Bulletin of Environmental Contamination and Toxicology (2019) 103:163–168
https://doi.org/10.1007/s00128-018-2521-3

Biochar Addition Enhances Phenanthrene Fixation in Sediment

Ying-heng Fei[1,2,3] · Yuxiao Chen[1] · Chengshuai Liu[4] · Tangfu Xiao[1]

Received: 8 October 2018 / Accepted: 8 December 2018 / Published online: 2 January 2019

Abstract
Biochar is believed to be promising for soil contaminant stabilization due to its large adsorption capacity. However, study in sediment is rare, especially with the aging effect. In the present study, a plant biomass-derived biochar was added to phenanthrene polluted sediment, in order to investigate its performance in sediment remediation. During the incubation period of 60 days, it was observed that the partition coefficient of phenanthrene increased in sediment either with or without biochar addition, as a result of aging process. Whilst, the biochar-added sediments showed much higher partition coefficients, as well as more curved adsorption isotherms, suggesting larger retention of the contaminant. Under the extreme extraction by strong surfactant, the release ratio of phenanthrene from polluted sediment was significantly reduced from 60% to 5% by 0.5% (w/w) addition of biochar. These results suggested that biochar would be applicable for improving the adsorption of organic pollutant in sediment, and the adsorbed organic pollutant would be stably fixed during aging as a result of the increased affinity.

Keywords Adsorption · Biochar · Phenanthrene · Fixation · Sediment

Biochar attracted much public attention in recent years. As Lehmann and Joseph (2009) defined, biochar is a carbon-rich material produced by thermal decomposition of biomass, which is usually fine-grained with porous structure. While, the International Biochar Initiative further specified that the material described above could be referred as biochar only when it is purposefully applied to soil for both agricultural and environmental gains (Manya 2012). Actually, ever from the beginning, biochar was found to be with multiple eco-functions, including improving soil fertility and plant productivity, sequestering carbon sources (Lehmann and Joseph 2009), as well as a promising adsorbent for hydrophobic organic compounds (Jin et al. 2016).

From the aspect of chemical composition and physical properties, biochar is commonly compared as black carbon, which is widely existed in natural soil and sediment, and often exhibited huge affinity with organic compounds and dominate the adsorption behavior rather than other natural organic matter (Cornelissen et al. 2005). Up to 10–1000 times of stronger adsorption capacity by black carbon or biochar makes it possible to apply biochar for fixation of organic pollutants in polluted soil and sediment. With the advantages such as easy production and low cost, biochars are widely applied for soil remediation as the artificial mimicking of natural black carbon (Chen and Yuan 2011). It has been reported by others that even a small amount of biochar (e.g. 0.1%) could dominate the overall sorption of organic contaminants, and with elevated dose of biochar, the adsorption by the soil–biochar mixture could be generally enhanced (Chen and Yuan 2011; Teixido et al. 2013).

So far, studies on biochar adsorption as well as its efficiency in fixation of soil contaminants have been extensively explored (e.g. Chen and Yuan 2011; Garcia-Jaramillo et al. 2015; Jin et al. 2016; Teixido et al. 2013), while investigation on sediment is rarely found. For the similarity in most

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00128-018-2521-3) contains supplementary material, which is available to authorized users.

✉ Chengshuai Liu
liuchengshuai@vip.gyig.ac.cn

[1] Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China

[2] Guangzhou Institute of Advanced Technology, Chinese Academy of Sciences, Guangzhou 511458, China

[3] Shenzhen Institute of Advanced Technology, Shenzhen 518055, China

[4] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

physical–chemical properties of soil and sediment, these two matrices are usually compared. However, as others reported that the possible interactions of biochar with soil components might attenuate the potential of biochar adsorption behavior (Garcia-Jaramillo et al. 2015), the difference in organic matter origins as well as the moisture condition and specific variety in mineral and particle structure between soil and sediment may bring difference in the biochar performances in pollutants fixation. Thus, in the present study, sediment was intentionally studied.

More importantly, this study aimed to assess the performance of biochar amendment during an aging period rather than based on static points. Though the sorption process is commonly considered as fast, the initial fast sorption is usually followed by a slow sorption process that may last for weeks or much longer period (Zhao et al. 2010). Most of the studies only focused on the fast effect of adsorption or desorption, which would result in an underestimation of pollutants retention and inaccurate estimation of mobility and bioavailability of the concerned chemicals (An et al. 2017).

