autoclaved under the conditions described in the previous paragraph,
178 cooled, then filtered and made up to 5 mL.

179 Extractable PTEs in the soils were determined by extracting 1.5 g of soil with 15 ml of $(NH_4)_2SO_4$ 0.1M
180 in 50 ml tubes and shaking for four hours at 180 rpm. The samples were then filtered and 0.1 ml of
181 HNO_3 was added (Vázquez et al., 2008).

182 *2.3 Statistical and data analysis*

183 Statistical analyses were carried out on SPSS. Data were checked to fit the hypothesis of normality
184 and homoscedasticity; log transformation was applied to data as necessary. Hypotheses were tested
185 with ANOVA. Tukey's post-hoc test was used for mean comparisons of the homoscedastic data.
186 Games-Howell's test was used for the comparisons of heteroscedastic data.

187 BSAFs (biota-soil accumulation factor) were calculated for the PAH concentrations in maize shoots
188 by use of the following equation: $C_{PAH\ shoot}/(C_{PAH\ soil}*f_{OM})$, where shoot PAH concentrations for each
189 treatment were divided by the soil PAH concentrations (from the control soils) normalised to the
190 soil organic matter (OM) fraction (for each treatment) (Jakob et al., 2012).

191 3. Results and discussion

192 *3.1 Soil PAH concentrations*

193 PAHs were grouped according to the number of benzene rings in their structure, due the similar
194 statistical patterns observed from analysis of the individual compounds: 3 ring PAHs (fluorene,
195 phenanthrene, anthracene), 4 ring PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene,
196 benzo(b)flouranthene, benzo(k)flouranthene) and 5/6 ring PAHs (benzo(a)pyrene,
197 dibenz(a,h)anthracene, indeno(a)pyrene, benzo(ghi)perylene). Hexane-acetone extracted
198 concentrations are presented in Fig S1 of Supporting Information (SI). Observed reductions in the
199 amended soils compared to the unamended soil are considered to represent the sorbent bound
200 PAHs, due to the higher black carbon content of carbonaceous sorbents, which affected PAH
201 extractability by hexane-acetone and has also been noted for other solvents (n-heptane) (Beesley et
202 al., 2010; Hale et al., 2012). As such, total PAHs in the soil are considered to be the total derived
203 from the unamended soil extraction plus the PAHs native to the biochars and activated carbon for
204 the relevant amendments, although this sorbent PAH input is not significant.

205 *3.2 Effect of sorbent amendment on PAH bioavailability and plant uptake*

206 POM extractions suggested there were no difference in porewater PAH concentrations between
207 unplanted and planted replicates within amendment groupings (Fig. 1), apart from the 5/6 ring PAH
208 class where MB-P had significantly higher porewater PAHs than MB+P. The results for the 3 and 4
209 ring PAHs is in contrast with the findings by Marchal et al (2014), where the unplanted soil had
210 higher anthracene, fluoranthene and pyrene values than the planted soil, while phenanthrene did
211 not differ between the two scenarios. No data is available from this study for the differences
212 between unplanted and planted amended soils for comparison. A number of possible reasons could
213 account for the differences observed in our study, from the use of spiked soil in the cited study
214 versus the field contaminated soil used in our study, to the different timescales employed, 60 days in
215 the cited study versus 21 days in the current study.

