Effect of exogenous carbonaceous materials on the bioavailability of organic pollutants and their ecological risks

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Abstract

The presence of exogenous carbonaceous materials (ECMs) in organic contaminated soil is widespread because of their intentional application as carbonaceous amendments (e.g. biochar and activated carbon) or unintentional discharge (e.g. carbon nanomaterials). Most research so far has focused on the sorption behaviors of ECMs in soil. However, the impact of ECMs on the bioavailability of organic pollutants (OPs) and their ecological damages remain unclear. This paper presents an overview on how the ECMs affect bioavailability of OPs to different organisms, such as microorganisms, plants and earthworms. This is affected by different biological response and properties of ECMs. Moreover, the possible risks of ECMs on soil biota are also discussed at different level. This review presents a unique insight into risk assessment of ECMs. Further researches should focus on possible change in physicochemical characteristics of ECMs when exposed to the natural environment and the consequent influence on their sorption ability and ecotoxicity outcomes.

Keywords: Organic pollutants; Exogenous carbonaceous materials; Adsorption; Bioavailability; Ecological risk

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1. Introduction

Currently, increasing concern has been raised concerning the issue of soil organic contamination resulting from intensive industrial and agricultural activities (Cheng et al., 2016; Liu et al., 2012; Tang et al., 2014b; Yang et al., 2015; Zhou et al., 2016). The coexistence of exogenous carbonaceous materials (ECMs) and organic pollutants (OPs) is possible in the soil environment (Pang et al., 2011; Zeng et al., 2013a). ECMs can be divided into carbonaceous amendments and carbon nanomaterials (CNMs). Carbonaceous amendments, such as activated carbon and biochar, are highly recommended in soil remediation because of their large surface area, high porosity and great sorption capacity (Feng et al., 2010; Ghosh et al., 2011; Tang et al., 2016). In addition, the rapid development of nanotechnology and unique physicochemical properties of carbon nanomaterials (CNMs) have caused a sharp increase in the production and utilization (Tang et al., 2015; Tang et al., 2014a; Tang et al., 2012; Zhou et al., 2017). Various CNMs such as carbon nanotubes (CNTs), graphene and fullerene have been widely applied in numerous fields, which inevitably release into the natural environment (Tang et al., 2014; Liu et al., 2012; Zhang et al., 2007). Besides, the potential use of CNMs in environmental remediation has also been reported (Gong et al., 2009; Song et al., 2017). Accordingly, whether intentionally (e.g. pollution remediation) or unintentionally (e.g. accidentally spill), the existence of ECMs in soil is possible. In this case, two sides should be considered.

On the one hand, sorption behavior of ECMs would decrease bioavailability of

OPs (Fan et al., 2008; Hu et al., 2011; Huang et al., 2008; Yang et al., 2010). The sediments amended with 1% of carbon materials showed a decrease in freely dissolved concentration (C_{free}) of polybrominated diphenyl ethers (PBDEs) in sediments, up to 98.3% with activated carbon, followed by 78.0% and 77.5% with biochar and charcoal, respectively (Jia and Gan, 2014). Towell et al. (2011) also found that extractability of polycyclic aromatic hydrocarbons (PAH) significantly decreased with increasing addition of fullerene soot and CNTs. When evaluating the impact of ECMs on OPs bioavailability, microorganism is mostly studied as it is the primary degrader of OPs and is widely exist in natural environment (Ren et al., 2017; Rodrigues et al., 2013; Zhu et al., 2016a). However, considering the agronomical value and engineering application of plants in soil remediation, it is also important to investigate its impact on plants uptake of OPs (Hamdi et al., 2015; Zhou and Hu, 2017). In addition, earthworms are considered as predominant soil fauna in terrestrial ecosystem and perform many beneficial functions in soil, including soil structure improvement, carbon and nutrient cycling, and bioaccumulation of OPs (Rodriguez-Campos et al., 2014; Shan et al., 2014). Therefore, the influence of ECMs on earthworm accumulation of OPs should also be considered. Meanwhile, due to different uptake route of organisms to OPs, the impact of ECMs can be contradictory. More than by porewater uptake, some species are able to access adsorbed OPs or direct ingest soil particles (Chen et al., 2017; Huang et al., 2017; Hurtado et al., 2017; Khorram et al., 2016). Therefore, how the ECMs affect bioavailability of OPs to microorganism, plants and earthworm should be separately studied.

On the other hand, although positive role of ECMs in environmental remediation has been recently reported, environmental risks associated with ECMs has become an issue of growing concern (Zeng et al., 2013b). For example, the application of biochar has been questioned due to the release of toxic compounds that are detrimental to soil organism (Buss et al., 2015; Oleszczuk et al., 2013). Altered soil microbial community, reduced seed germination and earthworm avoidance in biochar amended soil have been documented (Buss and Masek, 2014; Masiello et al., 2013; Tammeorg et al., 2014). Moreover, CNMs exhibit stronger toxicity than biochar due to smaller size and higher content of catalyst metals. Potential risks of CNMs have long been studied. Knowledge of CNMs-induced toxicity is diverse, which can be roughly divided into those mediated by inherent toxicity of CNMs (e.g. oxidative stress), or by attachment to organisms and consequently hindering their physiological activity, but also by toxic substances along with CNMs (Barbolina et al., 2016; Rajavel et al., 2014; Tu et al., 2013). Hence, a comprehensive understanding of how ECMs adversely affect soil biota is essential.

