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The influence of facility agriculture production on phthalate esters distribution in black soils of northeast China

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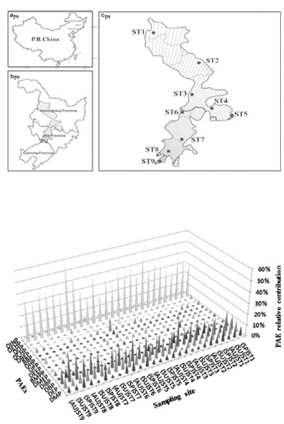
HIGHLIGHTS

- DEHP, DBP, DEP, and DMP were the main PAE contaminants in the black soil region studied.
- Facility agriculture black soils in northeast China shows higher pollution situation.
- Utilization of mulching film and increase in fertilizer usage increased soil PAEs in summer.
- Significant difference existed in the concentration of PAEs with different seasons.

GRAPHICAL ABSTRACT



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ABSTRACT

The current study investigates the existence of 15 phthalate esters (PAEs) in surface soils (27 samples) collected from 9 different facility agriculture sites in the black soil region of northeast China, during the process of agricultural production (comprising only three seasons spring, summer and autumn). Concentrations of the 15 PAEs detected significantly varied from spring to autumn and their values ranged from 1.37 to 4.90 mg/kg-dw, with a median value of 2.83 mg/kg-dw. The highest concentration of the 15 PAEs (4.90 mg/kg-dw) was determined in summer when mulching film was used in the greenhouses. Probably an increase in environmental temperature was a major reason for PAE transfer from the mulching film into the soil and coupled with the increased usage of chemical fertilizers in greenhouses. Results showed that of the 15 PAEs, di(2-ethylhexyl) phthalate(DEHP), di-n-butyl phthalate (DBP), diethyl phthalate (DEP) and dimethyl phthalate (DMP) were in abundance with the mean value of 1.12 ± 0.22, 0.46 ± 0.05, 0.36 ± 0.04, and 0.17 ± 0.01 mg/kg-dw, respectively; and their average contributions in spring, summer, and autumn ranged between 64.08 and 90.51% among the 15 PAEs. The results of Principal Component Analysis (PCA) indicated the concentration of these four main PAEs significantly differed among the facility agricultures investigated, during the process of agricultural production. In comparison with foreign and domestic results of previous researches, it is proved that the black soils of facility agriculture in northeast China show higher pollution situation comparing with non-facility agriculture soils.

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1. Introduction

Phthalate esters (PAEs) are the main components of plastic products which are being used as plasticizers and to improve the softness and flexibility of poly vinyl chloride (PVC), rubber, cellulose and styrene materials (Wang et al., 2013; Qureshi et al., 2013). PAEs are studied as hazardous substances and their presence in soil can be of possible threat to human beings and wildlife by different paths (Guo and Kannan, 2011). The potential routes of human exposure to phthalates are inhalation, skin absorption, dietary intake and so on (Guo and Kannan, 2011; Schettler, 2006; Wormuth et al., 2006). Current study reported that PAEs have estrogenic effects on animals and human as mentioned earlier that they can interfere with the endocrine system and procreation ability (Duty et al., 2003; Moore, 2000; Higuchi et al., 2003). Rising plastic industries are producing many common agricultural plastic films to use in on-site agricultural activities; but the subsequent environmental and associated human health problems cannot be ignored.

PAEs as plasticizers have good inter-miscibility in plastic products, and plastics. Chemically, they did not form a covalent bond with plastic substrates; rather they are linked together by the hydrogen bond and van der Waal force. Hence, with the passage of time these PAEs are readily migrated into the soil (Chen et al., 2011; Kong et al., 2012). Consequently, the phthalate molecules are able to drift from the soil into other spheres of the ecosystem (Kong et al., 2013; Yin et al., 2003).

In China, plasticizer production level for the years 2006 and 2007 reached up to 1.25 and 1.45 million tons, respectively (Xu et al., 2008); and in 2011 it was marked up to 2.2 million tons, most of which were used in the plastic film production (CPPIU, 2011). In early 2004, the global production of PAEs reached about 6 million tons (Xu et al., 2008); hence the PAEs were enlisted as the most potential pollutants. The use of polyvinyl chloride (PVC) as greenhouse film, especially in mulching materials, is about 50000 tons per annum in northeast China. PVC contents were about 20–30% in actual manufacturing of agricultural films, but for more flexibility of the material it is usually increased up to 60% of the final product (Chen et al., 2011; Liu et al., 2010a). As the utility of mulch material increases in per agricultural production year, there is an increase in the pollution level, which affects the quality of agricultural production (Chen et al., 2011; Fu et al., 2011).

