

Leaching Characteristics of Phenanthrene and Pyrene in Biochar-amended Contaminated Soil

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Abstract

Contamination of soil with persistent organic contaminants has been of great concern due to their long-term effects in the environment. Polycyclic aromatic hydrocarbons (PAHs) are a well-known group of organic contaminants characterized by their resistance to biodegradation and high hydrophobicity. Mobilization and migration of PAH compounds in hydrocarbon-contaminated site may endanger groundwater resources. The main objective of this study was to investigate the influence of pulverized biochar on immobilization and release characteristics of model PAHs. Column leaching test was used to simulate leaching of PAH compounds from contaminated solid phase towards aqueous phase. Results showed strong sorption of both studied PAHs i.e. phenanthrene and pyrene to soil particles, however, at the end of the experiment 5.32% and 0.99% of the initial solid phase content of, respectively, phenanthrene and pyrene released into water in unamended soil. Application of pulverized biochar could finally reduce mobilization and cumulative release of the above-mentioned PAH compounds significantly. Similar trend was also obtained for sum 16 US EPA PAHs. Variation of pH during the leaching process and its contribution to mobilization and release of selected PAH compounds, which has scarcely studied previously, were also addressed. Results indicated that pulverized biochar as a cost-effective alternative to other carbon-rich amendments e.g. activated carbon can be effectively employed for site remediation purposes to reduce mobilization of PAHs in soil.

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Introduction

Industrial development in recent decades has enhanced living standards and trade growth in different countries [1]; however, millions of contaminated sites have been left contaminated and/or abandoned due to industrial activities around the world. Soil pollution is known to be a serious problem throughout the world which can not only endanger food chain, but also threaten scarce water resources. Contamination of soil with persistent organic contaminants has been of great concern due to their long-term effects in the environment [2]. Among various persistent organic compounds, polycyclic aromatic hydrocarbons (PAHs) have been received remarkable attention in recent years and continue to be unremittingly investigated, due to the fact that they are among the most mutagenic, carcinogenic and toxic contaminants in the environment [3, 4]. PAHs as a category of organic contaminants characterized by their resistance to biodegradation and high hydrophobicity can originate from natural sources such as volcanoes as well as anthropogenic sources such as incomplete combustion of fossil fuels, wood burning, and municipal and industrial waste incineration which are known to be the main sources of PAHs occurrence in the environment [5]. PAHs are ubiquitous in the environment [6] and several PAH compounds have been listed as priority pollutants by the US Environmental Protection Agency (EPA) and their serious adverse impacts on human health and the environment

such as cancer development and DNA damage is extensively investigated in the literature [7-9].

Many drawbacks are attributed to application of conventional soil remediation techniques to remove persistent organic contaminants e.g. PAHs and Polychlorinated Biphenyls (PCBs) from soil. Such approaches are mainly costly, require excavation and therefore disruptive to the ecosystem [10, 11]. In addition, some of the treatment processes might release harmful secondary byproducts which further affect human health and environment [12]. Several alternative cost-effective technologies have come into existence and investigated in recent years such as bioremediation and plant-aid remediation; however, being cost-effective might not be sufficient for a remediation method to be considered suitable for a remediation purpose. For instance, phytoremediation can be successfully employed as a cost-effective technique in remediation of different types of brownfields [10, 13]; however, that may not be an appropriate remediation choice in case of a superfund site which is in need of urgent response, because long time period is usually required for various plant species to establish meaningful biomass and remove contaminants from soil to meet legal requirements in a given nation that remains a significant barrier for effective use of this remediation technology in superfund rehabilitation programs. Therefore, development and assessment of applicable environmental friendly approaches to restrict

mobilization of contaminants in soil matrix is highly needed to reduce and control threats imposed by migration of contaminants from solid phase i.e. soil towards ground-water resources.

Among various treatment techniques, sorption can be a promising method to treat PAHs in an environmental friendly and economical manner because PAH compounds have low aqueous solubility and high sorption ability into the hydrophobic solid media. In addition, taking advantage of sorption to treat PAHs-contaminated soils has other benefits such as simplicity in design and operation as well as production of no harmful by-product during the process [12, 14]. However, various factors can influence the sorption properties of a given organic contaminant such as particle size, temperature, pH, contact time, and salinity [15]. The main idea behind application of carbon-rich material in treatment of soil contaminated with organic pollutants is to enhance the sorption capability of soil which can significantly control bioavailability and fate of such contaminants in the environment [16], thereby controlling their leaching from solid phase e.g. soil to aqueous phase e.g. groundwater resources to protect them from being contaminated with dangerous organic contaminants e.g. PAHs. High sorption capacity of activated carbon for treatment of PAHs-contaminated water and soil media has been reported in the literature [17]. Enhanced removal effectiveness of phenanthrene, anthracene, fluorine, pyrene, benzo(a)pyrene and chrysene from pore water of PAHs-contaminated soil was achieved when pulverized activated carbon was employed rather than granular activated carbon [18]. Brandly *et al.*, (2008) found that application of 2% pulverized activated carbon can efficiently remove PAHs from contaminated water [19].