Overall, research on the interactions among ECMs, OPs and organisms is important to advance our understanding of the environmental impacts of ECMs and their performance in contaminated soil remediation. In this paper, firstly, we explored the impact of ECMs on the bioavailability (i.e. biodegradation/bioaccumulation) of OPs to various organisms. Subsequently, the possible risk of ECMs on soil biota is discussed at different levels (e.g. cellular, individual and community level). Moreover, future research needs of the risk assessment of ECMs are highlighted.

2. How do ECMs affect bioavailability of OPs?

ECMs are generally thought to decrease bioavailability of OPs in soil due to their strong sorption capacity. A modeling experiment by Marchal et al. (2013b) showed that it was the low desorption rate of PAH rather than bacterial activity that restricted PAHs mineralization. Moreover, microbial debromination ratio of BDE-47 was dropped by 92.8%–98.2% with 5.0% amendment of ECMs (Zhu et al., 2016a). Similar findings have been observed in plant accumulation of OPs. This may be attributed to the decrease of freely dissolved fraction of OPs in soil pore water, which is the primary form to be assimilated by plants roots in soil (Khorram et al., 2016). For example, addition of 5% biochar decreased turnips uptake of PAH by approximately 84% in the study of Khan et al. (2015), and a 2.5% and 5% amendment of biochar reduced concentration of emerging organic contaminants (i.e. bisphenol A, caffeine, carbamazepine, clofibric acid, furosemide,ibuprofen, methyl dihydrojasmonate, tris(2-chloroethyl)phosphate, triclosan, and tonalide) by 34–48% in lettuce roots and 23–55% in lettuce leaves in the study of Hurtado et al. (2017). Hamdi et al. (2015) also reported that CNTs significantly reduced bioaccumulation of pesticide by lettuce, with 88% decrease in roots and 78% in shoots by decreasing pesticide bioavailability. In addition to plant uptake, after amendment of 2% biochar, earthworm accumulation of fomesafen also decreased by 49.5%–52.9% compared to the control treatment (Khorram et al., 2016). Petersen et al. (2009) also proved that soils amended with 3.0 mg/g CNTs significantly decreased pyrene bioaccumulation in earthworms. Moreover, it has been reported that the acute toxicity to earthworm *Eisenia fetida* induced by complex of multi walled carbon nanotubes (MWCNT) and sodium pentachlorophenate was lower than MWCNT or sodium pentachlorophenate alone (Zhang et al., 2014). Overall, the adsorption behavior of ECMs would reduce the bioavailability of OPs.

While it is straightforward to conceive that ECMs decrease freely dissolved portion of OPs and their bioavailability to porewater-uptake-dominated organisms, some special cases where exposure route of OPs to certain species are not directed by porewater, are not well understood. Uptake mechanisms of OPs vary with different organisms. As for most species, such as plants, porewater absorption is the dominant pathway. However, for some microorganisms, the dissolved and adsorbed OPs are both available. As to earthworm, besides dermal absorption and porewater uptake, direct ingestion of soil particles is also possible. Mechanisms and possible effects of ECMs to the bioavailability of OPs can be seen in Table 1.

2.1. Microorganism

There is a possibility that bacteria utilize the adsorbed OPs by directly adhesion or formation of biofilm on ECMs (Kuśmierz et al., 2016). The observation that adding ECMs in soil caused a decline in desorption of phenanthrene, but not an equally decline in biodegradation and mineralization, evidenced the degradation possibility of adsorbed phenanthrene (Marchal et al., 2013a; Rhodes et al., 2012).

Xia et al. (2010) clearly proved the existence of *Agrobacterium* bacteria in the pores of carbon materials by scanning electron microscopy. Highly retained nutrients, available water and well-developed pores in biochar offer a good habitat to microorganisms. It provides available site for microbial attachment via hydrophobic attraction or electrostatic forces (Ding et al., 2016). Moreover, Zhang et al. (2016a) observed attached bacteria on functionalized MWCNTs and graphite, but not in other ECMs, indicating that this process was structural specific. Similarly, Jiang et al. (2017) found that interactions between MWCNTs and biological membrane were electrostatically mediated. Negatively charged MWCNTs prefer to interact with positively charged lipids by electrostatic forces and formation of H-bonds and C-O-P bonds. MWCNTs with defects (surface functional groups and dangling bonds) could provide more active site for the MWCNTs-biological membrane interactions (Jiang et al., 2017). However, not all bacteria are able to attach on ECMs, especially when immobilized with OPs. Sorption of PAH in MWCNTs truly decreased their availability to low-tolerant microbes, but the high-tolerant microbes were able to colonize on the surface of MWCNTs, which explained why MWCNTs treatment had no difference on PAH biodegradation with the control group (Shrestha et al., 2015). This from another point of view revealed that only fraction of bacteria could attach on MWCNTs.

In addition, the cytotoxicity of ECMs would inhibit biodegradation activity, indirectly affecting the bioavailability of OPs. Yang et al. (2017) found that addition of 100 mg/L biochar or CNTs led to significant reduction of atrazine biodegradation, with 47.6% and 68.9% respectively. This was attributed to the cell membrane damage by ECMs. Besides, biodegradation rate of atrazine was less decreased in biochar than CNTs, indicating that CNTs had higher toxicity to *Acinetobacter lwoffii*DNS32 than biochar, as was demonstrated by less bacterial viability (Yang et al., 2017).