For this purpose, the present study was conducted in laboratory in order to investigate: (1) the impact of biochar addition on the marine sediment adsorption of typical organic pollutants; and (2) whether this effect could last after a period of sediment aging. The results would help to evaluate the possibility of employing biochar as a promising stabilization material for organic pollutant contaminated sediment.

Materials and Methods

Natural marine sediment samples were collected from Victoria Harbour, Hong Kong, recorded as #0 for no artificial addition of biochar. The basic properties of the sediment was listed in Table S1 (Supplementary Information, SI). The sediment samples were collected from the top 30 cm surface of the sediment and stored below 4°C before the experimental use.

Dried biomass of giantreed (*Arundo donax Linn.*) was anaerobically ignited under 350°C for 4 h. And then the obtained biochar was incorporated into the sediment by the ratio of 0.2% and 0.5%. The sediment samples with added biochars were recorded as #2 and #5, respectively. When biochar was added, the sediment was kept at its original wet condition, and was manually agitated to mix well.

Model chemical, phenanthrene (PHE) powder (98%), was provided by Aldrich Company. It is very hydrophobic [Log $Kow = 4.57$ (Zhao et al. 2010), and $Sw = 1.1$ mg/L (Plaza et al. 2009)]. Stock solution was made in acetonitrile freshly before use.

At the start of sediment aging process, PHE was spiked into the natural sediment, with or without biochar addition. Amber glass screw-cap vials with Teflon-lined septa were employed as the sediment incubators. In each 15 mL-vial, about 1 g (dry weight) of natural sediment was spiked with 0.5 mL of PHE solution (20–200 mg/L, in acetonitrile), resulting in the final spiking concentration in the range of 10–100 mg/kg. Manual agitating and standing with cap unscrewed for 1 h was conducted to let the solvent be evaporated before incubation.

After PHE spiking, 10 mL of 200 mg/L NaN_3 (analytical grade, Aldrich Company) was added to each sediment-containing vials as cover water and also inhibitor of microbial activity. Vials were sealed and statically kept at 4°C refrigerator for incubation. For each kind of sediment, that is #0, #2 and #5, at each varied levels of PHE spiking concentration, 18 vials were prepared. On the day of 1, 4, 7, 15, 30 and 60, 3 vials were sacrificed for each 18-vial group, respectively.

The cover water was retrieved through centrifugation at 4000 rpm for 5 min followed by filtration through 0.45 µm polytetrafluoroethylene (PTFE) membrane, and then the concentration of PHE was determined. Residual PHE content in the aged sediment was estimated based on mass balance. Desorption isotherms were developed based on that.

The sediment was also extracted afterward. Briefly, the extraction was conducted by 10,000 mg/L SDBS solution (sodium dodecyl benzene sulfonate, 88%, Acros Company, powder dissolved in de-ionized water for usage). After equilibrated for 24 h in a shaker at the rate of 150 rpm, the mixture was centrifuged and the supernatant was sampled. The equilibrated concentration in SDBS solution was considered as extracted fraction and extraction efficiency was calculated.

HPLC system with diode array detector and fluorescence detector (Perkin Elmer, Series 200) was employed for PHE concentration determination. A C18 column (Phenomenex, 250 × 4.60 mm) was applied for the sample separation. The HPLC program for PHE determination was optimized by using 90% acetonitrile as the mobile phase, with the flow rate at 0.8 mL/min. Peak of PHE can be obtained within 15 min under the UV detection wavelength of 250 nm. The limit of detection and quantification was 0.05 mg/L and 0.15 mg/L, respectively. For concentrations under 0.1 mg/L, fluorescence detector (excitation and emission wavelengths were 250 nm and 370 nm, respectively) was employed for the quantification, limit of detection and quantification was 2.5 ng/L and 7.5 ng/L, respectively.

The desorption isotherm data of sediment adsorption of PHE were arranged to fit for typical adsorption models, including the linear partition model, and Freundlich model (Eqs. 1, 2) (Xing et al. 2011), i.e.,

$$Q_e = K_d C_e \tag{1}$$

$$Q_e = K_F C_e^{1/n} \tag{2}$$

where C_e and Q_e are the equilibrium concentrations of the chemical in the aqueous phase and sediment, respectively; K_d is the partition coefficient in the linear model; K_F and $1/n$ are the affinity coefficient and curvature index, respectively, in the Freundlich equation.

Unless stated otherwise, all tests and analyses were conducted in triplicate. The experimental data were analyzed by using Microsoft Office Excel (2013). Statistical analyses, such as *t* test and one-way analysis of variance (ANOVA), were carried out by SPSS (20.0) at the significance level of $p < 0.05$.