Alternative economical carbon-rich materials such as biochars have also recently been used for removal of PAHs from contaminated water and remediation of contaminated soil with PAHs [12]. Application of biochar which is mainly produced by heating biomass in an oxygen limited environment has significantly increased in the last decade not only because of its potential to improve soil fertility and long-term soil carbon sequestration, but also for its sorption capability [20, 21]. Application of biochar is known to be a novel technology to remediate contaminated sites and has received considerable attention in recent years because of its significant affinity to persistent organic compounds e.g. PAHs. Biochars which can be produced from various sources might be employed to alter sorption characteristics of organic contaminants thereby controlling their leaching from soil into groundwater. In a study by Chen and Yuan (2013), application of the high temperature-produced biochar (700°C) promoted sorption of PAHs to solid phase remarkably [22]. Biochar is quickly gaining in popularity, however there are still only a limited number of researches evaluated the capability of biochar to reduce the bioavailability and mobility of contaminants in soil [23, 24]. The main objective of this study was to investigate the influence of organic amendment of soil with forest wood-derived biochar on leaching behavior and release of selected polycyclic aromatic hydrocarbon compounds from solid phase i.e. soil to aqueous phase i.e. water.

Biochar was applied in pulverized form in order to enhance effective contact between biochar particles and PAH compounds in soil. To the best of our knowledge, the effect of forest wood-derived biochar on leaching behavior and release of phenanthrene and pyrene, which were selected as the model PAH compounds in this study, has rarely been studied. In addition, variation of pH in column percolates and its implication in the context of leaching behavior of PAHs has also been addressed in the preset study for the first time.

Materials and Methods

Contaminated soil used in this study as a reference material was provided from the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany. Reference material used in the column leaching test had particles size of less than 2 mm and density of the particles was 2.65 g/cm³. In order to evaluate the role of a carbon-rich material in leaching behavior of PAHs from soil, forest wood-derived biochar prepared under the pyrolytic temperature range of ca. 600°C - 750°C and selected for evaluation in this study. Carbon fraction of the biochar was measured at 79.5 percent by weight with the bulk density of 1.5 g/cm³. Prepared biochar chips were originally in granular form with a wide range of particle sizes. After being air-dried for one week, some biochar chips were milled using a zirconium oxide planet ball mill to yield homogeneous pulverized biochar to be mixed with the PAHs-contaminated soil and used in the column leaching test.

PAHs-Contaminated soil was completely mixed with pulverized biochar to be placed in the column. Three different columns were prepared in this research; Column B1: PAHs-contaminated soil (100%), Column B2: PAHs-contaminated soil (95%) and pulverized biochar (5%), and Columns B3: blank column containing only clean quartz sand to determine probable residual contaminants in order to make sure that there is no residual contamination in the leaching system e.g. within plastic tubes. Based on what mentioned above, results of the leaching test for column B3 would only be considered to control the possible residual contamination in the system and might not contribute to research finding and implications regarding interpretations of leaching behavior of PAHs under the specified test conditions.

In order to conduct leaching tests glass columns with the capacity of ca. 425 cm³ were used. Columns were filled in accordance with DIN CEN/TS 14405 (2004) [25]. Each column was filled with contaminated soil as well as the mixture of contaminated soil and pulverized biochar (based on the above-mentioned ratios) by placing them into the columns in five sub-layers. Each layer was slightly compacted using a plastic rammer as defined in DIN CEN/TS 14405 (2004) [25]. Table 1 presented the experimental set-up of column leaching tests. In order to prevent loss of column materials i.e. soil and soil/biochar, glass wool was used to seal the bottom of each column. Clean quartz sand (ca. 1 cm height) was placed in the bottom of the columns to distribute the water flow through the solid material evenly; then columns were filled by solid mate-

rials i.e. PAHs-contaminated soil or mixture of soil and organic amendment at a height of approximately 12 cm. Upper quartz sand filter layer was also placed above the soil (1 cm) to prevent flotation of materials particularly during the initial saturation stage where considerably higher water flow rate is applied. Column were saturated and run up-ward to minimize trapping of air bubbles and prevent preferential flow patterns during the leaching process. A multi-channel peristaltic pump was used to pump water into the columns at a constant flow rate (Table 1). Deionized water was used in this research to avoid interference with probable non-target ions and compounds in water. Columns were initially saturated with the leachant using a higher pump velocity. The column leaching procedure used in this research followed German industrial standards [26]. Percolates from columns were collected in dark brown bottles by connecting the columns to the bottles using a stainless still tube.