2.2. Plant

Understanding uptake of OPs in plants provides insight into how ECMs affect plants accumulation of OPs. Generally, OPs in soil are in intimate contact with the plant root system. In this case, rhizosphere soil is the most important region where plant systems interact with OPs, concerning roots, root exudates, rhizosphere soil and microbes (Gerhardt et al., 2009; Zeng et al., 2017). Movement of OPs into the root zone is often blocked as OPs are bounded to the soil before reaching rhizosphere or are hydrophobic and insoluble in water. Bioavailable fractions of OPs include water-soluble fraction that can be desorbed by water and acid-soluble fraction that can be desorbed by root exudates (Wu and Zhu, 2016). Plants provide impetus to this process by releasing root exudations such as carbohydrates, organic acids, and amino acids. Sun et al. (2013) examined the effect of different root exudate on pyrene availability in soils and found enhanced availability of pyrene with increasing root exudate at concentrations of 0–21 g/kg. Metal or mineral dissolution and release of dissolved organic matter (DOM) by root exudate are responsible for the enhanced availability. Dissolution of metal cations or soil minerals break up the structure of mineral-organic matter and soil organic matter

(SOM) is released from solid to solution, thus increasing the content of DOM (Sun et al., 2013). In view of the peculiarity of root exudates, the strong adsorption capacity of ECMs could have been masked. In the experiment conducted by Denyes et al. (2016), either biochar or activated carbon caused no effect on dichlorodiphenyltrichloroethane (DDT) accumulation in plants *Cucurbita pepo spp.pepo*, but biochar reduced DDT accumulation in earthworm. This was linked to the effectiveness of root exudates facilitating DDT desorption and uptake.

Meanwhile, there is a possibility that toxicity of CNMs increase bioaccumulation of OPs despite their sorption behavior. The increased content of dichlorodiphenyldichloroethylene (DDE) in agricultural crops in the presence of C_{60} was observed by De La Torre-Roche et al. (2012). This could be that C_{60} was absorbed by plant roots, so was the absorbed DDE on C_{60}, or that C_{60} induce cell membrane damage. CNMs usually occurred as a co-contaminant in soil and they might similarly accumulate in plants, just as OPs (De La Torre-Roche et al., 2012).

2.3. Earthworm

Earthworms have been recognized as important decomposer animals in soil and indicator of soil health (Gomez-Eyles et al., 2011; Gu et al., 2016). As a result, earthworms are widely used to measure the bioavailability of OPs. Comprehensive knowledge of earthworm behavior (especially feeding behavior) in contaminated soil is necessary to understand how ECMs affect OPs bioaccumulation in earthworm. Uptake of OPs by earthworm is realized either through passive absorption from soil pore water across dermis or direct ingestion of soil particles through gastrointestinal route and final accumulation of OPs in lipid-rich tissues (Johnson et al., 2002; Safaei Khorram et al., 2016). However, this process is species-dependent. In a study done by Wang et al. (2014a), bioaccumulation of atrazine in epigeic *Eisenia fetida* (*E. fetida*) was 5 times lower than that in endo-anecic *Metaphire guillelmi* (*M. guillelmi*). This was explained by the finding that dermal absorption was dominating uptake mechanism of atrazine in *E. fetida* while gut process played a key role in *M. guillelmi*. Chen et al. (2017) also showed that the total gut:skin accumulation ratios of Tetrabromobisphenol A in *M. guillelmi* was 2.7:1, which indicated that uptake of Tetrabromobisphenol A by *M. guillelmi* was mainly through the gut pathways. However, dermal absorption of uptake of Tetrabromobisphenol predominated in *E. fetida* (1:1.7). Accordingly, the dominating uptake mechanisms in *E. fetida* and *M. guillelmi* is usually determined by measuring the accumulation ratios of contaminants in body wall and gut of earthworm (Chen et al., 2017; Huang et al., 2017; Wang et al. 2014a). Besides, atrazine predominantly resided in biochar rather than soil in this study, where atrazine was hard to be extracted by *M. guillelmi* (Wang et al. 2014a). Therefore, biochar amendments led to higher reduction of bioaccumulation in *M. guillelmi* than *E. fetida*. On the contrary, in another study of Li et al. (2017a), addition of biochar or CNTs resulted in a larger decrease in *E. fetida* than *M. guillelmi*. For example, the reduction degree of γ-hexabromocyclododecanes bioaccumulation in *E. fetida* reached to 67.3% while in *M. guillelmi* it was only 47.4% after amendment of 0.5% CNTs. Uptake route of hexabromocyclododecanes by earthworm was through soil particles digestion, which was a characteristic feeding strategy of *M. guillelmi*, thus less affected by ECMs than *E. fetida*. The contrasting result was probably attributed to different sequestration potentials of atrazine and hexabromocyclododecanes by biochar (Li et al., 2017a). However, further studies are needed to confirm if the chemical properties of OPs would affect the biochar-induced decrease in bioaccumulation of OPs by different species of earthworms. Moreover, biochar reduce OPs bioavailability to earthworms more than just through increasing adsorption on biochar. It is suggested that biochar act as food source competing with OPs, thus decreasing OPs availability to earthworms (Gomez-Eyles et al., 2011).

However, Shan et al. (2014) found that biochar increased bioaccumulation of ^{14}C-catechol by earthworm *M. guillelmi*. Similarly, Gu et al. (2016) reported that biochar associated phenanthrene and 2,4-dichlorophenol were not accessible to microorganisms but remained available to *M. guillelmi*. Gut passage of earthworms freed biochar-associated OPs and then increased bioavailability. This was linked to feeding behavior of earthworm: grinding of soil particles and intestinal digestion exposed OPs to gut fluid of earthworm and/or surfactant-like substances in gut fluid increased desorption of OPs (Gu et al., 2016; Shan et al., 2014).