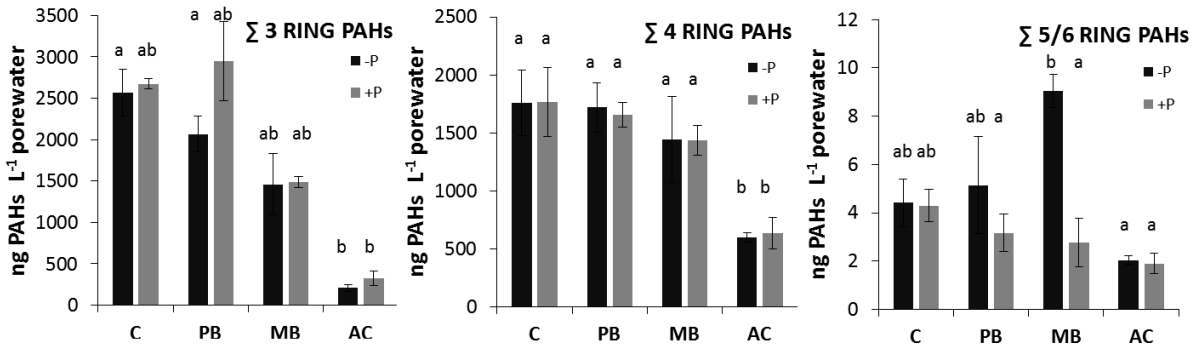
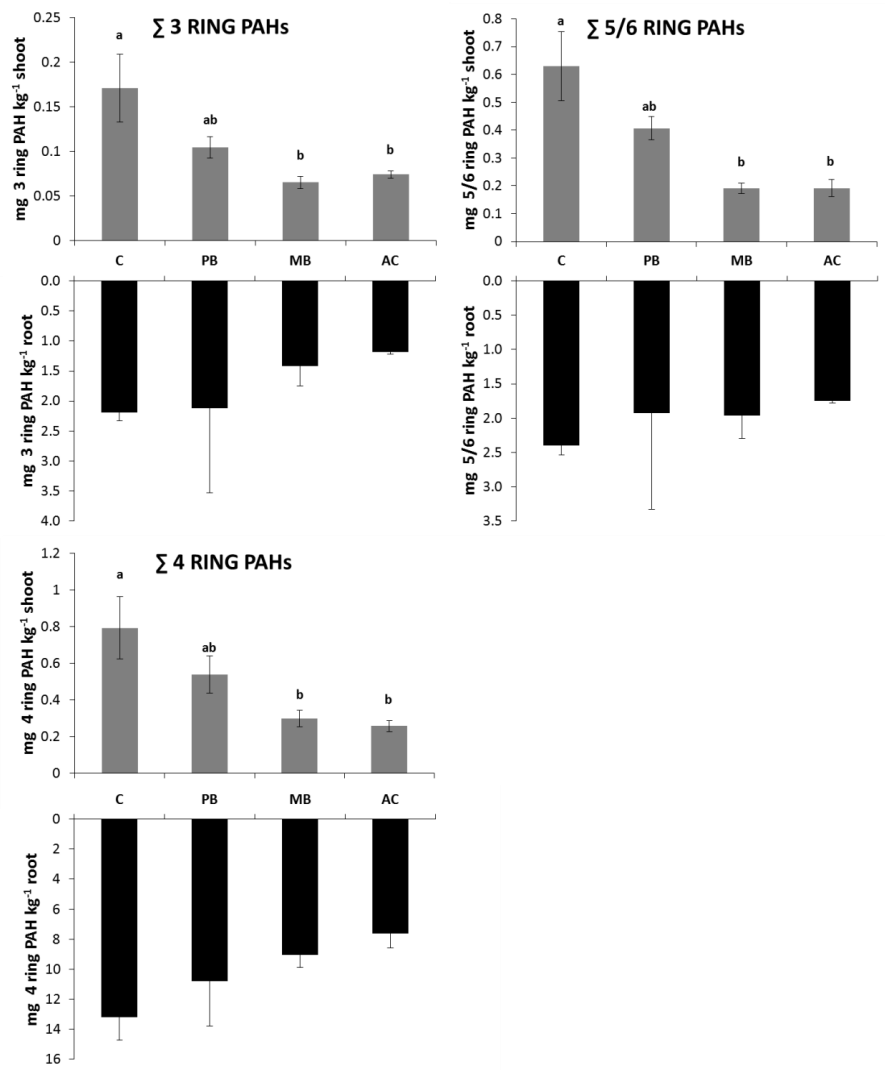


Fig. 1 Porewater concentrations of PAHs in planted (+P) and unplanted (-P) contaminated soil with different biochar treatments, C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Mean ± SE (n=4).Different letters signify statistical differences between treatments at $p<0.05$.

Assessing porewater PAHs according to amendment type, biochar had no effect on porewater concentrations for 3 and 4 ring PAHs, while AC showed a significant reduction in porewater concentrations compared the control. For 5/6 ring PAHs, none of the studied amendments reduced the porewater concentrations. Indeed, the MB-P demonstrated a significant increase in porewater concentrations compared to the controls (Fig 1). While this increase may partly be accounted for by the native PAHs in the MB biochar (Table 1, 14.5 mg kg^{-1} ∑13 EPA PAH), it is unlikely (Freddo et al., 2012). The observed increase is likely to have been caused by other factors and this increase is no longer observed when plants are in the system (see MB-P vs. MB+P in Fig. 1). Possible factors are increased dissolved organic carbon fluxes with biochar addition or 5/6 ring PAH mobilisation due to interactions with inorganic or organic co-contaminants.

The AC results reflect findings from other short term studies where rapidly desorbing fraction of lower molecular weight PAHs bound quickly to the studied GAC amendment compared to the unamended control soil (Brändli et al., 2008), while the heavier 5/6 ring PAHs showed limited differences between controls and amended soils in the short term. The cited study had similar contact times to the current study. Longer contact times using field amended soils have previously

