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Co-occurrence and interactions of pollutants, and their impacts on soil remediation—A review

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Abstract:	With the development of industrialization and agriculture, the phenomenon of soil contamination by combination of potentially toxic elements and organic pollutants has been a terrible environmental issue. The co-occurring pollutants exhibit complicated interactions in chemical processes, adsorption behaviors and biological processes. These interactions are of concern for any kind of remediation to be implemented, since they make great influence on soil remediation efficiency. Exploring the interactions and impacts of multiple pollutants is important for actual soil remediation. This review expounds several interactions of pollutants in soil, which would be helpful to better understand their impacts on remediation efficiency and further study directions in this field.

Co-occurrence and interactions of pollutants, and their impacts on soil remediation—A review

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ABSTRACT

With the development of industrialization and agriculture, the phenomenon of soil contamination by combination of potentially toxic elements and organic pollutants has been a terrible environmental issue. The co-occurring pollutants exhibit complicated interactions in chemical processes, adsorption behaviors and biological processes. These interactions are of concern for any kind of remediation to be implemented, since they make great influence on soil remediation efficiency. Exploring the interactions and impacts of multiple pollutants is important for actual soil remediation. This review expounds several interactions of pollutants in soil, which would be helpful to better understand their impacts on remediation efficiency and further study directions in this field.

Keywords: Soil combined contamination; Interaction; Remediation efficiency; Potentially toxic elements; Organic pollutants

1. Introduction

The industrial revolution has promoted the economic prosperity, along with releasing a variety of pollutants into the environment (Tang et al., 2008; Wuana & Okieimen, 2011). Especially due to the characteristics of concealment, accumulation and difficult restorability, there is not any appropriate treatment for the remediation of contaminated soil until recent years (Zeng et al., 2013a, 2013b). Moreover, soil co-contaminated with potentially toxic elements (PTEs) and organic pollutants (e.g. hydrocarbons, pesticides and emerging pollutants) has caused huge global environmental issues due to the rapid industrial development (Lohmann et al., 2007). A complex suite of organic chemical and PTEs occurs frequently in many situations. For instance, PTEs and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) etc. are widely co-existing in soil, since they are often released simultaneously from several sources like burning of coal, oil and wood, waste incineration and vehicle exhaust emissions (Jiang et al., 2015). The increasing re-utilization of sewage sludge, wastewater irrigation and conventional employment of pesticides also caused co-occurrence of PTEs and organic pollutants in contaminated soil (Hechmi et al., 2014).

Compared with single pollution, processes on remediation of soil contaminated by combination of different pollutants tend to be more complicated. A growing number of researches have been focusing on the remediation technologies for the purposes of multiple PTEs passivation and organic pollutants elimination through a wide variety of

pathways (Chen et al., 2015; Nsanganwimana et al., 2014; Tang et al., 2014; Ye et al., 2017; Zhang et al., 2007). Ecological toxicity of PTEs will be reduced either by immobilizing, chelating or shifting the valence (Beesley et al., 2010; Fan et al., 2008; Huang et al., 2017; Lee et al., 2012; Wu et al., 2016; Zhu et al., 2012), and the removal of organic pollutants mainly depends on decomposition by microbial activity and partitioning effect on the surface of biomass (Chen et al., 2010a; Dong et al., 2013; Jin et al., 2014; Wild et al., 2005). However, the complexity of multi-element contaminated soil brings certain difficulties to the remediation.

In the remediation processes of co-contaminated soil, the complexes between PTEs and organic pollutants formed by chemical reaction would alter their own solubility and bioaccessibility (Almeida et al., 2008; Almeida et al., 2009), and it is therefore an impact to change the biotoxicity of pollutants and the biological metabolic processes on microbial consortium (Alisi et al., 2009). Besides, the adsorbed amount of pollutants would be affected through competition or joint-adsorption on the binding sites (Jin et al., 2014). Moreover, based on above-mentioned discussion, the co-occurring pollutants would contribute to the synergistic or antagonistic effects on chemical process, adsorption behaviors and biological processes. The synergism or antagonism on the process of remediation would change the remediation efficiency of co-contaminated soil.

This review focuses on soil contamination by combination of different pollutants, and the interactions of multiple pollutants are of concern for any kind of soil

remediation to be implemented. With an increasing number of studies in this field, in this review we aim to: (1) summarize the interactions of multiple pollutants classified as the chemical processes, adsorption behaviors and biological processes; (2) discuss the impact of these interactions on remediation efficiency; and (3) identify future directions for research on this field.

2. Interaction in chemical process

2.1 Complexation reaction

Complexation is the direct result in the case of co-occurrence of PTEs and organic pollutants, the formation of PTE-organic complexes might change the solubility and bioavailability of pollutants in soil, since the complexes significantly alter the physico-chemical fraction and behavior of pollutants. When the chromium ions combined with the dissolved negatively charged 2,4-dichlorophenol (2,4-DCP) in aqueous solutions (sand soil: pH 7.2-7.4), the mobility of both pollutants were reduced by forming a neutral complex in the process of electrokinetic remediation (Ma et al., 2010). However, study from Almeida et al. (2009) reported that the presence of organic pollutants such as 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (DDE) or monobutyltin (MBT) tended to strengthen the solubility of Cu in sediment and further enhanced the availability and toxicity of pollutants to soil biota. After the addition of PAHs, the concentration of water-extractable Cd in loam soil reduced while insignificantly changed in EDTA-extractable fraction of Cd. However, it could not rule out that PAHs have chelating capacities for PTEs (Zhang et al., 2011b). Metal cations

have high affinities with electron-rich organic pollutants in the formation of cation-π bonding, causing solubilization which is described as "salting in" effect (Gokel et al., 2001). Complexes formed by self-assembly through coordination bond between bidentate or multbentate organic ligand and PTEs change the existing forms of pollutant. A report indicated the co-occurrence of Pb^{2+} and/or Cd^{2+} could enhance the adsorption of phenanthrene in soil. It might be derived from the cation-π bonding between the aromatic ring of phenanthrene and the adsorbed soft metal cations on clayey soil particles (Zhang et al., 2011a). Larger bioavailable amounts of phenanthrene were extracted by $CaCl_2$ and hydroxypropyl-β-cyclodextrin (HPCD) in the presence of Al and Cu (500 mg/kg) on sandy loam texture (Obuekwe & Semple, 2013). Toxicity of pollutants is depended on their existing forms, transition in existing forms of pollutants by complexation changes their solubility and bioavailability. The solubility of complexes makes influences on the remediation efficiency of pollution. On one hand, the low solubility of complexes is helpful to reduce the biological toxicity of pollutants and enhance pollutants immobilization; on the other hand, the high solubility of complexes is beneficial to improve the bioaccessibility and biodegradation efficiency of pollutants.