Nonetheless, several studies have proved the bioaccumulation of C_{60} and CNTs by earthworm *E. fetida* (Li et al., 2010; Petersen et al., 2008). There is a possibility that CNMs-adsorbed OPs are easier to be transported to organisms. Hu et al. (2013) reported that MWCNTs could act as a carrier of OPs and increased nonylphenol bioavailability to earthworm *E. fetida*. The possible reason for this phenomenon could be that CNTs penetrated intestinal cells, and then released more CNTs-adsorbed nonylphenol into the earthworms (Hu et al., 2013).

3. Potential ecological risks of ECMs for soil biota

3.1. Carbonaceous amendments

Although biochar has been widely regarded as a safe material with promising application in environmental remediation, there are still some reports about its harmful impact on soil biota (Lehmann et al., 2011). Undesirable impacts related to biochar were caused by unfavorable living environment (e.g. excessive salinization, water and nutrient deficiency or liming) and/or potential introduction of pollutants along with biochar. Among all the possible causes, pollutants released from biochar have been a focus in recent research. Pollutants in biochar can be divided into poisonous organic chemicals, toxic elements and volatile organic compounds (VOCs), which are derived from feedstocks (e.g. sewage sludge and heavy metal hyperaccumulators) and/or production process of biochar (Keiluweit et al., 2012; Zielińska and Oleszczuk, 2015). Pyrolysis process decompose part of organic compounds, along with synthesis of condensed aromatic structures (e.g. dioxins, furans and PAH), and VOCs (e.g. phenols, alcohols, organic acids) that are end up trapped and re-condensed in pyrolysis liquid phase (Buss et al., 2015; Hale et al., 2012; Kuśmierz et al., 2016). Besides, Liao et al. (2014) proposed that nonconventional pollutants from biochar such as persistent free radicals were accounted for its phytotoxicity. Pyrogenic radicals in biochar induced the formation of OH radicals, which could cause plasma membrane damage, thus inhibiting seed germination and growth (Liao et al., 2014). From the cost-effective perspective, feedstocks of biochar should be organic wastes that were of little economic value. However, those materials inherently contain PAH and heavy metals.

It has long been suggested that PAH should be responsible for the toxicity of biochar to various organisms (Oleszczuk et al., 2013). However, toxic extent of PAH in biochar vary with different sources. Pyrogenic PAHs (formed from incomplete combustion) had higher mutagenicity potential than petrogenic PAHs (originated from soil petroleum), as reported by Anjum et al. (2014). The final content of PAH in biochar is dominated by both process of degradation and formation of PAH during pyrolysis. Zielińska and Oleszczuk (2015) found that sewage sludge-derived biochar had lower content of PAH compared to the corresponding original material, except for naphthalene. The presence of trace metal (e.g. Cd and Zn) catalyzed the degradation process of PAH. Meanwhile, pyrolysis process contributed to the formation of PAH, which accounted for the increased content of naphthalene (Zielińska and Oleszczuk, 2015). During thermal process, organic macromolecules are broken into smaller fragments with abundant reactive free radicals and consequently produce stable PAHs (Hale et al., 2012).

Nevertheless, the toxicity of VOCs from biochar should not be ignored. In the study of Oleszczuk et al. (2014), almost none of the ecotoxicity parameters were related with PAH content. Moreover, Buss and Masek et al. (2014) proposed that it was the mobile VOCs rather than PAH that posed a threat to seed germination, as bioavailability of PAH in biochar was much low in this study. Those mobile organic compounds could be nitrogen-containing or volatile fatty acids-like substances that derived from pyrolysis of labile proteins or lipids, as reported in poultry litter biochar (Rombola et al., 2015). Buss et al. (2015) suggested that VOCs usually co-occurred with PAH in biochar and were more likely responsible for the phytotoxicity. This was supported by the fact that: i) negative impact of biochar was time-dependent and would disappear in around seven days (Gell et al., 2011), which was consistent with the dissipation characteristic of VOCs with time; ii) the reported noxious biochar had low pH, which was consistent with the presence of organic acids (Buss et al., 2015).

While organic compounds from biochar are mainly controlled by their formation conditions, the heavy metal content is primary determined by original materials of biochar. PAH is likely to mineralize under high temperature but most heavy metals are retained in biochar (Oleszczuk et al., 2016). What's more, mass loss during pyrolysis increase concentration of toxic elements. Conversion of sewage sludge to biochar increased trace metal concentration such as Zn, Ni, Cu and Pb, with the exception of Cd, as Cd could be evaporated at high temperature (Zielińska and Oleszczuk, 2015).

3.1.1. Interference of biochar to microbial community

Microbial communities are the foundation of the soil ecosystem and are the key players of soil biogeochemical cycling. Soil microorganisms respond quickly to environmental stressors, due to their high surface-to-volume ratio and low homeostasis (Boivin et al., 2002). Therefore, microbial change in activity, community structure and abundance will be a sensitive signal of soil ecosystem alterations (Huang et al., 2017; Ren et al., 2015). Lehmann et al. (2011) reviewed that microbial abundance are affected by the sorption behavior, pH, mineral matter and pore structure of biochar. Alteration of bacterial and fungal community structure and composition due to biochar amendment has also been observed. This cause some type of microorganisms to be dominant or restriction of certain microbes. For instance, mycorrhiza, as a kind of beneficial soil microbes, could be adversely affected by added biochar due to nutrient effects (Lehmann et al., 2011; Warnock et al., 2007). Especially in acidic soil, biochar amendment reduced carbon sequestration potential, as the microorganism capable of degrading organic matter was stimulated by biochar (Sheng et al., 2016). In addition, intraspecies and interspecies communications between bacteria are realized by signaling molecule, such as flavinoids, indole and quinolones. Biochar adsorb those biochemical signals and thus disrupt microbial communication. This kind of effect further inhibits gene expression of microbial-related process (e.g. nitrogen and carbon sequestration) (Masiello et al., 2013).

