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Soil contamination by phthalate esters in Chinese intensive vegetable production systems with different modes of use of plastic film

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ABSTRACT

The concentrations of six priority phthalic acid esters (PAEs) in intensively managed suburban vegetable soils in Nanjing, east China, were analyzed using gas chromatography–mass spectrometry (GC–MS). The total PAE concentrations in the soils ranged widely from 0.15 to 9.68 mg kg^{-1} with a median value of 1.70 mg kg^{-1}, and di-n-butyl phthalate (DnBP), bis-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP) were the most abundant phthalate esters. Soil PAE concentrations depended on the mode of use of plastic film in which PAEs were incorporated as plasticizing agents and both the plastic film and poultry manure appeared to be important sources of soil PAEs. Vegetables in rotation with flooded rice led to lower concentrations of PAEs in soil. The results indicate that agricultural plastic film can be an important source of soil PAE contamination and further research is required to fully elucidate the mechanisms of PAE contamination of intensive agricultural soils with different use modes of use of plastic film.

1. Introduction

Phthalic acid esters (PAEs) are commonly used to increase the flexibility, pliability and elasticity of plastic products (Chou and Robert, 2006). They are widely used in general plastic products, cosmetics, personal care products, food packaging and medical products (Van Wezel et al., 2000; Hens and Caballos, 2003; Cai et al., 2008; Xia et al., 2011). The global consumption of PAEs is about 6.0 million tons per annum (Xie et al., 2007). As a result of their large-scale production and widespread application, PAEs can enter into the environment during the manufacture, use and disposal of plastics (Kong et al., 2012). Numerous studies have revealed the presence of PAEs in various environmental media such as water (Xie et al., 2007), air (Wang et al., 2012), sediments (Cai et al., 2008; Srivastava et al., 2010) and soils (Ma et al., 2003; Zeng et al., 2008; Kong et al., 2012), and they have also been detected in epoxidized soybean oil, soft spreadable cheese, sauces, and peanut butter (Pedersen et al., 2008) and in many types of vegetable (Fu and Du, 2011). DnBP, DEHP, butyl benzyl phthalate (BBP), diethyl phthalate (DEP) and diheptyl phthalate have endocrine disruptive effects *in vivo* (Hens and Caballos, 2003). Furthermore, their metabolites are suspected endocrine disrupting chemicals exhibiting carcinogenic action (McKee et al., 2004). Human Leydig cell development and function may be vulnerable and incomplete virilization in infant boys due to perinatal exposure to some phthalates (Main et al., 2006). Moreover, inhalation of substantial amounts of phthalates or their metabolites by women during pregnancy can result in abortion (Adibi et al., 2003). The United States Environmental Protection Agency (USEPA) has classified dimethyl phthalate (DMP), DEP, DBP, BBP, DEHP and DnOP as priority environmental pollutants (USEPA, 2013). PAEs have become one of the most widespread classes of organic contaminants, which have attracted much attention on a global scale (Kong et al., 2012).

Urbanization and industrial modifications of the environment in China interact strongly with agricultural production (Khai et al., 2007; Zeng et al., 2008) and land use in suburban areas has changed from paddy fields to more economically lucrative intensive vegetable systems. Many agricultural soils have been severely degraded by agricultural activities and urban development (Zeng et al., 2009; Gu et al., 2011). Numerous studies have indicated that agricultural soils and vegetables have been contaminated by toxic pollutants (Gao et al., 2005). Some investigators have found that toxic pollutants such as heavy metals (Hu and Ding, 2009), polycyclic aromatic hydrocarbons (PAHs) (Yin et al., 2008), persistent organic pollutants (POPs) (Gao et al., 2005), organochlorine