Table 1. Experimental set-up for the column leaching test.

Parameter	Description
LS ⁻¹ ratio	Increasing up to LS ⁻¹ = 4 L kg ⁻¹
Leachant	DeminerIALIZED water
Filling height	12 cm
Flow rate	0.4 ml/min, up-flow percolation
Ambient temperature	20±1°C
Test execution	DIN CEN/TS 14405:2004

Phenanthrene and pyrene were selected as model PAHs to be monitored for leaching behavior under various conditions in this study. Initially 30 ml of leached water at the very early stage of leaching process was collected in separate bottles at assigned LS⁻¹ ratios to be analyzed for initial pH and turbidity, followed by leachate collection in dark brown bottles containing 10 ml cyclohexane (solvent) which was added to the bottles initially to avoid probable PAHs loss during the experiment. In order to extract PAH compounds from column effluents 10 µl of internal standard was added to the collected column effluent followed by 30 min shaking of the bottles to facilitate and accelerate mass transfer of the solutes (PAHs) from water phase into cyclohexane. PAH compounds within cyclohexane were extracted and measured using a GC/MS HP 6890 series which was equipped with DB-5MS column (30 m long, with 0.25 mm internal diameter and 0.25 µm film thickness). Initial column temperature was adjusted to 65°C for 4 min, firstly heated to 270°C at 10°C min⁻¹ and held for 10 min, finally to 310°C at 10°C min⁻¹ and held for 6.5 min. Initially collected leachates (30 ml) at specified LS⁻¹ ratios were measured for pH and turbidity. HACH 2100N Turbidimeter was used to measure turbidity levels in column leachates. In order to measure pH in column percolates a calibrated pH meter (pH 540 GLP) was used.

Results and Discussion

Phenanthrene and pyrene were selected as model PAH compounds in this research to investigate the leaching behavior in organic amended and unamended soil due to their widespread distribution in the environment and frequent occurrence where soil is contaminated with

PAHs. In addition detectable concentrations of both selected PAH compounds in groundwater resources due to leaching from solid phase have been reported in the literature [27]. Some chemical properties and the initial concentrations of the phenanthrene and pyrene are presented in Table 2 which indicates that pyrene has lower water solubility and higher Log K_{ow} compared to phenanthrene i.e. higher hydrophobicity. Phenanthrene which is known to have low to intermediate aqueous solubility and hydrophobicity has reported to have significant sorption to soil particles; however, it might still leave detectable contents in aqueous phase e.g. in groundwater resources beneath PAH-contaminated sites. Strong sorption of pyrene to soil particles in contaminated areas has also been reported [28].

Table 2. Chemical characteristics and initial solid phase content of the model PAH compounds [5, 29].

PAH compound	Number of benzene rings	Molecular Weight (g/mol)	Water solubility	Log K _{ow}	C _s (mg/kg dry soil)
Phenanthrene	3	178.2	1.10E+00	4.57	14.6
Pyrene	4	202.3	1.32E-01	5.18	8.2

Effluent concentration of phenanthrene and pyrene from organic amended and unamended contaminated soils are shown in Fig. 1. High initial concentration of phenanthrene was observed for unamended soil i.e. in column B1. Phenanthrene concentration in the leachate of unamended contaminated soil decreased almost steadily from 150.87 µg L⁻¹ at liquid to solid ratio of 0.3 L/Kg to 94.26 µg/L at LS ratio of 4 L/Kg, represents 37.5 % reduction over the course of the leaching process. Pyrene concentration in percolates of unamended column B1 had similar trend as phenanthrene after the LS ratio of 0.3 L/Kg; however, reduction of pyrene during the experiment was considerably less than that of phenanthrene, almost by the factor of ca. 2.7 implying the stronger sorption of pyrene to soil organic matters compared to phenanthrene. In a study by Zhang *et al.*, (2010), the aqueous concentration of phenanthrene was used as a measure of the effect of Pinus radiata-derived biochar on the sorption of PAHs in soil, where addition of 0.1-0.5 percent of biochar increased the soil sorption capacity by one order of magnitude compared to the unamended soil [30]. Results demonstrated that pyrene which has four benzene rings in its structure has stronger sorption to soil particles, in absence of biochar particles, compared to phenanthrene with three benzene rings, with leached amount of 12.24 µg/L at LS ratio of 0.3 L/Kg. Leached amount of pyrene in unamended soil decreased by only 13.8% from LS ratio of 0.3 to 4 L/Kg.