2.2 Catalytic redox reaction

When the organic pollutants meet some PTEs with high oxidative potential (e.g. Cr^{6+}, Fe^{3+} and As^{5+}) in soil, redox reaction would occur under certain conditions for their synchronous remediation (Dong et al., 2014; Yan & Lo, 2013). In the

co-contaminated soil (sandy loam; pH: 5.09) amended by *Geobacter metallireducens*, toluene and arsenic were treated as the electron donors and accepters, respectively. The degradation rate of toluene was promoted with the reduction of co-dissolved Fe (III) and As (V) on bacterial surface, and further achieved the synchronous remediation through the mechanism of electron transfer (Lee et al., 2012). Previous research revealed that the Fe^{3+} would accept electrons from naphthalene, whether naphthalene is dissolved or partitioned in soil particles, and resulted in naphthalene oxidation (Yan & Lo, 2013). The co-occurring PETs could be served as the source of metal coat according to the value of the redox potential. The metal-coating, formed *in situ*, enhanced the dehalogenation reaction of organic pollutants (Gong et al., 2009; Lien et al., 2007). In the remediation process of PCP by Pd/Fe bimetallic particles, Shih et al. (2011) proved that the degradation efficiency of PCP increased dramatically in the present of Cu^{2+} ions. A substantial portion of Cu^{2+} was spontaneously reduced to Cu, and the formed elemental Cu coated on the surface of Pd/Fe nanoparticles could not only induce the electron transfer, but also accelerate the corrosion of Fe and unlock the active site of iron nanoparticle surface (Shih et al., 2011). These phenomena contribute to the simultaneous achievement of catalytic degradation of organic pollutants and immobilization of free PTEs (Feng et al., 2010; Xu et al., 2012). Moreover, studies also showed the Cu^{2+}, Zn^{2+}, Co^{2+} and other Lewis acids including their metal oxides and hydroxides could catalyze the decomposition of the organicphosphorus pesticides and enhanced the hydrolysis rate of phosphate and phosphorothioate (Seger & Maciel,

2006; Smolen & Stone, 1997). This phenomenon was owing to the fact that the formation of complex with six-membered ring could concurrently reduce the electron density on the phosphorus atom and increase the ester leaving capacity in the process of hydrolysis (Uchimiya et al., 2012). However, some hydrolysis products with higher solubility are more toxic and bring greater risk to the ecosystem, increasing the difficulty of soil remediation. On the contrary, study also reported that the metal oxides might inhibit the hydrolysis of pollutants via blocking nucleophile attack on the remediation process (Dannenberg & Pehkonen, 1998). Concentrations of pesticides in solution phase would be decreased by sorption on metal oxides, and the collision frequency between pesticide molecule and nucleophilic reagent was also reduced (Dannenberg & Pehkonen, 1998). PTEs are excellent electronic deliverers which can be used as catalysts to accelerate decomposition of organic pollutants. However, the ecological toxicity of the incomplete decomposition products in degradation process is rarely analyzed and evaluated. It is still difficult to distinguish the effect of this interaction on remediation efficiency.

2.3 Other chemical reactions

Biosurfactant, saponin, has been reported for simultaneously removing Cd and phenanthrene from the co-contaminated soils (Song et al., 2008). Zhou et al. (2011) illustrated the solubilization effect of saponin on phenanthrene was magnified in the presence of Zn or Cd. It was due to the fact that Zn^{2+} and Cd^{2+} decreased the electrostatic repulsion of the head group of phenanthrene with saponin molecules, and

more effective in enhancing solubilization capabilities was observed at lower solution pH (Zhou et al., 2011). In addition, the co-occurrence of some PTEs (e.g. Hg and Sn) and organic pollutants lead to organic reaction, which might generate more hazardous toxic PTE-organic compounds (e.g. methylmercury and trimethyltin) into environment (Pounds et al., 2004).

Different types of co-occurring pollutants in soil may mutually affect the subsistent forms and migration-transformation of each other. Interactions of pollutants in chemical process, containing complexation, catalytic redox reaction, electrostatic interaction and organic reaction, significantly change the original form of pollutants in soil, further change their physico-chemical property, such as bioavailability to living organisms (affecting bioremediation), solubility (affecting washing and electrokinetic remediation) and binding status (affecting adsorbent remediation). Some chemical reactions of co-occurring pollutants are susceptible to soil properties, like temperature, pH and Eh values, and thus affect the remediation efficiency. The impact of specific environmental factors on this interaction still needs to be further explored.

3. Interaction in adsorption behavior

3.1 Competition on adsorption sites

The more similar on the chemical structure and physical properties of combined pollutants, the more easily the mutual inhibition occurs among them due to competition for the active binding sites. Overlapping of the binding sites contributes to intense competition (Wu et al., 2014). This effect is showed on Fig. 1. Previous work proved

the adsorption/desorption kinetics of pollutants was mutually affected by their competition, thus changed their retention/release and subsequent transport in soil environment (Table 1). Yang et al. (2006) proved the most intense competition occurred at a relatively low concentration of the initial solute with a high concentration of competitors owing to the heterogeneous energy distribution of surface adsorption sites. Moreover, they also found the role of competition seemed to disappear when the relative concentration of the primary solute (C_e / C_s) was close to 1 (Yang et al., 2006). Multiple-PTEs in soil amended by biochar are adsorbed on biochar surface mainly controlled by the forces of functional group binding, ion exchange and co-precipitation (Hu et al., 2011; Zhang et al., 2013a). Intense adsorption competition will occur associated with the similar in dominant binding mechanisms. With the increase in mobility and eco-toxicity of PTEs, the remediation of multi-element contaminated soil becomes more difficult.

The competition adsorption also appears between PTEs and organic pollutants, since the polar organic pollutants might be adsorbed on binding sites by electrostatic interactions and hydrogen bonding (Sun et al., 2012), which is comparable with PTEs. Compared with organic pollutants, PTEs are usually easier to overcome the outside resistance of the binding surface to form strong complexes. Moreover, the direct competition for adsorption sites between organic pollutants and hydrated metal ions further go against the pore-filling mechanism (Jin et al., 2014). Study confirmed the adsorption of Cu^{2+} decreased due to the direct competition with organic pollutants, it

could be manifested on the dropped distribution coefficient for PTEs sorption with the increasing concentration of organic solute (Chen et al., 2007). On the graphite structure, polar interactions with the functional groups are insignificant adsorption driving force, thus PTEs are outcompeted by hydrophobic organic pollutants in the competition for graphite surface sorption site. A study showed negligible influence of Ag^{+} or Cu^{2+} on the adsorption of organic pollutants, since the graphite surface is characterized by high hydrophobicity and almost no functional group for the PTEs binding (Chen et al., 2007). Data in Table 1 indicate that regardless of the type of pollutant, if the binding site or mechanism is similar, there would be a fierce competition of adsorption among the co-occurring pollutants. However, due to the different remediation methods applied, the adsorption competition might result in either inhibiting or promoting effect. The adsorption competition reduces the immobilized amount of pollutant and increases their mobility. This adversely influence the immobilized remediation, but the high mobility of pollutants is conducive to enhance electrokinetic and washing remediation. Furthermore, the soil characteristics, important factors influenced the interactions of pollutants, are only mentioned in previous studies and no systematic research has been done. Future researches can be explored in depth.

