Original Article

Contribution of Dissolved Organic Carbon in Mobilizing and Releasing High Molecular Weight Polycyclic Aromatic Hydrocarbons From Carbonaceous Material-Amended Soil

Ali Daryabeigi Zand[1]*

[1]School of Environment, College of Engineering, University of Tehran, Tehran, Iran

Corresponding Author: Ali Daryabeigi Zand, PhD, Assistant Professor, School of Environment, College of Engineering, University of Tehran, P.O. Box 14155-6135, Tehran, Iran. Tel: +98-9123107933, Email: adzand@ut.ac.ir

Abstract
Introduction: Migration and mobilization of recalcitrant organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) in contaminated sites may endanger groundwater resources if considerable amounts of these compounds are mobilized and leached from solid phase into aqueous phase. The aim of the present study was to investigate the influence of biochar in two forms i.e. crushed and pulverized on immobilization and leaching behavior of high molecular weight (HMW) PAHs from contaminated soil into water as well as evaluation of contribution of dissolved organic carbon (DOC) in mobilization and release of HMW PAHs in crushed and pulverized biochar-amended soil, which was addressed for the first time in this study.
Materials and Methods: Column leaching test was used to evaluate the leaching behavior of selected HMW PAHs from soil. Concentrations of PAHs in column leachates were determined using a GC/MS.
Results: Findings showed strong sorption of the studied HMW PAHs to solid phase in both unamended and amended columns. Dibenz[a,h]anthracene
was not mobilized by water flow in any of the examined treatments and showed the greatest affinity to solid matrix. Mobility and leaching of most HMW PAHs were enhanced in the presence of crushed biochar. Direct correlation between detected concentrations of HMW PAHs in column percolates and DOC was found in biochar-amended soil.
Conclusions: Biochar can be used as a promising cost-effective alternative to activated carbon in immobilization of PAHs in contaminated sites. However, contribution of DOC in mobilization of HMW PAHs from contaminated soils towards groundwater resources cannot be neglected.
Keywords: Immobilization, High Molecular Weight Polycyclic Aromatic Hydrocarbons, Crushed Biochar, Pulverized Biochar, Soil
Citation: Daryabeigi Zand A. Contribution of dissolved organic carbon in mobilizing and releasing high molecular weight polycyclic aromatic hydrocarbons from carbonaceous material-amended soil. J Appl Biotechnol Rep. 2020;7(2):125-134. doi:10.30491/JABR.2020.109288.

Introduction

Soil can be considered as a sink for various hydrophobic contaminants such as polycyclic aromatic hydrocarbons (PAHs),[1] in which migration and release of contaminants might occur over long periods of time, even after the contaminant source is removed. Contamination of soil with PAHs is a widespread environmental problem throughout the world.[2] The PAHs are mainly found in a mixture containing more than two of such compounds,[3] and may enter the environment through various routes. However, the widespread occurrence of them mainly takes root in their generation and escape to the environment in all processes involving incomplete combustion of organic materials.[4] The PAH compounds which are known to occur in the environment both naturally (e.g. from wild fires) and from anthropogenic sources (incomplete combustion of a wide variety of organic materials such as wood, fossil fuels, and wastes) were demonstrated to have mutagenic and carcinogenic properties and their hazards

to the environment and human health is usually increased by increasing molecular weight of a given PAH compound. For instance, benzo(a)pyrene as a heavy PAH compound with 5 benzene rings in its structure is highly carcinogenic and may cause genetic damage in lung cells while carcinogenicity bioassays with Anthracene which is a low molecular weight PAH compound (with three rings) generally giving negative results.[5-8] The PAHs generally have 2 or more aromatic rings in their structure. They are hydrophobic compounds with very little water solubility that decline with increasing molecular weight of PAH compounds.[9] In other words, high molecular weight (HMW) PAHs with four or more fused aromatic rings have less volatility, water solubility and thus a higher lipophilicity than light molecular weight (LMW) PAHs with three or less aromatic rings that can affect their desorption and mobilization behavior in contaminated sites.

Sorption of hydrophobic contaminants to organic matter in soils might be considered as a beneficial process restricting

migration of such compounds from soil to aqueous phase. However, mobile organic particles and colloids can promote transport of such compounds. For the restriction of migration and mobilization of hydrophobic compounds, applying carbon-rich materials to contaminated soil has received remarkable attention in recent years[10,11] since conventional remediation technologies are costly and potentially disruptive to the environment if e.g. contaminant mobilization is triggered.[12] Adding carbonaceous materials to soils and sediments reduces bioavailability of organic contaminants because sorption of hydrophobic contaminants is strongly enhanced. For instance, application of activated carbon could significantly reduce bioavailability of polychlorinated biphenyls (PCBs) in contaminated soil.[13]

Biochar is a high carbon content product generated by heating organic biomass in oxygen limited conditions and is typically added to soil to improve its fertility. Enhanced biodegradation of petroleum hydrocarbons in the presence of biochar in soil was also reported.[14] In addition to modification of soil structure and fertility, biochar may alter mobilization and leaching characteristics of PAHs in contaminated soil which will be addressed in this study for HMW PAHs. Organic carbon content of a soil amendment can considerably affect its performance in immobilization of organic contaminants in soil. For instance, lower effectiveness of compost containing less organic carbon fraction compared to biochar in immobilization of PAHs in soil has been reported in the literature.[15] Compost may enhance PAHs dissipation by improving soil texture, oxygen transfer and promoting microbial activity in soil[16] whereas biochar mainly increases sorption affinity of PAHs to soil organic matters. The type of biomass and the pyrolysis conditions such as temperature can significantly determine composition and characteristics of biochar[10] and its applicability for different purposes e.g. as soil amendment and/or for remediation purposes. Different types of wood, leaves, grasses, sludges and organic wastes can be used as feed stock to produce biochar. However, wood-based biochars generally have greater content of carbon,[17] which makes them favorable for their novel applications in immobilization and remediation purposes. Strong binding and slow desorption of pentachlorophenol was observed in the presence of carbonaceous material in soil.[18] Sheng et al[19] found that wheat char could adsorb pesticides effectively. Chars can be employed to alter sorption behavior of recalcitrant organic pollutants thereby changing their leaching behavior.[19] Biochar is quickly receiving popularity, however there are still only a limited number of studies who have examined the utilization of biochar to reduce the bioavailability and mobility of PAHs in soil.[20,21] Adding any kind of organic matter to soils may be associated with the risk of mobilizing organic particles, colloids and dissolved organic carbon (DOC), which is often overlooked. Facilitated transport would mainly affect the strongly hydrophobic compounds such as HMW PAHs.

