**ORIGINAL ARTICLE**

# Occurrence of phthalate esters around the major plastic industrial area in southern Taiwan

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## Abstract
The increasing usage and disposal of plastic products could cause the wide distribution of phthalate esters (PAEs) in various environmental media. In this study, six PAE compounds, namely dimethyl phthalate, diethyl phthalate, di-$n$-butyl phthalate, benzyl butyl phthalate, di(2-ethylhexyl) phthalate (DEHP), di-$n$-octyl phthalate, were analyzed in various samples collected from the major plastic industrial area of southern Taiwan, including soil, fertilizer and plastic products, for the purposes of identifying of the possible sources of PAEs and assessing the related health risk. The results show that PAEs in soil samples was dominated by DEHP, with the total concentrations in the range of $0.7 \pm 0.5$, $0.2 \pm 0.1$, and $0.3 \pm 0.2$ mg kg$^{-1}$ for soil samples from farmland, household back gardens and the roadside, respectively. Contents of PAEs in chemical fertilizer (ND—0 0.87 mg kg$^{-1}$) were higher than that in organic fertilizer (ND—0.08 mg kg$^{-1}$), and PAEs concentrations (ND—316 mg kg$^{-1}$) in plastic mulching films were much less than those in the other types of plastic products (ND—1719 mg kg$^{-1}$), implying that major sources of PAEs in agricultural soil could be the use of chemical fertilizer and plastic products other than plastic mulching films. Health risk assessment suggested that, via the exposure to PAEs in soil, the potential non-cancer and carcinogenic risks for adults and children are minimal in most cases, except that a "moderate" carcinogenic risk for children exposure to DEHP. The results of this study can serve as a reference for further pollution prevention and environmental protection plans in relation to the industrial operation and discharge as well as the farming practices.

**Keywords** PAEs · Plastic industrial area · Fertilizer · Plastic films · Health risk calculation

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## Introduction

Phthalate esters (PAEs) are a group of elastic chemicals that are used widely as plasticizers. They were found to exist in plastics, pesticides, toiletries, personal care products, medicines and even foodstuff (Liao et al. 2009; Niu et al. 2014). Annual global production of plastics is roughly 150 million tons and PAE consumption is from 6.0 to 8.0 million tons a year (Mackintosh et al. 2006; Net et al. 2015). PAEs are ubiquitous in different environmental media, e.g. soil, water, sediments, air and even found to exist in human body (Staples et al. 1997; Peijnenburg and Struijs 2006).

PAEs are known for a long time as environmental contaminant as well for their often-absent carcinogenic activity. They are also well known for their endocrine activities and exposure to them can lead to multiple negative health effects, including teratogenicity, mutagenicity and even carcinogenicity (Kozumbo et al. 1982; Kluwe 1986). Bester et al. (2010) reported their negative effects to either terrestrial or aquatic species. Particularly, six PAEs, namely dimethyl

phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (D*n*BP), benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (D*n*OP), have been listed as priority contaminants by the US Environmental Protection Agency (USEPA) (USEPA 2013).

Soils and sediments are the major "sink" for PAEs (Tran et al. 2015). Plastic mulching films are considered the main anthropogenic source of PAE contamination in agricultural areas due to the existence of great amount of PAEs in the films (Li et al. 2016a). PAE contamination can also come from pesticides, fertilizers, industrial discharge, sewage, etc. (Ma et al. 2013; Li et al. 2016a). PAE contamination of agricultural soil could result in PAE-contaminated agricultural products, therefore, raising concerns about subsequent health risks (Yang et al. 2015).

The incident that two Taiwanese chemical companies intentionally used PAEs as an emulsifier (or clouding agent) for their food processing has attracted wide public attention to health risks caused by PAE exposure (Wu et al. 2012). Kaohsiung City, located in the South of Taiwan, is the most industrialized city in the island with a population of 2.77 million. Ever since having been founded in the seventeenth century, Kaohsiung City has rapidly grown into an important economic and industrial center of Asia. Along with that, the demand for food and agricultural products has risen intensively. The North of the city is a large agricultural production area, providing agricultural products for the city itself and other provinces of Taiwan. This area is also where industries have blossomed in the recent decades, leading to the arrival of many industrial plants (Lin et al. 2017; Vu et al. 2017a). Therefore, there are increasing concerns about the potential contamination that those plants may cause to the agricultural production area and the potential associated health risks to humans.