237 highlighted effective reduction of freely dissolved heavier PAHs by GAC (Oen et al., 2011). Sorbent
238 particle size is another potential factor for the biochar and AC carbon results in this study, as
239 powdered activated carbon (PAC) has been shown to be more effective in the short term to mid-
240 term reduction of porewater PAHs (Brändli et al., 2008; Hale et al., 2012). Nonetheless, in the longer
241 term GAC and biochars may be more beneficial for overall effects on plant growth and soil biota,
242 perhaps partially due to the larger particle sizes, although this merits further study (Gomez-Eyles et
243 al., 2013; Jakob et al., 2012; Lehmann et al., 2011)
244 Root PAH concentrations were not significantly altered by PB, MB or AC (Fig 2). PAH shoot uptake
245 was significantly reduced by MB and AC for all PAH classes, but not by PB (Fig 2). It is not clear
246 exactly why PAH shoot uptake was reduced in MB amended soils and not PB amended soils, and
247 demonstrates that shoot uptake may be explained by differences in biochar properties creating
248 differences in soil conditions. Differences in EC, CEC, soluble NPK, bulk densities (Table 1) may be
249 contributing factors, but the influence of parameters not measured, such as particle size
250 distributions, oxygen contents cannot be ruled out (Atkinson et al., 2010). This trend in shoot uptake
251 was supported by the BSAF data, which showed significant reductions in BSAF for MB and AC
252 compared to the control. PB reduced BSAF by 33% (+/-5%) for 3 ring PAHs ($p=0.063$), 25% (+/-9%) for
253 4 ring PAHs ($p=0.202$), 27% (+/-7%) for 5 ring PAHs ($p=0.138$). MB reduced BSAF by 58% (+/-5%) for 3
254 ring PAHs ($p<0.01$), 57% (+/-7%) for 4 ring PAHs ($p<0.05$), 65% (+/-7%) for 5 ring PAHs ($p<0.001$). AC
255 reduced BSAF by 42% (+/-4%) for 3 ring PAHs ($p<0.05$), 44% (+/-14%) for 4 ring PAHs ($p<0.05$), 58%
256 (+/-6%) for 5 ring PAHs ($p<0.001$). These findings demonstrate the heterogeneous results produced
257 by biochars from different feedstocks and the activated carbon data support the results of other
258 studies where BSAFs of bio-relevant PAHs were reduced (Jakob et al., 2012).



259

260 **Fig. 2** PAH concentrations in shoots and roots of maize plants growing contaminated soils with
261 different biochar treatment, C: control, PB: pine woodchip biochar amended soil, MB: maize husk
262 biochar amended soil, AC: activated carbon amended soil. Mean ± SE (*n*=2-4, 2 reps in the case of C
263 and PB root data, 3-4 reps for all other data). Different letters mean statistical differences between
264 shoot groups at $p<0.05$, no root data showed statistically significant differences.

265

266 Fig 3 explores the relationship between actual root uptake (Table S1) and predicted values using
267 POM-derived data. A sorption prediction model proposed by Zhang and Zhu (2009) that accounts for
268 both carbohydrate and lipid PAH partitioning to plant roots was assessed for its efficacy in predicting
269 sorption to the plants used in the current experiment. Gomez-Eyles et al. (2011) used POM-derived

porewater PAH concentrations to apply the model and the same POM approach was used here. However, lipid and carbohydrate fractions were not determined for the maize plants used in this experiment and so lipid and carbohydrate fractions of wheat roots and shoots (Li et al., 2005) were used for the predictions presented (further details in SI). Despite this, the POM derived data provides a fairly accurate assessment of root uptake in the current study with all data falling within one order of magnitude on the log scale. AC PAH uptake to root is slightly under-predicted and PB data is variable (Fig 3).

