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RESEARCH ARTICLE

Reduced bioavailability and plant uptake of polycyclic aromatic hydrocarbons from soil slurry amended with biochars pyrolyzed under various temperatures

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Abstract

Biochar has high potential for organic pollutant immobilization due to its powerful sorption capacity. Nevertheless, potential risks may exist when biochar-sorbed organic pollutants are bioavailable. A direct plant exposure assay in combination with an organic solvent extraction experiment was carried out in this study to investigate the bioavailability of polycyclic aromatic hydrocarbons (PAHs) with the application of pine needle biochars pyrolyzed under different temperatures (100, 300, 400, and 700 °C; referred as P100–P700 accordingly). Biochar reduced solvent extractability and plant uptake of PAHs including naphthalene (Naph), acenaphthene (Acen), phenanthrene (Phen), and pyrene (Pyr), especially for three- and four-ring PAHs (Phen and Pyr) with high-temperature biochar. Plant uptake assay validates with organic solvent extraction for bioavailability assessment. Sorption of PAHs to biochars reduced plant uptake of PAHs in roots and shoots by lowering freely dissolved PAHs. Aging process reduced the bioavailability of PAHs that were bound to biochar. High pyrolysis temperature can be recommended for biochar preparation for purpose of effectively immobilizing PAHs, whereas application of moderate-temperature biochar for PAH immobilization should concern the potential risks of desorption and bioavailability of PAHs.

Keywords Biochar · Polycyclic aromatic hydrocarbons · Bioavailability · Plant uptake · Aging · Pyrolysis temperature

Introduction

The sorption of hydrophobic organic contaminants (HOCs) to geosorbents is an important process restricting their transport in natural environment, being largely affected by carbonaceous materials with great sorption capacity (Beesley et al. 2011; Chen et al. 2012c; Khan et al. 2013). Sorbents including humic acids, biochars, black carbon (such as soot and charcoal), activated carbon, surfactants, single-walled carbon nanotubes (SWNT), and engineered natural organic sorbents can reduce the bioavailability of HOCs in aqueous media, soils, and sediments (Chen et al. 2008c; Dettenmaier et al. 2009; Lu and Zhu 2009; McLeod et al. 2008; Millward et al. 2005; Smith et al. 2009; Tang et al. 2007; Wei et al. 2016; Wen et al. 2009; Yu et al. 2009). Among these materials, biochars can be easily obtained from various feedstocks (such as crop residues, livestock manure, sewage sludge, and paper mill waste) without sacrificing economic or environmental benefits. Biochars can effectively immobilize organic contaminants (Cao and Harris 2010; Oleszczuk et al. 2012; Waqas et al. 2015), unequivocally ascribed to the abundant surface functional moieties, large specific surface areas (SSA), and carbonized structure (Jeffery et al. 2015; Lehmann 2007; Lehmann et al. 2011; Renner 2007; Sun et al. 2013a). Physiochemical properties of biochar as determined by the pyrolysis temperatures are main factors controlling the sorption mechanisms of organic pollutants (Chen et al. 2012b).

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As a typical HOC, polycyclic aromatic hydrocarbons (PAHs) generated from incomplete combustion, pyrolysis of fossil fuels, and biomass are prevailing in surface water, sediments, and soils and are potentially harmful to human health due to their high bioaccumulation, potential mutagenic and carcinogenic properties (Cai et al. 2008; Chen et al. 2004; Jeong et al. 2008; Wang et al. 2016; Wang et al. 2011). High hydrophobicity of PAHs determines their main distribution in solid phase (organic matter for instance) rather than aqueous phase, and normally higher hydrophobicity is possessed by PAHs with more aromatic rings (Han et al. 2014). PAHs in soil matrix tend to go through an aging process, which considerably reduce their extractability and mobility (Luo et al. 2012; Ogbonnaya et al. 2014; Olson et al. 2008). Biochar can be used as soil conditioner for PAH remediation, benefitting from its high efficiency, low cost, and environmental friendly features. Biochar can enhance the adsorption of PAHs, particularly for biochars obtained at high temperature (Chen et al. 2008a; Chen et al. 2008b). Such biochars generally contain abundant functional groups that can effectively immobilize PAH molecules, such as aromatic CH that is capable of engaging in π-π and hydrogen bonding with PAH molecules (Chen et al. 2008a; Chen et al. 2008b). Strong sorption of PAHs usually leads to less availability for repartition of the compounds into environment, reducing the extractability and bioavailability, thereby reducing potential risks of PAHs (Alexander 2000; Cornelissen et al. 2005; Hauck et al. 2007; Northcott and Jones 2001; Yu et al. 2009).

However, PAHs that are sorbed into carbonaceous materials can possibly be bioavailable for plant uptake and microbial degradation (Wen et al. 2009), especially under changing environmental conditions (Cai et al. 2014; Marques et al. 2016; Noyes et al. 2009). This will raise the query on potential risks of PAHs sorbed on biochar. Therefore, it is essential to evaluate the bioavailability of PAHs following biochar immobilization. Both bioassays and chemical extraction have been used to assess PAH bioavailability in soils and sediments (Dettenmaier et al. 2009; Doick et al. 2005; Khan et al. 2013; Reid et al. 2000; Styrishave et al. 2008; Tao et al. 2006; Yang et al. 2008). Our study with simultaneous tests of both the assays aimed to evaluate the bioavailability and risks of PAHs that are immobilized in soil slurry with biochar amendment.

In this study, PAHs with different molecular weights were immobilized by pine needle biochar that were produced under different pyrolysis temperatures, and organic solvent extraction combined with bioassay (rice seedling uptake) was conducted to investigate the bioavailability of PAHs in soil and biochar. The primary objectives of this study were to investigate the following: (1) the bioavailability of PAHs to plants in soil slurry with biochar amendment and (2) the influence of aging process on the bioavailability of PAHs that are immobilized by biochar.