In this study, PAE contamination in soil, fertilizers and plastics was measured. Soil samples were collected from agricultural fields (AF), household back gardens (BG) and along the roadside (RS) around the major industrial area in Kaohsiung City. Additionally, the non-cancer and carcinogenic risks of the exposure to PAEs in the soil for adults and children were estimated via dietary and non-dietary pathways. In addition, PAE content in chemical and organic fertilizers, plastic mulching films and other types of plastics was measured and discussed concerning the potential sources of PAE contamination. The results of this study will provide a baseline for PAE contamination around the major industrial plants of Kaohsiung City, thus supporting a reliable reference for future environmental monitoring and protection plans.

## Methodology

### Site location and sampling

Kaohsiung City, located in the South of Taiwan, is one of the most rapidly growing industrial cities in Asia. Numbers of industrial plants with various large-scale industries have arrived in the northern area of the city, including Nanzih Export Processing Zone (NEPZ), Dashe Industrial Park and Renwu Industrial Park (Fig. 1). Renwu Industrial Park and Dashe Industrial Park specialize in plastic resin production, whereas NEPZ contains mostly metal-processing industries. These are the major industrial plants of Kaohsiung City and have been reported to be associated with various types of contaminants (Lee et al. 2018; Lin et al. 2009, 2010; Vu et al. 2017b). However, even though these industrial plants have resided in the northern agricultural and gardening area of the city for decades, there have been no studies examining the PAE contamination in the soil and investigating potential PAE contamination sources here. In this study, the sampling campaign covered a large area of three northern districts of Kaohsiung City, namely Renwu, Dashe and Nanzih districts. The vegetable planting area located within 2.5 km away from the abovementioned industrial plants were selected to be the sampling sites. The sampling sites included a large paddy/vegetable/flower field in the north-west of the city and numerous vegetable gardens located around the three industrial plants mentioned. To avoid the dilution and complication effects of precipitation, total 24 soil samples were collected in the AF, BG and RS sites around the three industrial plants within one week in the dry season (from February to June) of 2013. During this dry season, the ambient temperature fluctuated between 22 and 30 °C and precipitation was insignificant. Soil samples were collected on sunny days, between 9.00 am and 4.00 pm. The detailed sampling sites' characteristics (soil texture, planted vegetation, average temperature and climatic conditions) were given in Table S2.

Before sampling, some piled litter and debris on the soil surface were removed. Five surface soil samples (located on the crossing diagonals: four in the corners and one in the crossing point, depth 0–10 cm below ground surface) were collected from $5 \times 5$ m$^2$ or other smaller plots with a pre-cleaned stainless-steel scoop and homogeneously mixed to form a composite sample. Approximately 50 g of soil sample was collected from each sampling point. In addition, 13 fertilizer and 27 plastic samples were collected to investigate the source of PAE contamination in AF and BG sites. Similar to soil samples, five fertilizer samples were collected with the stainless-steel scoop and mixed together to create a composite sample. Meanwhile,
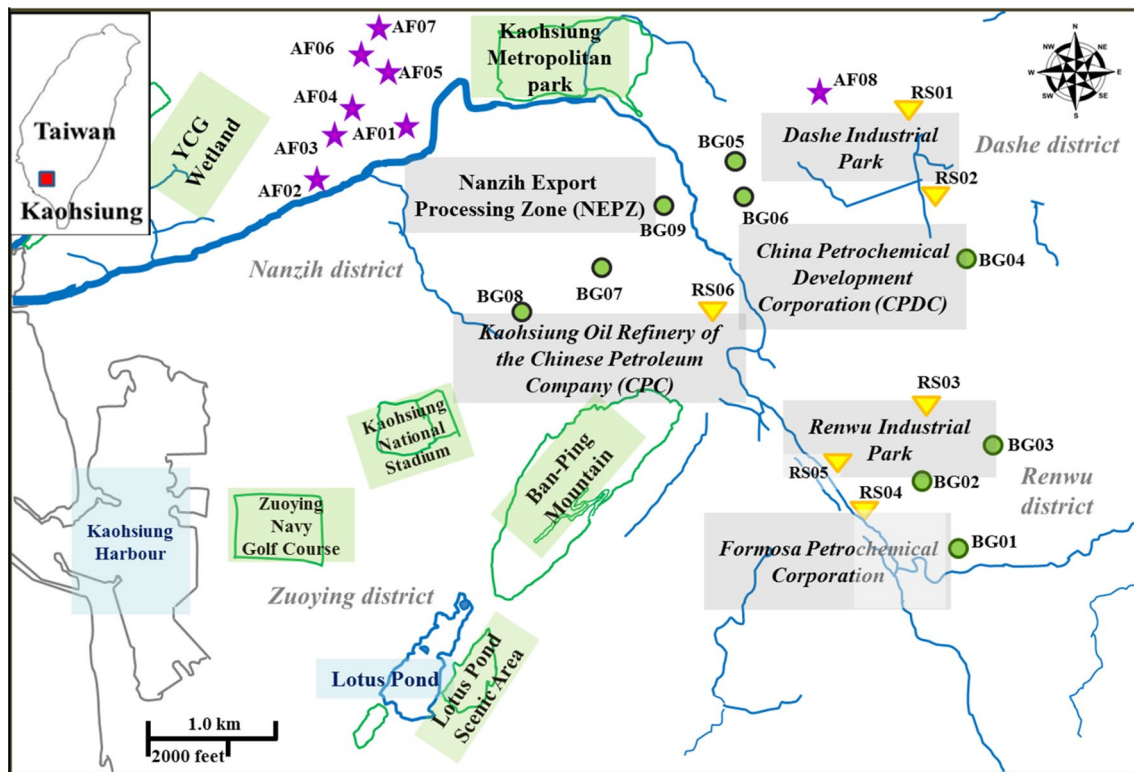
**Fig. 1** Sampling sites of agricultural fields (AF: purple star symbols), back gardens (BG: green circle symbols) and roadsides (RS: yellow trigonometry symbols) in Kaohsiung City, Southern Taiwan

