Biochar as An Effective Material on Sediment Remediation for Polycyclic Aromatic Hydrocarbons Contamination

To cite this article: Z Chen *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **281** 012016

Biochar as An Effective Material on Sediment Remediation for Polycyclic Aromatic Hydrocarbons Contamination

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Abstract. The mechanism of biochar as capping materials on polycyclic aromatic hydrocarbons (PAHs) removal in river sediments was investigated. When biochar was amended, pyrene was decreased through strengthened aging effects (1.6 times), which was attributed to high adsorption capacity of the biochar. While biochar did not alter the main microbial community, it provided a stable niche for PAHs degradation microorganisms, which attributed to the porosity and biological affinity of biochar. According to the results, biochar increased the opportunity for PAH-degraders to contact PAHs in sediments. When electron acceptors were available, the pyrene-degraders in biochar pore degraded the adsorbed pyrene rapidly (+103%). Therefore, biochar could be an effective material on PAHs removal in sediments.

1. Introduction

The high-speed urbanization and associated human activities have led to dramatic alternations on urban river ecosystems [1, 2], which consequently degrades surface water quality [3]. As a pollutant sink in the river ecosystem, sediment can accumulate various polycyclic aromatic hydrocarbons (PAHs), which derive from ship traffic petrol leaking and urban wastewater runoff [4]. PAHs are difficult to degrade under anaerobic conditions in the environments [5] and remain risks to ecosystems as well as human health [6]. Therefore, the removal of PAHs in sediment is a key technique in urban river remediation.

Several approaches were developed to remediate the PAHs contaminated sediments, including dredge, bioaugmentation, biostimulation and capping with clean material [7]. Among these methods, capping with viable substances were widely used as low-cost approaches for the natural recovery of sediments [8]. For the capping treatments, selection of cap-material is the critical part of this technology. These materials, such as clean sand, zeolite, and activated carbon [9], are all expected to have high adsorption capacities and be able to block the diffusion of organic pollutants from sediments. However, the utilization of these materials would consume natural resources (such as sand and zeolite) and require excessive energy in put (activated carbon). Development of a more environmental-friendly materials is of great concern on capping treatment for PAHs degradation.

Biochar is unknown as an environmental-friendly material, since it involve in carbon sequestration pathway and it always be produced from various agriculture wastes such as straws, branches, and nut shells [10]. The characteristics of biochar depend on its raw matrix and pyrolysis conditions. Biochar that derived from natural plants are usually porous and hydrophobic, which have high adsorption capacity for organic components [11]. Therefore, biochar has the potential capability to be used as a capping material for PAHs treatments. This study aims to investigate the mechanism of biochar as capping materials for PAHs removal in urban river sediments.

2. MATERIALS AND METHODS

2.1. Sediment and biochar preparation

Sediment samples were collected from surface sediments from the Pearl River segment in Guangzhou city, China (113°17′37″E, 23°6′24″N) where high PAHs contamination as reported [4]. Sediment samples were sieved through a 0.2-mm sieve and then homogenized with equivoluminal river water. Pyrene solution in acetone were spiked into the slurry achieved a final concentration of ~22.5 ng/g dry sediment, then incubated at dark for 120-day aging.

The biochar was made by crushed macadamia nut shells (φ=0.5-1.0 mm) pyrolyzed under a N2 atmosphere. The pyrolysis processes were set increasing temperature from 250 to 500 ℃ at 10 ℃ min−1 then kept 500°C for 1 h.

2.2. Setup of batch experiment

The batch microcosms were conducted in 40-mL airtight flasks, which contented 20 g of aged sediments and 10 mL of filtered river water. In biochar amending treatment (BC), 0.25 g of biochar was first added and mixed into sediment, while nitrate (1 mg N of NaNO3) was then added every 10 days for BCN treatment. Treatment without biochar and nitrate addition was set as the controls (CK).

The incubations were performed at 30 ℃ in dark, and triplicate sub-samples were collected at days 0, 10, 45 and 100. The inertial water centrifuged by 3000 rpm was used to determine nitrate concentration. Sediments after precipitated were used for extract the bulk (using dichloromethane) and mild-extracted (using hydroxypropyl-β-cyclodextrim) pyrene according to the methods described by Yang et al. [4]. DNA from sediment samples was extracted by PowerSoilTM DNA Isolation Kit (MoBio Laboratories, Carlsbad, CA, USA) with the recommended manuscript methods.