Figure 1 reveals that leached concentrations of pyrene declined not as fast as phenanthrene over the course of leaching process. One probable reason would be the fact that PAHs with lower solubility i.e. more hydrophobic compounds with higher K_d values tend to dissolve more slowly in pore water and the dissolution might last for a longer time compared to more soluble organic compounds. Strong sorption and extended tailing in leaching of higher molecular weight PAHs e.g. benzo(a)pyrene has been reported in the literature. Wick *et al.*, (2011) reported that leaching of PAHs from soil is more likely dominated by

colloidal organic matter rather than dissolution in water [5]. However, that would be more conservative to exclude more soluble PAH compounds e.g. naphthalene. Slight increase in pyrene concentration was observed at LS ratio of 1 L Kg⁻¹ (0.6%) that may be attributed to stronger sorption of pyrene to organic fraction of soil and therefore delayed mobilization and desorption of them from soil particles. Colloid-facilitated transport of higher molecular weight PAHs may also be considered as another explanation for unusual increase in leached amount of hydrophobic organic compounds from soil [31]. Obtained results indicate that the leaching fractions of initial amounts of the studied PAHs are declining with increasing hydrophobicity and molecular size which is consistent with previous studies conducted on leaching of PAHs [32]. Leaching of PAH compounds from column B3 in which only clean quartz sand where used (blank column) didn't occur indicating no residual contamination within the leaching system from previous studies. Biochar as a cheaper alternative to activated carbon was examined in this research with the aim of reducing leaching and release of PAHs from contaminated soils into water. Biochar may help further immobilization of PAHs in solid phase e.g. soil which is significantly beneficial in terms of site remediation. However, immobilization of organic compounds may not be favorable in all situations. For example, enhanced sorption of pesticides to soil particles may be favorable in the context of agricultural activity which can reduce pesticide residues in crops and therefore protect human health; on the other hand it may pose detrimental effects by reducing the effectiveness of herbicides that may lead to higher application rates of these hazardous chemicals [33]. Comparing leaching behavior of both studied PAH compounds in unamended and biochar-amended soil indicates the remarkable influence of soil organic amendment on immobilization of PAHs in soil (Figure 1). Application of pulverized biochar clearly reduced aqueous concentration of phenanthrene and pyrene at different liquid to solid ratios compared to the unamended column. Studying the variation of K_d between soil and organic amendments such as activated carbon and biochar has shown stronger affinity of some PAH compounds such as phenanthrene to organic amendment rather than soil organic matters and reduced desorption rate of such organic contaminants due to the application of organic amendments [32]. More than 84% reduction in phenanthrene concentration in column percolates was observed in presence of pulverized biochar in soil over the course of the present experiment with the highest value of reduction (90.5%) at LS ratio of 0.3 L/Kg. However, slight increase in leaching of phenanthrene in biochar-amended soil during the leaching experiment was observed. The highest leached concentration of phenanthrene reached at LS ratio of 2 L/Kg. Delayed release of phenanthrene in biochar-amended soil compared to unamended soil might be attributed to the strong sorption of phenanthrene to both soil and biochar particles and thus, slower dissolution kinetics which in turn postpone the required time to reach the maximum leached concentration of phenanthrene in aqueous phase. More insight into the long-term leaching and release of phenanthrene in biochar-

amended soil can be achieved if the leaching process is extended at higher values of LS ratio.

Results showed higher performance of pulverized biochar in immobilization of phenanthrene than pyrene. There might be two probable implications; first, suggesting interference of other controlling factors in leaching of pyrene (which has higher molecular weight and hydrophobicity than phenanthrene) such as colloid facilitated transport in presence of biochar particles and manipulating the original leaching pattern, and second, stronger sorption of pyrene to the solid phase compared to phenanthrene even in absence of an organic amendment as discussed earlier in this paper. However, application of pulverized biochar could still significantly reduce leaching of pyrene by 41.2 - 67.8 percent over the course of the leaching process. Initial leached amount of pyrene at LS ratio of 0.3 L/Kg declined from 7.2 µg/L in biochar amended column to 3.4 µg/L in amended soil with pulverized biochar i.e. 52.8% reduction. Aqueous concentration of pyrene in column B2 declined almost constantly with increasing LS ratios.