plastic samples were rinsed with deionized (DI) water, cut into $0.5 \times 0.5$ cm pieces, and dried by a vacuum freeze-drying machine (Eyela FDU-1200, Tokyo Rikakikai, Japan, $-50$ °C, 10 Pa, 24 h). At least, a duplicate sample (soil, fertilizer and plastic) was collected for each site.

The samples were kept in aluminium bags at 6–8 °C by a temperature-controlled box during the transportation to the laboratory. Precautions were performed during the sampling and sample analysis to avoid PAE contamination (Lin et al. 2009). Soil and fertilizer samples were homogeneously mixed and screened through a stainless-steel sieve (60 mesh). Then, all the samples were stored at 4 °C until sample extraction. Note that all samples were extracted within 14 days after the sampling.

## Chemicals

Six standard mixture PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP) (DnBP), benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP) (DnOP) were purchased from AccuStandard, Inc., New Haven, CT. The concentration of every PAE in the mixture solution was 1000 µg L$^{-1}$. Benzyl benzoate, in n-hexane (1000 mg L$^{-1}$), was used as an internal standard (Skrbic et al. 2016). All

other reagents and chemicals were of analytical grade and purchased from SUPELCO Analytical, Bellefonte, PA, USA.

## Sample extraction and instrumental analysis

The procedure of sample extraction and analysis in this study followed that in our previous study (Lin et al. 2009). Basically, samples (10 g each for of soil and fertilizer and 0.5 g each for plastic) were added and shaken in a conical flask with 30 mL dichloromethane (DCM) for 15 min. The process was repeated three times. The supernatants were combined and concentrated to 0.5 mL in a Turbo Vap (Biotage, USA) using gentle nitrogen flow (5 psi). Known quantity of the internal standard was added to the final extracts (0.5 mL) prior to the injection into the GC/MS for analysis. A 6890-5973 gas chromatography-mass selective detector (GC–MS) system was employed to quantify PAEs in an HP-5MS (30 m × 0.25 mm × 0.5 µm) capillary column (injection volume 1 µL, helium flow rate 1 mL min$^{-1}$). Oven temperature was initially set at 45 °C for 1 min before rising to 310 °C at the rate of 10 °C min$^{-1}$ and maintained there for 7 min. Selective ion monitoring (SIM) mode was performed with the specific retention time and characteristic ions in order to help increase the accuracy of an analysis. All calculation of concentrations and calibrations were performed according to

the previously built standard calibration curves. Eight calibration levels (1.25, 5, 10, 20, 40, 60, 80 and 100 µg mL$^{-1}$) were considered. Relatives response factor of all compounds were above 0.05, whereas the percentage of deviation of each compound was lower than 20%. In order to guarantee good data quality, a decafluorotriphenylphosphine (DFTPP) standard check was implemented to calibrate the mass selective detector before analysis. System proficiency calibration check (SPCC) was also performed once every 12 h of analysis. Blank and spike recovery tests were performed afterwards. Method detection limit (MDLs) were estimated from field blanks and seven samples of the same concentration. An individual MDL analyte was calculated from the product of the standard deviation by the appropriate one-sided 99% $t$ statistic. The MDL values ranged from 0.11 mg kg$^{-1}$ dry weight for DEP to 0.13 mg kg$^{-1}$ dry weight for DEHP. The blanks showed non-detected (ND) values. Standard mid-point and spiked-sample checks were performed every 10-sample batch. Standard mid-point and spiked-sample recoveries were from 94 to 108% and from 80 to 85%, respectively. Accuracies of the measures were $100 \pm 10\%$.

