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ScienceDirect
Journal of Hazardous Materials 150 (2008) 515–521
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Growth response of *Zea mays* L. in pyrene–copper co-contaminated soil and the fate of pollutants

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Received 17 November 2006; received in revised form 30 April 2007; accepted 30 April 2007
Available online 5 May 2007

Abstract

Phytoremediation, use of plants for remediation, is an emerging technology for treating heavy metals or a final polishing step for the high-level organic contamination, and may be suitable for remediation of heavy metal and organic co-contaminated soil. The aim of this study was to investigate the influence of co-contamination on the growth of *Zea mays* L. and the fate of both heavy metal and organic pollutants, using Cu and pyrene as the model pollutants. Results showed that shoot and root biomass were affected by the copper–pyrene co-contamination, although maize grown in spiked soils showed no outward signs of phytotoxicity. With the initial concentration of 50,100 and 500 mg/kg, pyrene tended to alleviate the inhibition of Cu to *Z. mays* L. Pyrene in both planted and non-planted soil was greatly decreased at the end of the 4-week culture, accounting for 16–18% of initial extractable concentrations in non-planted soil and 9–14% in planted soil, which indicated that the dissipation of soil pyrene was enhanced in the presence of vegetation probably due to the biodegradation and association with the soil matrix. With the increment of Cu level, residual pyrene in the planted soil tended to increase. The pyrene residual in the presence of high concentration of Cu was even higher in the planted soil than that in the non-planted soil, which suggested that the change of the microbial composition and microbial activity or the modified root physiology under Cu stress was probably unbeneficial to the dissipation of pyrene. A more thorough understanding of the mechanisms by which metals affect the dissipation of organic pollutants in the rhizosphere could provide a much better framework on which to base manipulation. Unlike pyrene, heavy metal copper cannot be degraded. Decontamination of Cu from contaminated soils in this system required the removal of Cu by plants. It was observed that the ability of Cu phytoextraction would be inhibited under co-contamination of high level of pyrene in highly Cu-polluted soil. In the treatment of 400 mg Cu/kg and 500 mg pyrene/kg, the accumulation of Cu was less than half of that in 400 mg Cu/kg treatment.

Keywords: Pyrene; Copper; Phytoremediation; Co-contamination; Heavy metal

1. Introduction

Since accumulated pollutants are of concern relative to both human and ecosystem exposure and potential impact [1], efforts are underway in many countries to control the release of contaminants [2] and to accelerate the removal or breakdown of existing contaminants by appropriate remediation techniques. Phytoremediation, use of plants for remediation, is one such highly appealing technology [2–6]. There are some promising results suggesting that these techniques might became viable alternatives to mechanical and chemical approaches in remediation of metal contaminated soils or a final polishing step for the high-level organic contamination [7–9].

Despite the wide study of phytoremediation in heavy metal or organic contaminated soil, little information was still available regarding the effectiveness and processes of phytoremediation of sites co-contaminated with organic and metal pollutants. It was reported that 40% of hazardous waste sites in the United States are co-contaminated with organic and metal pollutants [10,11]. Metals most frequently found include cadmium, chromium, copper, zinc and lead. Common organic co-contaminants include petroleum hydrocarbons (TPHs), and polyclic aromatic hydrocarbons (PAHs) coming from the exploration and consumption of fossil fuel, polychlorinated biphenyls (PCBs) widely used in the industrial process, and other chlorinated aromatics used as PCB replacement such as polychlorinated terphenyls

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doi:10.1016/j.jhazmat.2007.04.132

(PCTs), halogenated compounds like perchloroethylene (PCE) and trichloroethylene (TCE) and pesticides like atrazine and bentazon [12]. As the presence of metals can inhibit a broad range of microbial processes including nitrogen and sulfur conversions, dehalogenation, and reductive processes in general [13–19], and the changed bioavailability of heavy metals in the presence of organic co-contamination might occur [20], the efficiency and mechanism of phytoremediation probably was quite different.