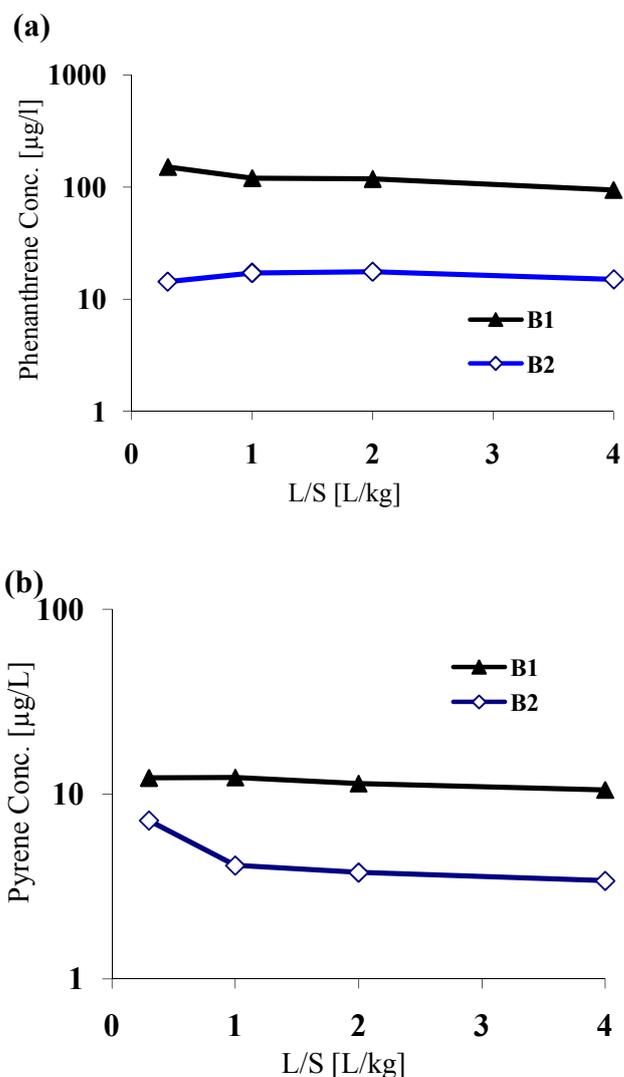


Figure 1. Leaching behavior of phenanthrene (a) and pyrene (b) in biochar-amended and unamended soils.

Figure 2 shows the accumulated leached amount of PAH compounds per kg soil at different liquid to solid ratios. Considering solid phase content of the phenanthrene and pyrene, results indicated that the cumulative release of the model PAHs reduced with increasing hydrophobicity and molecular size. At the end of the experiment, 5.32% of phenanthrene content in solid phase i.e. soil was mobilized and released into the water in column B1 in which no amendment was applied, whereas only 0.84% of phenanthrene was mobilized and released from biochar-amended soil indicating more than 6 times reduction in cumulative release of phenanthrene in presence of biochar in soil.

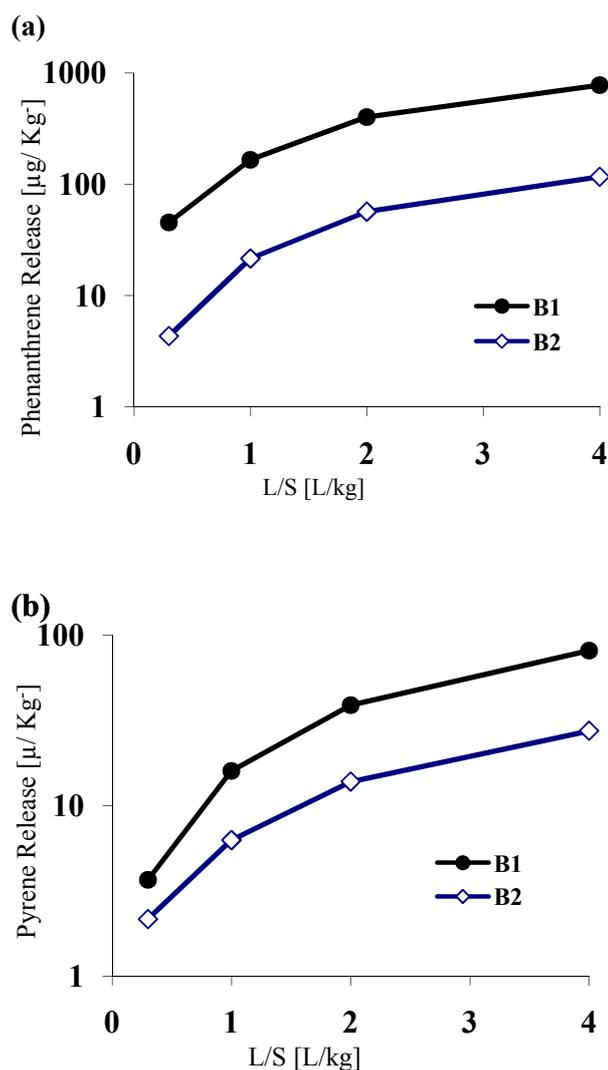


Figure 2. Cumulative release of phenanthrene (a) and pyrene (b) from biochar-amended and unamended soils.