3.1.2. Potential damages of biochar to plant growth

Plants, as a vital component of the soil ecological systems, are important ecological receptors and food supplier (Zhu et al., 2008). They are directly impacted by contaminants in soil. Seed germination and root elongation are highly responsive and are commonly used bioindicator to check toxic substances (Farrell et al., 2013). Delayed cress seed germination and reduced shoot/root growth by biochar was reported (Buss and Masek, 2014). Seed germination of *Cucumis sativus* L. was reduced at high application rate of biochar (>10%), while root elongation, a more sensitive parameter, was strongly inhibited even at low application rate (>0.5%) (Visioli et al., 2016). Electrical conductivity and metal release (e.g. Cu and Zn) were responsible for its phytotoxicity (Visioli et al., 2016). Another study done by Chi and Liu (2016) also found the reduced *V. spiralis* growth and PAH bioaccumulation after biochar amendment. Negative effects were associated with limited nutrient and water availability due to biochar retention and biochar sorption of plant signaling molecules to symbiotic microbes (Chi and Liu, 2016). Moreover, Li et al. (2015) observed that the influence of biochar on germination rate and early growth of shoot and root followed the pattern of promotive at low dosages and subsequent suppressive at high dosages. However, the early inhibition on root growth could be relieved after 11 days. Biochar provided sufficient nutrition element in seedling growth stage, and weakened its toxicity. They further observed molecular-level reaction to biochar toxicity. Toxicity response was followed by decreased antioxidant enzyme activities (e.g. superoxide dismutase, peroxidase, and catalase), increased malondialdehyde (MDA) content (an indicator of lipid peroxidation) and morphologic change (swollen and necrotic root tip cell) (Li et al., 2015; Song et al., 2016).

3.1.3. Stressful environment to earthworm caused by biochar

Earthworms are generally used as model organisms in ecotoxicological studies, for the reason that their behaviors in environmental perturbations can be measured, including mortality growth rate, reproductive rate and avoidance behavior (Li et al., 2011). Biochar generates a stressful environment to earthworm. The absence of feeding cavities in charcoal amended soil was reported, indicating the altered burrowing activity of earthworm *Pontoscolex corethrurus* (Topoliantz and Ponge, 2003). Liesch et al. (2010) observed higher earthworm death and weight loss in poultry litter biochar amended soil, due to the rapid increment in soil pH or excessive salinization and the generation of ammonia. Other researchers suggested that desiccation caused by high water-retention potential of biochar was the main reason for earthworm avoidance to biochar amended soil (Li et al., 2011; Tammeorg et al., 2014). Earthworm avoidance behavior indicated reduced activity of earthworm populations. Moreover, Malev et al. (2016) reported that application of biochar at the rate of 100t/ha (beneficial rate for crop production) could cause damage to earthworm, with survival rates decreased to 78% in clay soil and 64% in sandy soil. They proposed that biochar was not just a good habitat for soil microorganisms, but also for pathogen. The promoted proliferation and bioavailability made earthworms more susceptible to pathogen (Malev et al., 2016). However, considering the effect of mass concentration of biochar and exposure time, there might be contradictory results. Despite that earthworms were negatively affected by biochar addition in 14 days, in the field experiment after four and half month, soil biomass and earthworm density were the highest in biochar amended soil (Tammeorg et al., 2014). No significant long-term toxicity on earthworm population was found after biochar addition, indicating that the temporary negative effects reduced with time. Besides, in a study done by Cui et al. (2009), crop residues char did reduce genotoxicity of soil OPs at application rate of 5%, however, when added at the rate of 10%, induced DNA lesion to earthworm even in the absence of soil OPs.

In conclusion, biochar is likely to cause damages to organisms. Nevertheless, considering the effect of dose and exposure time, there might be contradictory results. Appropriate amount and sufficient exposure time of biochar amendment would show promotive effect. Meanwhile, there are concerns whether the contaminants in biochar will pose any risk to organisms or not. Application of biochar in soil clearly increased soil PAH content (Kuśmierz et al., 2016), however, it did not add to C_{free} PAHs and did decrease the indigenous C_{free} PAHs (Oleszczuk et al., 2016). Similarly, Farrell et al. (2013) observed that biochar increased concentration of toxic element in soil but decreased its phytoavailability. If the pyrolysis conditions are well adjusted and feedstock source are carefully selected, pollutants from biochar can be omitted. The pollutant source of biochar and its damage to different organisms can be seen in Fig. 1.

3.2. Carbon nanomaterials

The antibacterial mechanisms of CNMs have been extensively studied. This can be concluded as follows (Fig. 2): i) physical impairment. Cell membrane and cell wall will be destroyed by sharp edges of CNMs, especially those structured as nanosheet, nanotube or with branches. Furthermore, direct physical contact leads to leakage of intracellular substances. For example, it was demonstrated that graphene disrupted cell membrane either by directly insertion into cell membrane or by destructive extraction of membrane lipids (Tu et al., 2013). Particularly, due to the specific thin-film structure, graphene were capable of wrapping bacterial membrane, thus isolating cell from nutrition substrate, triggering hypoxic microenvironment and inhibiting their growth (Zou et al., 2016); ii) oxidative stress. CNMs induce the production of intracellular reactive oxygen species (ROS) (e.g. OH, O^{2-} and H_2O_2) that will destroy DNA and proteins (Rajavel et al., 2014); iii) disturbance of the electron and energy transfer. For example, MWCNTs induce *S. cerevisiae* death by mitochondrial impairment pathway (Zhu et al., 2016b) and iv) release of impurities (amorphous carbon and catalyst metal contaminants). Barbolina et al. (2016) found that highly purified graphene oxide had no effect on the growth of *E.coli*. In contrast, impure graphene oxide exhibited antibacterial properties owing to the release of soluble acidic impurities. However, it was found that metal residue (e.g. Co, Mo) released from CNTs alone may not contribute to negative effects on microbes, but their association with CNTs augmented the toxic effect (Jin et al., 2014; Tong et al., 2012). Antibacterial action of CNMs suggests that biological activities in natural system might be suppressed as well.

