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Enhanced organic contaminants accumulation in crops: Mechanisms, interactions with engineered nanomaterials in soil☆

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ABSTRACT

The mechanism of enhanced accumulation of organic contaminants in crops with engineered nanomaterials (ENMs) were investigated by co-exposure of crops (*Ipomoea aquatica Forsk* (Swamp morning-glory), *Cucumis sativus* L. (cucumber), *Zea mays* L. (corn), *Spinacia oleracea* L. (spinach) and *Cucurbita moschata* (pumpkin))to a range of chemicals (polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polybrominated diphenyl ether (PBDE)) and ENMs (TiO_2, Ag, Al_2O_3, graphene, carbon nanotubes (CNTs)) in soil. Induced by 50 mg kg^{-1} graphene co-exposure, the increase range of BDE-209, BaP, *p,p′*-DDE, HCB, PYR, FLU, ANT, and PHEN in the plants were increased in the range of 7.51−36.42, 5.69−32.77, 7.09−59.43, 11.61−66.73, 4.58−57.71, 5.79−109.07, 12.85−109.76, and15.57−127.75 ng g^{-1}, respectively. The contaminants in ENMs-spiked and control soils were separated into bioavailable, bound and residual fractions using a sequential ultrasonic extraction procedure (SUEP) to investigate the mechanism of the enhanced accumulation. The bioavailable fraction in spiked soils showed no significant difference ($p > 0.05$) from that in the control, while the bound fraction increased in equal proportion ($p > 0.05$) to the reduction in the residual fraction. These results implied that ENMs can competitively adsorbed the bound of organic contaminants from soil and co-transferred into crops, followed by a portion of the residual fraction transferred to the bound fraction to maintain the balance of different fractions in soils. The mass balance was all higher than 98.5%, indicating the portion of degraded contaminants was less than 1.5%. These findings could expand our knowledge about the organic contaminants accumulation enhancement in crops with ENMs.

1. Introduction

The estimated globe production of Engineered nanomaterials (ENMs) will reach 58,000 tons by 2020 (Kunhikrishnan et al., 2014). The particles of ENMs are more and more discharged into the environment with their increasing production and application. (Kahru and Dubourguier, 2010; Kunhikrishnan et al., 2014; Liu et al., 2014; Wu et al., 2017; Zhang et al., 2012). ENMs are inevitably discharged into environment and thus are ubiquitous in different environmental media, such as surface water, sediment, and soil, at concentrations in the range of μg kg^{-1} to mg kg^{-1} (Deng et al., 2017; Sun et al., 2014).

Because of their unique physiochemical properties, such as small particle size and large surface area (Deng et al., 2017; Jr et al., 2008; Li et al., 2013; Wilson et al., 2008), most of ENMs can easily enter soils, and contact/adsorb organic contaminants. Both organic contaminants and ENMs in crops pose potential risk to food production (Deng et al., 2014). Most previous studies focused on the toxicity of ENMs or organic contaminants themselves, and knowledge is still quite limited about their joint biological effects (Deng et al., 2017; Miralles et al., 2012b; Tan et al., 2018; Zuverza-Mena et al., 2017). Dr. White (De La Torre-Roche et al., 2012) reported that the bioaccumulation of *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE) in crops was increased in the presence of C_{60} fullerenes, indicating that ENMs affected soil as a function of co-exposure to plant. Although it has been confirmed that ENMs affected the bioaccumulation of organic contaminants in agriculture farmland, the underlying mechanism remains unknown (Tan et al., 2018).

ENMs can alter the migration and transformation of organic pollutants in soils (Wilson et al., 2008). There are many reports on

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the adsorption behavior of ENMs to organic compounds in water solutions (Li et al., 2016; Pan and Xing, 2008; Yan et al., 2008). However, the interaction between organic contaminants and ENMs in soils is unclear. The organic contaminants in soils can be roughly divided into four fractions using a sequential ultrasonic extraction procedure (SUEP) described in our previous studies, which were the water-soluble fraction, the acid-soluble fraction, the bound fraction, and the residual fraction (Liang et al., 2015; Wang et al., 2015; Wu and Zhu, 2016). The water-soluble and acid-soluble fractions are bioavailable, while the bound and residual fractions are difficult or impossible for plants to uptake, resulting in little or no bioavailability. The bioaccumulation of contaminants in crops is determined not only by the total amount of contaminants in soil but more vitally by the amount of bioavailable fraction (Clarke and Smith, 2011; Semple et al., 2004). In addition, the bound fraction can potentially be hitchhiked into crops with ENM carriers. The adsorption behavior of different fractions of ENMs to organic contaminants has been seldom reported.

ENMs and organic contaminants transferred from the soil to the edible parts of crops and accumulate in the food chain, resulting adverse health effects (Holden et al., 2016; Lahiani et al., 2016; Wilke et al., 2016). At present, there is insufficient information about the organic contamination of crops exposed to ENMs to accurately evaluate the ecological risk of contaminants in farmland soils. To understand the effect of ENMs on the adsorption, uptake and translocation of organic contaminants, a range of organic contaminants (five PAHs, two OCPs and one PBDE) and five engineered nanomaterials (TiO_2, Ag, Al_2O_3, graphene, CNTs) on the uptake of both types of contaminants by five crop species (*Ipomoea aquatica Forsk* (Swamp morning-glory), *Cucumis sativus* L. (cucumber), *Zea mays* L. (corn), *Spinacia oleracea* L. (spinach) and *Cucurbita moschata* (pumpkin)) in soil was investigated. The purpose of the current study is to investigate the interaction of ENMs with organic contaminants in farm soil and their uptake by crops.