Materials and methods

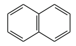
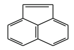
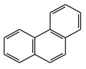
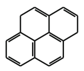
Chemicals, biochar and soil preparation, and rice seeding cultivation

Naphthalene (Naph), acenaphthene (Acen), phenanthrene (Phen), and pyrene (Pyr) with purities greater than 98% were purchased from Aldrich Chemical Co. (St. Louis, MO, USA), and selected physicochemical properties of the compounds are listed in Table 1. Uncontaminated soil, without records of crop residues burning or industrial input, was collected from Huajiachi campus of Zhejiang University. The soil was air-dried and passed through a 0.154 mm sieve. Biochars were produced via pyrolyzing pine needles under oxygen-limited conditions at different temperatures (100, 300, 400, and 700 °C; referred as P100, P300, P400, and P700, respectively), biochar characters as described in our previous studies (Chen et al. 2008a). To remove the ash components and labile fractions of biochar so as to focus on the function of stable fractions (Sun et al. 2013b), biochars were treated with HCl (1 mol L^{-1}) for 12 h to remove the ash components, then filtered, washed with distilled water (18 MΩ cm) until pH in aqueous phase got neutral, oven-dried at 80 °C for 24 h, then passed through 0.154 mm sieve to guarantee a homogeneous mixing during application. Increased total pore volume and surface area for biochar were found along with an increased pyrolysis temperature (Chen et al. 2008a). Rice seeds were germinated in vermiculite, and then, rice seedlings were transferred to a tray containing the half-strength Hoagland solution (Table S1), to grow in a climate chamber at 25–30 °C during daytime (16 h) and at 20–25 °C during night (8 h). Three weeks later, when the seedlings grew up to approximately 15 cm in height, plants that were healthy and without injuries were used for plant uptake experiment.

Solvent extraction of biochar-immobilized PAHs (with and without aging)

Stock solution of PAHs was prepared by separately dissolving Naph, Acen, Phen, and Pyr into acetonitrile, respectively, reaching concentrations of 6000, 1000, 400, and 40 mg L^{-1} for experimental use. Biochars (P100, P300, P400, and P700) with a dry weight of 20 mg were, respectively, added into the glass vial, and 100-μL PAH solutions of each were applied on biochars. After acetonitrile evaporated in dark under the fume hood, five different solvents were used to extract PAHs that were immobilized with biochars. The solvents were as below: (1) dichloromethane, (2) mixture of acetone and hexane with a volume ratio of 1:1, (3) mixture of acetone and hexane with a volume ratio of 1:3, (4) mixture of toluene and methanol with a volume ratio of 1:4, (5) mixture of toluene and methanol with a volume ratio of 1:6, with corresponding solvents serving as blank controls. Three replicates were set up for each treatment. Triplicate solution with the same amount of PAH

Table 1 Selected physico-chemical characters of naphthalene (Naph), acenaphthene (Acen), phenanthrene (Phen), and pyrene (Pyr) (Chen et al. 2004)

PAHs	Molecular Formula	Structural Formula	Molecular Weight (g mol^{-1})	C_s (25 °C) [a] (mg L^{-1})	K_{ow} [b]
Naph	$C_{10}H_8$		128.2	31.02	1.95×10^3
Acen	$C_{12}H_8$		154.2	3.47	8.4×10^3
Phen	$C_{14}H_{10}$		178.2	1.00	2.8×10^4
Pyr	$C_{16}H_{10}$		202.3	0.13	8.0×10^4

[a] C_s: aqueous solubility at 25 °C

[b] K_{ow}: octanol-water partition coefficients

addition but without biochars served as control for the calculation of the recovery rate of PAHs. Samples were extracted with ultrasonication by 10 mL solvents for three successive extractions (each for 30 min). The extraction was collected, evaporated nearly to dryness using a rotary evaporator, re-dissolved in 5 mL of hexane. The aging experiment of PAHs immobilized with biochar was conducted at 4 °C for different aging periods (respectively, at 0, 7, and 30 days, all following 24-h equilibration after the application of biochars), with the same amount of PAHs and biochars as that in the successive extraction experiment. Reagent blank and control (without biochar) were set up as well. After the corresponding aging time, dichloromethane (10 mL) was introduced to extract PAHs from biochars, with ultrasonication for 60 min. The extracting solution (both in solvent extraction and aging experiments) was then centrifuged at 3600×*g* for 15 min, cleaned up through 2.5 g silica gel columns with 15-mL mixtures of hexane and dichloromethane (1:1, *v*/*v*), and then evaporated and re-dissolved in acetonitrile to a final volume of 4 mL. After filtration through 0.22-μm filters, PAH concentrations were measured with a high-performance liquid chromatography (HPLC, Agilent 1200, USA) equipped with a reverse phase XDB-C18 column (4.6 × 150 mm) and a fluorescence detector (FLD) using acetonitrile-water (90:10, *v*/*v*) as the mobile phase with a flow rate of 1 mL min^{-1}. The excitation wavelengths for Naph, Acen, Phen, and Pyr were 240, 240, 244, and 237 nm, while the emission wavelengths were 360, 360, 360, and 385 nm, respectively. Detection limits for Naph, Acen, Phen, and Pyr with HPLC-FLD were, respectively, 97.3, 52.7, 9.82, and 1.05 pg (Table S2).