3.2.1. Microbial community response to CNMs

Cytotoxicity of CNMs is initiated from their attachment to cell surface and then internalization into the cell. Uptake of CNMs by microorganisms was realized either by direct piercing of cell membrane or endocytosis and membrane channels (Zhu et al., 2016b). Cellular membrane injury (Zhu et al., 2014), DNA damage (Lan et al., 2014), mitochondrial impairment (Zhu et al., 2016b), metabolic disturbance (Su et al., 2015) have been observed after exposure to CNMs. Although CNMs have shown toxicity to microbes in pure culture, their effects on soil microorganisms remain elusive. This is due to the complexity of soil microbial community.

Some studies reported the impact of CNMs on soil microbial community (Ge et al., 2016; Jin et al., 2014; Tong et al., 2016). This is reflected in microbial biomass, microbial community composition and microbial activity (indicated by extracellular enzymes). Single walled carbon nanotubes (SWCNTs) reduced biomass of major microbial populations (Gram-positive and Gram-negative bacteria, and fungi) especially at higher concentration (Jin et al., 2014). Tong et al. (2016) also observed lower total microbial biomass and altered microbial community structure after C_{60} treatment. However, in the study of Khodakovskaya et al. (2013), MWCNTs did not interfere with the diversity and abundance of soil microbial communities, but slightly affected community compositions, with an increase in *Bacteroidetes* and *Firmicutes* but a decrease in *Proteobacteria* and *Verrucomicorbia*. It is reported that CNMs show species dependent effects on soil microbial community. This was also demonstrated in the work by Rodrigues et al. (2013) that after amendment of SWCNTs, the main soil microbial populations remained unaffected, but microbes that were related to biogeochemical cycles of carbon and phosphorus, such as *Actinobacteria*, *Chloroflexi* and *Penicillium*, were largely affected. Likewise, graphene was found to act negatively on nitrogen cycle bacteria (e.g. *Nitrospira* and *Planctomyces*), but positively on pollutants-degrading microorganisms (Ren et al., 2015). In addition, the change of extracellular enzymes also reflect microbial community response to CNMs. SWCNTs at the concentration of 300–1000 μg/g significantly depressed activities of soil enzyme that involved in degradation of cellulose (mostly produced by fungi), chitin and organicphosphate (Jin et al., 2013). Similarly, in a recent study, after 21 days of exposure at 0.5–1.0 mg/g graphene oxide, soil enzyme activity (e.g. phosphatase and xylosidase) were decreased by 15%–50% (Chung et al., 2015).

However, some researchers suggested that CNMs cause little effect on soil microbial community (Chung et al., 2015; Oyelami and Semple, 2015; Tong et al., 2007). This is related to the exposure time and concentration of CNMs. For example, graphene had time-dependent effects on soil enzyme (e.g. dehydrogenase and fluorescein diacetate esterase) and bacterial population. In a short-term exposure these parameters were promoted, but then disappeared after long time exposure (Ren et al., 2015). The same case was found in CNTs where altered bacterial community was recovered after 14 days. On the contrary, the impacts on fungal community were persistent during the experiment (Rodrigues et al., 2013). Most importantly, the toxicity of CNMs was concentration-dependent. Generally, only in high concentration of CNMs can we observe obvious impacts on soil microorganism. For instance, at low concentration (10 mg/kg), MWCNT made no difference on soil microbial composition, but high concentration (1000 mg/kg) could cause an increase in fungal groups and the modified microbial community with an increasing proportion of tolerant microbes (Shrestha et al., 2013).

3.2.2. Uptake route and the damage of CNMs to plant

Toxic effect of CNMs to plants depends on whether they can be absorbed by plants roots. Lin et al. (2009) confirmed the existence of C_{70} in rice roots, stems and leaves, thus demonstrating the possibility of fullerene entering into plants. Cano et al. (2016) quantitatively detected different functioned-SWCNTs uptake in corn roots (0–24 μg/g) and bioaccumulation in stems and leaves (2–10 μg/g) after 40 days of exposure. This process was facilitated by the polysaccharide and mucilage that were secreted by roots tips and hairs (Begum et al., 2011). Besides, CNMs enter into plants by complexing with membrane carrier protein, directly passing across pores in cell wall or piercing into cell wall, and then enter into epidermal cells cytoplasm either through energy-dependent endocytosis or directly penetrating cell membrane (Hatami et al., 2016; Lin et al., 2009). There are two pathways of CNMs transportation in plants: i) apoplast pathway where CNMs transport between intercellular space and get into xylem; ii) symplastic pathway where CNMs transport to xylem by plasmodesmata. Xylem and phloem play an important role in translocation of CNMs from root to shoot. Whether symplastic or apoplastic pathway depend on the size of CNMs. Tripathi et al. (2016) found that only C-dots (4.5 nm) and SWCNTs (<10 nm) could travel through symplastic pathway while all the tested CNMs were likely to be transported by apoplastic route, as the intercellular spaces were in 50–60 nm range and cell membrane pores were in the 10–150 nm range.