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pesticides (Tao et al., 2005) and PAEs are present in suburban agricultural soils (Chen et al., 2011; Xia et al., 2011; Kong et al., 2012). PAEs are among the most abundant semi-volatile organic chemicals found in Chinese soils (Cai et al., 2008). Soils are environmental matrices that can transfer pollutants to plants and the human food chain. DnBP has negative impacts on the vitamin C and capsaicin contents of capsicum fruit (Yin et al., 2003). The uptake of DEHP by nine types of greenhouse vegetable varied from 10.14 to 36.16 mg kg^{-1} (Fu and Du, 2011). The use of large amounts of agricultural plastic film and fertilizers containing PAEs in intensive vegetable cultivation might increase the health risk of PAEs through the food chain (Mo et al., 2008; Pedersen et al., 2008; Kong et al., 2012). High levels of PAEs in agricultural soils have already been reported in the Pearl River Delta (Cai et al., 2005; Zeng et al., 2008; Zhang et al., 2009) and northeast China (Xu et al., 2008). The respective mean concentrations of DnBP and DEHP found in greenhouse soils were 1.63 and 1.96 mg kg^{-1} in Jinan, Shandong province (Meng et al., 1996), 0.60 and 0.63 mg kg^{-1} in Beijing (Ma et al., 2003), 15.5 and 4.61 mg kg^{-1} in Handan, Hebei province (Xu et al., 2008) and 0.21 and 1.48 mg kg^{-1} in Hangzhou, Zhejiang province (Chen et al., 2011). The concentrations of DnBP and DEHP in plastic film greenhouse and polytunnel soils may been influenced by differences in the use of irrigation, fertilizers and plastic film as well as meteorological conditions and external pollutant sources (Mo et al., 2008; Cai et al., 2008; Kong et al., 2012). Soil PAEs can also lead to atmospheric or water pollution by evaporation, leaching, deposition and drainage (Xu et al., 2008; Zeng et al., 2009; Wang et al., 2012).

The consumption of PAEs in China in 2011 was about 2.2 million tons, most of which was used in the production of plastic film (CPPIU, 2011). Plastic film generally comprises the walls of polytunnels or for mulching at the soil surface in intensive vegetable cultivation. The total mulching area in China was 15.6 million hectares by 2010 (China Agriculture Yearbook, 2011). Different plastic films, fertilizers and pesticides containing PAEs are applied to intensive vegetable production soils and different use modes of plastic film are practiced (Fu and Du, 2011). However, there is little information on the distribution of PAEs in soils used for vegetable production. The primary objectives of the present study were therefore to investigate PAE concentrations in suburban vegetable soils with different use modes of plastic film use, to identify the sources of the PAEs found, and to determine their environmental risk. The study was designed to provide preliminary data to help inform land managers for the control of PAEs in agricultural soils used to grow vegetables for human consumption.

2. Materials and methods

2.1. Soil sampling

One hundred and twenty-seven soil samples (0–15 cm depth) from vegetable production with different use modes of plastic film and thirty-two samples of plastic film and poultry manure were collected from four vegetable production areas in Jiangning and Lishui districts of Nanjing, east China in January 2012. The sampling locations were recorded by GPS and are shown in Fig. 1. Forty-one soil samples were collected from Guli (GL) where the vegetables had been cultivated for 8–12 years with double polytunnels and a single layer of mulch film. The outer polytunnel film remained in position throughout the year and the small inner polytunnel was used during winter to spring (Fig. 2A). Thirty-three samples were collected from Hushu (HS) where the typical production system comprised vegetables and flooded rice in rotation for about 4 years (Fig. 2B). Twenty-nine samples were collected from Suoshi (SS) where vegetables had been cultivated for over 10 years with a single layer of polytunnel and mulch film (Fig. 2C). Twenty-four samples were from Pulangke (PK) where vegetables had been grown for over 10 years with the sequence of single layer polytunnels during the whole year for two years with mulching film and then one year with mulching film but without polytunnels (Fig. 2D). The first two soil samples from each location (representing each use mode of plastic film) were collected from where the vegetables had been grown without polytunnel and mulching film and served as controls (CK). All of the soil samples collected from each site were obtained from different field sites in the locality. The physico-chemical properties of the top 15 cm of the soil at the four sites were determined and the mean values were: pH (H_2O), 7.4; soil organic carbon, 25.2 g kg^{-1}; total N, 1.53 g kg^{-1}; total P, 1.80 g kg^{-1}; and clay, 15.2% (v/v). Both polytunnel film and mulch film were used and were composed of polyethylene. Two colors of mulch film were used, namely black and white. The thickness of the greenhouse film at GL, SS, HS and PK was 0.12, 0.14, 0.60 and 0.15 mm, respectively. The mulch film width × thickness at GL, SS, HS and PK was 2000 × 0.003, 2000 × 0.004, 2000 × 0.006 and 2000 × 0.002 mm.