To reduce the possible cross-contamination during the PAE analysis, laboratory glassware was free of plastics and pre-treated with continuous heating and rinsing as described by Skrbic et al. (2016). Moreover, simple preparation was employed to reduce preparation time. High-purity DCM was used, and plastic materials were avoided. In this study, blanks always showed ND values, meaning that the contamination during sampling and instrumental analysis was well controlled.

## Measurement of basic soil properties

Soil samples were measured for basic properties, including pH, soil texture, total organic carbon (TOC), cation exchange capacity (CEC), total nitrogen (TN) and C/N ratio. The analytical methods and results for basic soil properties are shown in Table 1. Briefly, pH value was measured by a pH electrode (YSI 6600 V2-4, Xylem Inc., USA) according to ASTM standard method D4972-13. Soil texture was determined using hydrometer method and United States Department of Agriculture's (USDA) classification. TOCs of the soil were measured using ASTM method D2974–14. The Taiwan NIEA S202.60A method was used to determine soil CEC, whereas Kjeldahl digestion method was employed for soil TN (Flowers and Bremner 1991).

## Health risk calculation of PAE contamination

Non-cancer and carcinogenic risk calculation, including dietary and non-dietary exposure to PAEs in soil, was performed for adults and children according to USEPA (2013). We included dietary (considering food or vegetables grown in the soil) and non-dietary (through incidentally ingestion, dermal contact and inhalation) pathways because they should cover all the main exposure routes of PAEs to humans (Niu et al. 2014). The exposure risks for children and adults were calculated using the equations shown below.

Among the PAEs studied, only DEP, D$n$BP and D$n$OP were listed as compounds posing potential non-cancer risks by USEPA (2013). Non-cancer risk or hazard index (HI) was calculated as follows:

$$HI_{dietary} = \frac{C_{soil} \times BAF \times FIR \times EF \times ED \times CF}{RfD \times BW \times TA},$$

where $C_{soil}$ is PAE concentration in soil samples (mg kg$^{-1}$); BAF is bioaccumulation factor of PAEs to foodstuff; FIR is food ingestion rate (kg person$^{-1}$ day$^{-1}$); EF is exposure frequency (days year$^{-1}$); ED is exposure duration (years); CF is conversion factor (kg mg$^{-1}$); RfD is oral reference dose (mg kg$^{-1}$ day$^{-1}$); BW is average body weight (kg); and TA is average exposure time (days).

$$HI_{non\text{-}dietary} = HQ_{ingest} + HQ_{dermal} + HQ_{inhale}$$

- $HQ_{ingest} = \frac{C_{soil} \times SIR \times EF \times ED \times CF}{RfD \times BW \times TA},$
- $HQ_{dermal} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED \times CF}{RfD \times BW \times TA},$
- $HQ_{inhale} = \frac{C_{soil} \times EF \times ED \times 10^3}{RfD \times PEF \times TA},$

**Table 1** Basic properties of soil samples collected in AF, BG and RS sites in Kaohsiung City, Taiwan

| Soil properties | AF and BG ($n=18$) | RS ($n=6$) | Analytical methods |
|---|---|---|---|
| pH | $6.04 \pm 0.065$ | $7.34 \pm 0.110$ | ASTM D4972-13 |
| Sand (%) | 80.52 | 74.20 | Hydrometer method |
| Slit (%) | 6.58 | 16.09 | |
| Clay (%) | 12.91 | 9.70 | |
| TOC (g kg$^{-1}$) | $4.20 \pm 0.820$ | $4.08 \pm 0.443$ | ASTM D2974-14 |
| CEC (cmol kg$^{-1}$) | $8.52 \pm 3.214$ | $8.95 \pm 2.281$ | NIEA S202.60A |
| TN (%) | $0.10 \pm 0.012$ | $0.10 \pm 0.021$ | Kjeldahl digestion (Flowers and Bremner 1991) |
| C/N ratio | $0.49 \pm 0.353$ | $0.45 \pm 0.116$ | |

where HQ is hazard quotient; SIR is soil ingestion rate (mg day$^{-1}$); SA is soil surface area (cm$^2$ day$^{-1}$); AF is soil adherence factor (mg cm$^{-2}$); and ABS is fraction of dermally absorbed contaminant (dimensionless); PEF is particulate emission factor (m$^3$ kg$^{-1}$).

For HI, a value under 1 means that PAE content causes almost no adverse effects on human health, whereas a value above 1 indicates possible negative health risks to whom intake the food or soil (USEPA 2013).