The main aim of this study was to investigate the contribution of DOC in leaching and releasing HMW PAHs from contaminated soil amended with biochar as well as the effect of biochar on the leaching behavior of HMW PAHs. The contribution of DOC in mobilization and release of HMW

PAHs in the presence of crushed and pulverized biochar in soil has been rarely investigated. In addition, biochar was employed in two different forms i.e. crushed and pulverized forms in order to examine the impact of biochar particle size on the leaching behavior of HMW PAHs.

Materials and Methods
Soil and Biochar Preparation
Contaminated soil used in this study was prepared from the Federal Institute for Materials Research and Testing in Berlin, Germany. Reference soil had the particles size of less than 2 mm with the particle density of 2.65 g cm^{-3}. Feed stock material used to provide biochar was forest wood. The forest wood-derived biochar employed in this research had the organic carbon content of 79.5% and bulk density of 1.5 g cm^{-3}. Pyrolytic temperature was as high as ca. 600°C-750°C in order to produce forest wood-biochar to be utilized in this investigation. Produced biochar chips were kept in dry condition; however, they were air dried for a week before applying to soil. In order to investigate the impact of biochar particle size on leaching behavior of HMW PAHs, biochar was applied to soil in 2 forms; crushed and pulverized. A ceramic mortar equipped with a pestle was used to crush the air-dried chips of biochar. Crushed chips were then sieved with a sieve of 2 mm before applying to contaminated soil. Zirconium oxide planet ball mill was used in order to prepare pulverized biochar.

Column Leaching Test Procedure
Columns were filled with contaminated soil and the mixture of contaminated soil/biochar was in the following order; Column S1: 100% PAHs-contaminated soil, column S2: 95% PAHs-contaminated soil and 5% crushed biochar particles (w/w %) and column S3: 95% PAHs-contaminated soil and 5% pulverized biochar particles (w/w %). A separate column containing only clean quartz sand was also prepared and run as a blank to ensure lack of background contamination with PAHs. Small glass columns with an inner diameter of 6 cm were used for the leaching studies. Columns were filled with contaminated soil as well as the mixture of contaminated soil and biochar in five sub-layers up to the height of 12 cm. The experimental set-up of column tests is presented in Table 1. On the top and bottom of the columns a layer of 1 cm of clean quartz sand was used in order to facilitate uniform distribution of water flow within columns as well as preventing loss of soil and biochar particles. The leaching tests were performed in accordance with DIN 19528.[22] The technical committee CEN/TC 351 "Construction products- Assessment of the release of substances to soil, surface water and groundwater" has been conducting investigations on a harmonized leaching test method. The German standard DIN 19528 is believed to be the most advanced leaching test method.[23] Experiments were conducted in a room having a constant temperature of 20°C. Columns were percolated from the bottom (upward flow direction) to prevent trapping of air bubbles. Milli-Q water which was kept in a 50-L vessel was used in this study as a leaching agent to avoid interference with probable non-target ions and compounds in water. Water was pumped into

Table 1. Column Leaching Test Experimental Set-up Used in This Study

Parameter	Description
LS^{-1} ratio	Increasing from 0.3 to 4 L kg^{-1}
Column diameter	6 cm
Filling height	12 cm
Flow rate	0.4 mL min^{-1}, up-flow percolation
Leachant	MilliQwater (Millipoer, MA, USA)
Ambient temperature	20±1°C
Contact time	5 h

columns using a multi-channel peristaltic pump at a constant flow rate (Table 1). Columns were initially saturated with the deionized water using a higher flow rate. Tests were started not later than 1 hour after the completion of the saturation. Columns percolates were collected in dark glass bottles by connecting the columns to the bottles using a stainless still tube. Also, 10 mL cyclohexane (solvent) was added to collection bottles in order to prevent PAHs biodegradation during the test. Before connecting the main bottles, 30 mL of initially collected eluates were collected in 50 mL dark glass bottles to be analyzed for other parameters e.g. turbidity and DOC. Collection bottles containing eluate fractions were changed at specified liquid/solid (LS^{-1}) ratios up to 4 L kg^{-1} and kept at 4°C before analysis.

PAHs Extraction and Analysis

Column percolates were analyzed for PAHs in this study. Internal standard (10 μL of PAH-Mix 31 deuterated, Dr. Ehrenstorfer GmbH, Germany) was added to the samples, and bottles containing percolates were gently shaken for 30 minutes and stored overnight to facilitate mass transfer of the solutes PAHs from the water phase into the cyclohexane phase. Then the organic compounds accumulated at the top of the bottles were extracted to be analyzed for PAHs. Also, sodium sulfate was used to oxidize the extracted water in order to assist water/organic phase separation whenever appropriate. The column percolates were then measured for PAH content using a GC/MS HP 6890 series equipped with DB-5MS column with 30 m long, with 0.25 mm internal diameter and 0.25 μm film thickness. The temperature of the device column was initially adjusted to 65°C for 4 minutes, then heated to 270°C at increasing rate of 10°C min^{-1} and held for 10 minutes, before increasing to 310°C at the same

gradient (10°C min^{-1}). Temperature was held at 310 °C for 6.5 minutes. Results of the tests were expressed as a function of liquid to solid (LS) ratio in terms of mg of a given PAH compound measured per liter of leachate.

