Journal of Environmental Management xxx (2017) 1–7

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Effect of cetyltrimethyl ammonium bromide on uptake of polycyclic aromatic hydrocarbons by carrots

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A R T I C L E I N F O

Article history:
Received 22 September 2017
Received in revised form
6 December 2017
Accepted 9 December 2017
Available online xxx

Keywords:
Polycyclic aromatic hydrocarbons
Cetyltrimethyl ammonium bromide
Bioavailability
Daucus carota L
Leaching loss

A B S T R A C T

This is the first study investigating the effect of cationic surfactants on the mobility of polycyclic aromatic hydrocarbons (PAHs) in aged contaminated soils and on PAH bioaccumulation in tuberous vegetables. In an aerobic soil incubation experiment, 150 mg/kg cetyltrimethyl ammonium bromide (CTMAB) decreased the bioavailability of PAHs primarily via immobilization (by 13%). In a carrot pot experiment, the effectiveness of CTMAB to reduce PAH uptake by carrots decreased with time. Accordingly, the bioavailability of PAHs in the soil decreased in the first 90 days and then increased and remained stable until harvest. In the leaching test, the leaching loss of CTMAB (15%) was lower in soils treated with small amounts of CTMAB in several applications than it was in soils (24%) treated once with CTMAB. Therefore, CTMAB, when applied in appropriate doses via addition methods, can effectively reduce the environmental risk of PAH entering humans and livestock through the food chain.

1. Introduction

Recently, the contamination of polycyclic aromatic hydrocarbons (PAHs) in farmland soils near industrial areas has attracted considerable attention (Wang et al., 2017). The main sources of the pollution are anthropogenic activities, such as wastewater irrigation and transportation emissions (Khan et al., 2015). The available fraction of PAHs in soils can be taken up by food crops and then transferred to humans and other organisms (Usman et al., 2016). The recommended level of total 16 PAHs, declared carcinogenic by United States Environmental Protection Agency (USEPA), in the environmental quality standards for soils in China (GB 15618-2008) was 4.9 mg/kg. To reduce the environmental risk of PAHs in soil and ensure safe agricultural production, various geosorbents have been studied and applied to reduce the migration of PAHs from soils to plants.

Cationic surfactants have been proposed as additive reagents for the remediation of soils contaminated with PAHs (Boyd et al., 1988; Zhu et al., 2010; Garcia-Galan et al., 2017). Below the critical micelle concentration (CMC), monomeric cationic surfactants can help shape the pseudo-organic phase on the solid substrate through the interaction of the positive charge with the negatively charged soil particles. Subsequently, this phase allows more PAHs to be distributed into the soil (Zhao et al., 2010). The process of PAH sorption to cationic surfactants is similar to the distributive role played by soil organic matter, and the distribution intensity of cationic surfactants is 10–30 times stronger than that of natural organic matter (Boulakradeche et al., 2015). Cationic surfactants, e.g., cetyltrimethyl ammonium bromide (CTMAB) and dodecylpyridinium bromide (DDPB), have been observed to effectively inhibit the solid-vapour volatilization of PAHs, enhance the soil retention of PAHs and reduce their bioavailability (Boyd et al., 1988; Smith and Galan, 1995; Zhu et al., 2000; Lu and Zhu, 2012). Our previous study demonstrated that when CTMAB was applied at appropriate concentrations, PAH desorption from the soil was retarded (Ni et al., 2017). To date, one study investigating the effects of cationic surfactants on dry farming in PAH-contaminated soils has been reported. Lu and Zhu (2009) demonstrated that the concentrations of phenanthrene and pyrene in chrysanthemums, cabbages, and lettuces decreased with increasing doses of CTMAB and DDPB in soil over a 30-day experiment ($p < .05$). This study focused on the ability of the cationic surfactants to immobilize

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https://doi.org/10.1016/j.jenvman.2017.12.024
0301-4797/

artificially spiked PAHs in soils and the bioaccumulation of those PAHs in the vegetables with short growth cycles. On the one hand, pore water concentrations and soil sorption coefficients of PAHs were widely different in freshly spiked and aged soils (Ter Laak et al., 2006; Škulcová et al., 2017). On the other hand, the various growth periods of crops may strongly impact the effectiveness of cationic surfactants. However, no study has examined the potential of cationic surfactants to limit the bioavailability of PAHs in aged contaminated soils and their bioaccumulation in crops with relatively long growth cycles. Moreover, compared with leafy crops, tuberous vegetables (e.g., carrots, radishes and turnips) contain much higher PAH concentrations because the accumulation of PAHs is higher in roots than in other parts of the plant (Florence et al., 2015). Thus, it is worth examining the potential of cationic surfactants to enable the safe production of tuberous vegetables with long growth cycles in PAH-contaminated soils.

Therefore, this study aims to explore whether and how cationic surfactants can reduce PAH bioavailability in aged contaminated soils and their bioaccumulation in tuberous vegetables throughout the entire growth period. CTMAB was selected as the cationic surfactant and used to amend PAH-contaminated farmland soil. An incubation experiment was performed to investigate the effect of CTMAB on the mobility and availability of PAHs in aged contaminated soil. A pot experiment was conducted in a greenhouse using carrots (*Daucus carota* L.) as a typical root vegetable. A leaching experiment was performed with soil columns to elucidate the effect of different CTMAB addition methods on the leaching loss of CTMAB with daily watering and the PAH bioavailability in soil. To the best of our knowledge, this is the first study to apply a cationic surfactant to aged contaminated soils to reduce PAH bioaccumulation in tuberous vegetables.