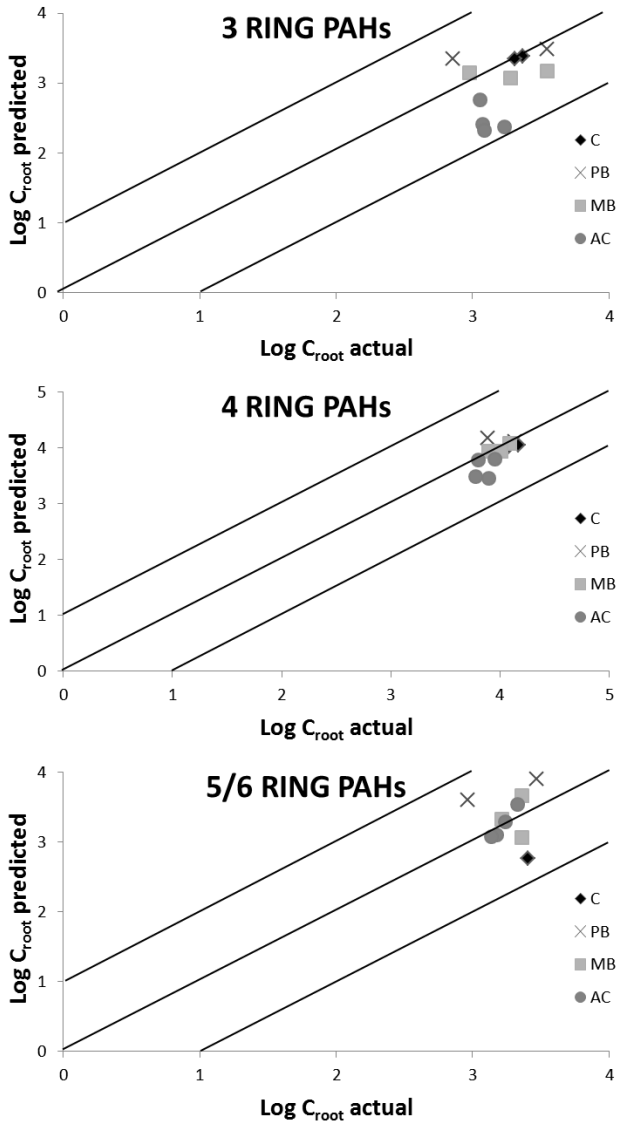


Fig. 3 Predicting root concentrations using POM. Middle line indicates a 1:1 relationship while the lines on either side represent one order of magnitude either way.

AC showed the greatest decrease in porewater concentrations, yet had similar PAH uptake to roots and shoots as MB (Figs 1 and 2). It is not clear why this occurred, as previous studies investigating PAH uptake to plants have demonstrated the importance of water soluble fractions in PAH root uptake and subsequent translocation to shoots (Gao et al., 2011; Gao and Collins, 2009). As suggested by other authors (Gomez-Eyles et al., 2011; Yoshitomi and Shann, 2001) interactions with root exudates may affect uptake and in the current study, differences in root exudate production among treatments may have affected uptake, although this would need to be confirmed by further study. As we have shown (Fig 3), measuring PAHs in soil porewater and comparing to PAH plant uptake may contribute to further understanding of the mechanisms behind PAH uptake to plants, particularly with regards to amended soils. Even if is this does not prove to be the case, using POM remains an inexpensive and straightforward method for monitoring changes in freely dissolved PAH concentrations.

Taking both PAH porewater data and PAH plant uptake data into account, AC displayed consistent improvements compared to controls. Nonetheless, MB proved effective at reducing PAH shoot uptake and no detrimental effect on porewater concentrations was observed in the planted MB soils. PB appears unsuitable for addressing problems with PAH contamination, at least in the short term.

3.3 Effect of sorbent amendment on PTE extractability and plant uptake

Similarly to the PAH data, the ammonium sulphate extractions (Fig 4) highlighted no differences in PTE mobility between unplanted and planted replicates of each treatment group. Across C, PB, MB and AC amendment groups, Cu and As exhibited significant differences in some cases. Amendment had no statistical effect on Zn behaviour in the soil. Cu and As in unplanted PB, MB and AC did not differ significantly to the unplanted control. Similarly for the planted replicates, Cu and As were unaffected by any of the amendments compared to the control. However, when comparing differences to the control across planted and unplanted replicates, planted MB and AC significantly

reduced Cu and As compared to the unplanted control. Unplanted PB had significantly higher concentrations of Cu and As compared to the planted control (Fig 4).

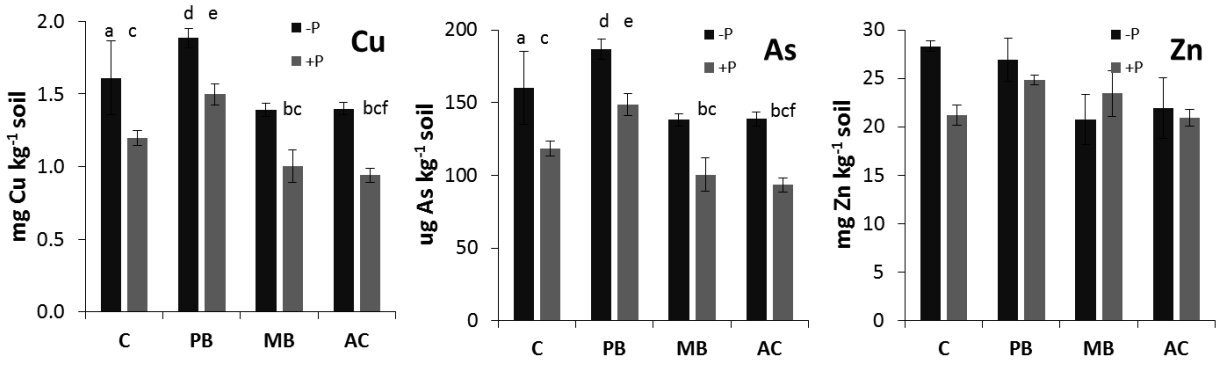


Fig. 4 Ammonium sulphate-extractable Cu, As and Zn in planted (+P) and unplanted (-P) contaminated soil with different biochar treatments, C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Mean ± SE (n=4).Letters signify statistical differences between treatments at $p<0.05$ and are divided into independent group pairs, a vs. b, c vs. d, e vs. f, where no letters are indicated, no differences are observed.

pH did not change across treatments in this study (data not shown), similar to previous work (Brennan et al., 2014), and may explain the small changes in extractability observed. Studies that observed increases in soil pH with biochar amendment also observed increases in porewater As (Beesley et al., 2013) and decreases in porewater Cu linked to increase in amended soil alkalinity over time (Karami et al., 2011). The differences observed compared to our study may be a result of the different amendment approaches used (3% w/w basis in our study compared to a volumetric approach). To our knowledge, no data is available on interactions of AC and PTEs in contaminated soils, despite widespread use of AC for metal removal in the water filtration industry.