PAE pollution has become a serious issue in the field of environmental researches. Many researchers have reported the presence of PAEs in different mediums such as the atmosphere (Kong et al., 2013; Wang et al., 2012), surface water and sediments (Srivastava et al., 2010), sewage sludge (Cai et al., 2007), and in soil (Wang et al., 2013; Kong et al., 2012; Yin et al., 2003; Zeng et al., 2009). Detected PAE concentrations in these mediums were noted to be higher than those reported in the Netherlands and Denmark (Zeng et al., 2009). PAE contaminations have been reported to be higher in China than in US (Cui et al., 2010); similarly, when compared with other parts of the world, PAE pollution in China was reported to be relatively severe (Zeng et al., 2008a, 2009).

Different studies investigated the soil PAE contamination in the east, south, southwest, north, northwest and northeast regions of China (Hu et al., 2003), Tianjin (Liu et al., 2010b), Guangzhou (Zeng et al., 2009), Handan (Xu et al., 2008), Hangzhou (Chen et al., 2011). According to different researches of soil PAE analysis from different regions, DEHP and DnBP detection was high; while DMP, DEP, BBP and DnOP detection was relatively low (Cui et al., 2010). Although there already exist many researches focusing on PAE concentration in the environment, yet only a few reports are available on the PAE content in facility agriculture soils (Wang et al., 2013; Chen et al., 2011), As per our knowledge and information, there has not been any study conducted on the black soils of facility agriculture in northeast China, especially during the periods of agricultural production.

The aims and objectives of this study were to investigate the PAE concentration of black soils (0–20 cm) collected from different locations in northeast China, and to discuss the contamination profiles with seasonal variation characteristics. This study will provide a reliable data set for soil bioremediation and risk assessment of the facility agriculture soil of the northeast, and will encourage a full use and protection of the declining black soil resources, which are of great significances to agricultural production.

2. Materials and methods

2.1. Reagents and chemicals

Fifteen PAE standard mixtures, containing dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-n-butyl phthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), bis(4-methyl-2-pentyl)phthalate (BMPP), di(2-ethoxyethyl) phthalate (DEEP), diphenyl ortho-phthalate (DPP), diheptyl phthalate (DHP), butylbenzyl phthalate (BBP), di(2-n-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), di(2-ethylhexyl) phthalate (DEHP), dioctyl phthalate (DOP), and di-iso-nonyl phthalate (DINP) at 1000 mg/L each were dissolved in hexane. The pure standard mixture (>99%) was purchased from AccuStandard Inc., USA. Internal standard of di(2-ethylhexyl) phthalate-D4 (DEHP-D4) was acquired initially as a solid of 99% purity (Dr. Ehrenstorfer GmbH, Germany). The acetone and n-hexane (HPLC grade) were supplied by Tedia Inc., USA.

2.2. Description of the sampling sites

The black soil zone of China cuts across the north of Nenjiang in Heilongjiang province to Changtu in the south of Liaoning province, specifically located along the Binbei-Binchang railroad area. Nine representative locations were selected from this black soil region based on change in latitude, which covers three provinces of Songnen, Liaohe and Sanjiang plain (Xu et al., 2010). All sampling points were located in the temperate zone monsoon climate, with a wide variation in winter and summer temperatures. The zones are also characterized with warm summer and low winter temperatures; the lowest temperature in winter is usually around −40 °C, and soil freezing depth was reported up to 0.5–1.3 m; thus, the winter season has not been usually suitable for agricultural production (Jing et al., 2008). The average temperatures of the three seasons across the different sampling sites varied between 21.1 and 25.8 °C. The crops cultivated at these sampling sites are cucumbers, and the average sizes of the greenhouses were all about 90 × 10 × 4.5 m (as length, width, and Empyrean). The locations of the sampling sites are given in Fig. 1 and the information of the location is given in Table 1.

2.3. Soil sample collection

Soil samples at depth of 0–20 cm (surface soil) were collected from greenhouse facilities in nine cities (Jiusan, Hailun, Harbin, Shangzhi, Songyuan, Mudangjiang, Changchun, Siping and Changtu), all within the three provinces of Heilongjiang, Jilin, and Liaoning. It is necessary to report that all sampling sites used agricultural films of 0.008 mm thickness. The sampling soil was characterized as black soils of the northeast region of China. A total of 27 soil samples were taken in May, August and November of 2013, depicting each climatic season at the nine sites.

At the greenhouse, surface soils were collected into pre-cleaned aluminum foil envelopes using a pre-cleaned stainless steel soil sampler. Before sample collection, particles of small vegetation or/and litters were removed where necessary (Wang et al., 2013). From each site, and each season, one soil sample (within 5 × 5 m^2, 500 g each) composed of five sub-samples were collected. The soil samples were cooled in a temperature-controlled box filled with ice bags during transport to the laboratory.

In the laboratory, soils were sieved to remove stones and visible roots and fauna, and divided into two parts: one part was directly