Biochar amendment to reduce plant uptake of PAHs (plant uptake experiment)

Half-strength Hoagland solution was used for the cultivation of rice seedlings in this experimental section (Table S1). Phen and Pyr were separately added into 500 mL of the half-strength Hoagland solution in conical flasks, reaching an initial concentration of 1.00 and 0.1 mg L^{-1}, respectively. For different treatment setup, quantitative soil (10 g), biochars (100 mg, P100-P700), and biochar-soil mixtures (100 mg biochar: 10 g soil) with biochar application rate of 1% were then separately brought into the corresponding solutions. One set of blank was with the same Hoagland solution and the cultivation of rice seedlings yet without any PAH addition, while a second set of blank (reagent blank) was with the Hoagland solution and PAHs (Phen and Pyr), yet without the cultivation of seedlings. The control was designed with Hoagland solution, PAHs, and rice seedling cultivation, yet without biochar or soil application. Treatments were all with rice seedlings cultivated in Hoagland solutions and with PAH application (in the same concentrations as in blank and control), respectively, with soil, biochar P100, soil + P100, P300, soil + P300, P400, soil + P400, P700, and soil + P700. Three replicates were set up for each experimental group.

The cultivation solution for the above treatments was homogenized and equilibrated for 24 h; then, 2-mL equivalents were diluted with acetonitrile (1:1, *v*/*v*) and filtered through 0.22-μm filters to measure the initial concentration of PAHs (Phen and Pyr) with HPLC (C_{e24h}). After the measurement of biomass, rice seedlings (with loose banding with Teflon tapes on the lower part of the shoots) were transplanted into the conical flasks through a drilled hole in the cap, keeping the roots just immerged below the surface of the solution. The growing conditions in the climate chamber were the same for the cultivation of seedlings as described in the mentioned section. Fourteen days later, plants were harvested, rinsed with distilled water, separated between roots and shoots, and biomass was measured. PAH exposure period was defined as the time interval between the transplant and the harvest of seedlings. Meanwhile, cultivation solution was transferred into 8-mL vials and centrifuged at 3600×*g* for 15 min to collect the supernatant. The residual

PAHs in solutions were filtered through 0.22 μm filters, diluted with acetonitrile (1:1, *v*/*v*), and quantified with HPLC. Soil slurries were transferred into 40-mL vials and centrifuged at 2025×*g* for 15 min. The supernatant was removed, and the solid phases were left under natural drying in dark. Dichloromethane was then used to extract the PAHs from the solid phase, following the same procedures as described before in the aging experiment. The residual PAHs in plant tissues (roots and shoots) were extracted by ultrasonication for 30 min with 10-mL mixtures of acetone and hexane (1:1, *v*/*v*) for three successive extractions (Singh et al. 2011). The extractions were collected and evaporated nearly to dryness using rotary evaporator, then re-dissolved in 5 mL of hexane, followed by a clean-up procedure through a 2.5-g silica gel column with 15-mL mixture of hexane and dichloromethane (1:1, *v*/*v*). Samples were evaporated again and re-dissolved in acetonitrile to a final volume of 4 mL. After filtration through 0.22-μm filters, PAH concentrations were quantified with HPLC. To control the extraction efficiency, certain amount of external standard (mixed Phen and Pyr dissolved in acetonitrile) was added to the media, following with the same extraction and detection procedures as that for samples, giving average recovery rates between 89.92 and 110.39% for water, soil, roots, shoots, and biochars (except for low recovery rates for P700 due to strong sorption, Table S3).

Statistics

Differences of PAH concentrations in solution, solid phase, and plant tissues between the treatments with biochars, extraction solvents, aging time, and plant cultivation were calculated with the software SPSS 18.0 (IBM, NY, USA). One-way ANOVA and multiple comparison with the least significant difference (LSD) were carried out at the significance level lower than 0.05. Figures were drawn with the software SigmaPlot 10.0 (Systat Software Inc., CA, USA).

Results and discussion

Solvent extractability of biochar-immobilized PAHs

Interactions between PAHs (Naph, Acen, Phen, and Pyr) with biochars produced under different temperatures (P100, P300, P400, and P700) resulted in different extraction efficiencies, as presented in Fig. 1. PAHs (Naph, Acen, Phen, and Pyr) sorbed on low- and moderate-temperature biochars (P100, P300, and P400) were completely extractable (nearly 100%), regardless of the molecular weight of PAHs, indicating high availability of PAHs on those biochars. On the contrary, high-temperature biochar (P700) had stronger sorption of high molecular PAHs (Phen and Pyr) than low molecular PAHs (Naph and Acen), resulting in extraction efficiencies, respectively, ranging from 21.14 to 61.41% for Phen and from 6.56 to 15.69% for Pyr (depending on the solvents) and nearly 100% for Naph and Acen. Extractability for Phen from P700 was dependent on the varieties of organic solvents. The acetone-hexane mixture (1:1, *v*/*v*), acetone-hexane mixture (1:3, *v*/*v*), dichloromethane, toluene-methanol mixture (1:4, *v*/*v*), and toluene-methanol mixture (1:6, *v*/*v*), respectively, achieved ordinally higher extraction rates for extracting Phen from P700 (respectively, being 21.14 ± 1.00, 25.85 ± 1.16, 41.97 ± 1.30, 58.67 ± 2.97, and 61.41 ± 1.21% of the initial applied Phen, Fig. 1c). Variations in extraction efficiencies of Phen with different organic solvents can be related with their polarity. The extractability of Phen was generally higher than Pyr for each corresponding extraction.