2.3. Pyrene determination and microbial community analysis

After bulk and mild extraction, pyrene was analyzed with a gas chromatograph/mass spectrometer detector (Agilent 7890A/5975C, GC/MS, USA) as primary described [4]. The surrogate recovery of chrysene-d12 was 92.1% ± 8.6%.

The extracted DNA was amplified with primers 515f/806r targeting the V4 region of 16S rRNA gene, and then sequenced on Illumina Hiseq platform. Sequence data were processed with Usearch pipeline and treated with Qiime software as described by Pan et al. [12]. The 8023 qualified sequences were re-extracted randomly from each sample database and result in 2854-4785 OTUs at the cutoff of 97% sequence identify. The Illumina sequence raw data reported here was submitted to the NCBI Sequence Read Archive (http://www.ncbi.nlm.nih.gov/sra) under accession number SRP110548.

3. RESULTS AND DISCUSSION

3.1. Bulk pyrene removal as biochar addition

PAHs are difficult to be degraded because contaminated sediments are often in an anaerobic state and lacking effective electron receptors. In fact, sediments, particularly urban river sediments, are rich in PAH-degraders, but their activities are limited due to the lack of electron receptors. In our experiments (such as sediment collection and homogenization), it was impossible to avoid oxygen from air to conduct aerobic pyrene degradation, although the dissolved oxygen level is low. As Figure 1 showed, about 18.0% of pyrene was decreased in the control treatment during 100 days.

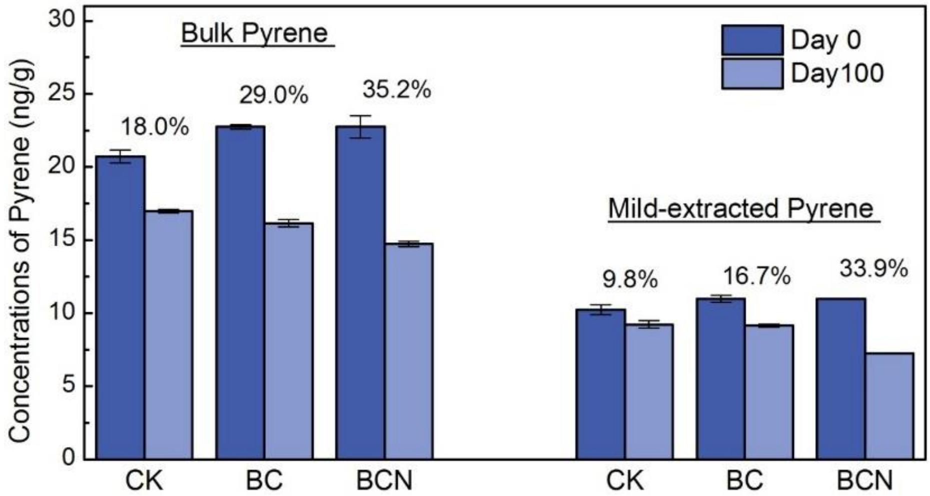

Figure 1. Concentrations of bulk and mild-extracted pyrene in sediment. The percentages were represented the decrease rate in 100 days.

In engineering projects, biochar was used to improve soil texture, such as to increase soil porosity and soil's carbon content [13]. In this study, the addition of biochar significantly decreased the amount of pyrene at the end of the experiment (Figure 1). This could be due to three reasons: (1) The aged PAHs are less bioavailable and hard to be extracted [14]. The added biochar improved the aging effect in the matrix because biochar is a high carbon content material that has been proved to be effective in the adsorption of hydrophobic organic matter including PAHs [15]. (2) The biochar could serve as the sediment skeleton and increased the soil ventilation [16], which led the electron receptors to get farther diffusion. The more widely distributed electronic receptors would promote more widespread polycyclic aromatic hydrocarbon degradation. (3) The porous biochar provided as a stable carrier for PAHs degrader. These three mechanisms will be further discussed below.

3.2. The mechanisms of pyrene removal

PAHs in sediments mainly exist in the adsorption phase. The strength of adsorption is related to the content of organic matter, the particle size of sediment matrix and the residence time of PAHs entering the sediment, all of these have influences on the PAHs aging effect [4, 14]. The aged PAHs are difficult to extracted from sediment, and not degradable by microorganisms. In contrast, the weak adsorbed fraction of PAHs which could be extracted by mild-extraction agent, such as n-butanol, methanol, Tenax, and hydroxypropyl-β-cyclodextrin, are considered as more bioavailable and easy to be degraded by microorganisms [17]. In this study, mild-extracted pyrene was determined to investigate the real degradation compared with the decrease of bulk pyrene. As Figure 1 shows, the initial concentrations of mild-extracted pyrene were comparable during different treatments. Afterwards, the higher decreases were observed in biochar treatments, these means that more pyrene was degraded with biochar adding. This result supported the hypothesis that biochar could stimulate electron acceptor diffusion as well as provide the suitable niche for PAH-degraders and thus increased the pyrene biodegradation.