Determination of Dissolved Organic Carbon and Turbidity

The DOC and turbidity were measured within one day after sampling. Initially collected eluates i.e. 30 mL of initially leached water at assigned LS^{-1} ratios were analyzed for this purpose. Each sample was filtered through 0.45 μm filtration membranes (MILEXHA) before being analyzed for DOC using HighTOC analyzer (Elementar). A HACH 2100N Turbidity meter was used to determine turbidity levels in the remaining fraction.

Results and Discussion

In addition to evaluation of leaching behavior of HMW PAHs from contaminated soil, the impact of forest wood-derived biochar in crushed and pulverized forms on mobilization and leaching characteristics of HMW PAHs was investigated in this research. Concentrations of total PAHs (C_{tot}) in water increase as function of DOC:

$$C_{tot} = C_{w,free}(1 + K_{DOC}C_{DOC})$$
(1)

Where $C_{w,free}$ denotes the freely dissolved concentration and the second term the DOC associated PAHs. K_{DOC} is the distribution coefficient [L kg^{-1}] between freely dissolved PAHs and colloidal organic carbon dissolved in water (C_{DOC} [kg L^{-1}]). Since C_{DOC} is typically less than 100 mg/L only compound with K_{DOC} higher than 10 000 are significantly affected. Generally, these are PAHs with log K_{ow} larger than 4.5 and water solubility less than1 mg L^{-1}.

Benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(k) fluoranthene, benzo(ghi)perylene and dibenz(a,h)anthracene were selected as target HMW PAH compounds in this research. Initial solid phase concentration of the HMW PAHs and some of their characteristics are presented in Table 2. As it can be seen in Table 2, all the studied PAH compounds have low water solubility and high K_{ow}, with the greatest Log K_{ow} for benzo(ghi)perylene and Dibenz(a,h) anthracene having 6 aromatic rings in their structure with the highest molecular weight among the selected HMW PAHs. Leached concentrations of the selected HMW PAHs

Table 2. Solid Phase Concentrations of Selected High Molecular Weight PAHs in Contaminated Soil and Their Chemical Properties[6]

PAH Compound	C_s (mg kg^{-1} Dry Soil)	Number of Benzene Rings	Molecular Weight (g mol^{-1})	S_i (mg L^{-1})	$(f^s/f^l)_i$ at 25°C	$S_{i, sub}$ (mg L^{-1})[a]	Log K_{ow}
Benzo(a)anthracene	1.47	4	228.29	0.014	0.04	0.350	5.91
Chrysene	1.16	4	228.29	0.002	0.0097	0.206	5.91
Benzo(a)pyrene	0.36	5	252.32	0.0038	0.03	0.127	5.91
Benzo(k)fluoranthene	0.19	5	252.32	0.00323	0.039	0.083	6
Benzo(ghi)perylene	0.01	6	276.34	0.00026	0.003	0.087	6.50
Dibenz(a,h)anthracene	0.01	6	278.35	0.0005	0.004	0.125	6.75

[a] The solubility of the subcooled liquid.

from different columns at specified LS ratios are shown in Figure 1. Concentrations of HMW PAH compounds were plotted versus liquid to solid ratio (LS) rather than time as it facilitates comparison of findings from various leaching tests. The LS ratio is defined as the amount of leachate (water in this case) percolated through column materials (i.e. soil and soil/biochar mixture) after a certain time relative to the dry weight of solids in a column. The LS ratio is directly proportional to the average flow rate, porosity of material in the column and time, and reversely related to distance travelled by contaminants within soil and dry bulk density of materials used in the column.[24]