Cumulative release of pyrene in percolates of column B1 in which unamended soil was used was significantly lower than that of phenanthrene i.e. by the factor of 5.4, indicating stronger sorption of pyrene to soil particles in comparison with phenanthrene as well as slower desorption kinetics. Soil amendment with biochar further reduced

cumulative release of pyrene from solid phase into aqueous phase in this study demonstrating the effectiveness of biochar in immobilization of pyrene in PAH-contaminated soil. Pyrene release from biochar-amended soil reduced by a factor of three compared to unamended soil. Cumulative release of phenanthrene and pyrene reduced by 85.0% and 66.2%, respectively, in presence of 5% pulverized biochar compared to unamended soil. Remarkable decrease in release of the model PAHs in this study from soil into aqueous phase in presence of organic amendment may be attributed to the stronger sorption of phenanthrene and pyrene to biochar particles than soil particles thereby reducing mobilization and migration of the PAH compounds from soil into water. Greater sorption of hydrophobic organic compounds on black carbon and soot-like materials than soil organic matter has been reported in the literature [17]. Additionally, increase in organic carbon content of soil/biochar system compared to unamended contaminated soil would be another probable interpretation for enhanced sorption of phenanthrene and pyrene to the solid phase and their reduced desorption and release. Pyrene is also shown to be more bioavailable in soils with low organic matter content than those with higher content of organic matter [34], implying the possible influence of carbon addition to soil on pyrene stabilization in soil through organic amendment as observed in this study for pulverized biochar. Decreasing concentrations of a solute in aqueous phase which was observed in this study indicates a non-equilibrium condition in a given column. The shift between equilibrium and non-equilibrium situations depends on various factors such as flow velocity, grain sizes, etc. Concentration of a given compound in the column percolates might also decline because of the depletion of that compound in solid phase, which was not the case in this study as no sharp decline and extended tailing was observed.

Leached behavior and release of sum 16 US EPA PAHs is shown in Fig. 3. The total concentration of 16 US EPA PAHs has declined to some extent at the end of the leaching process in both column effluents. Measured concentration of sum 16 US EPA PAHs in percolates of column B1 dropped from 1087.09 µg/L at LS=0.3 L/Kg to 928.61 µg/L at LS=4 L/Kg, implying 21.8% reduction in absence of biochar in soil that might be attributed to the initial mobilization of the more soluble PAHs followed by slower release governed by diffusion. The observed trend for the sum 16 US EPA PAHs in unamended soil was rather comparable with leaching trend of the studied 3-, 4-ring PAHs (Fig. 1) where higher initial concentrations of the PAHs was observed at LS=0.3 L/Kg. In this experiment, initially higher concentration of sum PAHs in column effluents followed by a slight drop was observed suggesting the establishment of non-equilibrium condition in column B1. Application of biochar to soil reduced aqueous concentration of sum PAHs during the experiment compared to unamended treatment. Leached concentrations of sum 16 US EPA PAHs in biochar-amended soil reduced by 4.4%, from LS ratio of 0.3 L/Kg to LS ratio of 4 L/Kg. Application of biochar decreased concentration of sum PAHs in columns effluents by more than 85% compared to

unamended treatment, over the course of leaching test. Findings of Cornelissen *et al.*, (2005) showed that employing carbon rich material e.g. charcoal and activated carbon can increase the sorption of hydrophobic organic compounds (HOCs) in soils and sediments by 1 to 3 orders of magnitude [35]. Enhanced sorption of polychlorinated biphenyls (PCBs) in biochar-amended soil and activated carbon-amended soil was also reported in the literature [23]. Surface area of an organic amendment can also contribute to the sorption process. In general, biochar have higher surface area than native soil organic matter that causes higher sorption capacity of persistent organic contaminants, like PAHs.