3.2 Surface modification

The adsorbed pollutant has ability to modify the surface properties of binding sites thereby make influence on the adsorption of other pollutants. Research indicated the co-occurrence of Al drastically reduced the absorbed amount of Cd on biochar. In

addition to the competitive mechanism, aluminium ions play a role on soil acidification which contributes to both release of the adsorbed ions and decrease in adsorption sites (Qian et al., 2015). Another study showed the adsorption capacity of dibutyl phthalate (DBP) on biochar increased in the presence of phenanthrene (PHE). In addition to their different adsorption sites of biochar (PHE as π-donor while DBP as π-acceptor), the synergistic effect was attributed to the additional adsorption sites generated by the conformation of "biochar-PHE-DBP" (Jin et al., 2014). Those organic molecules, adsorbed on the surface of adsorbent, might exhibit attractive forces to other types of organic pollutants, namely, the solute-coated surface of adsorbent is still available for the adsorption of other pollutants. On the other side, the adsorbed DBP on binding sites could improve the surface characteristics of biochar (e.g. organic matter). In turn, the modified surface has an attraction for PHE and facilitates its adsorption (Jin et al., 2014; Yang et al., 2006). Pore blockage, another interaction mechanism on adsorption, also affects the surface properties of binding sites (Wang et al., 2006). The detained organic pollutants not only clog the micro-pores, but also increase the surface hydrophobicity of binding sites. Pore-filling mechanism associated with the swelling to micro-pores would further alter the pore volume of surface (Yu & Huang, 2005). These changes in surface characteristics would cause promoting or inhibiting impact on pollutants adsorption depended on the characters of the co-occurring pollutants.

It is complicated about the influences of interaction on the adsorption between PTEs and organic pollutants on binding sites, due to the different dominant mechanism

from various types of pollutants (Liang et al., 2015). In general, the functional group binding of PTEs is more frequent than that of organic pollutants. The adsorbed PTEs can modify the chemical properties and pores structure of binding sites. Study demonstrated that PTEs attached on the surface of negatively charged microbes by electrostatic attraction, which is stronger than Van der Waals forces between PAHs and the microbes (Zouboulis et al., 2004). However, the microbial surface turns to lower hydrophilicity, when surface is neutralized with the increasing amount of PTEs. It is noteworthy that the surface, turned to hydrophobicity by PTE-binding, could contribute to the PAHs adsorption (Al-Turki, 2009). Metal ions which belong to soft Lewis acid would like to replace the original metal ions on binding sites by the formation of out-sphere complexation. Study found the adsorbed Ag (softer cation) by wood biochar was effective to reduce the dimension of hydration shells of dense water and contributed to a decrease in hydrophilicity of the adsorption sites (Chen et al., 2007). The above-mentioned phenomena are advantageous for the sequestration of organic pollutants by wood biochar. A study reported that Cd^{2+} usually combines with the electron rich site of biochar, which is similar to the DBP that behaved as π-acceptor. Logically, it could be expected mutual inhibitive competition on their adsorption. However, data revealed that Cd^{2+} increased the DBP sorption through enhancing the hydrophobic sorption, as a result of the metal-complex functionalities (metal ions expand the hydrophobic of sorption sites by alleviating the competitive adsorption of water molecules) (Chen et al., 2007; Jin et al., 2014). Moreover, the formation of

cation-π bonding complex between Cd^{2+} and electron-rich PHE was beneficial to promote mutually their adsorption on biochar (Jin et al., 2014). Research showed when added a low concentration of pollutants, ofloxacin (OFL) might be bridged by the adsorbed Cu^{2+} and the Cu^{2+} was bound to the adsorbed OFL (Wu et al., 2014). In addition, study indicated the bond-bridge roles of PTEs induced the dissolve organic matter moving to solid phase, thereby promoting the adsorption of PAHs on a solid substrate by partition (Gao et al., 2006). In these cases, the PTEs bound on the adsorbent are in favor of the adsorption of organic pollutants by partitioning effect or combined-adsorption. However, the adsorbed "hard" cations (such as Cu^{2+}) are likely to cause hydration shell in the local area around metal-complexes. The inhibition in adsorption of organic pollutants is obvious, especially when the hydrated metal ions have considerable sizes with micro-pore of biochar due to the thermodynamic steric constraint to char pores (Ohtaki & Radnai, 1993). The complexes between PTEs and organic pollutants in adsorption behavior exhibit dual effects on the remediation efficiency. On one hand, the negative effect occurs because complexes reduce the amount of pollutants which reach the surface of binding sites (Zhang et al., 2011b). On the other hand, the formed structure of "adsorbent-PTE-organic pollutant" (or "adsorbent-organic pollutant-PTE") due to the intense cation-π interaction might surpass the competitive effect (Zhang et al., 2011a). Generally, the amount of adsorbed PTEs becomes the leading factor that determines the adsorbed amount of pollutants (Jin et al., 2014).

Interactions of multiple pollutants in adsorption behavior include the competition and surface modification. Competitions among different types of pollutants, depended on their binding affinity with adsorption site, usually increase the mobility of pollutants. Surface, modified by the co-occurring pollutant through acidification, hydrophobization, pore-blockage, bond-bridge, and so on, shows different adsorption properties for other pollutants. However, the interactions of pollutants in adsorption behavior result in different effects on the efficiency of different remediation methods. Climate change (e.g. temperature, rainfall) significantly affects the composition of soil medium, thereby changing the interaction of multiple pollutants in adsorption and migration behavior, which increases the difficulty of soil remediation in actual field. Impacts of climate change on interactions of pollutants require further study because of the lack of available reference.

4. Interactions in biological processes

The co-occurring pollutants usually change a portion of biological processes thereby affect the remediation efficiency of other pollutants on plants and microbes (Fig. 2). For instance, PTEs could make influence on root exudates, which affects biodegradation of organic pollutants through the changes in microbial growth, or inhibits the biodegradation through the changes in bioavailability of organic pollutants. Organic pollutants could promote the root uptake of PTEs by the impacts on development of apical apoplastic barrier. The mutual influences of PTEs and organic pollutants on soil remediation in biological processes mainly include three aspects: (1)

co-occurring pollutants might influence the bioremediation capability of soil biota by changing their biological growth and biomass; (2) co-occurring pollutants might affect the biological intracellular metabolic degradation pathway of pollutants by altering the structure and composition of biological cells; and (3) co-occurring pollutants might influence the extracellular conversion processes of pollutants by transforming the production and activities of secretion (e.g. enzymes, organic acids and biosurfactants).