Figure 1 shows that leaching behavior of benzo(a)anthracene and chrysene has similar trend in both unamended contaminated soil and biochar-amended soil. However, the observed leaching behavior for each compound was markedly different among different treatments i.e. in unamended soil (column B1), crushed biochar-amended soil (column B2) and pulverized biochar-amended soil (column B3). Relatively constant increase in concentrations of benzo(a)anthracene and Chrysene is measured up to the LS ratio of 2 L kg^{-1}. This is in contradiction with the results reported by Marchal et al where initial high concentrations of an LMW PAH compound i.e. phenanthrene in column percolates followed by a quick drop in concentration was observed.[11] This might be attributed to the fact that lighter fractions of PAHs in soil may be rapidly desorbed and leached while more hydrophobic compounds such as benzo(a)anthracene and chrysene can form much stronger bonds with soil organic matter preventing their fast depletion during a leaching test, that's why their leaching with water is an slow time-dependent process and might be gradually enhanced slightly as time goes on. A slight declining trend was established in the aqueous concentration of benzo(a)anthracene and chrysene in percolates from LS of 2 L kg^{-1} to 4 L kg^{-1}. At the end of the experiment, leached concentrations of benzo(a)anthracene and chrysene increased by 73.7% and 75.0%, respectively, compared to LS ratio of 0.3 L kg^{-1}, in the absence of biochar in soil. The impact of the addition of 2% biochar to soil on the fate of volatile petroleum hydrocarbons was studied by Bushnaf et al.[25] They observed more rapid biodegradation and depletion of volatile petroleum hydrocarbons in the presence of biochar in soil and suggested the greater degradation of less strongly sorbed compounds because of the reduced availability of strongly sorbed compounds in presence of biochar in soil. In general, solid phase depletion of organic contaminants might
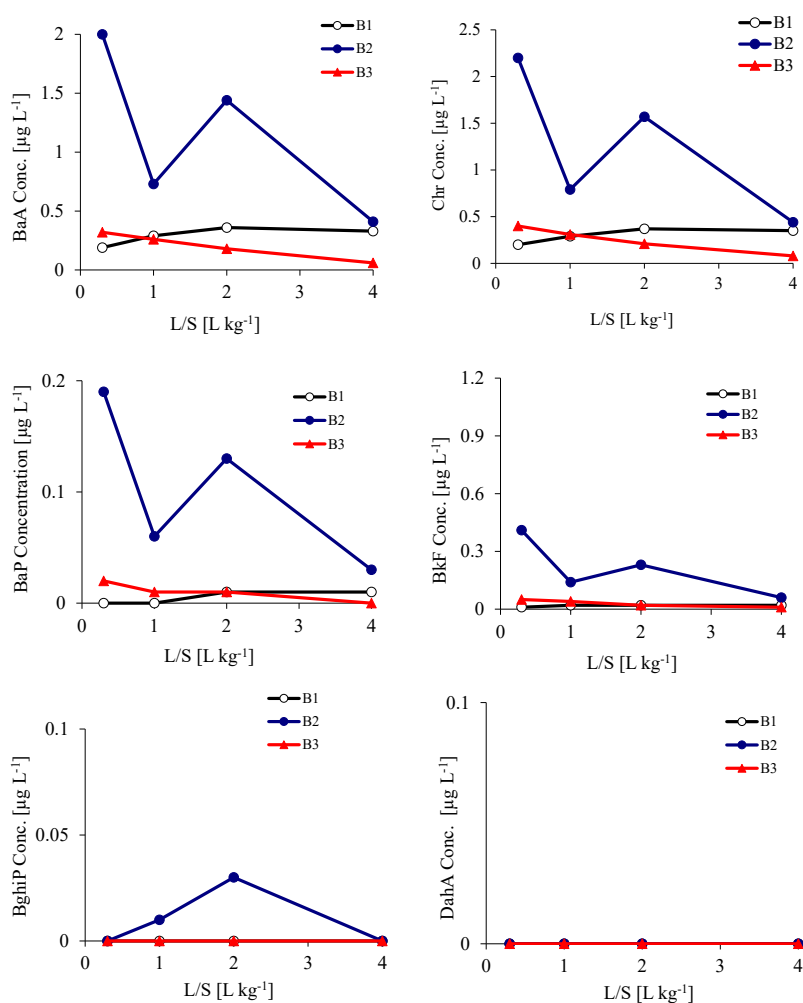

Figure 1. Concentration of Benzo(a)Anthracene (BaA), Chrysene (Chr), Benzo(a)Pyrene (BaP), Benzo(k)Fluoranthene (BkF), Benzo(ghi)Perylene (BghiP) and Dibenz(ah)Anthracen (DahA) in Percolates of unamended Column (B1) and Amended Column With Crushed Biochar (B2) and Pulverized Biochar (B3)

be more relevant to less hydrophobic organic compounds rather than highly hydrophobic contaminants such as HMW PAHs studied in this research.

Results showed that initially benzo(a)anthracene and chrysene were highly mobilized after application of crushed biochar to contaminated soil. Initial concentration of benzo(a)anthracene in leachate of amended soil with crushed biochar drastically increased by 11 times, compared to unamended soil at LS of 0.3 L kg^{-1}. Application of crushed biochar enhanced leached concentrations of benzo(a) anthracene and chrysene at all examined LS ratios compared to unamended soil, however, the final leached concentrations of them in column percolates were only slightly more than the corresponding values in unamended soil. Pulverized biochar remarkably reduced aqueous concentrations of both benzo(a) anthracene and chrysene at higher LS ratios in comparison to unamended soil as well as crushed biochar-amended soil.

In general, leaching concentrations of benzo(a)anthracene and chrysene in crushed biochar-amended soil showed a declining trend during the leaching test. Declining concentrations of a solute indicated a non-equilibrium condition in column. The shift between equilibrium and non-equilibrium conditions depends on various parameters like flow velocity, grain sizes, diffusion distances, and the sorption capacity. The concentration of a compound in the column effluent may decrease due to depletion of a given compound or due to non-equilibrium conditions established in the column.[24] For example, in column B2 concentration of benzo(a)anthracene and chrysene declined initially indicating the non-equilibrium conditions in the column. Benzo(a)anthracene and chrysene concentrations increased in percolates at LS ratio of 2 L kg^{-1}. A sudden increase in the leaching of the both studied 4-ring PAHs at LS ratio of 2 L kg^{-1} (Figure 1) may be caused by heterogeneous distribution of crushed biochar in soil/biochar mixture and delayed release of these PAH compounds attached to colloids associated with application of crushed biochar in soil. The impact of the amount of mobilized suspended particles and DOC on the mobility of some hydrophobic organic compounds has been reported in the literature.[26,27]