2. Experimental section

2.1. Standards and reagents

Standards of five PAHs (Anthracene (ANT),Phenanthrene (PHEN), Pyrene (PYR), Fluoranthene (FLU) and Benzo[a]pyrene (BaP)), two OCPs (Hexachlorobezene (HCB) and p,p′-Dichlorodiphenyldichloroethylene (*p,p′*-DDE) and one PBDE (Decabrominated diphenyl ether (BDE-209)) in soil and crop samples were used in this study. The physical properties of these chemicals are provided in the supplementary information section (SI, Table S1). Standards of eight contaminants (analytical grade) and 1,2,3,4,5,6,7,8,9,10-decadeuteriophenanthrene (D-PHEN) were purchased from AccuStandard (NewHaven, USA). Five ENMs, including titanium dioxide nanoparticles (nano-TiO_2 (25 nm)), silver nanoparticles (nano-Ag (60–120 nm)), aluminum oxide nanoparticles (nano-Al_2O_3 (30 nm)), graphene (4–20 nm) and carbon nanotubes (CNTs (500–2000 nm)), were purchased from the Aladdin® Chemical Reagent Co., Ltd., China. The physicochemical properties of these ENMs are described in Table S2. All solvents (n-hexane, dichloromethane, n-nonane, and acetone) were of HPLC grade. The florisil, silica gel and anhydrous sodium sulfate used in the clean-up procedure were activated or pretreated in advance (Niu et al., 2013).

2.2. The co-exposure experiments

The main properties of the paddy soil used in this study are summarized in Table S3. The concentrations of the eight organic contaminants were measured in all blank soil samples, and all were lower than the limit of detection (LOD). The LOD of tested organic contaminants is provided in the SI section (Table S5). The seed were purchased from the Zhejiang seed Co., Ltd., China. Swamp morning-glory (*Ipomoea aquatica Forsk*), cucumber (*Cucumis sativus* L.), corn (*Zea mays* L.), spinach (*Spinacia oleracea* L.) and pumpkin (*Cucurbita moschata*) were sown in separate pots. After the seeds were germinated in vermiculite, the seedlings were transferred to a tray containing 1000 ml a half-strength Hoagland solution (Hoagland and Arnon, 1950). The seedlings were maintained in a greenhouse at 25–30 °C during the day and at 20–25 °C during the night. After three weeks, the crops were approximately 15 cm tall, and healthy roots were developed.

The contaminants were dissolved in acetone and spiked in one soil sample (50 g) to make a fortified soil, one type at a time, and mixed by mechanical agitation and roll oscillation, the soil were thoroughly shaken to make the contaminant distribute evenly. Then the fortified soil were exposed to the ambient air (10 °C) overnight to evaporate the acetone. After the soils were aged for 30 days, 50 g of the fortified soil, 50 mg ENM, and 950 g of clean soil were mixed together. The homogeneity of contaminant thorough the soil was checked by five extraction of random soil samples (Wu and Zhu, 2016), and the standard error of the five parallel samples was less than 1.52%. The soils were then stored in dark at room temperature (25 ± 1 °C) and aged for 200 days. The concentrations of the contaminates were quantified before use. The concentrations of PHEN, ANT, PYR, and FLU in the soil were 0.85 ± 0.016, 0.92 ± 0.017, 0.93 ± 0.014, and 0.80 ± 0.028 mg kg^{-1}, respectively. For HCB, BDE-209,BaP, and p,p′-DDE, the concentrations were 0.45 ± 0.010, 0.42 ± 0.018, 0.09 ± 0.036, and 0.08 ± 0.010 mgkg^{-1}, respectively. Those concentrations were all lower than the limits in the Farmland Environmental Quality Evaluation Standard for Edible Agricultural Products (HJ 332–2006) and the draft of the Environmental Quality Standard for Soils (GB15618-2008). The crop uptake of organic contaminants was conducted using a batch technique (Li et al., 2002). Twenty-one day old seedlings were used for the experiment. For each type of five crops, nine units were loosely bundled together with a Teflon tape, cultured in a 1000 mL amber glass container through a hole drilled through the cap. Each amber glass was placed in the greenhouse in a growth chamber programmed for a 16 h light (25° ± 1 °C)/8 h dark (20 ± 1 °C) culture cycle with the addition of 700 g dry weight of the contaminated soil, during which the soil moisture content was 60% of the field capacity. After 25 days of exposure, the crop was collected. The remaining 300 g dry weight of the contaminated soil was used as the baseline for further analysis.

2.3. Sequential ultrasonic extraction procedure

A SUEP method was developed in our previous work for extracting different fractions of organic contaminants. The detailed information about SUEP was shown in Table S4. D-PHEN was added as an isotope-labeled standard in soil at 5% of the concentration of PHEN when exposed. This method was shown to be precise and replicable.

2.4. Crop extraction

The crops separated from the soils were washed with distilled water and then dried with filter paper. The crop samples were dried in a vacuum freeze dryer and ground to powder in liquid nitrogen. The roots and shoots were treated together to reduce systematic errors. The samples were ultrasonically extracted in a 10-mL mixture of hexane/dichloromethane (DCM) (1:1; v/v) for 10 min, and this extraction process was repeated 6 times. After the extraction procedure, the extracts were concentrated to less than