Results and Discussion

Desorption isotherms of sediment without biochar incorporation (#0) and the model fitting results are shown in Fig. 1 and Table 1. As the R^2 parameters indicated, both the linear and the Freundlich model could describe the isotherms well, while linear model performed better overall. For sediment organic matter, it was found that the content of nonhydrolyzable carbon and black carbon content in sediment is lower than that in soil, and the sediment organic matter is usually more aliphatic (Sun et al. 2010). Compared with more aromatic organic matter, sediment with higher aliphaticity may usually lead to a higher nonlinearity index $1/n$ (Zhang and He 2010).

Values of K_d or K_F was in the range between 2 and 3 orders of magnitude (Table 1), suggesting the big affinity of PHE to organic matter, which was consistent with its hydrophobic properties (Xu et al. 2010). Looking into the dynamic change of desorption isotherms and model fitting parameters, it could be obviously noticed that the desorption of PHE from the sediment became more and more difficult along with the extended aging time, as the isotherms gradually approached the vertical axis (Fig. 1) and the value of either K_d or K_F increased significantly (Table 1). Remarkably, the curvature index, $1/n$, also decreased noticeably, indicating that the desorption isotherms may tend to be more curved rather than straight lines. This observation is in accordance with other's finding that the time dependence changes of K_F increased while $1/n$ decreased during PHE and pyrene sorption by soil (Zhao et al. 2010). Consistently with Zhao's study on soil, the change in sediment reached to an equilibrium at around 30 days in this study.

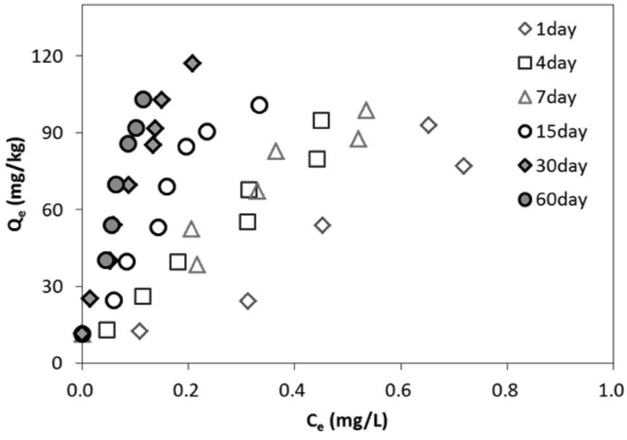

Fig. 1 Desorption isotherms of PHE from sediment with varied aging time

Table 1 Parameters for model fittings of PHE desorption from aged sediment

Aging time (days)	Linear		Freundlich		
	Log K_d	R^2	Log K_F	$1/n$	R^2
#0					
Day 1	2.08^{a}	0.9676	2.07^{a}	1.07^{a}	0.9123
Day 4	2.31^{b}	0.9889	2.25^{b}	0.86^{c}	0.9788
Day 7	2.32^{b}	0.9573	2.31^{c}	0.95^{b}	0.7715
Day 15	2.56^{d}	0.9837	2.48^{e}	0.85^{c}	0.9641
Day 30	2.79^{e}	0.9747	2.57^{f}	0.71^{d}	0.9701
Day 60	2.95^{f}	0.9940	2.67^{g}	0.69^{d}	0.9866
#2					
Day 1	2.41^{c}	0.9808	2.29^{c}	0.69^{d}	0.9914
Day 4	2.55^{d}	0.9725	2.38^{d}	0.64^{e}	0.9974
Day 7	2.79^{e}	0.9716	2.54^{f}	0.60^{f}	0.9523
Day 15	3.02^{g}	0.9510	2.29^{c}	0.65^{e}	0.9680
Day 30	3.24^{h}	0.9226	3.00^{j}	0.68^{d}	0.8913
Day 60	3.39^{j}	0.9771	2.96^{i}	0.70^{d}	0.9938
#5					
Day 1	3.01^{g}	0.9625	2.76^{h}	0.62^{f}	0.9883
Day 4	3.32^{i}	0.8844	2.98^{ij}	0.60^{f}	0.9590
Day 15	3.72^{k}	0.8726	3.15^{k}	0.54^{g}	0.9453
Day 30	4.16^{l}	0.8590	3.44^{l}	0.57^{f}	0.9519
Day 60	4.21^{m}	0.8754	3.52^{m}	0.60^{f}	0.9649

