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Distribution of phthalate esters in agricultural soil with plastic film mulching in Shandong Peninsula, East China

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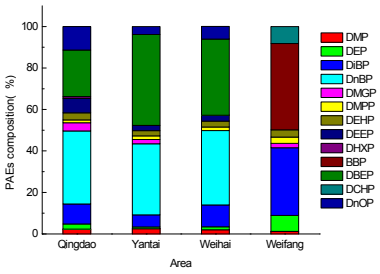
HIGHLIGHTS

- The PAEs in soils of vegetable fields with plastic film mulching were investigated.
- The total contents of the 16 PAEs ranged from 1.374 to 18.810 mg/kg with an average of 6.470 mg/kg.
- The ratios of DMP, DEP, and DnBP that exceeded the allowable concentrations were 63.9–100%.
- The long-term application of plastic film increases PAE concentrations in the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

The content of phthalate esters (PAEs) was investigated in 36 vegetable fields with plastic film mulching in Shandong Peninsula, East China. Soils at depths of 0–10 cm, 10–20 cm, and 20–40 cm were collected, and 16 PAEs were analyzed by gas chromatography–mass spectrometry. PAEs were detected in all the analyzed samples. The total contents of the 16 PAEs (Σ_{16}PAEs) ranged from 1.374 to 18.810 mg/kg, with an average of 6.470 mg/kg. Among the four areas of Shandong Peninsula, including Qingdao, Weihai, Weifang, and Yantai, the highest Σ_{16}PAE in the soil was observed in Weifang district (9.786 mg/kg), which is famous for large-scale vegetable production. Despite the significant differences among the Σ_{16}PAEs, the PAE compositions in soils with plastic film mulching in Shandong Peninsula were comparable. Diethyl phthalate (DEP), diisobutyl phthalate, and di(4-methyl-2-pentyl) phthalate were present in all the samples, whereas di-*n*-hexyl phthalate was detected only in Qingdao (~1%) and dicyclohexyl phthalate was observed only in Weifang (5.7–8.2%) in low proportions. The ratios of dimethyl phthalate, DEP, and di-*n*-butyl phthalate, which exceeded allowable concentrations, were 63.9–100% at different soil depths, indicating high PAE pollution. The concentration of butyl benzyl phthalate detected only in Weifang exceeded the recommended allowable soil concentration. Overall, the high PAE content in the soil with plastic film mulching in Shandong Peninsula is an issue of concern because of the large amounts of plastic film used.

1. Introduction

Phthalate esters (PAEs) are a class of manufactured chemicals that are widely used as plasticizers in industrial products and households (Staples et al., 1997). The global production of PAEs is estimated to be 6.0 million tons per year (Mackintosh et al., 2006),

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and the current consumption of PAEs in China is above 0.87 million tons per year (CPPIU, 2004). PAEs are ubiquitous environmental contaminants because these materials are widely produced and applied (Bauer and Herrmann, 1997; Amir et al., 2005; Wang et al., 2008; Buszka et al., 2009; Lin et al., 2009; Zhang et al., 2012). PAEs have been detected in the air, water, soil, sediments, and even in the human body (Peijnenburg and Struijs, 2006; Teil et al., 2006; Jambeck et al., 2015). The various toxic and biological effects of PAEs, such as teratogenicity, carcinogenicity, and mutagenicity, have been a subject of discussion and public concern (Fukuwatari et al., 2002; Gómez-Hens and Aguilar-Caballos, 2003; Scholz, 2004; Net et al., 2015). Six PAEs, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), and di-*n*-octyl phthalate(DnOP), have been classified as priority environmental pollutants by the U.S. Environmental Protection Agency (U.S. EPA, 2013).

Soil is a major reservoir for a diverse range of pollutants such as PAEs (Wu et al., 2016). Farmland soil environments extensively deteriorate because of the increasing application of agricultural plastic films. The consumption of plastic films in China in 2011 was approximately 2.29 million tons. Meanwhile, the total mulching area reached 19.8 million hectares (Department of Rural Survey National Bureau of Statistics of China, 2012). Soil plays a vital role in our life because of the agricultural products it produces. However, agricultural products may be contaminated by the agricultural soil containing PAEs, which increase health risk to humans (Mariko et al., 2008).

Shandong Peninsula, which is known as the largest peninsula in China, is a fast-growing and economically developed area. The peninsula comprises the cities of Qingdao, Yantai, Weifang, and Weihai. Urbanization is occurring at a high rate, which is characterized by a high population density of 550 people/km^2. Plastic films are widely used in this area because it is a primary vegetable-producing region. Approximately, 30,000 tons/year plastic film is used only in Shouguang, Weifang (Chen et al., 2014). Concerns about the potential health risk of PAEs through the food chain were raised because of the increasing usage of agricultural plastic films (Mo et al., 2008; Pedersen et al., 2008; Kong et al., 2012). However, information on the characteristics of PAEs in agricultural soils with plastic film mulching in Shandong Peninsula is limited.