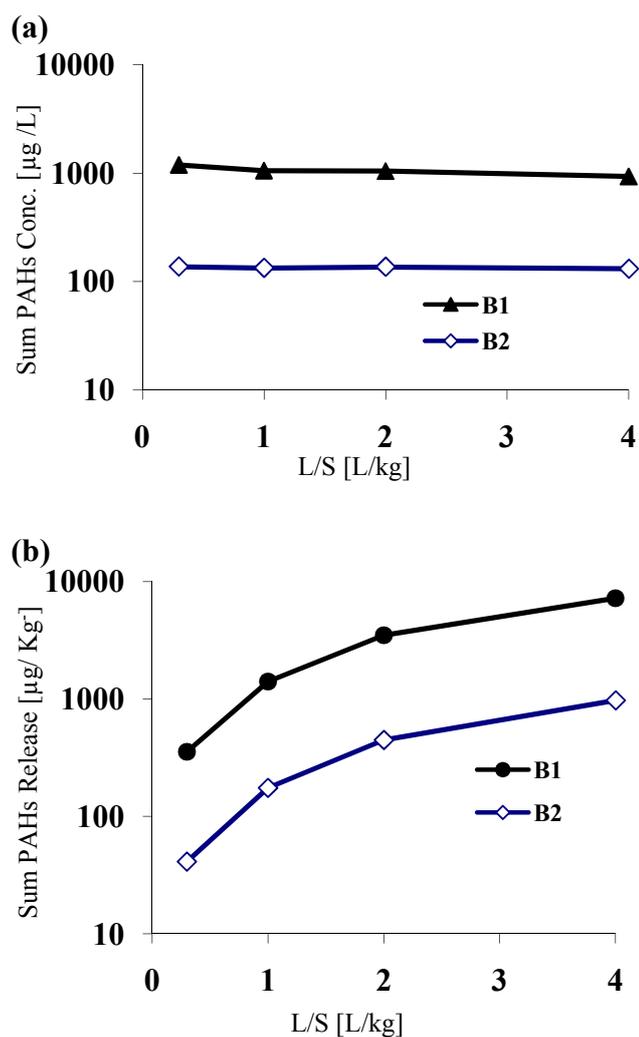


Figure 3. Concentration (a) and cumulative release (b) of sum 16 US EPA PAHs in percolates of biochar-amended and unamended soil.

As the aqueous concentration of sum PAHs in both amended and unamended columns did not dropped and depleted rapidly over the course of leaching test extended leaching and release of PAHs in both column is probable over extended periods of time which needs complementary investigations at higher LS ratios to be identified; however, in real-world scale it takes several decades to reach

that time. Slight increase in leaching of sum PAHs at LS ratio of 2 L/Kg was observed in this research suggesting the heterogeneous distribution of biochar particles in solid phase and delayed mobilization of some PAH compounds relevant to confined biochar particles in soil. It can be inferred from Fig. 3 that totally 7207.53 µg/Kg (ca. 7.2 ppm w/w) of the 16 US EPA PAHs in unamended contaminated soil released from soil into the water; i.e. 9.2% of the initial solid phase content of sum PAHs in soil. Application of pulverized biochar to soil showed remarkable influence on immobilization of sum 16 US EPA PAHs in soil and reduced release of sum PAHs from soil by the factor of 7 demonstrating great impact of biochar addition to soil on immobilization of hydrophobic PAH compounds. Obtained results suggest that strong affinity of PAHs to biochar particles might be a critical factor restricting mobilization and migration of PAHs from soil towards water. In biochar-amended column only 1.3% of the initial soil content of sum 16 US EPA PAHs mobilized and released into aqueous phase over the course of the leaching experiment. Results of the present study showed that pulverized biochar can promisingly reduce mobilization and release of the selected PAHs as well as sum of 16 US EPA PAHs from soil that is markedly favorable in terms of soil remediation.

Leachates were also analyzed for pH values. Measurement of pH is important as change in the chemical environment may alter the mobility of particles. Figure 4 shows that pH values of the percolates of column B1 remained fairly constant with slight steady decrease during the leaching process. Variation of pH values in column B1 were not so high during the leaching test that can affect the PAHs leaching result. Application of biochar in pulverized form increased pH values of leachates slightly, especially at higher LS ratios (Fig. 4).

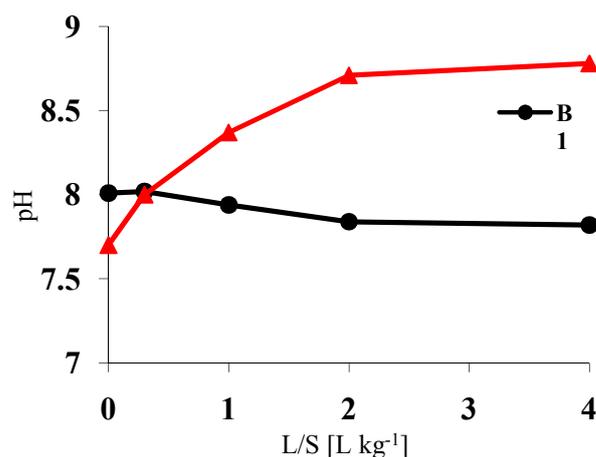


Figure 4. Variation in pH values in percolates of biochar-amended and unamended soil.