Among the PAEs studied, only DEHP was nominated as a potential carcinogen by USEPA (2013). Carcinogenic risk (TR) calculation for DEHP was performed as follows:

$$TR_{dietary} = \frac{C_{soil} \times BAF \times FIR \times EF \times ED \times CF \times CSF}{BW \times TA},$$

where CSF is cancer slope factor (mg kg$^{-1}$ day$^{-1}$).

$$TR_{non-dietary} = TR_{ingest} + TR_{dermal} + TR_{inhale}$$

- $TR_{ingest} = \frac{C_{soil} \times EF \times SIR_{adj} \times CF \times CSF}{TA}$,

- $TR_{dermal} = \frac{C_{soil} \times EF \times SDC_{adj} \times ABS \times CF \times CSF}{TA}$,

- $TR_{inhale} = \frac{C_{soil} \times EF \times ED \times 10^3 \times CSF \times IR}{PEF \times TA}$,

where SIR$_{adj}$ is age-adjusted soil ingestion rate (mg year kg$^{-1}$ day$^{-1}$); SDC$_{adj}$ is age-adjusted dermal contact rate (mg year kg$^{-1}$ day$^{-1}$); IR is inhalation risk ((mg m$^{-3}$)$^{-1}$).

For TR, if the value is lower than $10^{-6}$, the carcinogenic risk is negligible. If the value is greater than $10^{-4}$, the carcinogenic risk is unacceptable. Between $10^{-6}$ and $10^{-4}$, it is an acceptable range of the risk (Li et al. 2016a). The values of abovementioned parameters are provided in Table S1.

## Statistical analysis

SPSS for Windows, Version 22, was employed for statistical analysis in this study. Pearson's bilateral test was used to analyze the correlation between soil PAEs and basic soil properties. Student's *t* test was employed to examine the correlation between PAE concentrations in two fertilizer groups and similarly in two plastic groups. Differences were regarded as significant with 95% confidence interval.

## Results and discussion

### PAE contamination in soil

#### Basic soil properties

Table 1 shows the methods and results of basic properties of soil samples taken from AF and BG, and RS sites. Soil samples taken from AF and BG sites were grouped together because the soil in these sites was used for similar purposes, i.e. growing rice and vegetables. The pH values of surface soil varied from moderately acidic for samples taken from AF and BG sites to sub-alkaline for those taken from RS sites. Results for TOC, CEC and TN measurements were similar between the two groups, AF and BG, and RS soils. TOC, CEC and TN measured values fluctuated around 4.0, 8.5 and 0.1, respectively. The C/N ratios of AF and BG soils (0.49 ± 0.353) were slightly higher than those of RS soils (0.45 ± 0.116). The soils taken from AF, BG and RS sites could be categorized "sandy" soils according to the results of soil texture analysis.

#### PAEs concentration in the different soil samples

Figure 2 and Table S3 provide information about PAE composition in soils taken from AF, BG and RS sites. For AF sites, the total of six PAE concentrations ranged from 0.1 to 1.61 mg kg$^{-1}$ (0.65 ± 0.47 mg kg$^{-1}$). Among the six PAEs, DEHP was the most popular PAE compound in soil samples. The highest and second highest concentrations of DEHP were observed at the sites AF08 (1.53 mg kg$^{-1}$) and AF02 (0.95 mg kg$^{-1}$), respectively. In three other AF sites, DEHP was also the most popular PAE compound, indicating the widespread contamination of DEHP in AF sites. A large area of the site AF08 was planted with lemon and gurva (Table S1). During the sampling, plastic bags used to cover the ripening fruit were observed on the ground and nearby grasses at this site. Those plastic bags were discarded after the harvesting of the fruit and not collected for further disposal and/or treatment. This environmentally unfriendly practice of the local farmers probably contributed to the very high PAE concentrations in soil in site AF08. In addition, during the sampling, we observed that the sites AF01, AF02, AF05, AF06 and AF08 were receiving an additional amount of chemical fertilizer as these fields were near to the harvest. Chemical fertilizer was known to contain high concentrations of PAEs and other organic contaminants (Staples et al. 1997; Mo et al. 2008; Wang et al. 2013a) and the effects of applying fertilizer on soil PAE contamination will be discussed in "PAE contamination in chemical and organic fertilizers". D*n*OP was the most popular PAE at the sites AF05 (0.61 mg kg$^{-1}$) and AF06 (0.64 mg kg$^{-1}$), making it the second most popular PAE compound in AF soils. DEHP and D*n*OP have been well documented to occur in plastic mulching film, and many chemicals and fertilizers used for farming practices (Mo et al. 2008; Wang et al. 2013a; Li et al. 2016a). The differences in observed PAE composition at different AF sites were mainly due to the use of different types of plastic mulching film, fertilizers and other plastic farming materials and equipment.