It is well known that phytoremediation of organics is based on the beneficial effects of roots on degradation. A multitude of changes occur in soil in the presence of roots that may be apprehended as changes in its chemical characteristics, modified microbial composition, and enhanced microbial activity. In heavy metal–organic pollutant combined system, heavy metal not only cause the positive or negative effects on the root growth and thereafter affect the root enhanced dissipation, but also exert direct effects on microorganisms and cause direct and indirect effect for degradation of organic pollutants. Lin et al. [21] reported that in copper co-contaminated soil with the initial pentachlorophenol (PCP) concentration of 50 mg/kg, plants grew better with the increment of soil Cu level (0, 150 and 300 mg/kg), implying that combinations of inorganic and organic pollutants sometimes exerted antagonistic toxic effects on plant growth. The observed higher PCP dissipation in soil spiked with 50 mg/kg PCP in the presence of Cu and the less difference of PCP residual between strongly and loosely adhering soils further suggests the occurrence of Cu–PCP interaction and the enhanced degradation and mass flow are two possible explanations. In copper co-contaminated soil with the initial PCP concentration of 100 mg/kg, however, both plant growth and the microbial activity were inhibited with the increment of soil Cu level. The lowered degrading activity of microorganisms and the reduced mass flow were probably responsible for the significantly lower levels of PCP dissipation in copper co-contaminated soil. Besides, Zhu et al. [22,23] reported that the exposure of bacteria to a combination of PCP and copper at non- or sub-toxic concentrations resulted in enhanced cytotoxic effects in a synergistic mode as measured both by growth inhibition and colony-forming ability. Pollutant biodegradation was thus inhibited due to the decrease of microbial biomass and activity [24]. In some cases, however, addition of metals has also been observed to stimulate microbial activity. It is suggested the stimulatory effect may also be due to metals reducing competition for equivalents or nutrients between metal-resistant degraders and metal-sensitive non-degraders [11]. Kuo and Genthner [24] reported that the addition of some metals at low levels stimulated biodegradation. Hexavalent chromium (0.01 mg total chromium/L) increased the biodegradation rate of phenol by 177% and that of benzoate by 169% over controls containing no metals. Copper and cadmium (both at 0.01 mg total metal/L) increased the benzoate biodegradation rate by 185% and the 2-chlorophenol biodegradation rate by 168%.

Unlike organic pollutants, the most effective but also technically the most difficult phytoremediation strategy of heavy metal is phytoextraction [6]. Several bottleneck processes limiting heavy metal accumulation in plants include the mobilization of poorly available contaminant trace elements in the soil, root uptake, symplastic mobility and xylem loading, as well as detoxification and storage inside the shoot [25]. The effect of organic pollutant on the phytoextraction of heavy metal is not fully understood yet. However, organic chelators increase metal ion uptake and translocation in plant is widely researched. For example, when ethylene diamine tetra-acetic acid (EDTA) is added to lead contaminated soils, there is a >100-fold increase in the uptake and transport of the lead–EDTA–chelate into stems and leaves [26,27]. Therefore, in stress condition, plants altered to increase their secretion of particular organic matter such as organic acids will probably increase the uptake and translocation of metal pollutants.

In sum, phytoremediation of sites co-contaminated with organic and metal pollutants is very complex. The objective of this paper was to investigate the influence of co-contamination on the growth of *Zea mays* L. and the fate of pollutants in soil and plants. Cu and pyrene were selected as the model pollutants. Maize (*Z. mays* L.) was chosen as the tested plant species because of its high biomass yields and heavy metal tolerance. Ali et al. [28] studied maize tolerance and proposed this plant as a possible solution for the stabilization and restoration of Cu-polluted soils. Additionally, maize may create particularly good environmental conditions for soil microorganisms and microfauna [29–31]. Dillewijn et al. [32] reported that the extractable TNT content in rhizosphere soil associated to maize roots decreased by more than 96% in 60 days regardless of inoculation and considered that under field conditions, maize is potentially useful alternative to remediation surface soils contaminated with medium levels of TNT.

2. Material and methods

2.1. Soil and subsamples

Soil samples used in the present study were collected from Jiaxin county, Zhejiang province, China. The soil is classified as Paddy soil (course-loamy, nonacid). Soil testing results showed pH (1:2.5 water) 6.10; OM content 5.2% and CEC 4.28 cmol/kg. The levels of Cu and pyrene added into soil were 0, 200, 400 mg Cu/kg soil and 0, 50, 100, 500 mg pyrene/kg soil. Briefly, the bulk soil was first mixed thoroughly with Cu (as $CuSO_4$), urea (0.11 g/kg), KH_2PO_4 (0.10 g/kg) and KCl (0.11 g/kg) in an aqueous solution, incubated at a moisture condition for 4 weeks. Then the subsamples were air-dried naturally, fully homogenized again and stored for use. The subsamples containing pyrene was prepared with the above subsamples. High purity pyrene in acetone was spayed onto the soil. After acetone had evaporated off, the spiked soils were sieved again through 2 mm sieve to ensure the homogeneity and stored for use.

2.2. Incubation experiment

Two hundred grams of each subsample (including control subsamples without an addition of Cu and pyrene) were put in open plastic pots and pre-incubated in the greenhouse for 1 week with 60% of the water holding capacity. Then, two pre-