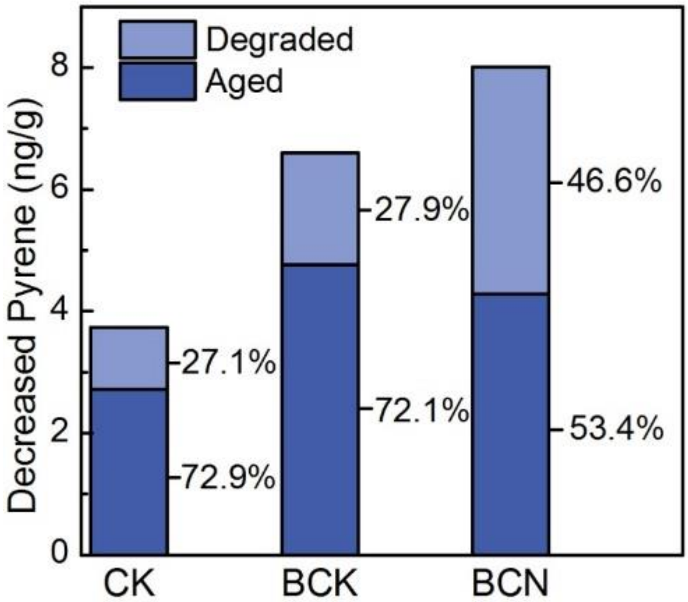

Figure 2. Portion of decreased bulk pyrene. The percentages were represented the degraded and aged portions in decreased bulk pryene.

As discussed above, the bulk decrease of pyrene could be divided into two phases: the biodegraded phase and the aged phase (Figure 2). As shown in Figure 2, biochar addition increased the concentrations of aged pyrene, which suggested that more pyrene was adsorbed into biochar. The adsorbed pyrene could then distribute on the surface and in the pores of biochar particles. Therefore, biochar actually increased the exposure opportunities for pyrene and pyrene-degraders. When the electron acceptor nitrate was added, even more pyrene was degraded (Figure1 and 2, BC vs BCN).

3.3. Effects on microbial community

Previous studies suggested that biochar addition would alter the microbial structure since biochar can change the soil textures significantly [18]. However, the microbial communities on the phylum level were similar between the control and the biochar treatment in this study (Figure 3). This might be attributed to the sediment characteristics of it being a saturated soil. Interstitial water increased the mobility rate for microorganisms and let them showing similarities on a high taxonomic level. Getting insight into OTUs level (Figure 4) allowed the switch of microbial communities becomes more obvious between the control and biochar treatment.

On the other side, nitrate triggered the alternation of microbial communities by increasing the group of β-Proteobacteria (Figure 3). Higher nitrate concentration increased the abundances of Gallionella spp., Thiobacillus spp. and species in class Rhodocyclaceae (Figure 4, Cluster B). These species were reported as nitrate reducers [19, 20] with some of them also being PAH-degraders [20]. As more nitrate was used, the more pyrene was degraded. Therefore, although biochar did not significantly alter the composition of microbial communities, it served as the stable carrier for pyrene-degraders, when electron acceptors were available, the adsorbed pyrene in biochar could be degraded effectively.