The sorption of organic pollutants on biochar is an important process as it controls their fate and environmental risks. The solvent extraction is the desorption and redistribution process of labile PAHs in organic matters from soils and sorbents, and the extractability of PAHs from organic matters (as geosorbents) depends on molecular weight of PAHs, surface properties of the sorbents, fractions of organic matter, and the interaction between the sorbents (biochar) and PAH molecules (Khan et al. 2013; Luo et al. 2012). Biochar characters that are determined by pyrolysis temperatures, including chemical composition, functional groups, pore volumes, and specific surface areas (SSA), play vital roles on the sorption of PAHs (Chen et al. 2012b). High pyrolysis temperature generated higher SSA of biochar, resulting in higher adsorption capacity of P700 than that of P100, P300, and P400 (Chen et al. 2012c). The sorption capacity of biochar can be ascribed to different mechanisms for biochars obtained at different temperatures (Chen et al. 2008a). Sorption of PAHs to low-temperature pyrolyzed biochars is determined by the partition to the noncarbonized biopolymers within biomass (Cao et al. 2009; Chen et al. 2008a), and the re-partition of PAHs from biochar to the solvents results in the extractability. Biochars produced at higher temperatures have more unsaturated functional groups that are capable of engaging in π-π bonding to PAHs with more aromatic rings, thereby resulting in high adsorption efficiencies of PAHs to biochars (Ahmad et al. 2014; Chen et al. 2008a). The sorption capacity of HOCs with a geosorbent is related with the aromatic and (reversely) polar constituents of the sorbent, that nonpolarity and aromaticity of biochar enhanced the sorption of Phen at low concentration (Abelmann et al. 2005; Kang and Xing 2005; Wang et al. 2013).The polarity of pine needle biochars, indicated by atomic (O + N)/C, decreased when pyrolysis temperatures increased, while the aromaticity the other way around (Chen et al. 2008a). Increasing aromaticity and decreasing polarity of biochar produced under high temperature (P700) can result in an increase of adsorption processes (Abelmann et al. 2005; Chen et al. 2008a). Although high immobilization of PAHs with high temperature biochars while low immobilization with low temperature biochars was found, it should be noticed

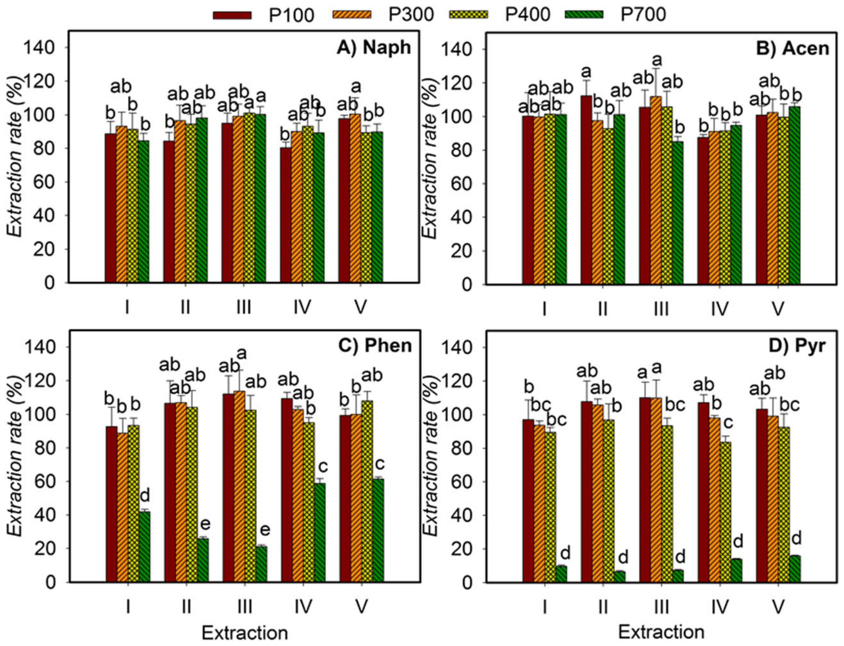


Fig. 1 Extraction rate of naphthalene (Naph), acenaphthene (Acen), phenanthrene (Phen), and pyrene (Pyr) from biochars produced under 100, 300, 400, and 700 °C (referred as P100, P300, P400, and P700) by different solvents: (I) dichloromethane, (II) acetone and hexane (1:1, *v*/*v*), (III) acetone and hexane (1:3, *v*/*v*), (IV) toluene and methanol (1:4, *v*/*v*), and (V) toluene and methanol (1:6, *v*/*v*). Extraction rates were calculated as the percentages of the extractable amount of PAHs relative to that from control (without biochar). The same letter above the bars indicates no significant differences between groups (both the solvents and biochars compared together) at *p* level lower than 0.05 according to one-way ANOVA and LSD analysis

that the relationship between the production temperature and adsorption capacity of biochars can be non-linear (Lamichhane et al. 2016). In addition to adsorption, pore filling and diffusion effects in high-temperature biochar can contribute to the immobilization of PAHs with more aromatic rings as well (Vithanage et al. 2016).

Aging of biochar-immobilized PAHs

The extraction rates of Naph, Acen, Phen, and Pyr from biochars (P100, P300, P400, and P700) at different aging periods (0, 7, and 30 days) are shown in Fig. 2. Although only extracted for one time, the extraction efficiency of PAHs in the aging experiment (at 0 day) was comparable with that of three successive extractions introduced shortly (0 day) after the adsorption (the extraction experiment mentioned above), with respect to the same organic solvent (dichloromethane) (Fig. 1). Aging of PAHs at 7 and 30 days with the application of biochars was found, which became more remarkable with the treatment of P700 for Naph and Acen, with the extraction rate, respectively, reduced from 88 ± 12 to 57 ± 4% and from 100 ± 12 to 70 ± 1% at 30 days interval compared with the initial content (Fig. 2a, b). The lowest extractability for Phen and Pry was found with P700 treatment at day 30, where extraction rates were reduced to 31 and 8%, respectively (Fig. 2c, d). The extraction rates of Phen and Pry with P700 treatment were much lower than that of Naph and Acen, and the immobilization of Phen and Pry was faster and more stable than that of PAHs with lower molecular weight (Naph and Acen). Regardless of biochar types, the extractability of PAHs notably decreased along with aging period (from 0 to 30 days), suggesting a descending PAH bioavailability due to biochar sorption. It can be speculated that aging will likely result in a reduced PAH concentrations in soil pore water (Oleszczuk et al. 2012).

