



## Effect of wetland reclamation and tillage conversion on accumulation and distribution of phthalate esters residues in soils

Xiaoli Wang<sup>a,b</sup>, Qianxin Lin<sup>a,c</sup>, Jian Wang<sup>a</sup>, Xianguo Lu<sup>a</sup>, Guoping Wang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Wetland Ecology and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, 3195 Weishan Road, Changchun 130012, China

<sup>b</sup> College of Plant Sciences, Jilin University, 5333 Xian Road, Changchun 130062, China

<sup>c</sup> Department of Oceanography and Coastal Sciences, School of the Coast & Environment, Louisiana State University, Baton Rouge, LA 70803, USA

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### ABSTRACT

Accumulation and distribution of phthalate esters (PAEs) in the soils of natural and reclaimed wetlands for different cultivation purposes were investigated. The selected reclaimed soils have only been under cultivation since 1995, thus the behaviors of PAEs may precisely reveal their recent distribution patterns. Dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) were all detected in surface soil samples. The vertical distribution of PAEs differed between the natural wetlands and cultivated fields. The concentration of PAEs in wetland soil decreased from 0 cm to 30 cm, and then increased from 30 cm to 40 cm soil depth. However, the concentrations in 3 types of cultivated fields consistently increased from 0 cm to 40 cm soil depths. The total concentration of DMP, DEP, DnBP, and DEHP in the wetland surface soil was 109.2 ng/g. The total concentrations in rice fields tended to be higher than that of the wetland soil although the difference was not statistically significant, most likely due to the short tillage history. The conversion of bean field to rice field has had a significant effect on accumulation of PAEs. The total concentrations of PAEs in the 1-year rice field were significantly higher than that in the bean field. This was partly due to differences in pesticide and fertilizer usage between rice and bean cultivations; slower biodegradation, abiotic degradation, and evaporation behavior resulting from water covering of rice field probably also contributed to the higher PAEs concentrations in the rice field.

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### 1. Introduction

Phthalate acid esters (PAEs) have been in use for over 50-years, mainly in the manufacture of resins and plastics such as PVC (Fromme et al., 2002). PAEs are also used in other non-PVC applications such as paints, rubber products, adhesives and some cosmetics. Some widely-used fertilizers in China have also been found to contain PAEs (Mo et al., 2007). In addition, many pesticides and herbicides contain PAEs as solutizers. Six PAE compounds, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di-n-octyl phthalate (DOP) and di(2-ethylhexyl) phthalate (DEHP), have been classified as priority organic pollutants by USEPA.

During the last few decades, investigations on the occurrence and degradation of PAEs in various soils have been increasing (Vikelsø et al., 2002; Peijnenburg and Struijs, 2006). The six PAEs mentioned have been frequently identified in the soils from

different regions in China (Cai et al., 2008). The studies covered different cultivated fields, such as upland fields, including plastics film greenhouse, vegetable fields, orchard fields, cotton fields and crop fields, as well as paddy fields, including rice fields. Different cultivated types and land usages induced different distribution patterns of PAEs in soils. The higher PAE concentrations were observed in greenhouse and vegetable soils (Xu et al., 2008), likely due to the widespread usage of polyvinyl chloride plastics films containing PAEs, as well as fertilizers containing PAEs (Mo et al., 2007). Vegetable and orchard fields showed higher PAEs concentrations than rice and cotton fields since vegetable and orchard fields generally require intensively pesticide and fertilizer use, and plastic packing (Liu et al., 2010). However, among these agricultural fields, there were no studies on a bean field although bean fields are one of the most important upland fields. Furthermore, the previous studies mainly focused on comparing PAEs residues in different agricultural fields; there were few studies to compare the residues and distribution pattern of different PAEs between upland and paddy fields. The great difference in geochemical characteristics between upland and paddy soils most likely influence the occurrence and distribution characteristics of PAEs residues in these two

\* Corresponding author. Tel.: +86 431 85542339; fax: +86 431 85542298.  
E-mail address: [wanguoping@neigae.ac.cn](mailto:wanguoping@neigae.ac.cn) (G. Wang).

representative agricultural fields. For example, PAEs concentration in rice field has been found to be higher than that in a cotton field (Liu et al., 2010). Different land usages could affect PAEs distribution patterns (Vikelsøe et al., 2002; Xu et al., 2008; Liu et al., 2010). However, information on PAEs residue's changes with the tillage conversion of wetland to bean field, and then to rice field is very scarce, especially given the short cultivation history of bean fields and rice fields.

In the present study area of the Sanjiang Plain region, a wide range of wetlands have been cultivated to bean field, and recently to rice field. However, environmental and ecological consequences derived from these large-scale reclamation and tillage activities have been little known. To address these issues, the objectives of this research were: (i) to assess the impact of short-term reclaiming and tillage of wetland to cultivated fields on PAEs occurrence and distribution in soils; (ii) to determine whether the tillage conversion of bean fields to rice fields influenced the soil PAEs accumulation.

## 2. Materials and methods

### 2.1. Reagents and chemicals

A mixed phthalate esters solution containing 6 PAEs namely DMP, DEP, DnBP, DEHP, BBP, and DnOP in n-hexane respectively at  $2014 \pm 6.9$ ,  $2026 \pm 9.7$ ,  $2072 \pm 42.0$ ,  $2123 \pm 72.2$ ,  $2127 \pm 61.9$ , and  $2124 \pm 91.4$  mg/L (SUPELCO, USA) were used in the present study. The surrogate standard of di-n-benzyl phthalate, and an internal standard namely benzyl benzoate were also used in the study.