Soils with plastic film mulching in Shandong Peninsula might be highly contaminated. Thus, determining the concentrations, compositions, and distributions of the 16 PAEs in this area is crucial. In this study, we investigated the concentrations, compositions, and distributions of the 16 PAEs at different depths. The congener profiles, sources, and risks of PAEs were discussed.

2. Materials and methods

2.1. Chemicals and materials

Sixteen standard-mixture PAEs, containing DMP, DEP, diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), dimethylglycol phthalate (DMGP), di(4-methyl-2-pentyl) phthalate (DMPP), DEHP, di(2-ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DPP), di-*n*-hexyl phthalate (DHXP), BBP, di(2-*n*-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), DnOP, diphenyl phthalate (DPhP), and di-*n*-nonyl phthalate (DNP), were purchased from O2SI, Inc. (USA). The concentration of each PAE in this mixture solution was 1000 mg/L, and an internal standard, benzyl benzoate, in *n*-hexane at 1000 mg/L was used. Petroleum ether, acetone, and diethyl ether were of analytical grade and re-distilled before use to avoid PAE contamination. N-hexane, which was obtained from Anpel Company Inc., was of high-performance liquid chromatography grade. Sodium sulfate (granular, anhydrous) was purified by heating at 420 °C, and Florisil (60–80 mesh) was activated at 650 °C for 4 h in a muffle furnace. All the glassware for the experiment was soaked with K_2CrO_7/H_2SO_4 solution for 12 h, washed with redistilled water, and baked at 400 °C for 4 h.

2.2. Sampling

A total of 108 soil samples were collected from 36 vegetable fields with plastic film mulching from Qingdao (number of samples: 30), Yantai (number of samples: 30), Weifang (number of samples: 24), and Weihai (number of samples: 24) in Shandong Peninsula from May 28 to 30, 2012. The location and topographical map of Shandong Peninsula and the sampling sites are shown in Fig. 1. In each site, the samples were collected from depths of 0–10 cm, 10–20 cm, and 20–40 cm, and five subsamples were collected from the same area (in a 100-m^2 area) and then bulked together to form one composite sample. The soil samples were stored in glass bottles at −20 °C until analysis, after being freeze-dried, ground, and homogenized by sieving through a stainless steel sieve (60 mesh).

2.3. Sample extraction and purification

The extraction of PAEs was conducted using Wang's methods (Wang, 2007). For each sample extraction, 5.0 g soil was placed in a grinding mouth triangle bottle spiked with a surrogate standard (benzyl benzoate) and extracted through a shaking table shock for 20 min with 90 mL of acetone/petroleum ether (1:3, v:v). The extracts were combined, filtered, and concentrated using a rotary evaporator to approximately 3–5 mL. The concentrated extracts were cleaned and fractionated on a glass column (1 cm i.d.) filled from the bottom to the top with anhydrous sodium sulfate (4 g), Florisil (6 g), and anhydrous sodium sulfate (4 g). Twelve milliliters of petroleum ether/diethyl ether (10:0.4, v:v) were used to wash the column, and 90 mL of petroleum ether/diethyl ether (10:3, v:v) was used to elute the PAEs. The extracts were reduced to 1.0 mL in hexane, and the known quantities of the internal standard were

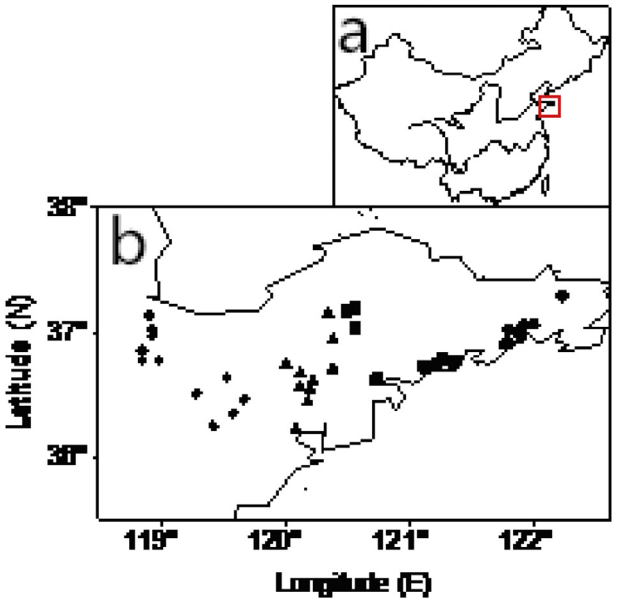

Fig. 1. Schematic showing the geographical location of (a) Shandong Peninsula and (b) the vegetable soil sampling sites in the four regions in Shandong Peninsula (solid diamond: Weifang; solid triangle: Qingdao; solid square: Yantai; solid round: Weihai).