Diffusion of organic pollutants to geosorbents is a rate-limiting step for their sorption (Chen et al. 2012b). Along with the aging process, freely dissolved PAH content would be reduced with the diffusion of PAHs from soil matrix to micropores of biochar, which is hypothesized as pore filling mechanism (Oleszczuk et al. 2012). Meso- and micropores in soil and biochar play a significant role in rapid diffusion of PAHs from labile to stable domains, and the diffusion process may slow down for PAHs with relatively higher molecular weight and higher K_{ow} (lower water solubility) (Luo et al. 2012), because these PAHs may need longer time to reach the complete equilibrium, which can result in slow mass transfer (Oleszczuk et al. 2012). Biochar properties may affect the aging process of PAHs as well because those properties determine the interaction mechanism between biochar and PAHs (Ren et al. 2016). For low-temperature biochars, the sorption rate of PAHs is determined by the polarity of biochars and the partition of PAH molecules to the uncarbonized biopolymers remaining from biomass, while for high-temperature biochar, rapid

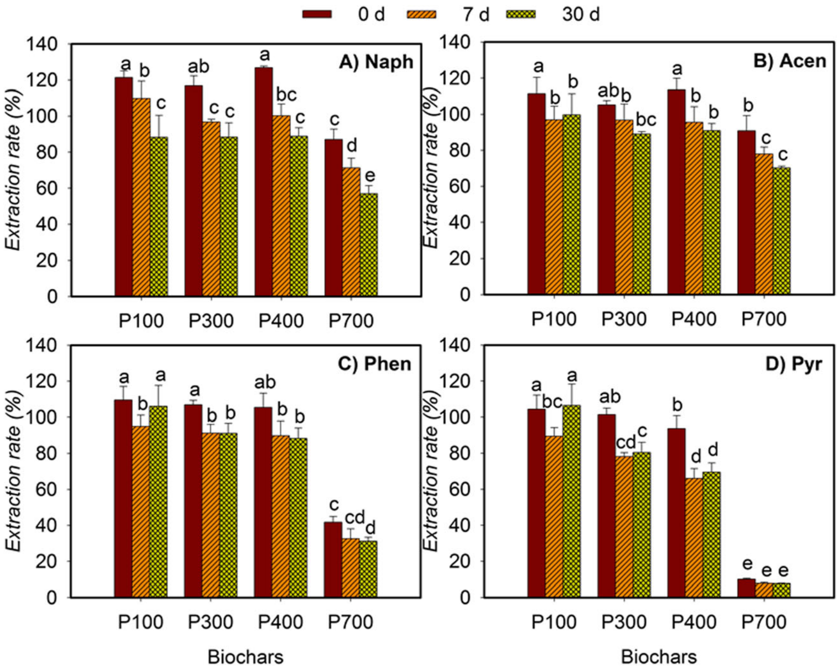


Fig. 2 Extraction rate of naphthalene (Naph), acenaphthene (Acen), phenanthrene (Phen), and pyrene (Pyr) by dichloromethane, from biochars produced under 100, 300, 400, and 700 °C (referred as P100, P300, P400, and P700) at different aging times (0, 7, and 30 days). Extraction rates were calculated as the percentages of the extractable amount of PAHs relative to that from control (without biochar). The same letter above the bars indicates no significant differences between groups (both aging time and biochars) at *p* level lower than 0.05 according to one-way ANOVA and LSD analysis

adsorption can be obtained, ascribing to higher surface areas and well-developed micro- or nano-pores within the highly carbonized biochar (Chen et al. 2008a; Chen et al. 2012b). In addition, humic substances, microbial activities, and plants may affect the aging and dissipation process of PAHs with biochar application in natural environment (Liu et al. 2015).

Reduced plant uptake of PAHs from soil amended with biochars

Sorption of PAHs to soil, biochars, and soil-biochar mixtures. The exposure to PAHs did not lead to visible damage or death of rice seedlings in this study, indicating no lethal toxicity from the PAH dose or the applied biochars. There is possible risks of biochars concerning of the release of certain PAHs produced at different temperatures (Fabbri et al. 2013; Freddo et al. 2012; Kusmierz and Oleszczuk 2014; Lehmann 2007; Oleszczuk et al. 2014; Quilliam et al. 2013). Some study revealed that PAHs produced consequently with biochar pyrolysis were dependent on the pyrolysis conditions and feedstock types, that biochars produced from wood and rice hull by slow pyrolysis yield low PAH concentration (10 and 0.02–0.45 μg g^{-1}, respectively, for the former and the latter) (Fabbri et al. 2013; Liu et al. 2015). To eliminate the impact of PAHs possibly released from biochars, we extracted bicohars to test their PAH contents. Nevertheless, PAHs extracted from biochars per se (P100, P300, P400, and P700) were negligible in this study (nearly the same as that in the reagent blank, results not shown).

The extractability of PAHs from solid phase (biochar and soil) after 14-day cultivation of rice seedlings are shown in Fig. 3. After short-term exposure (14 days), larger amount of PAHs were sorbed to pure biochars produced at higher temperatures, so was the case for soil-biochar mixtures (Fig. 3). Less PAHs could be extracted from high-temperature pure biochars (P700), which is quite significant for Pyr (Fig. 3b). Biochar characteristics as function of pyrolysis temperatures dominate the respective sorption behaviors (Chen et al. 2008a). Soil-biochar mixtures with P100 and P300 immobilized more PAHs than the corresponding pure biochars, attributing to a synergy effect, possibly due to the dominant partition effect that is noncompetitive (Chiou et al. 2015). However, soil caused an attenuation effect to the sorption of PAHs to high-temperature pure biochars (P400 and P700), suggesting that soil-biochar mixtures suppressed the PAH sorption to the corresponding pure biochars. This finding is in coincidence with our previous study where actual sorption of Phen to soil-biochar mixtures was lower than the predicted values that was simply a sum of the both (Chen and Yuan 2011). Therefore, we speculate that when adsorption dominates the sorption effects, for biochars produced under relatively high temperature, soil organic matter (e.g., humic acids) may compete with PAHs and occupy the adsorption sites, causing the attenuation effects of sorption. When activated carbon is applied into soil for organic pollution amendment, this attenuation phenomenon can possibly be even greater, since although activated carbon with its carbonized structures potentially has stronger adsorption capacity of organic pollutants than some biochars, meanwhile, its adsorption sites can be more easily occupied by soil organic matters (Chen et al. 2008a; Koltowski et al. 2016).