2. Materials and methods

2.1. Chemicals and soil preparation

Analytical grade CTMAB was purchased from Nanjing Chemical Factory (Nanjing, China). The molecular formula and CMC of CTMAB are $C_{19}H_{42}BrN$ and 360.8 mg/L respectively.

A sample of arable field soil that had been contaminated with PAHs for more than 40 years was collected from the top 20 cm in an area near a steel mill in a suburb of Nanjing, China. The soil was air-dried and passed through a 2-mm sieve. The soil had a pH of 7.4, a dissolved organic carbon content of 309 mg/kg, and a composition of 9% clay, 64% silt, and 28% sand. The total soil concentration of the 16 PAHs included in the United States Environmental Protection Agency (U.S. EPA) priority pollutant list was 7582 mg/kg. The concentration of each PAH, grouped according to the number of rings in the PAH structure, was reported previously (Ni et al., 2017).

2.2. Soil incubation experiment

The collected soils were spiked with an aqueous solution of CTMAB to reach a concentration of 50 mg/kg or 150 mg/kg (dry soil) in a cylindrical polyvinyl chloride pot (20 cm in height and 20 cm in bottom diameter). The microcosms were watered to up to 60% of its water holding capacity and allowed to equilibrate weekly. The three treatments were 50 CTMAB, 150 CTMAB and Control (without amendment), and each treatment was performed in triplicate. All the microcosms were incubated in a greenhouse under natural diurnal light conditions from May to October 2015. Every 30 days, 10 g of soil from each pot was sampled using a soil borer to measure the total and bioavailable concentrations of PAHs.

2.3. Carrot pot experiment

In each cylindrical polyvinyl chloride pot, the collected soil was mixed with 2.58 g of N (ammonium nitrate), 1.23 g of P (potassium dihydrogen phosphate), 1.35 g of K (potassium sulfate), and then spiked with an aqueous solution of CTMAB to reach a concentration of 50 mg/kg or 150 mg/kg (dry soil) and subsequently allowed to stand for 24 h. Carrot seeds were sterilized in a 30% H_2O_2 solution for 10 min and then immersed in deionized water on moist filter paper in culture dishes for one week. Ten uniformly germinated seeds were selected and sown in each pot. The same three treatments as described above for the soil incubation experiment, i.e., Control, 50 CTMAB and 150 CTMAB, were used. All the treatments were conducted in triplicate. The carrots were periodically watered with a certain volume of water according to the growth requirements. The plants were grown in the greenhouse under natural diurnal light conditions from May to October 2015. Every 30 days, 10 g of the soil was sampled from each pot using a soil borer to measure the total and bioavailable concentrations of PAHs. Carrots were sampled on days 90, 120 and 150 of the growth period, and two carrots were sampled at each time point. The collected shoots and roots were thoroughly washed with deionized water and freeze-dried for chemical analysis.

2.4. Leaching experiment in soil columns

Leaching tests were carried out in glass columns that were 5 cm in diameter and 18 cm in height, which was the same as the height of the soil in the carrot pot experiment. The columns were packed from bottom to top with 200 screen mesh, glass wool, quartz sand and 250 g of the collected soil to prevent the soil fractions from flowing through the column. The soils were first pre-wetted with ultrapure water to field capacity, and then, 50 mL of deionized water was slowly and evenly added to the top to simulate daily watering during the later stage of the pot experiment. CTMAB at a concentration of 150 mg/kg was introduced in three ways: by mixing with the soil before loading the column (T1) or by inclusion in the daily watering solution five times (every 6 days, T5) or ten times (every 2 days, T10). Every two days, the leachate was collected, weighed, and filtered, and then, the CTMAB concentration in the leachate was determined by an ultraviolet–visible spectrometer (UV-2401PC, Shimadzu, Japan). After 30 days, the PAH residues and bioavailable concentrations in the soil column were also measured.

2.5. PAH extraction and quantification in soil and carrots

The total PAH concentrations in soils/carrots were extracted by accelerated solvent extraction (ASE 200, Dionex, Sunnyvale, CA, USA) (Belo et al., 2017). Briefly, 1 g of soil or 0.5 g of a carrot sample was homogenized with 5 g of diatomaceous earth and extracted with hexane/acetone (4:1, *v/v*) at 100 °C and a pressure of 1500 psi. The extracts were rotary evaporated to 1 mL at 50 °C. The concentrated samples were loaded on a silica gel/anhydrous sodium sulfate column for the soil samples and a sulfonated silica/anhydrous sodium sulfate column for the carrot samples and then eluted with 15 mL of hexane/dichloromethane (9:1, *v/v*). The eluate was concentrated to 1 mL for the detection of PAHs by gas chromatography-mass spectrometry analysis (GC-MS, Agilent 7890A/5975C, Santa Clara, CA).

The available PAH concentrations in soil were determined by extracting the PAHs with hydroxypropyl-β-cyclodextrin (HPCD), which is an effective method for evaluating the bioavailability of PAHs (Guo et al., 2017). Briefly, 1 g of freeze-dried soil was extracted with 20 mL of HPCD (50 mmol/L) in a glass centrifuge tube by