For soils collected from BG, PAE contamination was far lower than that in AF soils. Total six PAE content varied
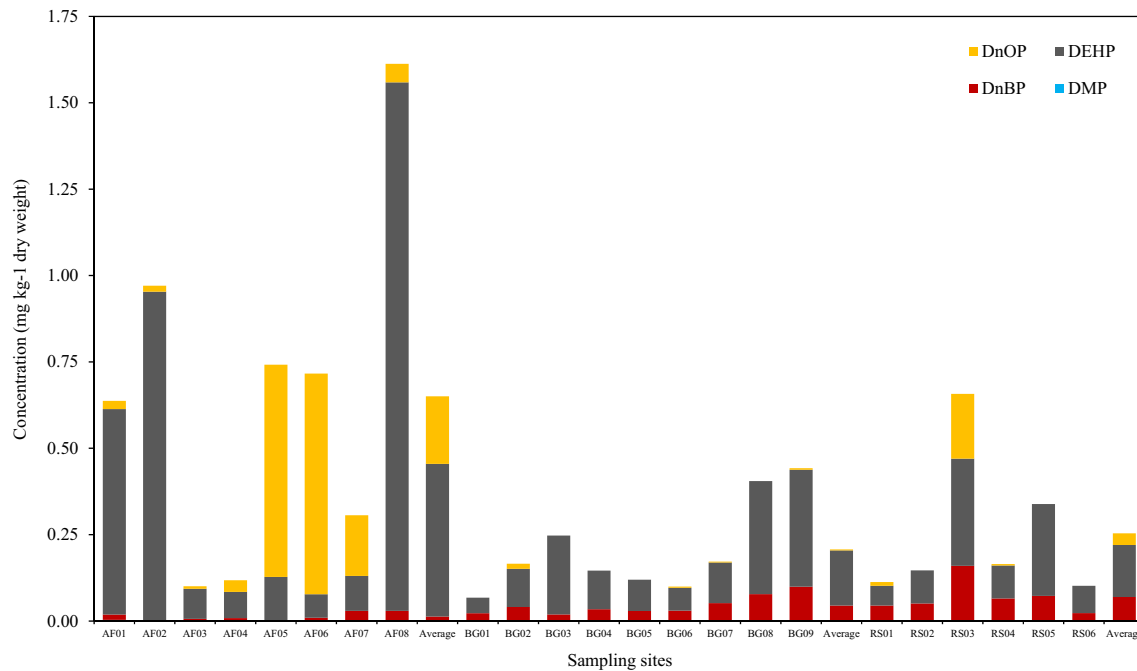
**Fig. 2** PAE composition in soil samples taken from AF, BG and RS sites in Kaohsiung City, Taiwan. DEHP and DnOP accounted for the most of PAE concentrations in soil (>90%). DEP and BBP were not found, while DMP was only detected in negligible amount in the soil sample collected at site AF01

from 0.07 to 0.44 mg kg$^{-1}$ (0.21 ± 0.13 mg kg$^{-1}$). Again, DEHP remained the most widespread PAE compound. DEHP concentrations were highest among the six PAEs at all BG sites. The most noticeable DEHP concentrations were observed at the sites BG08 (0.33 mg kg$^{-1}$) and BG09 (0.34 mg kg$^{-1}$). During the sampling, the sites BG08 and BG09 were receiving an additional amount of chemical fertilizer as these two gardens were near to the harvest and plastic bags used to cover the ripening fruit were also observed on the ground and nearby grasses at these two sites. In the back gardens, different types of vegetables, flowers and other vegetation were planted for owners' use and/or for sale. Compared to AF sites, vegetation in BG sites varied more in types, but was lower in quantity. Farming scale of AFs was far larger than the gardening scale of BGs. The amount of plastic mulching film, farming fertilizers, chemicals and other plastic materials and equipment used in BG sites was therefore sharply lower than that used in AF sites. Generally, PAE concentrations in BG soils were lower than those in AF soils.

Compared to BG soils, RS soils showed slightly higher PAE concentrations, ranging from 0.1 to 0.66 mg kg$^{-1}$ (0.25 ± 0.20 mg kg$^{-1}$). DEHP was still the most dominant PAE compound. At the site RS03, which locates near Renwu Industrial Park, the concentration of DEHP was particularly high (0.31 mg kg$^{-1}$). In addition, PAE concentrations in two RS sites near Renwu Industrial Park, RS03 and RS05, were

considerably higher than those in other RS sites. PAEs in RS soils could be attributed to the deposition of ambient PAEs, the convection and diffusion of indoor PAEs to outdoor environment, and PAEs spilled from daily activities from industrial, commercial and residential areas nearby (Peijnenburg and Struijs 2006; Pei et al. 2013; Wang et al. 2013b; Skrbic et al. 2016).