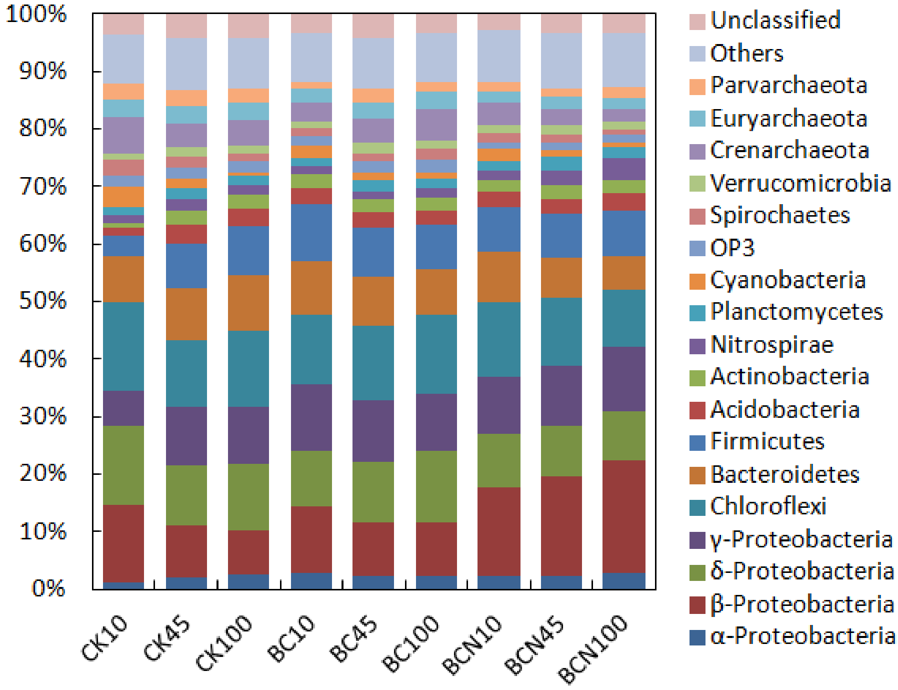

Figure 3. Microbial community structure on phylum level in different treatments.

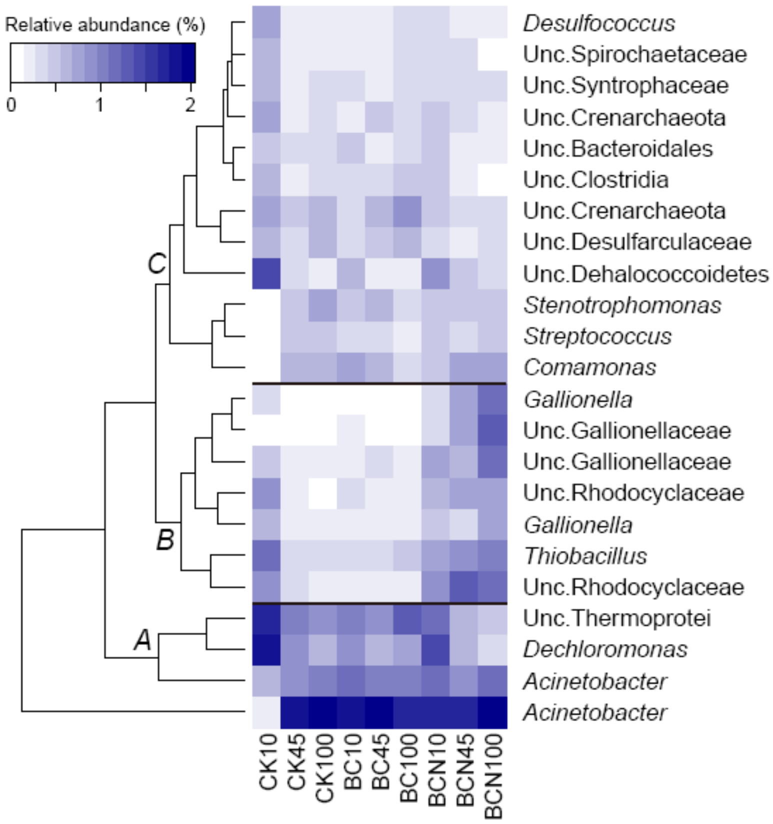

Figure 4. The relative abundance changes of major OTUs (relative abundance > 0.5%).

4. CONCLUSIONS

Biochar is an environmental-friendly material used in sediment remediation. It increased the aging effects for pyrene in sediment that decreased the ecological risk for aquatic organisms. Biochar can increase the interaction between adsorbed pyrene and pyrene-degraders. Although the major structure of microbial composition was not altered after adding biochar, the total diversity of the microbial community was increased. Biochar pore served as the stable niche for PAHs degradation bacteria, and available electron acceptors increased pyrene degradation rate effectively.

ACKNOWLEDGEMENTS

This work was supported by grants from the National Natural Science Foundation of China (No. 51508111, No. 41501278), Pearl River S&T Nova Program of Guangzhou, China (No. 201806010050), Program of International S&T Cooperation, the National Key Research and Development Program of China (No. 2016YFE0106600), Science and Technology Program by Guangdong Financial Department (No. PM-zx097-201601-024), Science and Technology Program of Guangzhou, China (No. 2016201604030057), the Research Fund Program of Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology (2018K10).

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