Root concentrations of Cu and Zn were not significantly affected by amendment (Fig 5), no data are available for root As concentrations due to insufficient root material for arsenic analysis. All amendments (PB, MB and AC) significantly reduced Cu in maize shoots compared to the control.

Shoot As was significantly reduced in MB compared to the control, but not in PB or AC. Shoot Zn concentrations were statistically unaffected by amendment.

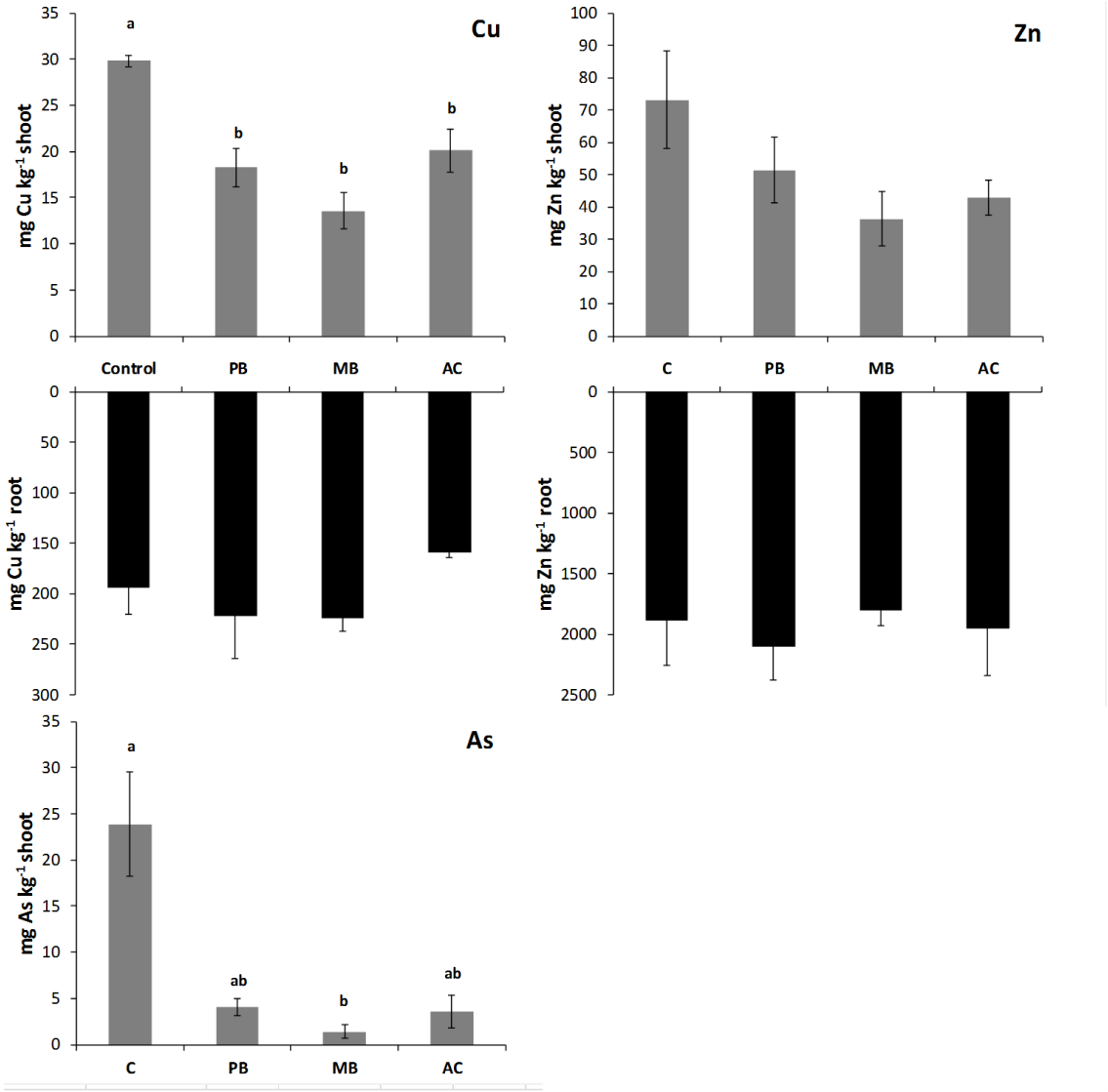


Fig. 5 Cu, As and Zn concentrations in shoots and roots (insufficient sample for root As analysis) of maize plants growing contaminated soils with different biochar treatment, C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Mean ± SE (*n*=3-4). Different letters mean statistical differences between groups at $p<0.05$, where there are no letters, no differences were observed.