The most abundant PAE compound in Kaohsiung City's soils was DEHP. This abundance of DEHP in soils could be attributed to the widespread involvement of this compound in plastic industries which have developed rapidly and intensely for decades in Kaohsiung City (Lin et al. 2009). Also, DEHP could be released to the soil through various farming practices, which include the use of plastic films (Niu et al. 2014). Compared to the soils taken from AF sites, soils collected in BG and RS sites displayed much lower PAE content, implying that the soil PAE contamination in Kaohsiung City's soils could be more likely due to the use of plastic mulching film, fertilizers and chemicals containing PAEs and other plastic equipment used in farming practices rather than the release of PAEs from industrial activities (Wang et al. 2013a; Yang et al. 2013; Li et al. 2016a).

PAE contamination in AF sites of this study was compared to the findings of other similar studies around the world to briefly assess the PAE contamination status in the agricultural soil of Kaohsiung City (Table 2). Most studies concerning PAE contamination in agricultural soil were

**Table 2** Comparison of PAE concentrations (values are shown in mean ± standard deviation or mean) between different similar studies in different geographical areas around the world (mg kg$^{-1}$)

| | DMP | DEP | D$n$BP | BBP | DEHP | D$n$OP | References |
|---|---|---|---|---|---|---|---|
| **Agricultural soil** | | | | | | | |
| Kaohsiung, Taiwan | 0.0004 ± 0.001 | ND | 0.01 ± 0.01 | ND | 0.44 ± 0.51 | **0.2 ± 0.25** | This study |
| Shandong Peninsula, China | **0.14 ± 0.2** | **0.34 ± 0.44** | **1.99 ± 2.55** | **0.49 ± 1.16** | 0.29 ± 0.46 | **0.36 ± 0.77** | Li et al. (2016b) |
| Paris, France | 0.001 | 0.005 | 0.004 | 0.0004 | 0.12 | 0.004 | Tran et al. (2015) |
| Hebei, China | 0.02 ± 0.01 | 0.003 ± 0.003 | 0.05 ± 0.01 | 0.02 ± 0.03 | 0.14 ± 0.05 | 0.04 ± 0.02 | Zhang et al. (2015) |
| 31 provinces in China | 0.01 ± 0.01 | 0.003 ± 0.002 | 0.07 ± 0.05 | 0.00004 ± 0.00004 | 0.82 ± 0.76 | 0.02 ± 0.03 | Niu et al. (2014) |
| Nanjing, China | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.26 ± 0.38 | 0.01 ± 0.01 | **2.45 ± 2.04** | **0.46 ± 0.45** | Wang et al. (2013a) |
| Yellow River Delta, China | 0.03 ± 0.003 | 0 | 0.41 ± 0.05 | 0 | **1.22 ± 0.11** | 0.01 ± 0.001 | Yang et al. (2013) |
| Five regions in Czech Republic | | | **1.1** | | **1.31** | | Daňková et al. (2012) |
| Tianjin, China | 0.02 ± 0.02 | 0.03 ± 0.02 | 0.07 ± 0.04 | 0.07 ± 0.27 | 0.26 ± 0.4 | 0.07 ± 0.13 | Kong et al. (2012) |
| Guangzhou, China | 0.01 | 0.01 | 0.12 | 0.004 | 0.6 | 0.01 | Zeng et al. (2008) |
| Heilongjiang, China | | | **15.46** | | **4.61** | | Xu et al. (2008) |
| Beijing, China | | | **2.96** | | **2.7** | | Ma et al. (2003) |
| Roskilde, Denmark | | | 0.002 | 0.0001 | 0.03 | 0.004 | Vikelsoe et al. (2002) |
| **Chemical fertilizer** | | | | | | | |
| Kaohsiung, Taiwan | ND | ND | 0.01 ± 0.03 | **0.01 ± 0.01** | 0.22 ± 0.35 | **0.1 ± 0.25** | This study |
| China | **0.02** | **0.0001** | **0.16** | 0.002 | 0.07 | 0.0002 | Mo et al. (2008) |
| Roskilde, Denmark | | | 0.09 ± 0.002 | **0.04 ± 0.01** | **1.1 ± 0.13** | 0.04 ± 0.004 | Vikelsoe et al. (2002) |
| **Organic fertilizer** | | | | | | | |
| Kaohsiung, Taiwan | ND | ND | 0.03 ± 0.02 | 0.03 ± 0.02 | 0.05 ± 0.03 | **0.04 ± 0.02** | This study |
| China | 0.001 | ND | 0.0004 | ND | 0.0008 | ND | Mo et al. (2008) |
| Roskilde, Denmark | | | 0.02 ± 0.01 | 0.02 ± 0.01 | 0.03 ± 0.01 | 0.001 ± 0.001 | Vikelsoe et al. (2002) |
| **Plastic mulching films** | | | | | | | |
| Kaohsiung, Taiwan | ND | ND | ND | 3.2 ± 1.8 | **67.06 ± 32.78** | **157.76 ± 96.23** | This study |
| Beijing, China | 0.09 | 0.04 | 3.2 | 0.08 | 5.15 | 0.04 | Li et al. (2016a) |
| Nanjing, China | 3.95 | **3.76** | **15** | **3.05** | **105** | 75 | Wang et al. (2016) |
| China | **1240 ± 111.6** | ND | ND | | | **270 ± 29.4** | Zhou et al. (2012) |