4.1 Impacts on biomass

Either PTEs or organic pollutants have influences on biomass of plants and microbes (which play critical role in the remediation of contaminated soil), but their combined effect on the bio-toxicity is not a simple superposition. Fig. 3 indicates the combined effect of multiple pollutants on the biomass of soil biota. Both PTEs and organic pollutants cause oxidative stress to the organisms (Khillare et al., 2012; Wu et al., 2015; Wu et al., 2013). On one hand, the co-occurrence of different pollutants might exert synergistic toxicity and further restrict the growth and biomass of plants and microorganisms (Sun et al., 2011). On the other hand, the formation of complex between PTEs and organic pollutant also decreases the bioavailability of pollutants thereby reduces the biological toxicity.

The bioremediation efficiency is influenced by the biomass changes of soil biota, when PTEs coexist in co-contaminated soil. Sometimes low dosage of PTEs (e.g. Cu, Ni and Zn) could increase the macronutrient contents, and further contribute to the positive effect on plant growth (Davari et al., 2015). However, toxicity of PTEs often

suppresses the growth of organism, and the negative effect of PTEs on the biomass is greater compared with organic pollutants in general (Wang et al., 2014b; Zhang et al., 2011b). A study reported that owing to the low solubility of benzo(a)pyrene besides the fact that benzo(a)pyrene is likely to be adsorbed on soil organic matter, plants exposed to benzo(a)pyrene contaminated soils did not show poisoning symptoms, yet did in the real landfill soil co-contaminated with PTEs (Gutierrez-Gines et al., 2014).

The toxic amplification effect of mixed organic pollutants reduces the survival rate of soil biota and makes the degradation rate dropped. Gao et al. (2011) found the lower degradation efficiency, caused by toxic amplification, resulted in higher residual concentrations of phenanthrene and pyrene in soil. Consequently, higher levels of phenanthrene and pyrene were obtained in plants body through uptake thereby induced greater toxicity (Gao et al., 2011). In addition, the inhibiting effect on microbial degradation, resulted from the competition among co-occurring multiple PAHs, was reported by Stringfellow and Aitken (1995). On the contrary, study confirmed the bacterial degradation of phenanthrene and pyrene was stimulated by the addition of naphthalene (McNally et al., 1999). The stress of organic pollutants might increase the intensity of cell respiration and enzymatic activity. Furthermore, the other organic pollutants can be stimulated to break down due to the adaptability of microorganisms and their ability to take advantage of xenobiotics as carbon and energy source (Baran et al., 2004). The positive effect of PAHs on plant growth might be associated with the metabolites and phytohormones that produced by the transformation of organic

pollutants in the abundance of rhizosphere microbes (Zhang et al., 2011b). According to the information of Table 2, perhaps plant/microbe species and the characteristics of pollutants cause different biomass response to multiple contaminants, as well as depending on soil parameters, like soil type, organic matter content and pH value. The biomass of the organisms used in remediation directly affects the bioremediation efficiency, suggesting that changes in growth (biomass) of the organisms caused by the interaction of pollutant really alter the efficiency of bioremediation.

4.2 Impacts on intracellular metabolism processes

The biodegradation of organic pollutants may be affected in co-contaminated soil, because the co-occurring one might change the intracellular metabolism processes of soil biota on the pollutant transformation (Huang et al., 2008; Thavamani et al., 2011). PAHs with low molecular weight could be used as co-metabolic substances to promote the mineralization of high molecular weight PAHs (Wang et al., 2014a). The degradation rates of anthracene, fluoranthene and pyrene by Micrococcus sp. PHE3 could reach more than 90% with adding naphthalene and phenanthrene, because the key enzymes were induced through the decomposition process of easily available one (Zhang et al., 2013b). A previous study showed the removal of available benzo[a]pyrene by microbes in soil was observably restrained with increasing Cd concentration (Wang et al., 2014a). PTEs usually influence the conversion and biodegradation process of organic pollutants by altering the cellular structure and related enzymatic properties (intracellular enzymatic reaction). The enzymatic activity

is adversely affected by denaturing the protein and masking the enzymatic active catalytic group (Liu et al., 2015). Changes in intracellular enzymes (e.g. metallothionein, dehalogenase and mixed function oxidase enzymes) influence the spread and metabolic conversion mode of pollutants and further affect their behaviors and metabolism in cells. According to the induced-fit hypothesis, PTEs with relatively low doses could serve as the cofactors and embed in protein for activating enzyme. The modified enzymes, embedded by metal, provide additional position corresponded with substrate for the formation of "enzyme-metal-substrate" complexes, and it is therefore a possible situation to accelerate significantly the degradation of organic pollutants (Liu et al., 2015). However, the excess PTEs may compete with the macronutrients which work as modification normally through camouflaged seizing the enzyme binding site. The deformation of enzymes caused by the extra metal-bindings is no longer suitable for the binding of substrates thereby reduce the catalytic ability (Liu et al., 2015). Generally, PTEs can partially or completely inhibit normal heterotrophic microbial activity depended not only on the nature but also on the concentration of an element. Moreover, they further hinder the metabolic degradation of organic pollution (Dong et al., 2013). Details are shown in Fig. 4. PTEs with high concentration influence the conversion of organic pollutants through more than one biochemical pathways in cell: (1) PTEs might combine with the certain functional groups of protein such as sulfhydryl, hydroxy and carboxy group, and then hinder the synthesis and metabolism of biological macromolecules (Guo et al., 2010); (2) PTEs might deplete

the antioxidant, especially glutathione, which induces the production of reactive oxygen species (ROS) and lead to injury in DNA and organelles (Ke et al., 2010); (3) PTEs could disrupt the cellular homeostasis by oxidation reaction with surface proteins on the plasma membrane, which affects the transport of ions (Na^+/K^+) and pollutants; (4) PTEs could impede the movement of cytoskeleton and further make the cell cytokinesis to be delayed (Su et al., 2009), and the acclimation periods might also be extended; and (5) PTEs could competitively inhibit the specific membrane-bound translocating proteins by occupying the binding sites thus interfere with the membrane active transport processes (Niu et al., 2009). The biodegradation of pollutants might be inhibited with the weakening in microbial metabolism by toxicity of PTEs.