Soil samples were collected from the top 15 cm of the profile using a pre-cleaned stainless soil auger and transferred into cloth bags. Small pieces of vegetation and litter were removed before transfer. Each soil and poultry manure sample consisted of five sub-samples collected from the area of each site (within 60 × 10 m^2, 1 kg each) and were cooled in an ice box during transport. Precautions were taken during sampling and sample processing to avoid PAE contamination. Soil and poultry manure samples were freeze-dried, ground and homogenized by sieving through a stainless steel sieve (60-mesh) after removing stones and residual roots and then sealed in brown glass bottles. The plastic film samples were rinsed clean with deionized water, allowed to dry at ambient temperature, cut into pieces 0.5 × 0.5 mm, and sealed in Kraft paper bags. All the soil, fertilizer and plastic film samples were stored at −20 °C until analysis.

2.2. Sample extraction

Mixed standard solutions containing DMP, DEP, DBP, BBP, DEHP and DOP (1 mg mL^{-1}) and isotope surrogate standard di-n-butyl phthalate-d4 (DnBP-D4, 100 μg mL^{-1}) were supplied by Dr. Ehrenstorfer GmbH, Augsburg, Germany. The stock solutions of six mixed phthalates were prepared in n-hexane at a concentration of 1 mg L^{-1}. Acetone and n-hexane were obtained from Nanjing chemical reagent companies and were re-distilled in glass before use to avoid PAE contamination. HPLC grade hexane was purchased from Tedia Company Inc., Fairfield, OH. All glassware was washed in detergent solution in a laboratory ultrasonic washer (KQ-600DB, Kun Shan Ultrasonic Instruments Co., Ltd., Jiangsu province, east China) and air dried, then immersed in sulfuric acid (guaranteed reagent) and

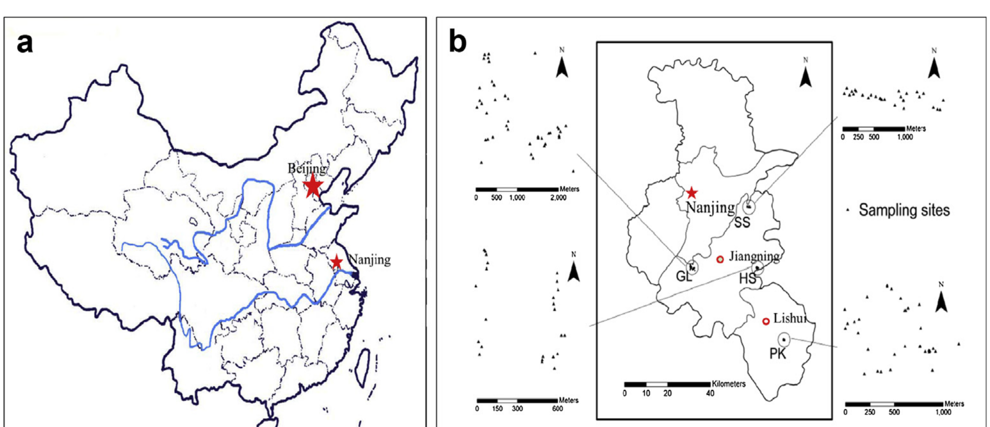

Fig. 1. Schematic map showing the geographical location of (a) Nanjing city and (b) the vegetable soil sampling sites in the Nanjing suburbs within the Nanjing region.