334 The zinc data overall is in agreement with other studies with a similar level (<5%) of sorbent
335 amendment (Waqas et al., 2014) while studies with higher biochar quantities observed reductions in
336 zinc availability and plant uptake (Beesley et al., 2010). Reductions in copper extractability and
337 uptake are commonly observed (Karami et al., 2011; Waqas et al., 2014); the reductions in uptake
338 were observed in this study for all amendments but extractability data was more ambiguous.
339 Interestingly, ammonium sulphate extractable As did not increase with amendment in this study.
340 Increases in porewater As have been observed occasionally elsewhere (Beesley et al., 2013) and this
341 is likely related to experiment-specific conditions such as biochar quantity and feedstock properties,
342 as well as changes in soil pH and dissolved organic matter fluxes.

343 *3.4 Plant parameters as affected by sorbent amendment application to contaminated soil*

344 Maize root biomass (dry wt.) was unaffected by PB, MB or AC amendment. However, maize shoot
345 biomass significantly increased ($p<0.05$) for MB and AC compared to the control. This increase in
346 shoot biomass then led to higher shoot: root ratio for these treatments ($p<0.05$) (Fig 6), which
347 follows a similar pattern to the contaminant uptake data. This pattern similarity could be due to
348 different factors for MB and AC amended soils. The physicochemical properties of MB (Table 1)
349 compared to PB, particularly differences in soluble NPK, may have contributed to the improved
350 shoot growth for MB. Meanwhile, the capacity for AC to bind contaminants in soils reduced
351 contaminant availability (as indicated by shoot uptake- Fig 2) in a way not accounted for by the POM
352 extractions (Fig 1), thereby leading to improved shoot growth.

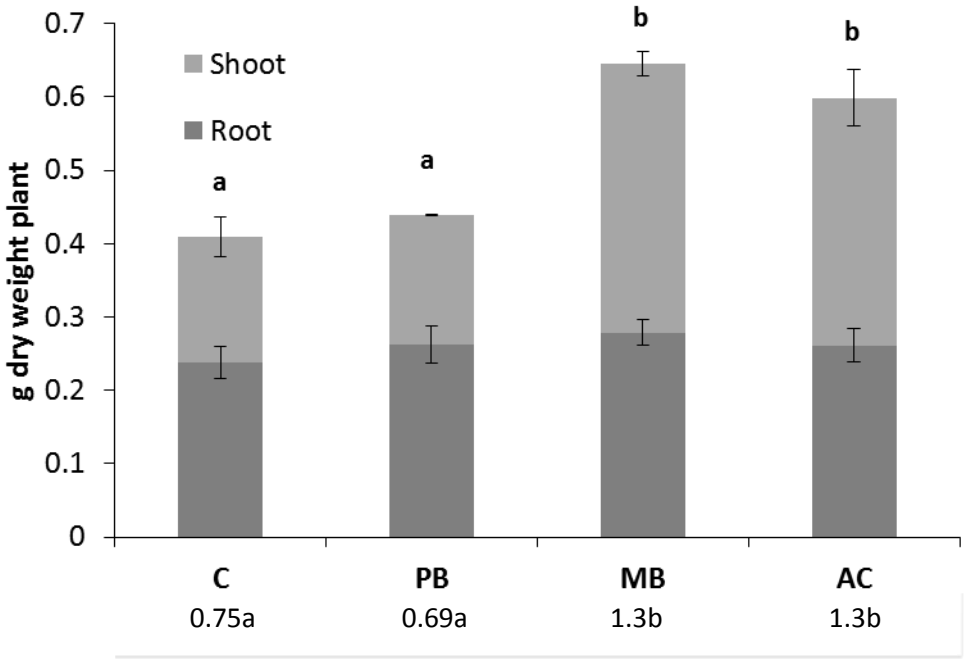


Fig. 6 Plant biomass (g of dry weight per maize plant) in the contaminated soil with different biochars, C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Mean ± SE (*n*=3-4). The shoot: root ratio was calculated and shown on the bottom of the *x* axis. Different letters indicate statistical differences between groups at $p<0.05$.

Chlorophyll *a* has previously been used as a biomarker to assess photosynthesis ability in plants and the presence of both PAHs and PTEs has been shown to inhibit photosynthesis (Kummerová et al., 2006; Oleszczuk, 2008; Wang et al., 2013). Chlorophyll *a* content increased with PB and MB amendment ($p<0.05$) compared to the control, but not with AC amendment. Chlorophyll *b* and total carotenoids were unaffected by amendment. When taken as a total of the different components, the pattern for total chlorophyll was as for chlorophyll *a* (Fig 7). Compared with the contaminant data, where PB has no effect on any PAHs or As compared to the control, this data suggests that chlorophyll content is less affected by reduction in PAH/As availability and PAH/As plant uptake than by the reduction in copper uptake and extractability (see PB data in Figs 4 and 5). Nonetheless, other factors related to differences in PB, MB and AC properties cannot be ruled out.