Accurately, PTEs would not certainly influence adversely the degradation of organic pollutants. A dose-dependent relationship between PTEs concentration and biodegradation rate of organic pollutants may be proposed (Carine et al., 2009; Lin et al., 2006; Zhang et al., 2011b). When facing with a certain range dose of PTEs, the biodegradation rate of organic pollutants might be promoted. For example, the higher degradation rate of 2, 4-dichloro-phenoxyacetic acid methyl ester (2, 4-DME) was observed in the presence of Cd at 100 μM than that exposed to 10 μM (Said & Lewis, 1991). It was noted that the better degradation at higher PTEs levels might be attributed, in part to the resource competitive advantage of degrading-microbes in soil, since the susceptible bacteria cannot survive in the presence of certain concentrations of PTEs. The propagation and metabolism of resistant bacterium species could be

enhanced, because they do not need to compete with other species for carbon and energy sources any more. It is beneficial for the resistant bacterium to exert their degradability on pollutant removal. A trial was conducted by composting application for co-contaminated soil with Pb and phenanthrene (PHE). It indicated that the across-membrane transport of PHE by microbes was facilitated (Niu et al., 2009). This phenomenon is explained by the fact that Pb^{2+} at appropriate concentrations could increase the hydrophobicity of microbial membrane through binding with polar functional groups, and the modification of cytomembrane by PTEs might promote the uptake of organic pollutants (Niu et al., 2009). Another possible explanation may be that the tolerance mechanism of bacteria plays a greater role in regulating and promoting metabolism when facing with PTEs (Said & Lewis, 1991), therefore the biodegradation rate of organic pollutants increased observably. The increasing concentration of reactive oxygen species (ROS) under a certain degree of PTEs stress might enhance the intracellular oxidative degradation of low molecular weight PAHs (Ke et al., 2010). The level of siderophores which are capable of chelating PTEs was up-regulated in the presence of Cd^{2+} on research reported from Dimkpa et al. (2008)

Toxicity of organic pollutants sometimes decreased the uptake potential of PTEs hyperaccumulator in co-contaminated sites (Tripathi et al., 2015). Generated reactive oxygen species (ROS) on the metabolic process of PAHs by cytochrome P450 might lower the bioremediation capability for treating PTEs (Kuang et al., 2013). However, a number of information indicated a positive effect of organic pollutants on the uptake

and translocation of PTEs by changing the biological structure (Almeida et al., 2008; Zhang et al., 2011b). Research found that PAHs might induce PTEs and/or PTE-organic complexes to penetrate passively through the root cell membrane without carrier (Almeida et al., 2008). Another interpretation was put forward that organic pollutants could hinder the development of apical apoplastic barrier whose function is to avoid excessive uptake of PTEs by root. It seems like to strengthen the uptake of Cd while increase the phytotoxicity with the increasing Cd concentration in plant tissue (Wang et al., 2014b). Gogolev and Wilke (1997) conducted agar-plate experiments and evidenced that even if the low doses of PTEs and fluoranthene (FLA) (which individual dose would not restrain the growth of bacteria) were added, the FLA showed a toxic synergistic effect with PTEs on bacteria, owing to the changes in permeability of microbial cell membranes. Hydrophobic organic pollutants which have a narcotic mode of toxicity (such as PAHs) could interact with the lipophilic components of plasma membranes (Li & Wong, 2012). The interference adversely influences the permeability and structure of cell membranes, making the penetration of PTEs through the plasma membrane into cells become easier (Shen et al., 2005). PAHs could also change the fluidity and electrical potential of membrane. The ionoregulation disruption, caused by PAHs, might reduce the activity of metal-ATPase, all affect the PTEs transportation and adsorption (Gauthier et al., 2015; Gorria et al., 2006). Co-occurring pollutants may cause the disturbance of biological barriers in structure and function. The barrier damage would change the permeability and further affect the transport

capacity (active or passive) of a barrier (Fig. 5). At higher concentration of PTEs, the addition of PAHs would not promote the uptake of PTEs any more (Gogolev & Wilke, 1997). This phenomenon is due to the fact that high concentration of PTEs significantly inhibits the microbial growth, which acts as the dominant mechanism. Furthermore, the non-specific bonding of PTEs on the bacterial surface restricts the interaction between organic pollutants and membrane components (Gogolev & Wilke, 1997).

The interactions of multiple PTEs in soil may influence the efficiency of phytoremediation (Khan, 2005). Research proved that co-occurrence of Cd and Pb had a synergistic effect on reinforcing the accumulation of Cd by *Brassica rapa*. The reason for this phenomenon was the Pb competed with Cd for the exchangeable sites on the surface of soil colloids, increasing the available concentration of Cd in solution phase for plant uptakes (Chen et al., 2010b). Cd may be accumulated through the Zn transporter channel in plant, and these two kinds of PTEs might compete with each other because of the similarity in chemical properties (Clemens, 2006). Although Zn can reduce the toxicity of other PTEs on soil biota by adjusting the level of glutathione (GSH) in general, it is the major contenders of Cd on the remediation process (Shen et al., 2005). Previous work confirmed the role of Zn (GSH regulating) was restrained by Cd, due to the fact that Cd inhibits the biosynthetic enzymes and then causes an adverse influence on plant defense system (Clabeaux et al., 2013). Study reported that competition between Cd and Zn for organic ligands would occur on the process of

forming protein complexes *in vivo*, showing negative implications on tolerance and uptake ability of plants (Thavamani et al., 2011). However, there was no significant influence of Zn on the uptake of Cd in *macrophytic alga*, shown on study from Lai & Chen (2006), owing to the fact that Cd^{2+} was also transferred through the channels of Fe^{2+} and Ca^{2+} instead of Zn^{2+} transporter.

4.3 Impacts on extracellular conversion processes

Extracellular conversion is another removal process of pollutants in soil. Extracellular secretions, produced by soil biota, on one hand could affect the transportation and bioavailability of PTEs by chelating effect (Christofi & Ivshina, 2002; Gorman-Lewis et al., 2013; Paquet et al., 2015). On the other hand, the exudates could promote the degradation of organic pollutants through their emulsifying capacity to increase the bioavailability, or play a direct role in organic pollutant molecules for catalytic degradation (Dong et al., 2013; Zheng & Obbard, 2002). Besides, a portion of the decomposition products of organic pollutants could serve as the substrate for biological growth. Co-occurring PTEs would interfere with the soil enzymes both in production and function, thereby inhibiting the decomposition of organic pollutants. Several studies have shown that the interaction of PTEs and organic pollutants has synergistic or antagonistic effects on activity of soil enzymes (e.g. urease, dehydrogenase and sucrase) at different concentrations and exposure time (Shen et al., 2005; 2006). Carine et al. (2009) investigated the different influences of various PTEs at different concentrations (range from 0 to 800 mM) on phenol oxidase activities in

soil. They also divided the influences on phenol degradation into inhibition, stimulation, stimulation followed by inhibition and no effect according to the experimental results (Carine et al., 2009). In addition to the above-mentioned effects of PTEs on the removal of organic pollutants by microorganisms, plant root also possess an important function in the interaction of multiple pollutants and their phytoremediation efficiency (Fig. 6). More root secretion could be released by plant under the pressure of PTEs (Zhang et al., 2009). On one hand, the secretion provides the substrate for biological growth. It is conducive to microbial biomass and enzymatic activity for the improvement of the degradation rate. On the other hand, the special root exudates might combine with organic pollutants and consequently decrease the bioavailability of pollutants (Zhang et al., 2009).