To avoid contamination, no plastic equipment was used during sampling and processing. All the glass apparatus were soaked in  $K_2CrO_4$  sulfuric acid solution for at least 24 h, rinsed with organic-free reagent water, and finally baked at  $180^\circ C$  for 6 h. All the solvents including dichloromethane, n-hexane, methanol, acetone, were of HPLC grade.

### 2.2. Study area

The Sanjiang Plain region is an extensive plain between three large rivers – the Heiron, Sonhua, and Wusuli in northeast China with a total area of  $0.9 \times 10^6$  ha in 2005 (Bao et al., 2011). This area was historically a contiguous wetland, but has experienced intensive cultivation over the past 50-years (Wang et al., 2006). Between the 1950s and 1980s, large areas of wetlands were cultivated and changed primarily to upland fields to plant bean; during the 1980s–2000s, 40% of uplands were shifted to a paddy fields to plant rice.

### 2.3. Soil collection

Soil samples for this study were collected in October of 2010 from the northeast corner of the Sanjiang Plain. The sampling sites where cultivation started in 1995 were selected. The cultivation field was remote and had limited influences from traffic, household and industry pollution. The effects of human were primarily from cultivation, including the application of pesticides, fertilizers, plastic film, and the operation of agricultural machinery. The field for the present study was initially reclaimed for bean crops; parts of the field were changed to farm rice recently. As such, three types of cultivation fields, i.e. the bean field, rice field with 1-year rice cultivation period and rice field with 6-years rice cultivation period, were included in the present study. These rice cultivation fields were originally reclaimed from the wetland with abundant water, and then changed to a bean cultivation field with relatively

inadequate water, and some fields were finally changed to a rice cultivation field with relatively adequate water.

Sampling sites were designed by considering cultivating types. According to the covered area of each sub-field for different types of cultivation, 23 sampling sites were chosen, including 5 sites for bean field, 9 sites for rice field with 1-year rice cultivation period, and 9 sites for rice field with 6-years rice cultivation period. In each site, samples were collected at 0–20 cm soil depth. Meanwhile, soil samples of natural wetland next to the cultivated fields and ditches between the cultivation fields were also collected. In addition, surface soils (0–5 cm) at two levels of irrigation ditch were collected and analyzed. One set of ditches was located between, but adjacent rice fields. This ditch directly irrigated the rice fields and received the runoff water from the fields. The communion of rice fields with the other environments was firstly via this ditch; which we defined as the first-level-ditch. The other ditches circumfused the rice fields and the first-level-ditches, and supplied water to the first-level-ditches and vice versa received the water discharged from the first-level-ditches. This ditch was defined as the second-level-ditch. Additionally, one deep soil core (0 cm–40 cm) from each of the 3 cultivation fields and the natural wetland was collected to determine the vertical distribution of the PAEs. Soil samples were air-dried, ground, and homogenized by sieving through a stainless steel 100-mesh sieve after removing stones and residual roots, and stored in aluminum foil bags below  $4^\circ C$  until extraction.

### 2.4. Soil analysis

PAEs in soil samples were extracted and analyzed by using the methods of Liu et al. (2010). Twenty grams of soil sample were spiked with  $20 \mu L$  100 mg/L surrogate standards, and extracted with dichloromethane for 24 h at a rate of 4–6 cycles/h using Soxhlet extractor. For the blank experiment, an empty filter paper bag spiked with the same surrogate standards was extracted in the same way with samples. Activated copper granules were added to the extraction flasks during the extraction to remove elemental sulfur. The extracts were concentrated, flowed through anhydrous sodium sulfate, solvent exchanged to n-hexane, and further reduced to approximately 1.0 mL using a rotary evaporator. Concentrated extracts were cleaned and fractionated on a 10-mm i.d. 1:2 alumina/silica gel glass column packed, from the bottom to top, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). The concentrated extracts were added into the column and washed with 40 mL of hexane. Then PAEs were eluted with 40 mL mixed solvent of acetone/n-hexane (2:8, v:v). The extracts were concentrated using rotary evaporator, and reduced to 0.2 mL under a stream of purified  $N_2$ . Known quantities of internal standard were added to the sample prior to instrumental analysis. Analyses of the samples were conducted in triplicate.

The samples were analyzed with a gas chromatograph with FID detector (Agilent 6890N, PA, USA), and a DB-5 MS capillary column ( $30 \mu m \times 250 \mu m \times 0.25 \mu m$ , Agilent, USA) for chromatographic separation. The detector temperature was maintained at  $280^\circ C$ . The column temperature program was initiated at  $80^\circ C$  for 1.0 min, increased to  $280^\circ C$  at a rate of  $6^\circ C/min$ , and held for 10 min. The flow rate of the carrier gas  $N_2$  was kept constant at 1.2 mL/min. The extracts ( $2.0 \mu L$ ) were injected onto GC in splitless mode with an inlet temperature of  $280^\circ C$ . Quantification was performed using the internal calibration method based on six-point calibration curve for individual PAEs and the correlation coefficients of calibration curves were all higher than 0.99. Benzyl benzoate was used as internal standard for the quantification of PAEs. Contents of PAEs in soils were normalized to dry soil weight and were surrogate recovered and blank corrected. The surrogate

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