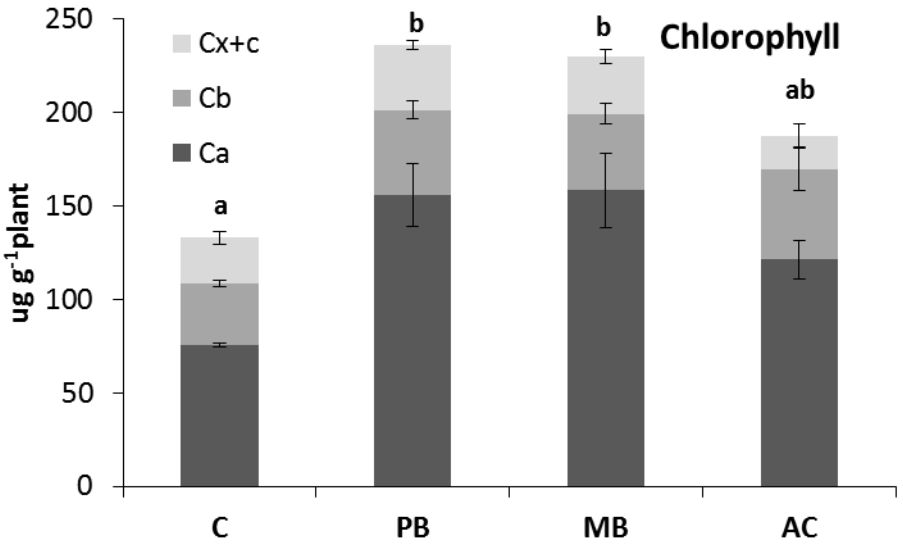


Fig. 7 Chlorophyll *a*, chlorophyll *b* and total carotenoids expressed in ug g^{-1}. Mean +/-SE (n=3-4). Soil treatments correspond to C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Different letters indicate statistical differences between groups at $p<0.05$.

3.5 Implications for using carbonaceous sorbent amendment on contaminated soils

Our findings show how carbonaceous sorbent amendment leads to an overall improvement in the condition of contaminated soils and are supported by data from other studies (Beesley et al., 2010; Fellet et al., 2014; Waqas et al., 2014). However, the short term effects noted in this study are unlikely to reflect sorption kinetics in the longer term, particularly for the most hydrophobic organic contaminants and this should be considered in future studies. Sorbent amendment improved measured plant health parameters and reduced contaminant uptake and extractability to varying extents. Although biomass in PB did not change significantly compared to the controls, plants had higher chlorophyll contents and reduced Cu uptake. MB increased plant biomass parameters and chlorophyll content, consistently reduced contaminant uptake to plants and metal extractability but had ambiguous effects on PAHs in porewater. MB reduced BSAF to the greatest extent. AC improved plant biomass production but did not increase chlorophyll levels, while consistently reducing organic and inorganic contaminant bioavailable fractions and measured uptake to plants.

3.6 Conclusions

Having examined the effect of sorbents in the early stages of plant growth, both biochar and AC warrant further investigation as part of an integrated phytomanagement approach for contaminated sites. Taking LCA considerations into account, these further investigations would benefit from comparisons of coconut shell-derived AC to different biochars in addition to coal-derived ACs. Our results illustrate the suitability of certain types of biochar for aiding plant establishment in degraded soils, giving comparable results to commercial AC. Biochars from different feedstock did produce different results; nonetheless, no detrimental effect was observed as a result of its addition to the soil. Activated carbon is an industry standard product but the choice over which amendment to use, if at all, is likely to be based on site-specific requirements, cost considerations and the need for result consistency. Given the heterogeneous behaviours of the different sorbents with regards to both plant growth and how they affect the mobility of organic and inorganic contaminants, this study highlights the necessity of treatability studies prior to using biochar or activated carbon in the field, in order to fully understand amendment effects prior to field deployment.

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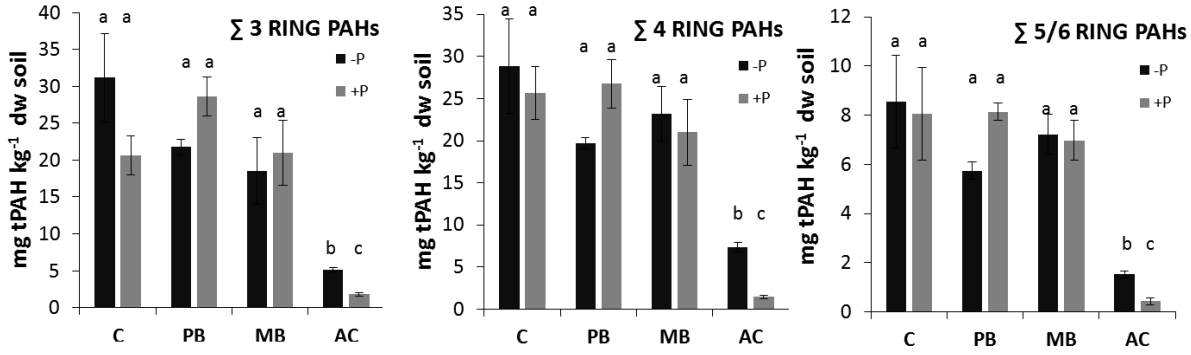