Organic pollutants could stimulate the enzymatic activity in a certain degree and affect the processes on uptake, adsorption, transformation and immobilization of PTEs in co-contaminated soil. Organic pollutants in a certain dose can raise the energy source of microbes and enhance biological respiration intensity. The metabolites generated by the transformation of organic pollutants also contribute to biological activity (Zhang et al., 2011b). A study conducted composting experiment and found the intermediate of PAHs, salicylate, could enhance the bacterial uptake of Cd (Rosner & Aumercier, 1990). However, research from Wen et al. (2011) proved the accumulation up to a high level of intermediate, like phthalic acid and salicylic acid, inhibited the pyrene degradation. Besides, organic pollutants co-existed in soil are promising to alter

the composition of root exudates. For example, PAHs induced salt marsh plants to secrete the Cu ligands in contaminated soil, and the secreted ligands have capacity for making the PTEs become soluble and available by complexation (Almeida et al., 2008).

Biological processes are affected by co-occurrence of pollutants, and the changes in biomass, biological intracellular metabolism, and extracellular secretion have been demonstrated in the presence of multiple pollutants. In general, certain levels of pollutants have the ability to promote bioremediation, due to chelating effect and respiratory stimulation, while toxicity of pollutants (excessive concentrations) often inhibits bioremediation, because of its damage to the enzyme protein and biological barriers. Besides the concentrations of pollutant, biological species used for remediation and their mechanisms also make difference on the interactions of multiple pollutants. Moreover, it is unclear for the detailed steps of the interaction of multiple pollutants on metabolism and oxidative stress in living organisms.

5. Conclusions and expectations

Researches on soil combined contamination are popular in recent years, and the interaction of co-occurring pollutants has attracted worldwide attention. Remediation of co-contaminated soil is not just a simple superposition of technologies for various pollutants. Mutual inhibiting or promoting effects constantly occur due to the interactions of different pollutants 1) in chemical processes: complexation, catalytic redox and other chemical reactions; 2) in adsorption behaviors, such as competition for

binding sites and modification of surface properties; and 3) in biological processes, as impacts on biomass development, biological intracellular metabolism and extracellular conversion processes. However, soil medium is relatively complex, and the interaction of pollutants is susceptible to the surrounding environment. In addition, the micro-mechanism of the interaction of pollutants is less explored, which hinders the assessment and prediction of pollution remediation in actual contaminated sites. In order to clarify the interaction of the increasingly serious combined contamination in the future, further researches for some aspects are needed as following:

1. Experiments should move from the laboratory into the natural environment to verify the influence of various variable environmental factors on the interaction of different pollutants in soil.
2. The mechanisms of the interaction of different pollutants are critical to further research. For instance, the speciation conversions of PTEs are caused by different types and concentrations of organic pollutants and/or their metabolites in remediation system. Besides, the toxicity of PTEs at different bioavailability influences the decomposition of organic pollutants by various pathways.
3. The implementations of remediation technologies might also change the soil properties. We need to understand the effects of the changes in soil organic matter content, pH value and other soil characteristics on the interactive relationship of different pollutants in soil remediation system.
4. The comprehensive influences of multiple stresses (PTEs and organic pollutants)

on biological effects of soil, especially on the bio-metabolic modes and detailed enzymes, are needed for the deeper analysis.

5. In many aspects of the interactions, it appears a dose-dependent on remediation efficiency with the dose of coexisting pollutants. Future researches need to be done to accurately illustrate this dose-effect relationship.

6. The ecological risk of combined contamination could be reduced through taking advantage of the favorable aspects of the interactions of different pollutants. On the premise of introducing as few contaminants as possible, future studies are needed to develop a technology which has the ability to trigger the remediation process by making use of one pollutant to react with other pollutants

7. There are several mechanisms of the interaction among multiple pollutants in soil and even result in opposite effect. For instance, competitive adsorptions of pollutants increase the desorbed amount and further strengthen the bioavailability of contaminants; on the contrary, the availability of organic pollutants and PTEs might reduce due to the formation of neutral complexes. However, the dominant mechanism of interaction and their main effect on remediation system require deeper experimental confirmation.

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Figure captions

Fig. 1 The effects of different pollutants on their adsorption behavior on binding sites

Fig. 2 The main influence pathways of PTEs on the biological degradation of organic pollutants, and the impact pathways of organic pollutants on biological uptake of PTEs

Note: Different color arrows represent the different pathways of the influence. The "+" ("-") represents the coexisting pollutant promote (inhibit) the remediation of other pollutants.

Fig. 3 Combined effect of PTEs and organic pollutants on biomass

Note: The "+" represents biomass promotion and "-" represents biomass inhibition.

Fig. 4 The inhibitive effect of PTEs on the microbial activity to pollutants degradation

Fig. 5 The influence of PTEs on the microbial uptake of pollutants (transport of pollutants across the membrane)

Fig. 6 The effect of coexisting pollutants on the bioremediation efficiency of other pollutants by changing extracellular secretion

Note: The "+" ("-") represents the promotion (inhibition).