Adverse effect of pH increase on sorption of some PAH compounds e.g. fluorene on soil particles [36] and leonardite [37] has been reported in the literature. One probable reason for the slight increase in leaching of sum PAHs from LS ratio of 1 L/Kg to 2 L/Kg that was observed in

this study for column B2 might be an increase in soil pH at the corresponding LS ratio in presence of pulverized biochar. In other words biochar may affect leaching behavior of PAHs in soil by exerting two contradictory effects; firstly strengthen the sorption capacity through enhancement of organic carbon fraction in of soil/biochar system and restrict their leaching, and secondly promote leaching of PAHs in soil due to pH enhancement up on addition of biochar to soil. However, results of the present study showed that the first mechanism is dominantly control the leaching behavior of both studied PAHs as well as sum 16 US EPA PAHs and potential adverse effect of pH increase due to application of biochar has far less impact on sorption/desorption of PAHs in biochar-amended soil. In another study by Olu-Owolabi *et al.*, (2014) the enhanced sorption of pyrene to soil at low pH values was attributed the reduced polarity of soil surfaces; and therefore, increased affinity to pyrene [34]. Increase in desorption of other organic chemicals from soil with increase in soil pH has also been reported in the literature. Organic amendments such as biochars that contribute to soil pH increase may reduce non-polarity of soil to some extent and thereby increase organic contaminant desorption from soil which is not favorable in terms of remediation. Sheng *et al.*, (2005) suggested that higher attraction between negatively charged soil particles and ametryne as a pesticide at low pH may be responsible for higher adsorption of ametryne to soil particles at low pH values due to the fact that ametryne is positively charged at low pH; however, organic amendment of soil dominated the effect of soil pH in immobilization of ametryne in soil [38] that is consistent with the results of the present study.

In addition, pH can also affect dissolved organic carbon (DOC) content in leachate and hence may alter leaching behavior of PAHs associated with DOC. However, in a study by Munch *et al.*, (2002) pH variation had negligible effect on mobilization of carbon and leaching of DOC from soil [39]. A sorption study by Rad *et al.*, (2014) showed that adsorption of phenanthrene on activated carbon did not change significantly as pH changed implying more significant role of organic amendment on sorption and fate of persistent organic contaminants in soil rather than pH variation [40]. There is no strong evidence in the literature proving significant influence of soil pH on mobilization of PAHs in soil when variation in pH is not substantial which is also inferred from the results of the present research. Results did not show remarkable effect of pH on performance of the used organic amendment in this study most likely due to the fact that changes in pH were marginal in (less than 1 pH unit in most cases) both as a function of LS ratio and among amended and unamended treatments. In other words, results of the present study indicates that slight increase in soil pH because of the addition of biochar to soil might not affect their performance in immobilization of PAHs in contaminated soil.

Conclusion

Leaching and release behavior of selected PAHs i.e. phenanthrene and pyrene as well as sum 16 US EPA PAHs were investigated in this research. Application of pulverized biochar markedly reduced leaching and release of

studied PAH compounds from contaminated soil into water. Relatively high initial concentration of phenanthrene, which has three benzene rings in its structure measured in percolate of column B1 in which no organic amendment was applied to soil. Addition of pulverized biochar to soil reduced cumulative release of phenanthrene by more than 6 times, during the leaching process. Pyrene showed stronger sorption to soil organic matter in unamended soil and far less cumulative release into aqueous phase compared to phenanthrene. Application of biochar could significantly reduce leaching and cumulative release of pyrene too. Application of biochar increased pH values of column percolates during the leaching test. The influence of pH variation during a leaching test on leaching properties of PAHs in biochar-amended soil which has rarely been addressed previously revealed that pH increase during a leaching test due to addition of biochar may adversely affect desorption of PAHs, however, no strong evidence on enhanced desorption and leaching of PAH compounds was found in this study, probably due to marginal pH change. It is recommended to slightly reduce pH during the leaching test in future studies to gain deeper insight into the variation of desorption and leaching behavior of PAHs under controlled and uncontrolled pH condition, when biochar is applied to soil. Moreover, wider variation of pH during longer periods of time may further reveal the impact of pH on leaching behavior of PAHs. Over the course of the experiment, up to the LS ratio of 4 L/Kg, 9.2% of the total solid phase content of PAHs was mobilized and leached in unamended soil that might be considered as a threat to the groundwater resources. Based on the obtained results, application of biochar in pulverized form demonstrated promising effect in immobilization of PAHs in contaminated soil and reduction of their leaching and release into the aqueous phase. Further lysimeter investigation over extended periods of time is recommended to gain deeper insight into the real-world contribution of biochar in reduction of PAHs migration from soil into water.

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