Environmental Pollution 231 (2017) 752–760

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Exploration of biodegradation mechanisms of black carbon-bound nonylphenol in black carbon-amended sediment☆

Guanghuan Cheng [a, b, c], Mingyang Sun [a, b], Xinlei Ge [a, b], Xinhua Xu [c], Qi Lin [c], Liping Lou [c, d, *]

[a] Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAEET), Nanjing University of Information Science & Technology, Nanjing, 210044, People's Republic of China
[b] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, People's Republic of China
[c] Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, People's Republic of China
[d] Key Laboratory of Water Pollution Control and Environmental Safety Technology, Zhejiang University, Hangzhou 310029, People's Republic of China

ARTICLE INFO

Article history:
Received 27 March 2017
Received in revised form
22 July 2017
Accepted 14 August 2017
Available online 30 August 2017

Keywords:
Black carbon (BC)
Nonylphenol (NP)
Adsorbed state
Biodegradation
Mechanism

ABSTRACT

The present study aimed to investigate biodegradation mechanisms of black carbon (BC)-bound contaminants in BC-amended sediment when BC was applied to control organic pollution. The single-point Tenax desorption technique was applied to track the species changes of nonylphenol (NP) during biodegradation process in the rice straw carbon (RC)-amended sediment. And the correlation between the biodegradation and desorption of NP was analyzed. Results showed that microorganisms firstly degraded the rapid-desorbing NP (6 h Tenax desorption) in RC-amended sediment. The biodegradation facilitated the desorption of slow-desorbing NP, which was subsequently degraded as well (192 h Tenax desorption). Notably, the final amount of NP degradation was greater than that of NP desorption, indicating that absorbed NP by RC amendment can be degraded by microorganisms. Finally, the residual NP amount in RC-amended sediment was decided by RC content and its physicochemical property. Moreover, the presence of the biofilm was observed by the confocal laser scanning microscope (CLSM) and scanning electron microscope (SEM) so that microorganisms were able to overcome the mass transfer resistance and directly utilized the absorbed NP. Therefore, single-point Tenax desorption alone may not be an adequate basis for the prediction of the bioaccessibility of contaminants to microorganisms or bioremediation potential in BC-amended sediment.

1. Introduction

Despite a general consensus among researchers that only the bioavailable fractions of contaminants in soils or sediments can be degraded by microorganisms (Cornelissen et al., 1998; Rhodes et al., 2010; Spasojević et al., 2015; Wang et al., 2017), recent studies have found that adsorbed contaminants can also be degraded when strong adsorbents such as black carbon (BC) are present in soils or sediments (Rhodes et al., 2008, 2012; Zhang et al., 2012). However, there have been debates in the field of microbial degradation over the questions of: does the degrading bacteria only utilize the contaminants dissolved in aqueous solution? In other words, can the compounds absorbed by the solid particles only be utilized by the bacteria after desorption, or the absorbed contaminants can be directly utilized by the degrading bacteria without desorption? Earlier studies suggest that only hydrophobic organic chemicals (HOCs) that have been desorbed into free form in the aqueous phase can be utilized by microorganisms and the bioavailability of HOCs can be assessed directly from the rapid-desorption fraction (Cornelissen et al., 1998). However, growing evidence supports the idea that certain degrading bacteria can directly utilize the solid-phase absorbed contaminants to degrade in the absence of the desorption process. Rhodes et al. (2012) compared the amounts of microbial degradation and desorption of phenanthrene in soils before and after the addition of BC. They found that without the addition of BC, the amount of degradation was equivalent to that of

☆ This paper has been recommended for acceptance by Dr. Harmon Sarah Michele.

* Corresponding author. Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, People's Republic of China.
E-mail address: loulp@zju.edu.cn (L. Lou).

http://dx.doi.org/10.1016/j.envpol.2017.08.061
0269-7491/

phenanthrene desorption. However, after adding BC to the soil, the amount of phenanthrene degradation became greater than that of its desorption. Their results suggested that the degrading bacteria of phenanthrene could directly make use of the phenanthrene absorbed by the BC. To account for this phenomenon, there are several possible explanations.

Firstly, BC contains P, C, Na^+, Mo and other nutrients and trace elements, which might stimulate the growth of microorganisms (Zhang et al., 2005). Especially in the high temperature-derived biochar, even more carbon sources and nutrients are likely to be available for microbial growth. Previous research has shown that the addition of biochar (Lehmann et al., 2011) or activated carbon (Meynet et al., 2012) to the natural soil can significantly increase the soil microorganism quantity and respiration intensity. The amount of increase is positively correlated with the amount of added carbon. In addition, adding biochar or activated carbon has also been shown to considerably affect the microbial community composition and enzyme activity. Secondly, BC sequestration can concentrate the contaminants and increase the local concentration level of contaminants. As the degrading bacteria tend to enrich in areas with high concentrations of contaminants (Van Loosdrecht et al., 1990; Leglize et al., 2008), the concentration of BC on contaminants can make the bacteria approach the BC surface, and the contaminants absorbed to BC and ready to be utilized by the bacteria. Thirdly, BC is likely to help with the formation of biofilms by serving as a shelter, where the microorganisms can attach and be protected from being washed away or preyed (Jin, 2010; Lin et al., 2013). So far, there has been limited research directly tapping into the effect of BC.