Cumulative leaching concentrations of HMW PAHs are shown in Figure 2. It can be inferred from Figure 2 that cumulative concentration of benzo(a)anthracene in the presence of crushed biochar increased by ca. four times at LS ratio of 4 L kg^{-1}, while the amendment of contaminated soil with pulverized biochar could reduce cumulative concentration of benzo(a)anthracene in comparison to unamended contaminated soil. A similar effect and trend
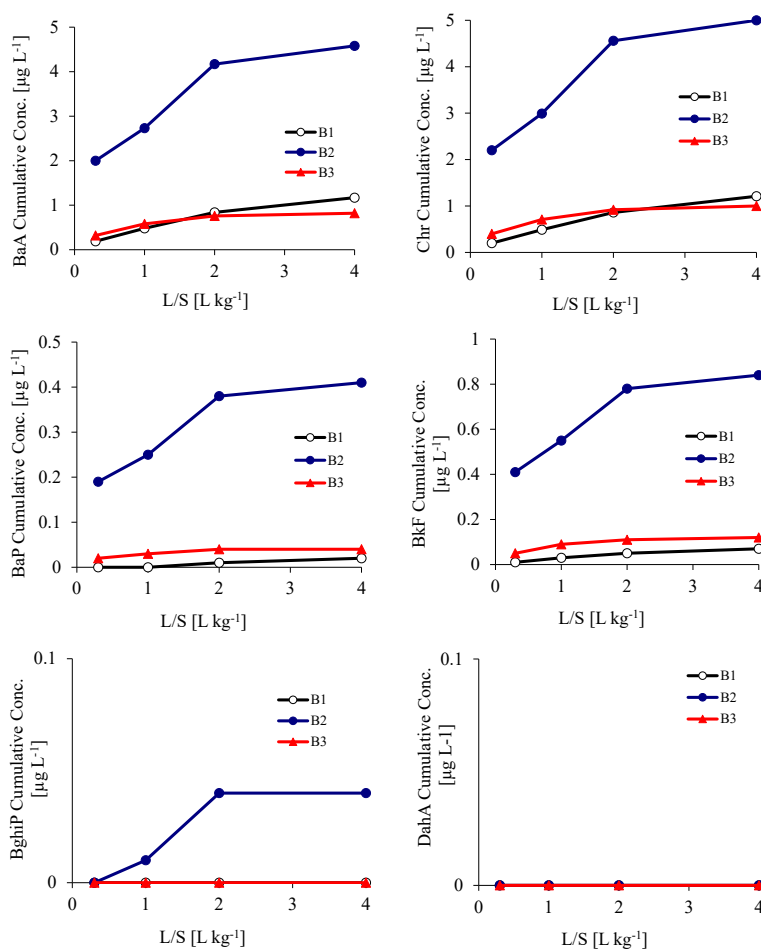

Figure 2. Cumulative leached concentrations of Benzo(a)Anthracene (BaA), Chrysene (Chr), Benzo(a)Pyrene (BaP), Benzo(k)Fluoranthene (BkF), Benzo(ghi)Perylene (BghiP) and Dibenz(ah)Anthracen (DahA) From Unamended Column (B1) and Amended Column With Crushed Biochar (B2) and Pulverized Biochar (B3)

was obtained for cumulative concentrations of chrysene in examined treatments. Comparison of cumulative release of benzo(a)anthracene in different treatments demonstrated that soil amendment with pulverized biochar can markedly reduce mobilization AOD release of benzo(a)anthracene from the solid phase towards the aqueous phase. Accumulated release of benzo(a)anthracene to water phase over the course of experiment declined by 59.9% in the presence of pulverized biochar in soil compared to unamended soil. However, addition of crushed biochar to soil caused a significant increase (by a factor of 2.4) in accumulated release of benzo(a)anthracene from soil to water. Application of 2% activated carbon in granular and powder forms reduced PAHs concentration in water phase by 3%-64% and 63%-99%, respectively, implying the significance of organic amendment size[28] as observed in the present research. Mobilization and release behavior of chrysene in the presence of both crushed biochar and pulverized biochar was comparable with that of benzo(a)anthracene; in other words addition of crushed biochar enhanced cumulative release of chrysene whereas employing pulverized biochar reduced mobilization and release of chrysene at the end of the leaching test. Finally, 0.57% and 0.1% of the initial solid phase content of chrysene was mobilized and released into the aqueous phase in the presence of crushed and pulverized biochar, respectively, that implies beneficial performance of pulverized biochar while crushed biochar did not show promising impacts on immobilization of chrysene in soil. Reduction in leaching of 4-ring PAHs may be attributed to the enhanced sorption of benzo(a)anthracene and chrysene to biochar particles as also suggested by other authors.[15] Results of the present study showed fairly higher effectiveness of the used biochar (5%) in reducing desorption and immobilization of HMW PAHs from soil compared to the obtained results by Gomez-Eyles et al[29] that might be attributed to biochar feedstock, pyrolytic temperature, and structure as well as biochar particle distribution in soil. Denyes et al has reported improvement enhanced sorption of PCBs in soil amended with biochar and activated carbon.[13] Organic amendment of soil using carbon rich amendments e.g. biochar and activated carbon can enhance sorption of PAHs in soil and reduce their bioavailability that is a favorable condition in terms of stabilization of contaminants in soil and reducing groundwater contamination risk through immobilization of contaminants in soil.