Means in the same column not sharing the same letter are different at the $p = 0.05$ level by one-way ANOVA

Adsorption of hydrophobic compounds like PHE is commonly believed to be dominated by organic matter, while the contribution from sediment or soil mineral fraction could be negligible (Mei et al. 2016; Xing et al. 2011). Under the framework of dual model by Xing and Pignatello (1997), different organic matter could be generally compared to rubbery and glassy domains, based on the chemical property and adsorption behaviors. For a certain sediment or soil, its organic matter is usually a mixture of different origins of various characteristics, and the overall adsorption can be well described by the sum of linear and curved models. When amorphous rubbery domain dominated, the sorption behavior might appear to be linear partition, and if condensed carbon or glassy domain take more charge, the sorption would be saturated at high loading concentration and could be described better by curvilinear models.

In the present study, aging effects may be attributed by several behaviors including partitioning into organic matter, strong surface adsorption, diffusion into micropores, etc. (An et al. 2017). Models were developed by Weber and Huang (1996) used to divided organic matter to inner condensed fraction and outer amorphous fraction, which in fact somehow perform similarly to the glassy domain and rubbery domain as described in Xing's dual model. Others (e.g. Xu et al. 2010) also observed similar time-dependent adsorption process of PHE on geosorbents like soils and peats. The partitioning domain is believed to be less energetically favorable, and can be reached faster. Provided with extended time, PHE molecules is possible to diffuse from readily accessible amorphous rubbery domain, which was considered as partitioner with linear adsorption, to condensed glassy domain, which had both partition and hole-filling mechanisms for adsorption and displayed multi-Langmuir models, made the overall adsorption change to more curved and higher affinity.

Desorption of PHE from the biochar amended sediment (#2 and #5) was also summarized in Table 1 by model fittings. Compared to sediment without biochar addition (#0), K_d and K_F values were much higher and $1/n$ was significantly lower. This result implied that incorporation of biochar enhanced the adsorption of PHE on sediment. The single adsorption of PHE by biochar at 3-day equilibration was found to be huge, suggested by Log $K_d = 4.7$ (Fig. S1, SI). By adding 0.2% and 0.5% of biochar to the marine sediment, the K_d was increased by 114% and 751%, respectively. The enhancement was much higher than predicted from the simple mass-based estimation (Fig. S2, SI). A pore-expanding effect on biochar was reported previously in mineral-treated biochars (Li et al. 2015). For the possible reason of elevated enhancement of PHE adsorption by the biochar-sediment mixture, further study is required.

Noticeably, the R^2 values also suggested that the fitting by Freundlich model were generally better than by linear model. The mixing of biochar changed the composition of sediment organic matter, mainly increased the content of condensed carbon. Considering the dominance of adsorption behavior by even small amount of black carbon or artificially amended biochar (Cornelissen et al. 2005; Chen and Yuan 2011), the curvilinear adsorption by added biochar would take more part in the overall sediment sorption behavior, leading to more curved isotherms.

The change of affinity parameters for #2 and #5, including K_d and K_F, was similar to that for #0, as shown in Table 1 and Fig. 2a. When the aging time extended, the affinity of PHE to sediment increased significantly. The most dynamic increase occurred during the first month of aging. After 60 days of aging incubation, K_d was 9.5 and 15.9 times of that before incubation, for #2 and #5, respectively. As a result of the artificially dosed black carbon (biochar), the diffusion of PHE molecules from easily accessible surface site to inner adsorption sites brought much higher increase to the strong affinity of PHE to the amended sediment.