A large number of studies demonstrated that CNMs could inhibit plant growth.

This is reflected in seed germination, growth of root and shoot, biomass and yields. At the concentration of 500 to 2000 mg/L, graphene significantly depressed root and shoot growth and leaves number of cabbage, red spinach, and tomato (Begum et al., 2011). Biomass of corn and soybean declined by 36.5%–45% at 500 mg/kg of C_{60} (De La Torre-Roche et al., 2013). Begum and Fugetsu (2012) clearly observed reduction in root and shoot growth (weight and height), leaves number and leaf area at different concentration of CNTs (from 125 mg/L to 1000 mg/L). Besides, Lin et al. (2009) reported that the presence of C_{70} retarded the rice flowering at least 1 month and decreased its seeds yields.

More than the individual level damage, in cellular level, morphological change of root and leaf was described by Begum and Fugetsu (2012). They observed wilted leaves (yellow and curling blade), elongated and irregular shaped cell, swelled epidermis, stomata closure. Moreover, CNMs also cause a series of damage to the organelles. SWCNTs induced condensed chromatin and cleavage of DNA in *Arabidopsis* tissue (Shen et al., 2010). More symptoms such as plasmolysis, suppressed cell division, nuclear chromatin aggregation and loss of chloroplast thylakoids by graphene oxide were reported by Hu et al. (2014a). While some studies presented that CNMs were likely to enhance plants photosynthetic efficiency as a result of enhanced photoabsorption and electron transfer rates (Giraldo et al., 2014). Due to oxidative stress, CNMs adversely affect chlorophyll synthesis and damage chloroplast structure (Hu et al., 2014a; Zhang et al., 2016b). Moreover, in metabolic level, Hu et al. (2014a) observed a down-regulation in sugars, amino acids and inositol and an up-regulation in unsaturated fatty acid. This was consistent with cytotoxicity of graphene oxide. Change of unsaturated fatty acid and inositol was related to the process of cell enclosure by graphene oxide and subsequent plasmolysis and graphene oxide internalization. Meanwhile, the production of ROS altered enzyme activity and thus inhibited sugars and amino acids metabolism (Hu et al., 2014a). Disordered nutrient elements in *Triticum aestivum L.* with long-term exposure to 500 mg L^{-1} graphene was reported by Zhang et al. (2016b). Contents of N, K, Ca, Mg, Fe, Zn, and Cu were decreased while P and Na were unaffected. This was attributed to the interactions between graphene and plants roots (Zhang et al., 2016b). Graphene attachment on root surface impeded entrance of nutrient elements into root (Zhang et al., 2015). In addition, graphene triggered-oxidation stress reduced hydraulic conductivity and root hair growth (Zhang et al., 2016b). Moreover, graphene had negative impact on plant growth-promoting rhizobacteria, which indirectly limited plants growth (Gurunathan, 2015). Recently, Zhou and Hu (2017) linked the phenotypes of rice roots under graphene oxide stress to molecular response: i) reduced hydraulic conductivity of roots (a response to resist graphene oxide uptake), was related to depressed aquaporin gene expression; ii) decreased antioxidant enzyme activity (SOD and POD) was linked to downregulation of class III peroxidase; iii) mitochondrial membrane potential loss was adjusted by upregulation of gene OS02G0741500 (nuclear-pore anchor translocated promoter) and gene OS05G0100500 (transcriptional repressor); iv) suppression of lateral roots and promotion of primary root were consistent with synthesis of phytohormones (decrease of salicylic acid and increase of jasmonic acid); v) cell wall synthesis were the result of downregulation of lignin and upregulation of laccases (Zhou and Hu, 2017). The uptake route and damage of CNMs to plants can be seen in Fig. 3.

3.2.3. Harmful effect of CNMs on earthworm

Given the low solubility of CNMs, they are absorbed by earthworms through oral digestion of soil particles (CNMs were associated with soil), and then CNMs are desorbed in the gut, and accumulated in fatty tissue (Petersen et al., 2008). Bioaccumulation of CNMs in earthworms has been demonstrated by Petersen et al. (2008) and Li et al. (2010). However, Li et al. (2013) found that even in hot spot soil, bioaccumulation factor of MWCNTs in earthworm was just 0.015±0.004, showing a low tendency to be ingested. This was influenced by soil conditions, physicochemical properties of CNMs and physiological behaviors of earthworms (Li et al., 2013).

Negative effect of CNMs on earthworm has been reported. Scott-Fordsmand et al. (2008) documented that hatchability, growth, and fatality of earthworms were not affected when exposed to CNTs or C_{60}, but their reproduction was substantially affected. Besides, Van der Ploeg et al. (2011) reported both individual and population level damage of C_{60} to earthworms. They observed a decline in cocoon production and juvenile growth, and an increase in juvenile mortality. However, it was found that only at the concentration of 50000 mg/kg did the earthworm cocoon production was inhibited by C_{60}, which was much higher than environmental level (Li and Alvarez, 2011).