Results of the present study showed strong sorption of both studied 5-ring PAHs i.e. benzo(a)pyrene and benzo(k) fluoranthene to soil organic matter. Benzo(a)pyrene was not initially detected in percolates of column B1 and only slightly leached at higher LS ratios (Figure 1). Benzo(k)fluoranthene was also determined to have very low concentrations in leachates of column B1 over the course of the leaching process; however, it was mobilized slightly more than benzo(a)pyrene. Much higher initial concentration of both benzo(a)pyrene and benzo(k)fluoranthene were observed in leachate of column B2 compared to column B1 suggesting that addition of crushed biochar to soil enhanced the mobility of the above-mentioned HMW PAHs and their leaching from soil into water. The highest leached amount of benzo(a)pyrene (0.19 µg L^{-1}) and benzo(k)fluoranthene (0.41 µg L^{-1}) was initially observed at LS ratio of 0.3 L kg^{-1} in the presence of crushed biochar in soil. For compounds which sorb strongly to the solid matrix i.e. soil in this case the equilibrium conditions can prevail over extended periods of time.[30] Addition of biochar to soil may alter the equilibrium conditions for hydrophobic organic compounds such as benzo(a)pyrene and benzo(k)fluoranthene through colloid-facilitated transport. benzo(a)pyrene leaching from soil in the presence of crushed biochar considerably decreased from 0.19 µg L^{-1} to 0.03 µg L^{-1} (84.2% reduction) which may be attributed to the depletion of mobilized and leachable biochar particles in soil. Rapid reduction and depletion of suspended solids and DOC associated with biochar particles can be inferred from Figure 3 and Figure 4, respectively, over the course of experiment. For instance, benzo(a)pyrene is a highly hydrophobic PAH compound with a very high K_{oc} value (Log K_{oc}=6.09)[31] that strongly sorbed to soil organic matter. Considerable increase in benzo(a)pyrene leaching and release in the presence of crushed biochar in soil may be attributed to facilitated transport and leaching of benzo(a)pyrene sorbed to crushed biochar particles and their mobilization. Effluent turbidity and DOC associated with biochar particles may be considered as the most prominent mechanism that enhanced leaching of benzo(a)pyrene from column B3 in which soil was mixed with crushed biochar. Mobilization of benzo(a) pyrene and benzo(k)fluoranthene sorbed to biochar particles followed by its leaching through suspended solids and DOC may be a probable reason for the enhancement of their
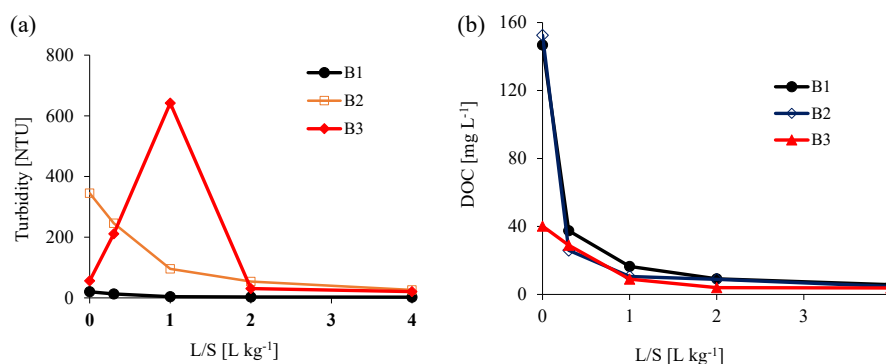

Figure 3. Leaching Behavior of Suspended Solids (a) and Dissolved Organic Carbon (b) in Unamended Soil and Amended Soil With Crushed and Pulverized Biochar.
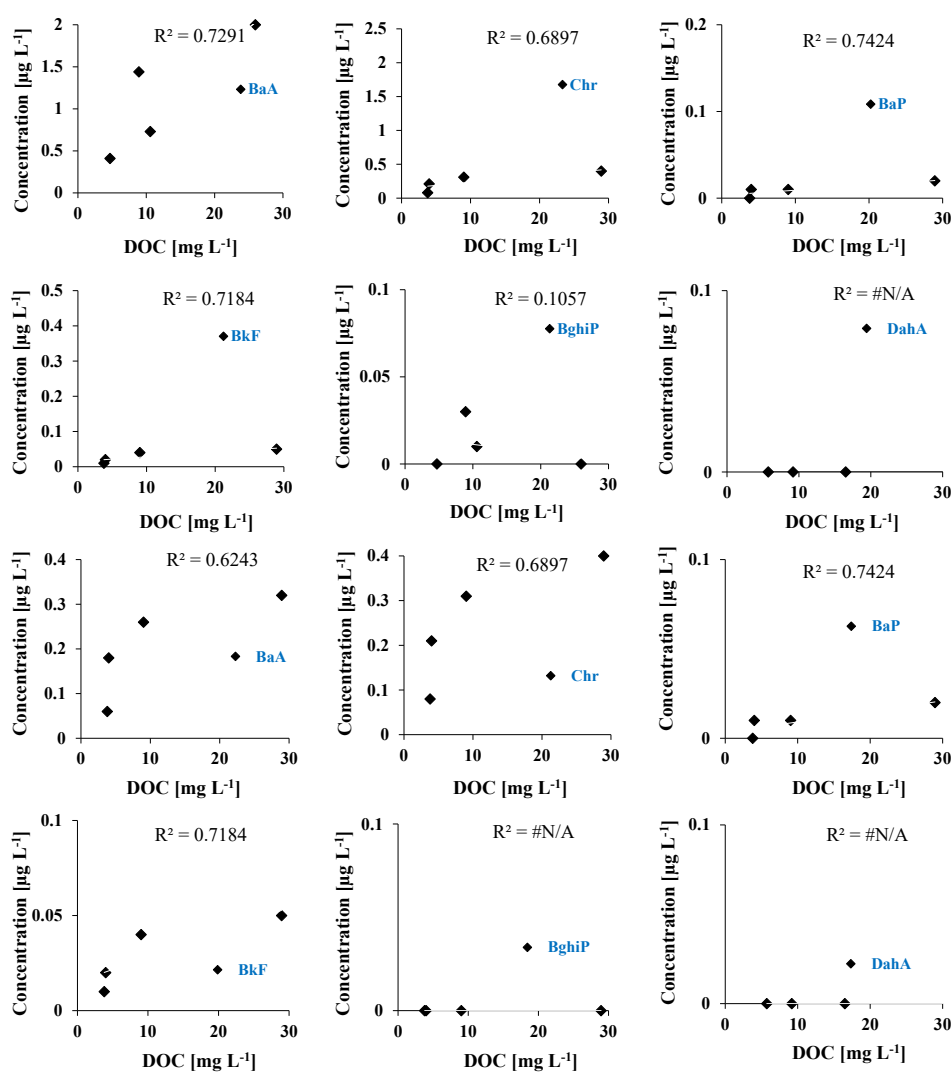
Figure 4. DOC Dependency of Leaching of HMW PAHs From Crushed Biochar-Amended (B2) and Pulverized Biochar-Amended (B3) Column. BaA: Benzo(a)anthracene; Chr: Chru=ysene; BaP: Benzo(a)pyrene; BkF: Benzo(k)fluoranthene; BghiP: Benzo(ghi)perylene; DahA: Dibenz(a,h)anthracene.* N/A: Not applicable.

concentration in leachate in the presence of crushed biochar in soil.