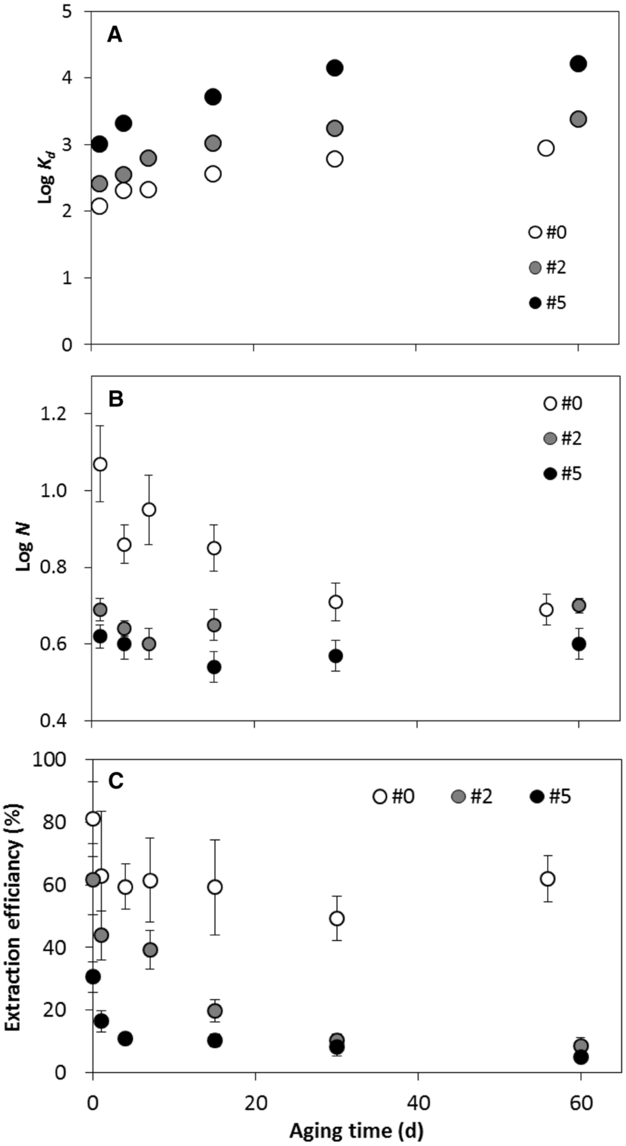

Fig. 2 Parameters of PHE desorption during aging incubation (**a** partition coefficient; **b** curvilinear index; **c** extraction efficiency)

The decline of curvature index, $1/n$, for #2 or #5 is not as significant as that for #0, though the initial values were already much lower (Fig. 2b). Values of $1/n$ were at around 0.6–0.7 and 0.5–0.6 for #2 and #5, respectively. All the $1/n$ values for biochar amended sediment were below the raw sediment. It is even lower for #5 than that for #2, probably due to the higher content of black carbon by addition.

Besides the apparent changes in adsorption capacity, the risk of release even at the extreme solution (strong extraction) was also largely reduced, demonstrated by the extraction efficiency (Fig. 2c). Surfactants like SDBS is usually employed as washing agent for contaminated-soil remediation (Yang et al. 2006; Guo et al. 2009). In the present study, extraction by SDBS was used to estimate the maximum possibility of PHE leaching from stabilized sediment.

During the aging process, the extraction efficiency declined significantly for #0, from 81% to 62%, implying that the extreme possibility of PHE release was greatly decreased. This was comparable with Zhao's report (2013) that the SDBS extraction efficiency of PHE from soils was reduced from around 90%–60% during a 120-day aging process. As discussed above, the equilibrium in soft partitioning domain could be reached faster, while this is more reversible, compared with that in the hard adsorption domain (Xu et al. 2010). The affinity of PHE became stronger and firmer by molecular diffusion from surface and amorphous sites to inner and condensed sites, leading to more and more difficult desorption and release.

While the biochar-added sediment showed much lower extraction efficiency. At the beginning of incubation (day 0), only 60% and 32% of spiked PHE could be extracted by SDBS, with 0.2% and 0.5% of biochar addition, respectively, which were already around or much lower than the level for #0 after 60 days of aging and stabilization. Incorporation of black carbon like biochar could efficiently improve the stability of sorbed pollutants in sediment.

After 2 months of aging, the retention of PHE in biochar amended sediment showed further improvement. The extraction efficiency decreased to 9% and 5% for #2 and #5, respectively, suggesting the difficulty of PHE extraction. Noticeably, this extraction was by strong surfactant, and release of PHE under general environmental conditions would be even harder. Condensed glassy domain provided by biochar played significant role in retaining the PHE in the sediment.

1. During the aging process, partition coefficient, K_d, displayed a significant enhancement in all the three sediments, suggesting that more PHE molecules were distributed into the sediment. Confirmed by the declined SDBS extraction efficiency, which meant less possibility of release to aqueous phase, the adsorbed PHE was stabilized in the sediment.
2. Amended with biochar with very small dosage (0.2% or 0.5%), the improvement in retention of PHE in the polluted sediment was already significant. The adsorption affinity of PHE to biochar-added sediment was more than double of that to non-amended sediment.
3. The performance of biochar immobilization was further better, giving time of sediment aging. For extreme extraction, the release ratio of PHE was limited to < 10% and 5% for 0.2% and 0.5% of biochar addition, respectively, suggesting it's capability as a promising technique for sediment stabilization.