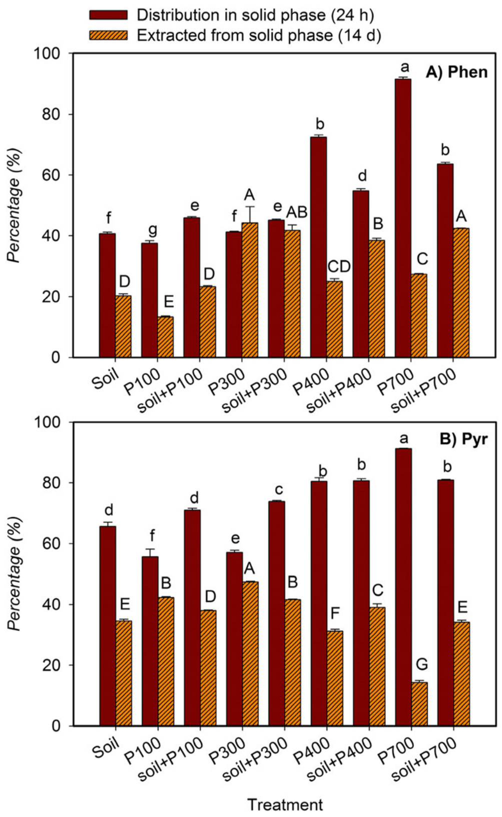


Fig. 3 Extraction of phenanthrene (Phen) and pyrene (Pyr) from solid phase after cultivation of rice seedlings for 14 days, in comparison with Phen and Pyr concentrations in solid phase 24 h after PAH application (which were calculated by the deduction of PAH concentrations detected in solution from the applied total concentrations). Biochar and soil were applied either separately or mixed (as indicated by soil, P100, soil + P100, and so on) in the solution with PAHs (Phen and Pyr). The same letter above the bars indicates no significant differences between groups at *p* level lower than 0.05 according to one-way ANOVA and LSD analysis, with small letters for distribution in solid phase at 24 h and capital letters for extraction from solid phase at 14 days

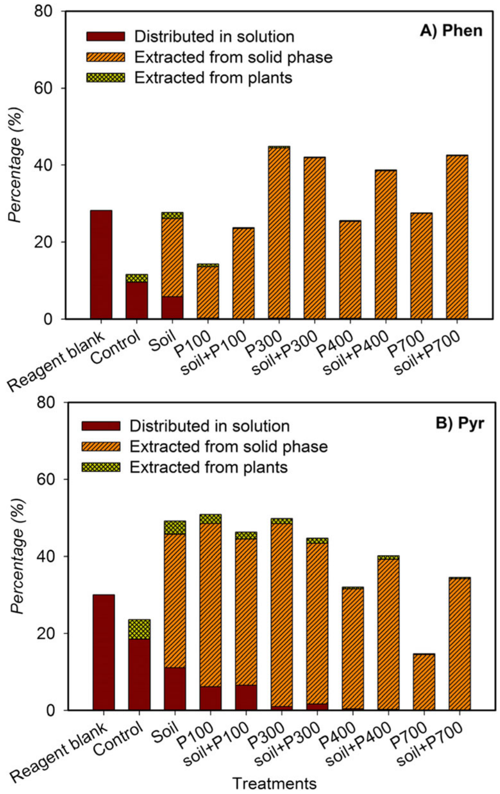


Fig. 4 Distribution of phenanthrene (Phen) and pyrene (Pyr) in solution, and that extracted from solid phase and plants, after 14-day cultivation of rice seedlings. Reagent blank was included to evaluate the evaporation of PAHs during cultivation. Control refers to plant seedlings grown in the solution with PAHs but without biochar or soil. Biochar and soil were applied either separately or mixed (as indicated by soil, P100, soil + P100, and so on)

Distribution of PAHs in solution, solids, and plants

Distribution of PAHs in solution, solid phase, and plants after 14-day cultivation were exhibited in Fig. 4. With the application of soil, biochars, and soil-biochar mixtures, a large number of PAHs were clearly presented in solid phase, while very little PAHs distributed in solution or sorbed by plants, indicating significant decrease in bioavailability of PAHs to plants. Soil and biochars both contribute to the immobilization of PAHs. Furthermore, moderate- and high-temperature biochars (P400 and P700) resulted in less distribution of PAHs (especially Pyr) in solution and less uptake by plants, namely less mobility and bioavailability. This can be attributed to an enhanced adsorption of PAHs with relatively higher molecular weight to biochar that are more completely carbonized. Besides the evaporation, non-extractable PAHs were possibly formed in this soil-biochar-plant system, and such PAH components may block some pore structures in biochars and soil-biochar mixtures, since great gaps of PAH concentrations exist between that in the solid phase after 24 h equilibration and that extracted from the solid phase after 14 days (especially for P400 and P700) (Fig. 3). The amount of non-extractable PAHs increased with the presence of biochars pyrolyzed at higher temperatures. Low extraction efficiency of PAHs from biochars P700 (Fig. 1) indicates greater inaccessibility of PAHs from solid residues to plants. This portion of non-extractable PAHs in solid phase is considered to be caused by aging.