Fig.1

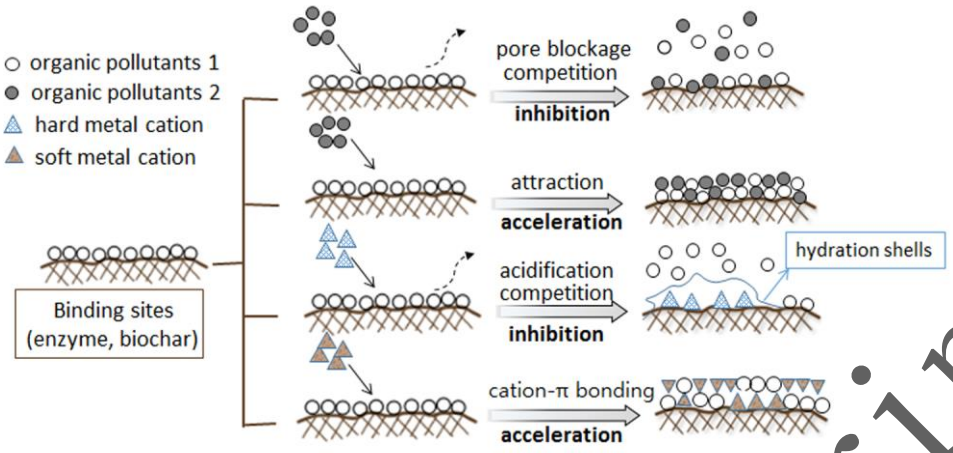


Fig.2

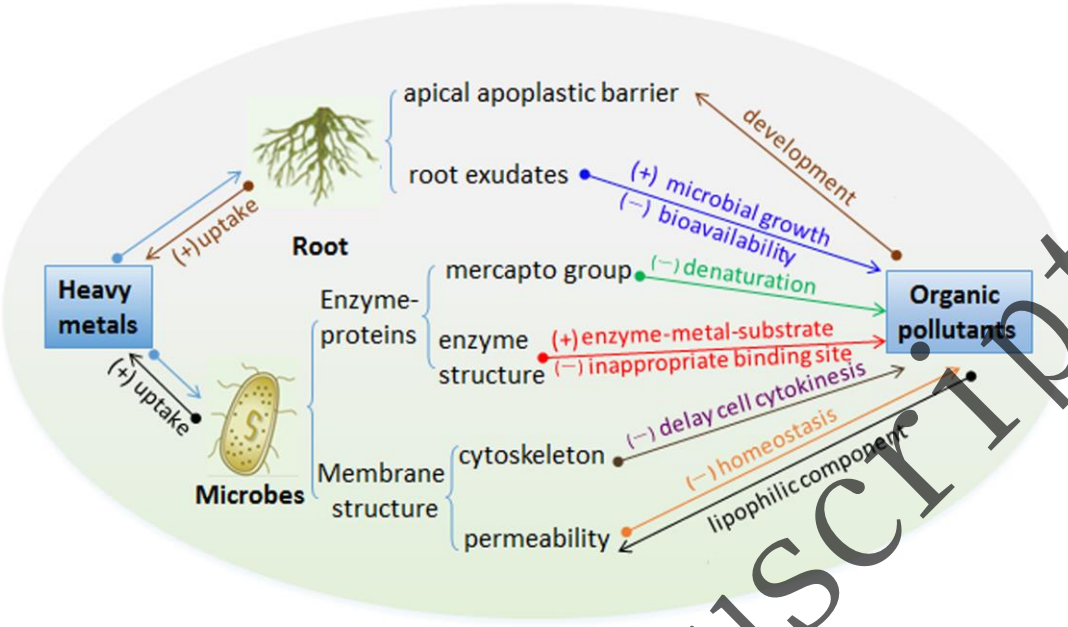
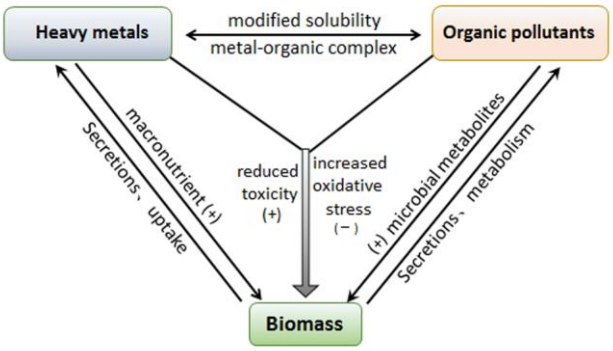


Fig.3



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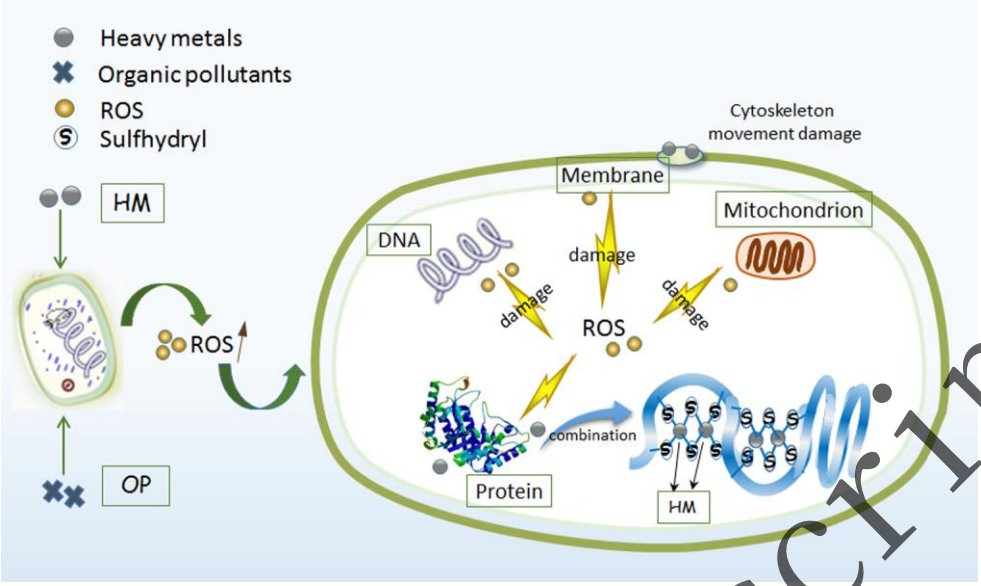