Acknowledgements This study was funded by the National Natural Science Foundation of China (Grant Nos. 41473124, 41673138, 41830753), Special Fund for Agro-Scientific Research in the Public Interest of China (201503107-4), the One Hundred Talents Program of the CAS, the Science and Technology Planning Project of Guangdong Province (Grant Nos. 2014A020216001, 2016B020242006), and the Science and Technology Planning Project of Shenzhen City (Grant No. JCYJ20150521094519490).

References

An XJ, Xiao BH, Di XY, Dong H, Tang HM (2017) Research progress on aging of organic pollutants in geosorbents: a review. Acta Geochim 36(1):27–43

Chen BL, Yuan MX (2011) Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. J Soils Sediments 11(1):62–71

Cornelissen G, Gustafsson O, Bucheli TD, Jonker MTO, Koelmans AA, Van Noort PCM (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ Sci Technol 39(18):6881–6895

Garcia-Jaramillo M, Cox L, Knicker HE, Cornejo J, Spokas KA, Hermosin MC (2015) Characterization and selection of biochar for an efficient retention of tricyclazole in a flooded alluvial paddy soil. J Hazard Mater 286:581–588

Guo HQ, Liu ZY, Yang SG, Sun C (2009) The feasibility of enhanced soil washing of p-nitrochlorobenzene (pNCB) with SDBS/Tween80 mixed surfactants. J Hazard Mater 170(2–3):1236–1241

Jin J, Kang MJ, Sun K, Pan ZZ, Wu FC, Xing BS (2016) Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine. Sci Total Environ 550:504–513

Lehmann J, Joseph S (2009) Biochar for environmental management: science and technology. Earthscan, London

Li JF, Li SJ, Dong HP, Yang SS, Li YM, Zhong JX (2015) Role of alumina and montmorillonite in changing the sorption of herbicides to biochars. J Agric Food Chem 63(24):5740–5746

Manya JJ (2012) Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs. Environ Sci Technol 46(15):7939–7954

Mei Y, Bai YC, Wang LY (2016) Effect of pH on binding of pyrene to hydrophobic fractions of dissolved organic matter (DOM) isolated from lake water. Acta Geochim 35(3):288–293

Plaza C, Xing B, Fernandez JM, Senesi N, Polo A (2009) Binding of polycyclic aromatic hydrocarbons by humic acids formed during composting. Environ Pollut 157(1):257–263

Sun K, Gao B, Zhang ZY, Zhang GX, Zhao Y, Xing BS (2010) Sorption of atrazine and phenanthrene by organic matter fractions in soil and sediment. Environ Pollut 158(12):3520–3526

Teixido M, Hurtado C, Pignatello JJ, Beltran JL, Granados M, Peccia J (2013) Predicting contaminant adsorption in black carbon (biochar)-amended soil for the veterinary antimicrobial sulfamethazine. Environ Sci Technol 47(12):6197–6205

Weber WJ, Huang WL (1996) A distributed reactivity model for sorption by soils and sediments. 4. Intraparticle heterogeneity and phase-distribution relationships under nonequilibrium conditions. Environ Sci Technol 30(3):881–888

Xing BS, Pignatello JJ (1997) Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. Environ Sci Technol 31(3):792–799

Xing BS, Senesi N, Huang PM (2011) Biophysico-chemical process of anthropogenic organic compounds in environmental systems. Wiley, Hoboken

Xu XY, Sun HW, Simpson MJ (2010) Concentration- and time-dependent sorption and desorption behavior of phenanthrene to geosorbents with varying organic matter composition. Chemosphere 79(8):772–778

Yang K, Zhu LZ, Xing BS (2006) Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS. Environ Sci Technol 40(13):4274–4280

Zhang JH, He MC (2010) Effect of structural variations on sorption and desorption of phenanthrene by sediment organic matter. J Hazard Mater 184(1–3):432–438

Zhao Q, Weise L, Li PJ, Yang K, Zhang YQ, Dong DB, Li P, Li XJ (2010) Ageing behavior of phenanthrene and pyrene in soils: A study using sodium dodecylbenzenesulfonate extraction. J Hazard Mater 183(1–3):881–887

Zhao Q, Xing BS, Tai PD, Li H, Song L, Zhang LZ, Li PJ (2013) Effect of freeze-thawing cycles on soil aging behavior of individually spiked phenanthrene and pyrene at different concentrations. Sci Total Environ 444:311–319