Moreover, in tissue and molecular level, exposure of C_{60} to earthworm *Lumbricus rubellus* resulted in low HSP70 gene expression, cuticle damage and tissue pathologies (i.e. epidermis and muscles) (Van Der Ploeg et al., 2013). Adaptive responses of earthworm to C_{60} toxicity were demonstrated by tissue repair, down-regulation of immune-related gene expression and change of metabolites (Lankadurai et al., 2015; Van Der Ploeg et al., 2013). Zhang et al. (2014) suggested that oxidation stress induced by MWCNTs led to higher content MDA in earthworm. Presence of MDA was initiated by lipid peroxidation in cell membrane. Similar conclusions were obtained by Wang et al. (2014b) that catalase activity was positively related to C_{60} exposure. Calisi et al. (2016) further observed morphologic alteration of earthworm immune cells (where MWCNTs most likely accumulate), enlargement of granulocyte lysosomal compartment, lysosomal membrane destabilization (which was related to releasing of cathepsin and lysosomal hydrolases), and metallothionein (Mt) concentration change (which initially increased and then decreased due to encapsulation by MWCNTs) (Calisi et al., 2016). Because that more energy was used to repair injured tissues, this also explained the low growth rate of earthworm under CNMs exposure (Calisi et al., 2016; Lankadurai et al., 2015; Van Der Ploeg et al., 2013). Selected reports on ecological risks of ECMs for soil biota can be seen in Table 2.

4. Conclusions and future perspectives

ECMs are widespread in soil, whether intentionally added as soil amendment or unintentionally release of CNMs. The presence of ECMs will increase/decrease bioavailability of OPs, depending on the uptake route of organisms to OPs and properties of ECMs. In the meantime, ECMs themselves could be co-contaminant and adversely affect soil biota. We can conclude and expect from this review that:

（1） In most case, the sorption behaviors of ECMs decrease bioavailability of OPs. However, as the access ways to OPs varied with different organisms, ECMs not always decrease bioavailability of OPs. Different physiological property of soil organisms, for example, microbial attachment, root exudates by plants and gut fluid of earthworm, make this more complicated. Moreover, high toxicity of CNMs and high availability of CNMs-adsorbed-OPs increase the bioaccumulation of OPs. This will lay the foundation for risk assessment to various organisms. It has been documented that ECMs would also affect the bioavailability of heavy metals, and the results vary with type of ECMs, heavy metals, co-existed OPs and species of organisms (Khan et al., 2015; Rizwan et al., 2016; Yu and Wang, 2013). Besides, the coexisted OPs would influence the bioavailability of heavy metal (Zhou et al., 2015). Therefore, the ECMs induced changes in bioavailability of co-existed OPs and heavy metals are interesting topics to explore.

（2） Biochar contains some pollutants, such as PAH, VOCs and toxic elements, which could be released into soil and damage soil organism. However, with appropriate pyrolysis conditions and feedstock source, this kind of effect could be avoided. In addition, sorption properties of biochar, such as adsorption of biogenic signaling molecule and nutrients, high water-retention potential and habitat for pathogen, result in an unfavorable living environment for organisms. Nevertheless, based on current research, no obvious damages are observed in the natural environment. Particularly, most studies that have proved biochar toxicity is conducted in pure medium or unpolluted soil. Actually, in strongly polluted soil, biochar mitigate pollutant-induced environmental stress, as a consequence, the risks of biochar are minimized. Another issue of biochar is the persistence of biochar-immobilized OPs. While biochar strongly sequestrated OPs and thus decreased their toxicity, they did not completely eliminate OPs. With time, the immobilized OPs could be released from ECMs. For example, Oleszczuk et al. (2016) found higher percentage of C_{free} PAHs in biochar amended soil after 851 days than in the first 105 days, indicating the weakened binding strength of PAH by biochar. Higher earthworm accumulation of thiacloprid in soil with 60 days-aged biochar than in unamended soil was also observed. In the long term, the absorbed thiacloprid in biochar will be released into pore water and enter into earthworm (Li et al., 2017b). This finding indicates a potential risk of biochar

(3) CNMs were much toxic than carbonaceous amendments. Understanding the cytotoxicity of CNMs was essential to exploring the detailed toxic mechanisms. However, individual and community level response are also important to reflect the overall biological response in real environment. Moreover, despite the increasing research regarding the risks of CNMs, investigation of their effect to soil biota in the presence of OPs is very scarce, especially whether the

coexisting OPs and CNMs had synergistic or antagonistic toxicity.

(4) Given that ECMs are used in the natural environment, soil properties (e.g. the content and type of organic matter, mineral composition) potentially change the state of ECMs (physical structure and surface chemistry). Consequently, ECMs in soil display remarkably different characteristics from the corresponding original materials, strengthening or weakening their sorption capacity, along with lessening or aggravating their adverse effects. For example, biochar undergo combined effect of surface oxidation, pore exposure and pore filling process in soil, which will increase or decrease its sorption capacity to OPs (Rechberger et al., 2017; Trigo et al., 2014; Zielinska and Oleszczuk, 2016). Also, Du et al. (2015b) comprehensively presented the change of graphene surface morphology and chemical activity in soil, which could affect its ecotoxicity. Moreover, some studies reported that natural organic matter has contradictory effect on the ecotoxicity of CNMs. Besides hindering the accessibility of CNMs to cell (Chi et al., 2016), HA could serve as natural detoxicant by regulating nanotoxicity-related metabolic pathways (Hu et al., 2014b), however, higher toxicity of HA-CNMs complex was also reported (Du et al., 2015a). Therefore, studies based on soil matrix with complex components are needed to estimate the actual risk of CNMs.

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Figure captions

Fig. 1. The pollutant source of biochar and its damage to different organisms. PFR, Persistent free radicals; VOC, Volatile organic compounds.

Fig. 2. Toxic mechanisms of CNMs to organisms. ROS, Reactive oxygen species.

Fig. 3. The uptake route and damage of CNMs to plants.