Aqueous concentration of both benzo(a)pyrene and benzo(k)fluoranthene decreased from LS ratio of 0.3 L kg^{-1} to 1 L kg^{-1}, followed by a sudden increase at LS= 2 L kg^{-1} in crushed biochar-amended soil, similar to the trend observed for benzo(a)anthracene and chrysene. The heterogeneity of the contaminated soil amended with crushed biochar and of the surface composition of pollutants adsorbed to the biochar particles is a probable reason for the unexpected increase of HMW PAHs at LS ratio of 2 L kg^{-1}. Addition of organic amendments to soil remarkably increased sorption of many PAH compounds in soil in many cases[28,32]; however, it was not successful enough in some studies. For example, in a study by Marchal et al, the application of compost to the different soil suspensions displayed a comparatively low influence on the phenanthrene desorption in soil, compared to unamended soil (only 3.1% decrease in aqueous concentration).[11] In this research, however, the application of pulverized biochar to contaminated soil markedly affected the leaching behavior of

the studied HMW PAHs in most cases.

Initial concentration of benzo(k)fluoranthene (0.01 µg L^{-1}) in percolate of column was more than 40 times greater than that of in effluent of column B1 at LS= 0.3 L kg^{-1}. Benzo(a) pyrene which was not leached initially from column B1 was found to be mobilized and leached at LS= 0.3 L kg^{-1} after application of crushed biochar to contaminated soil. Addition of pulverized biochar to soil also mobilized benzo(a) pyrene and benzo(k)fluoranthene slightly at early stages of the experiment, however, pulverized biochar could finally immobilize and reduce leaching of both studied 5-ring PAHs at higher LS ratios. In other words, leaching of benzo(a) pyrene and benzo(k)fluoranthene from pulverized biochar-amended soil declined by time. At the end of the leaching process, cumulative leached concentrations of benzo(k) fluoranthene from column B1 and B3 reached 0.07 and 0.12 µg L^{-1}, respectively (Figure 2). However, cumulative release of benzo(k)fluoranthene in the presence of pulverized biochar did not remarkably change compared to unamended soil and decreased slightly by 5.6%. Addition of crushed biochar to

contaminated soil mobilized benzo(k)fluoranthene. leaching and cumulative release of benzo(k)fluoranthene increased by 12 and 6.8 time, respectively, compared to the control treatment. In general, both studied 5-ring PAHs showed high hydrophobicity and strong sorption to solid phase in all treatments. The benzo(a)pyrene showed stronger sorption to solid phase than benzo(k)fluoranthene in both unamended and amended soil with the two forms of applied biochar. At the end of the experiment, cumulatively less than 0.02% of the initial content of benzo(a)pyrene in soil desorbed and released from solid phase into aqueous phase in unamended soil.

Benzo(ghi)perylene and dibenz(a,h)anthracene have six aromatic rings in their structure with the greatest molecular weight and log K_{ow} and the least water solubility among the studied HMW PAHs in this study (Table 2). Mobilization and release of benzo(ghi)perylene did not occur during the leaching process in unamended columns B1 and B3 (Figure 1) demonstrating very strong hydrophobicity and sorption of benzo(ghi)perylene to soil matrix no matter contaminated soil was amended with pulverized biochar or not. The addition of crushed biochar to PAH-contaminated soil slightly mobilized benzo(ghi)perylene at LS ratios of 1 and 2 L kg^{-1}, as observed earlier for other studied HMW PAH compounds. However, strong sorption of benzo(ghi)perylene reduced the adverse impact of crushed biochar on mobilization. Cumulatively only 0.04 µg L^{-1} of benzo(ghi)perylene leached into water. Considering the high hydrophobicity and sorption characterization of benzo(ghi)perylene there is only very small probability for this compound to be desorbed from the solid phase matrix and/or dissolved in water only by water flow. Therefore, mobilizing small fractions of benzo(ghi)perylene attached to biochar particles in soil through leaching and releasing biochar particles in forms of suspended solids or DOC seems to be more likely responsible for leaching benzo(ghi)perylene in crushed biochar-amended soil. Dibenz(a,h)anthracene with the highest molecular weight and log K_{ow} among the studied HMW PAHs did not leach from soil in any of the examined columns indicating very strong sorption to soil matrix in both amended and unamended soils.

Heterogeneous distribution of crushed biochar in column B2 seems to be a probable reason for a sudden increase in effluent concentration of the studied HMW PAHs in most cases. Results indicate that reduction in biochar particle size through pulverizing them may provide more homogenous distribution of biochar particles within the soil along the length of the column and therefore may have a more stable impact on the leaching concentration of the studied HMW PAHs. Comparison of results in column B2 and B3 suggests that the particle size of biochar in soil may be introduced as a limiting factor controlling PAHs desorption and mobilization during a leaching event. Providing effective contact between organic contaminants and biochar particles is a crucial factor to enhance its effectiveness to sorb and immobilize hydrophobic contaminants such as PAHs in soil.