Fig. S1 Hexane-acetone extractable concentrations of PAHs in planted (+P) and unplanted (-P) contaminated soil with different biochar treatments, C: control, PB: pine woodchip biochar amended soil, MB: maize husk biochar amended soil, AC: activated carbon amended soil. Mean ± SE (n=3-4). Different letters signify differences between groups at $p<0.001$. Data were log transformed to fit homoscedasticity for post hoc tests.

Table S1 Averaged values for individual PAH compounds in porewater (POM) and roots (n=3-4 POM, n=2-4 roots). Individual data points from +P data were used to compare root predictions using POM to actual root data.

	FLU	PHE	ANT	FLUA	PYR	BaA	CHR	BbF	BkF	BaP	IdP	DbA	BghiP
Freely dissolved concentrations in planted pots (± SE, expressed as ng L^{-1})													
C+P	560 ± 79.2	1542 ± 91.7	572 ± 42.2	1071 ± 173	644 ± 120	27.5 ± 3.04	18.4 ± 3.47	6.62 ± 1.01	1.55 ± 0.22	3.82 ± 0.65	0.19 ± 0.05	0.053 ± 0.014	0.237 ± 0.05
PB+P	741 ± 172	1631 ± 232	576 ± 83.8	1011 ± 64.2	579 ± 37.3	38.1 ± 14.7	22.3 ± 7.41	4.58 ± 1.16	1.17 ± 0.3	2.48 ± 0.6	0.24 ± 0.06	0.074 ± 0.008	0.366 ± 0.13
MB+P	293 ± 27	904 ± 63.4	291 ± 21.7	853 ± 70.6	548 ± 48.8	17.0 ± 4.22	14.4 ± 2.18	4.00 ± 1.48	0.993 ± 0.37	2.25 ± 0.82	0.205 ± 0.08	0.067 ± 0.028	0.241 ± 0.07
AC+P	30.9 ± 9.66	213 ± 56.3	77 ± 21.8	372 ± 82.6	241 ± 49.1	10.7 ± 2.25	8.20 ± 2.00	2.72 ± 0.62	0.681 ± 0.15	1.52 ± 0.35	0.153 ± 0.03	0.052 ± 0.014	0.180 ± 0.03
Root concentrations (± SE, expressed as µg kg-1)													
C+P	173 ± 10.8	1551 ± 93.4	465 ± 33.8	5113 ± 819	3677 ± 562	1324 ± 55.7	1388 ± 5.2	1195 ± 31	522 ± 55	955 ± 14.8	567 ± 55	228 ± 51	645 ± 41.2
PB+P	211 ± 162	1412 ± 824	498 ± 322	4091 ± 976	3139 ± 822	1174 ± 358	1441 ± 332	881 ± 351	383 ± 159	744 ± 368	494 ± 283	182 ± 100	505 ± 258
MB+P	145 ± 59.6	967 ± 199	304 ± 74	3003 ± 263	2367 ± 179	1262 ± 19.7	1050 ± 162	955 ± 152	418 ± 47.6	769 ± 134	483 ± 60.1	195 ± 0.8	515 ± 42.8
AC+P	88.7 ± 5.05	787 ± 3.3	305 ± 26.3	2601 ± 283	1945 ± 208	885 ± 85	955 ± 166	877 ± 146	379 ± 69.7	700 ± 83.7	429 ± 74.1	171 ± 37.3	446 ± 75

Method used to predict root values from POM data

K_{lip} and K_{ch} values were taken from the SI section of Gomez Eyles et al (2011). Lipid and carbohydrate fractions used (1.1% for lipids and 15.3% for carbohydrates in the roots of wheat plants) were taken from Li et al (2005).

The equation used for calculating predicted data was taken from Zhang and Zhu (2009):

$$C_{root\text{-}predicted} = C_{free}(f_{lip}K_{lip} + f_{ch}K_{ch})$$

Where $C_{root\text{-}predicted}$ is the predicted root concentrations, C_{free} is the freely dissolved calculation measured by POM, f_{lip} is the lipid fraction (0.011 in this study) K_{lip} is the lipid partitioning coefficient, f_{ch} is the carbohydrate fractions (0.153 in this study) and K_{ch} is the carbohydrate partitioning coefficient

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