Reduced plant uptake of PAHs from soil amended with biochars PAHs were accumulated in plant tissues through the solution-root-shoot system during hydroponic cultivation (Fig. 5). Biochar treatments reduced the distribution of free Phen and Pyr after 24 h equilibration, with variations observed for different biochar types (Fig. 5). Plant uptake of Phen and Pyr by roots, and the subsequent translocation to shoots, was dependent on different biochar types as well (Fig. 5). Rice seedlings dominantly accumulated PAHs in roots rather than in shoots, and they took up larger amount of Phen than Pyr (Fig. 6). Linear correlations between PAH concentrations in solution (equilibrated for 24 h after PAH application) with that in plants (both in roots and shoots), as well as close linear

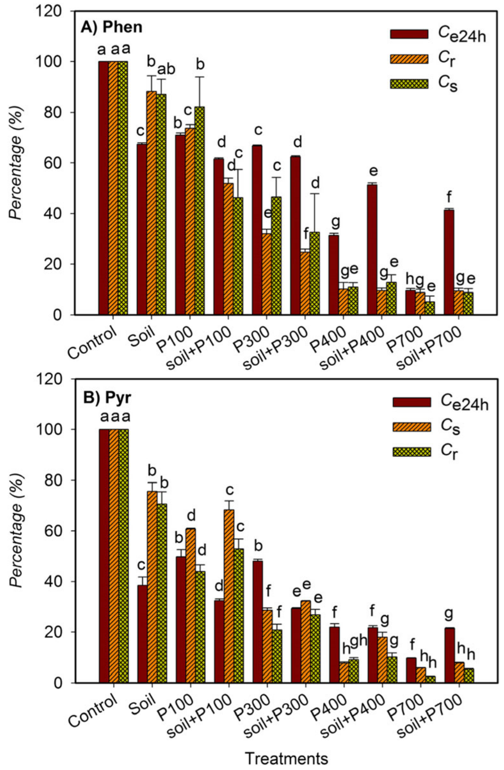


Fig. 5 Concentrations of free phenanthrene (Phen) and pyrene (Pyr) in equilibrium solution 24 h after PAH application (C_{e24h}) and that were extracted from plant roots and shoots after 14-day cultivation (C_r and C_s, respectively). Control refers to plant seedlings grown in the solution with PAHs but without biochar or soil. Biochar and soil were applied either separately or mixed (as indicated by soil, P100, soil + P100, and so on). Polycyclic aromatic hydrocarbon concentrations in treatments (with biochar and/or soil application) were compared with the control (growing plants in pure PAH solutions) for which the percentages of detected PAHs were set as 100%. The same letter above the bars indicates no significant differences between groups (separately for C_{e24h}, C_r, and C_s) at p level lower than 0.05 according to one-way ANOVA and LSD analysis

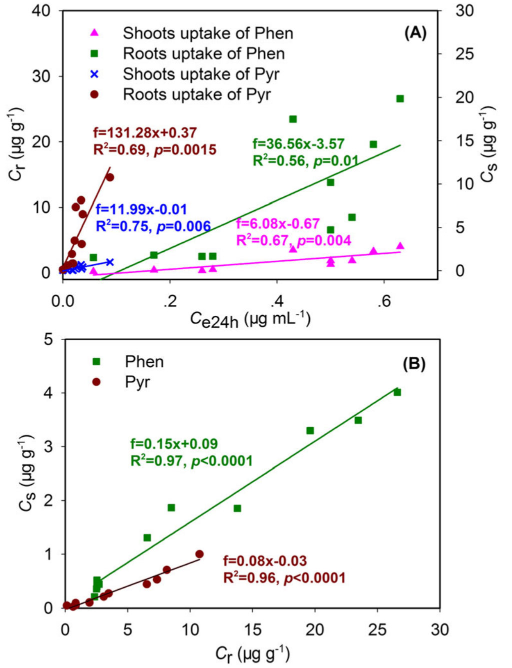


Fig. 6 Correlations of PAHs (phenanthrene = Phen and pyrene = Pyr) concentrations between that in equilibrated solution 24 h after PAH application and in plants (roots and shoots, respectively) after 14-day cultivation, as well as between that in roots and in shoots of rice seedlings after 14-day cultivation. The correlation coefficients (R^2) are labeled in the same color of the corresponding linear correlation curve, with the significance level (p) indicated as well, according to the calculation with the software SigmaPlot

correlations between roots with shoots were observed from Fig. 6, indicating that the uptake of PAHs from solution by roots and translocation to shoots is dependent on the freely dissolved PAHs in solution. It can be concluded that the accumulation of PAHs in shoots is dependent on PAH concentrations in roots. Previous study revealed that PAH uptake by plant tissues was driven by transpiration stream flux (Gao and Collins 2009) and affected by chemical properties of PAHs (Tao et al. 2009). Furthermore, our study shows that the binding of PAHs to soil matrix and biochars largely constrain the bioavailability of PAHs.

For cultivation systems with the application of biochar, soil, and soil-biochar mixtures, less PAHs were taken up by plants, in comparison with the control, indicating that the solids reduced the availability of PAHs. The presence of soil, biochar, and soil-biochar sorbents reduced Phen uptake by rice seedlings, respectively, by 23.76, 61.88–94.55, and 88.61–91.58%; and for Pyr, these percentages were, respectively, 32.35, 53.33–96.08, and 66.27–93.73%. Plant uptake of PAHs was dependent on PAH concentrations in equilibrium solution. Reduced plant uptake of PAHs from solid system was attributed to a reduction in freely dissolved PAH concentrations (Fig. 6), due to the sorption of PAHs by biochars and soil. Therefore, the bioavailability of PAHs is largely dependent on the application of biochars which are able to immobilize PAHs efficiently. What is worth noticing, with the only application of soil and after 24 h equilibration, Pyr in solution decreased to less than 40% of the applied concentration, immobilizing even a greater portion of Pyr into solid phase (soil) than that with the application of pure biochars pyrolyzed at low temperatures (P100 and P300) (Fig. 5). Nevertheless, after 14 days, rice seedlings grown in the cultivation system with pure soil accumulated larger amount of PAHs (especially Pyr) than that grown in biochar-amended soil, suggesting the re-distribution of PAHs from soil to solution, whereas more stable binding of PAHs to biochars than to soil.