Nevertheless, Rhodes et al. (2008, 2012) found that activated carbon could facilitate the formation of biofilms, which indirectly proved a facilitative role of BC. Rhodes et al. (2012) observed that the microorganisms attached to the activated carbon could continuously utilize the adsorbed phenanthrene in the micropores to facilitate the desorption and degradation of phenanthrene. The authors claimed that the biofilms formed on the surface of the activated carbon could utilize the HOCs of low solubility in water and high absorbability to overcome the mass transfer resistance during normal microbial degradation of HOCs. They assumed that it was the presence of biofilms that made adsorbed HOCs directly available to microorganisms. This would have important implications for the bioremediation of contaminated sites. Perhaps by concentrating on stimulating biodegradation during an initial phase when the BC amendments are freshly added, then the overall contaminant levels might be reduced. However, few studies have looked specifically at the biodegradation of contaminants that are freshly sorbed to such BC amendments and the underlying mechanism has also remained unclear. To better understand the phenomenon and its mechanism, it is crucial to study the adsorption and desorption of the contaminants.

In recent years, some studies have investigated this issue with the use of microbial degradation and desorption coupling models. The usage of some partial extraction techniques, e.g. hydroxypropyl-β-cyclodextrin (HPCD) extraction and Tenax extraction, are considered to be convenient and effective means to estimate the desorption kinetics of HOCs. Because Tenax beads have a density lower than water, making them float to the surface after centrifugation and easy to be recovered from the supernatant (e.g., by filtration). This economical property, when coupled with its hydrophobic nature for trapping HOCs, simplifies the measurement of HOC desorption. Combining it with microbial degradation results in a more effective, direct and accurate method for the study of microbial bioavailability of HOCs. However, continuous Tenax desorption experiments tend to be cumbersome and time-consuming. The single-point Tenax desorption technique is therefore proposed to replace the rapid-desorption fraction to characterize the bioavailability of HOCs. In current studies, a single desorption of 6 h, 24 h and 30 h is most often chosen in place of the rapid-desorption fraction. For example, Van Noort et al. (2002) used 6 h-Tenax desorption to assess the bioavailability and release risk of organic contaminants in sediments with different planar structures. Moermond et al. (2007) found that the 6 h-Tenax desorption amounts of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were consistent with their concentrations in organisms like invertebrates and fish. Shor et al. (2003) on the other hand, claimed that the 6 h-Tenax desorption underestimated the bioavailability of HOCs, whereas the 24-h Tenax desorption is a better alternative of the rapid-desorption fraction to assess the bioavailability of HOCs. Mackenbach et al. (2014) also found that the 24 h-Tenax extraction amount of PCBs was consistent with their accumulation amount in oligochaeta. Barnier et al. (2014), however, found that the 30 h-Tenax desorption amount was consistent with that in the rapid-desorption fraction. Thus, 6 h-, 24 h- or 30 h-Tenax desorption may all be used to assess the rapid desorption, i.e., bioavailability. Study of our research group showed that the 6 h-Tenax desorption amount of nonylphenol (NP) in the BC-amended sediment correlated the most with the amount in the rapid-desorption fraction. Therefore, it would be the optimal alternative of the rapid-desorption fraction to assess the bioavailability of NP. The desorption amount of 192 h-Tenax was also found correlated well with the desorbable amount and could serve as a predictor of the desorbable NP.

The present study investigated the microbial degradation of BC-bound NP in BC-amended sediment, with NP as the target contaminant and rice straw carbon (RC) as the strong absorbent. The single-point Tenax desorption technique was applied to track the species changes of NP during biodegradation process in RC-amended sediment. The correlation between NP desorption and the microbial degradation was then analyzed. In addition, whether biofilms formed were observed with the confocal laser scanning (CLSM) microscope and scanning electron microscope (SEM), so as to explore the microbial degradation mechanism of NP in the RC-amended sediment. Finally, the correlation between the amount of residual NP and RC content and properties in RC-amended sediment was analyzed using binary linear regression models to better understand the mechanism of RC's effect on NP biodegradation. Consequently, data from this study aid in understanding how BC-bound HOC was biodegraded by microorganism in BC-amended sediment and evaluating the feasibility of the application of BC on the HOCs pollution, and provide theoretical foundation for remediation of HOCs pollution in soils and sediments.

2. Materials and methods

2.1. Chemicals and materials

NP (Mixture of isomers) with a purity of >99% was purchased from Aladdin (Shanghai, China) and prepared as a concentrated stock solution with acetonitrile. Tenax TA (60–80 mesh) was obtained from Supelco (Bellefonte, Pennsylvania, USA). Tenax TA was activated or regenerated by ultrasonic washing with methanol, acetone and hexane in order (Cornelissen et al., 1997).

Sediment was obtained from the Qiantang River, Hangzhou, Zhejiang province, China, using a clamshell sampler (Juchang Company, Qingdao, Shandong province). The pH and cation exchange capacity (CEC) was 7.14 and 10.94 cmoL/kg, respectively, and the sediment was composed of 7.12% sand, 13.84% silt and 79.04% clay. The total organic carbon and BC content in the sediment was 0.964% and 0.37%, respectively. Some other details, such as background concentrations of heavy metals, were also described