Turbidity and DOC measurements were conducted on percolates collected at various LS ratios in this study to see the leaching behavior of suspended solids and DOC from soil under various scenarios as well as to reveal a probable role of them in leaching the studied HMW PAH compounds. Turbidity levels in percolates of column B1 that was packed only with contaminated soil was the lowest among all treatments over the course of the leaching process. In other word, adding biochar in both crushed and pulverized forms increased the turbidity of leachates at various LS ratios. Initial turbidity of leachates in the presence of crushed and pulverized biochar increased by 94.1% and 63.9%, respectively, compared to unamended soil. Leaching trend of suspended solids was comparable in columns B1 and B2 where a rapid decrease in the turbidity of percolates followed by an extended tailing of the concentrations was observed (Figure 3). For instance, initial turbidity of leachates from column B2 in which crushed biochar was added to soil dropped from 345 NTU to 26.2 NTU at LS ratio of 4 L kg^{-1} (more than 92% reduction). Initial turbidity level of percolates in presence of pulverized biochar (column B3) was considerably lower than that of in the presence of crushed biochar in soil (column B2). However, release of suspended materials increased dramatically p to the LS = 1 L kg^{-1} that might be attributed to trapping the fine particles of biochar within the soil along the length of the soil column. In general, suspended solids may play an important role in carrying and releasing a wide variety of pollutants in soil.[33] The DOC may act as a carrier for hydrophobic compounds and increase their mobilization and leaching.[34] Colloid-facilitated transport that is a transport process in which colloidal particles serve as transport vectors of contaminants can play an important role in the migration of strongly sorbing solutes in a porous media e.g. contaminated soil,[35] as observed for some HMW PAHs in this study. Increased mobilization and release of vigorously attached contaminants to soil matrix through colloid-facilitated transport has been also cited by other authors.[36,37]

Rapid decline in the DOC content of soil, followed by an extended tailing of the DOC concentrations were observed in columns B1 and B2, as shown in Figure 3. Depletion of highly soluble organic carbon resources in soil may be responsible for the rapid drop in the concentrations of DOC in percolates. For example, initial DOC concentration in leachate of column B1 which was 146.78 mg L^{-1} dropped to 37.5 mg L^{-1} at LS ratio of 0.3 L kg^{-1} (74.5% reduction) and finally to 5.73 mg L^{-1} at LS ratio of 4 L kg^{-1} (96.1% reduction). The DOC content of leachates decreased considerably when pulverized biochar was added to soil compared to unamended treatment indicating strong sorption capacity of pulverized biochar that inhibits mobilization and leaching of dissolved organic matters in soil that in turn reduces the facilitated transport of HMW PAH compounds in soil as obtained in the present study. Addition of crushed biochar to soil slightly increased the leaching of DOC initially which may be responsible for initial enhancement in leaching some HMW PAHs from crushed biochar-amended soil in this study.

As it can be seen in Figure 4, the correlation between the concentrations of DOC and the leached HMW PAHs for columns B2 and B3 (amended columns) is presented. The DOC is organic molecules present within the aquatic system

having molecular size less than 0.45 μm so is considered dissolved.[23] Some PAHs can form complexes with DOC and thus the solubility of such hydrophobic compounds may alter in the presence of DOC and they can be mobilized and released from soil into water attached to the leached DOC. Generally, it is challenging to directly track DOC associated with the release of organic and inorganic compounds, however, identifying correlation and coefficient of determination (R^2) might be beneficial to indirectly examine the probable relationship between a variation of leached concentration of a contaminant and DOC. Positive correlation between leached concentrations of HMW PAH compounds with DOC at corresponding LS ratios was observed in most cases which indicates that higher values of DOC were associated with higher values of aqueous phase concentrations of the studied compounds in amended columns (Figure 4).Positive correlation between leached concentrations of HMW PAHs and DOC was not obtained in column B1 in which only unamended contaminated soil was used implying a more important role of DOC in the leaching of HMW PAHs in biochar-amended soil compared to unamended soil. The closer Pearson correlation coefficient (R) - a statistical measure of the strength of a linear relationship between paired data- is to +1, the stronger the positive correlation. The Pearson correlation coefficient (R) showed strong positive correlation between DOC concentrations and eluted concentrations of benzo(a)anthracene, chrysene, benzo(a)pyrene, and benzo(k)fluoranthene in the presence of both crushed biochar and pulverized biochar. However, Figure 4 reveals a stronger correlation for crushed biochar-amended soil than pulverized biochar-amended soil in some cases such as benzo(a)anthracene. This might be a probable explanation for increasing concentrations of studied HMW PAHs in crushed biochar-amended soil compared to pulverized biochar-amended column as well as unamended column. Pearson's correlation coefficients (R) for benzo(a)anthracene, chrysene, benzo(a)pyrene and benzo(k)fluoranthene in pulverized biochar-amended soil (column B3) falls in the range of 0.8-1.0 i.e. very strong correlation according to Wuensch[38] suggesting a remarkable dependence of mobilization and leaching of the above-mentioned HMW PAHs on the release of DOC in column B2.

Conclusions

In this study, the leaching behavior of selected HMW PAHs i.e. benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(k) fluoranthene, benzo(ghi)perylene and dibenz(ah)anthracene in contaminated soil as well as biochar-amended soil were investigated using column leaching test. Results indicated strong sorption of all studied HMW PAHs to soil in all treatments over the course of the experiment. Cumulative release of benzo(a)anthracene, chrysene and benzo(a)pyrene was remarkably reduced by the application of pulverized biochar compared to unamended soil; however, pulverized biochar could not significantly decrease the leaching and release of benzo(k)fluoranthene. Very high hydrophobicity and vigorous affinity of the studied 6-ring PAHs i.e.

benzo(ghi)perylene and dibenz(ah)anthracene to soil organic matter prevented mobilization and desorption of them within both unamended and biochar-amended soil.

Application of crushed biochar enhanced mobilization of most of the studied HMW PAHs implying the significance of biochar particle size in the leaching behavior of HMW PAHs which can be further investigated in future studies. Reverse proportion of accumulated leached concentrations of the PAHs with molecular weight was found in this study.

Contribution of DOC in leaching of HMW PAHs in unamended soil as well as amended soil with crushed and pulverized biochar, which has rarely been studied previously, was also investigated in this research. Strong correlation between leached concentrations of HMW PAHs with DOC at corresponding LS ratios was found in biochar-amended soil. Pulverized biochar showed greater performance in a reducing release of most HMW PAHs from contaminated soil compared to crushed biochar. When biochar is used to control the migration of PAHs from contaminated soil, it is necessary to consider the impact of biochar particle size and DOC-associated mobilization.

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