Chemical extraction and biological exposure are versatile tools to assess the bioavailability of organic compounds (Dettenmaier et al. 2009; Wen et al. 2009). In our study, solvent extraction and plant uptake of PAHs from soils amended with biochars are simultaneously employed to assess the bioavailability of PAHs to plants. Immobilization of PAHs with biochars successfully reduced solvent extractability and their bioavailability to plants, resulting in a decreased plant uptake of PAHs (Fig. 7). Chemical solvent extractability and plant uptake capability of relatively high-molecular-weight PAHs (Phen and Pyr) both decreased, especially with the application of pure biochars produced at higher temperature (P700), and this trend became more remarkable with extended aging time (Fig. 2). When different biochars were applied individually, the accumulation of Pyr in plant tissues decreased with the increasing pyrolysis temperatures, accordingly from low (P100 and P300) to moderate (P400) and high temperatures (P700) (Fig. 5). A previous study shows positive correlation between organic solvent extractable Phen with the mineralization of Phen by PAH-degrading bacteria, indicating that extractability shares common results with the bioavailability (Ogbonnaya et al. 2014). Although potential risks exist when PAHs immobilized in low- and moderate-temperature biochar are possibly released back to the environment, a combination of biochar with bioremediation strategy will facilitate further degradation of PAHs by PAH-degrading bacteria (Chen et al. 2012a). Additionally, biochars can act as a promising carrier for such PAH-degrading bacteria, guaranteeing PAH degradation with high and stable efficiency (Chen et al. 2012a).

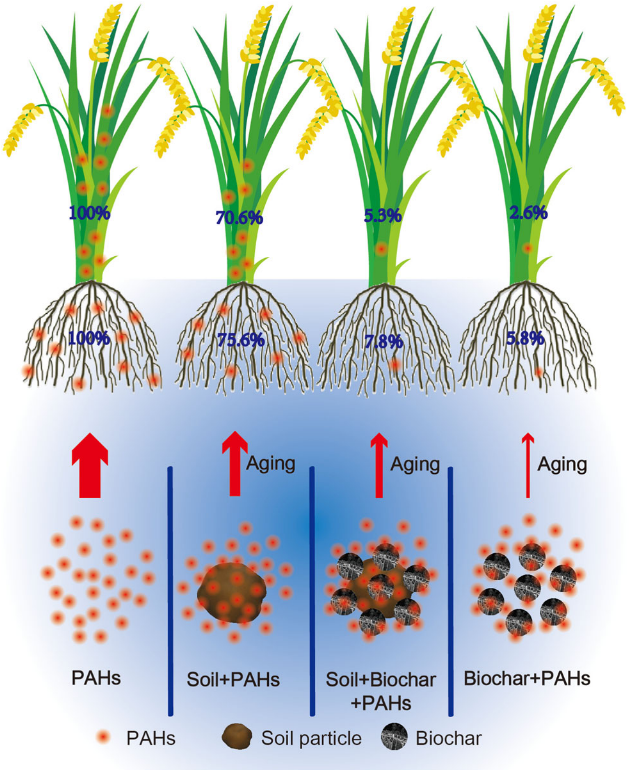


Fig. 7 Schematic diagram showing that soil amendment with biochar (P700 as a representative) can reduce the freely dissolved PAH (pyrene, Pyr as a representative) and decrease PAH uptake by roots and shoots when plants are exposed to PAHs. The size of red arrows represents the amount of freely dissolved Pyr, and the numbers of red dots on plants are the representative of the relative uptake amount of Pyr by roots and shoots, with the corresponding percentages labeled on the plants as well (from which the root and shoot uptake of Pyr by plants growing in the solution with PAHs but without biochar or soil were set as 100%). The sorption of Pyr by biochar and soil, as well as the aging process significantly reduce the freely dissolved PAHs (Pyr) and then decrease the plant root and shoot uptake of Pyr

Conclusions

Although natural soil could immobilize PAHs in short term, our study shows a higher risk of redistribution of soil-bound PAHs back to solution than that with biochar. Biochars are able to immobilize PAHs from soil more efficiently and more stable, especially for those produced at relatively higher temperatures (P400 and P700). Aging process can further reduce the bioavailability of PAHs. Different pyrolysis temperatures determine biochar properties that play an essential role in PAH sorption, including porosity, surface area, and functional groups. Biochar properties further decided the bioavailability of PAHs that were sorbed into biochar. Chemical solvent extraction and plant exposure assay simultaneously used in our study reach uniform conclusions for bioavailability assessment of PAHs following biochar sorption. It is found that biochars pyrolyzed at relatively higher temperature can reduce plant uptake of PAHs to larger extent than those pyrolyzed at lower temperatures.

The assessment of PAH bioavailability following soil amendment with biochar is not only essential to evaluate the potential risks of PAHs, but also can be pivotal to instruct the selection of biochars for the purpose of combined remediation together with PAH-degrading microbes. Single application of high-temperature biochar can benefit long-term PAH immobilization, while combined application of low- and moderate-temperature biochar with PAH-degrading microbes is speculated to enhance the degradation of PAHs, due to the resulting bioavailability of PAHs. Research in recent years have developed large amount of materials to produce biochars for the purpose of remediating soil organic contamination, many achieving satisfactory results. With our current study, we appeal that research concerning of biochar application for the purpose of soil organic pollution remediation should be followed with environmental risk assessment, because even for the same material different pyrolysis temperatures would change the biovailability of PAHs binding to biochars. In practical application for soil remediation, more types of biochars covering more types of feedstocks under various pyrolysis conditions should be compared in terms of bioavailability of organic contaminants, potential risks, and efficiency for combined remediation with microbes.

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