Fig.5

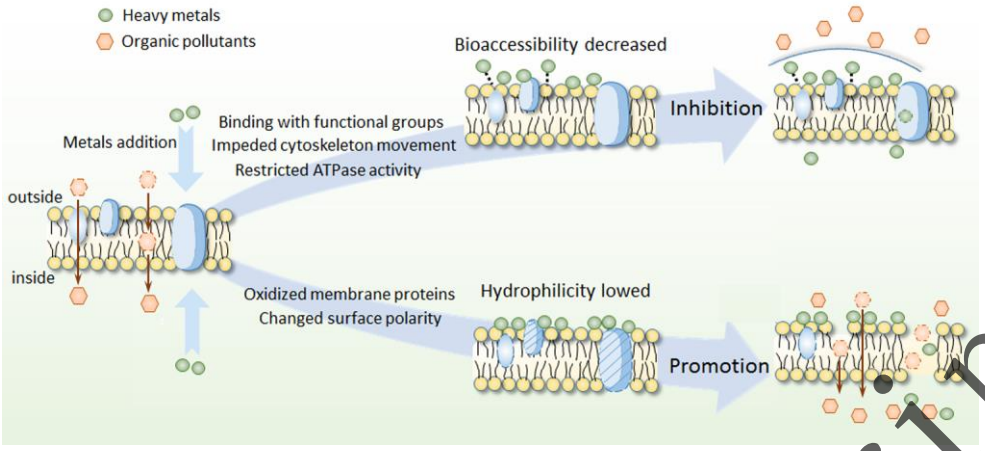

Fig.6

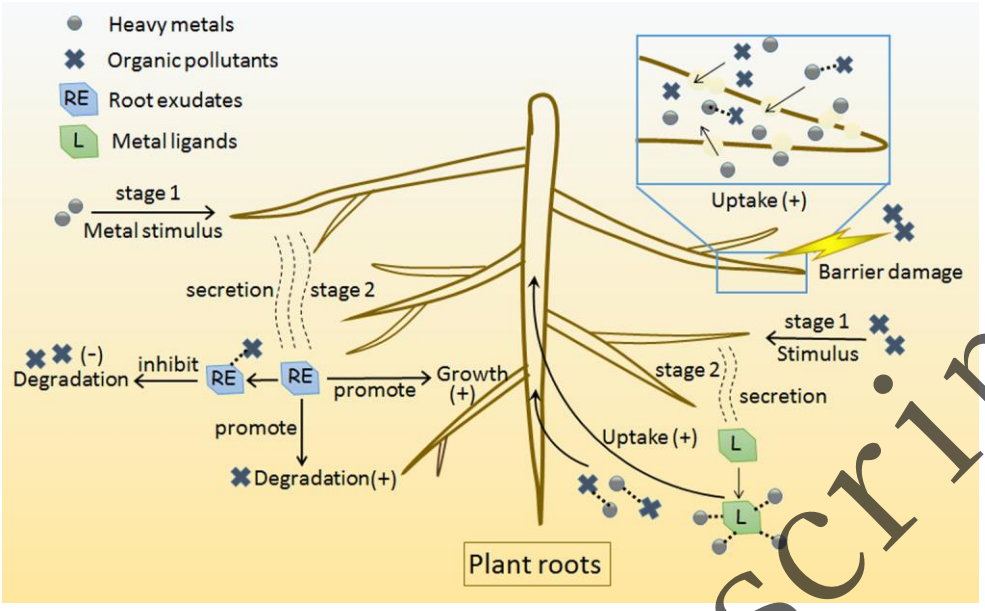

Table 1

Table 1 Competitive consequence of adsorption behaviour of multiple pollutants.

Soil characteristics	Pollutants	Binding sites	Interactions	Effects on remediation	References
Soil/spent mushroom compost mixture	Phenanthrene and tricyclazole	Active site of dioxygenase	Competition for enzymes, due to molecular similarity	Inhibited the degradation of phenanthrene, but the negative effect tended to decrease with the improvement of microbial diversity	(Liu et al., 2008)
Mineral soil, peat soil, and soil humic acid particles	Trichloroethene (TCE), atrazine and its analogues	Soil particles	Competition for adsorptive sites, due to similarity in adsorption mechanism	Significant competitive adsorption appeared between atrazine and its analogues while almost no competition between atrazine and trichloroethene	(Xing et al., 1996)
Calcareous soils pH: 7.60	Ni and Cd	Soil particles	Competition, due to similarity in adsorption behavior	Antagonistic effect was observed on the adsorption of Cd and Ni, and the negative effect of Cd on the sorption of Ni was larger than the reversed system, consistent with adsorption isotherms	(Davari et al., 2015)
Lacking	Pb, Cu and Zn	Green waste compost, coir, compost and wood bark	Competition, due to similarity in adsorption mechanism	The introduction of competitive metal cation reduced the adsorption amount of Pb to 50-60%, while the adsorption of Cu was reduced to 30-40% approximately	(Nwachukwu & Pulford, 2008)
Sandy loam pH: 7.74	Cd and 2,4-dichlorophenol	Soil particles and bamboo charcoal	Competition for sites, due to similarity in adsorption behavior	The desorption of both pollutants was favorable to the removal by electromigration and electroosmotic flow	(Ma et al., 2010)
Light sandy loam pH: 5.72	Cd, Ni, and Zn	Sewage sludge and soil particles	Competition, due to similarity in adsorption behavior	Great reduction in the distribution coefficient (K_d) of metal was obtained when multiple metals coexist in one system, especially the K_d of Cd to decrease by almost 50%	(Antoniadis et al., 2007)

Table 2 The effects of interaction of multiple pollutants in biomass on remediation.

Soil	Multiple pollutants	Remediation methods	Interactions on biomass	Effects on remediation	References
Lacking	Cu and Pyr	Phytoremediation by *Brassica juncea*	Cu- Pyr showed negative effect on the shoot and root dry matter of plant, changing the root physiology and restricting the rhizosphere microbial growth and activity	The inhibition of Cu phytoextraction and Pyr dissipation was confirmed	(Chigbo et al., 2013)
Sediment, pH:6.68 OM:11.21%	Cd and Pyr	Rhizoremediation by *Kandelia obovata*	High level of Cd- Pyr combined stress decreased the extension of roots and biological weight of plant, biotoxicity tended to amplify with increasing Cd on combined pressure	The degradation of pyrene was inhibited by Cd, as high Cd and Pyr contents might be toxic to specific groups of beneficial microbes	(Wang et al., 2014b)
Agricultural soil, pH:7.42	Cd and PHE	Mushroom (*Pleurotus cornucopiae*) and bacteria (FQ1, *Bacillus thuringiensis*)	PHE had interacted effect on easing up the toxicity of Cd in mushroom, increasing the biomass of *P. Cornucopiae*, and the greater alleviative effect was observed at low concentrations of phenanthrene	The co-existence of PHE promoted the Cd accumulation to some extent; up to100% and 95.07% of PHE were dissipated in 200 and 500 mg/kg groups	(Jiang et al., 2015)
Loam soil; pH:6.40	Cd and PAHs	Phytoremediation by *Juncus subsecundus*	Mixture of low Cd and low PAHs could obviously increase the total plant biomass and total number of microorganisms	Increased the Cd accumulation in plant tissues, and dissipation of PAHs in soils was apparently affected by interactions with Cd	(Zhang et al., 2011b)
Paddy soil (course-loamy). pH:6.10 OM 5.2%	Cu and PCP	Phytoremediation by *Lolium perenne L*, and *Raphanus sativus*	There is antagonistic effect on plant cytotoxicity with increasing Cu level at lower initial PCP level, while exerted synergistic effect at higher initial PCP level	The removal efficiency of extractable PCP was significantly influenced by coexisting pollutant depended on polluted level	(Lin et al., 2006)
Sandy loam pH:6.40	Cd and Pyr + PHE	Phytoremediation by *Juncus subsecundus*	Interaction of Cd and PAHs partly lessen Cd toxicity to plants, promoting plant growth, but abundance of	Cd accumulation and removal was significantly higher in treatments with PAHs,	(Zhang et al., 2012)

			PAH-degraders was not significantly influenced by Cd additions	dissipation of PAHs were not significantly influenced by Cd	
Agricultural soil pH:6.42 OM 1.63%	Cd and Pyr	Phytoremediation by maize (*Zea mays L.*)	A obvious decrease in roots and shoots dry weights was observed in Cd spiked soils combined with Pyr	The ability of Cd phytoextraction and Pyr degradation were restrained under co-contaminated soil	(Zhang et al., 2009)

OM: organic matter; Pyr: pyrene; PHE: phenanthrene; PCP: pentachlorophenol