In bold are values of 'high' concentrations for a specific PAE compound

*ND* not detected

carried out in China, suggesting that this country has been incurred a heavy PAE contamination (Li et al. 2016b). The comparison showed that PAE contamination in Kaohsiung City was not as serious as that in several parts of China but was still more serious than that in some other areas of China and other countries. The most serious PAE contamination in agricultural soil was found in the rapidly developed area of Shandong Peninsula (Li et al. 2016b), the intensive agricultural area of Heilongjiang (Xu et al. 2008) and the outskirts of Beijing (Ma et al. 2003) in China. High PAE contamination in those areas could be due to their intensive farming and usage of plastic mulching films (Li et al. 2016b). It is noticeable that although our findings of DMP were three orders of magnitude lower than those of the highest found in agricultural soil in Shandong Peninsula (Li

et al. 2016b), they were still one order of magnitude higher than the findings in the rural area fertilized by wastewater treatment sludge in Paris, France (Tran et al. 2015) and the rural area of Roskilde, Denmark (Vikelsoe et al. 2002). D$n$BP concentrations in our study were two to three orders of magnitude lower than those in the studies conducted in Czech Republic (Daňková et al. 2012), Beijing (Ma et al. 2003), Shandong Peninsula (Li et al. 2016b) and Heilongjiang (Xu et al. 2008). DEHP, though representing the highest concentrations among the six PAEs in Kaohsiung City's agricultural soil, showed much lower concentrations than those in the similar studies conducted in the agricultural and industrial areas of the Yellow River Delta (Yang et al. 2013), of the suburban areas of Nanjing (Wang et al. 2013a), of Heilongjiang (Xu et al. 2008), of Beijing (Ma et al. 2003)

in China and in Czech Republic (Daňková et al. 2012). Yet, Kaohsiung City's DEHP content was approximately twice and three times higher than that of the suburban soils of Tianjin (Kong et al. 2012) and the wastewater-irrigated soils of Hebei (Zhang et al. 2015) in China, respectively. D*n*OP content in this study, however, was among the three highest D*n*OP findings. Kaohsiung City's D*n*OP content was only lower than that of Shandong Peninsula (Li et al. 2016b) and of Nanjing (Wang et al. 2013a). Kaohsiung City's D*n*OP was in fact one and two orders of magnitude higher than that in the study conducted in 31 Chinese provinces (Niu et al. 2014) and the rapidly growing city of Guangzhou, China (Zeng et al. 2008), respectively.

In our rough ecotoxicological risk assessment, the content of all six PAEs in Kaohsiung City's soils was far lower than both the allowable and cleanup levels mentioned in the soil cleanup guidelines issued by the New York State Department of Environmental Conservation (NYSDEC 2010) (Table S3). Therefore, PAE contamination level in soils in Kaohsiung City was still within the tolerable range. However, due to the possibility of PAEs transferring from soil to cultivated products, long-term contamination and accumulation in the food chain could pose negative health effects on humans and thus monitoring and pollution management plans are still in need in order to avoid unnecessary risks (Li et al. 2016a; Skrbic et al. 2016).

Up to now, there have been no studies addressing PAE levels in BG and RS sites, making us incapable of creating a similar comparison to AF soils for our findings in BG and RS sites. In our study, BG sites were used to plant vegetables, flowers and some other types of vegetation, and at RS sites, vegetation coverage was negligible. BG and RS sites were selected due to their locations, which are near and around the circumference of the major industrial plants in Kaohsiung City. It is reasonable to speculate that the two giant plastic resin manufacturing complexes, Renwu Industrial Park and Dashe Industrial Park, release certain amount of PAEs into the surrounding environment (Lin et al. 2009). Our findings of PAEs in BG and RS sites can, therefore, provide a baseline for future environmental monitoring and management plans in relation to the operation and discharge of PAE contaminants by industrial activities in Kaohsiung City.

PAE concentrations could be affected by soil properties, especially by pH values and organic matter content (Niu et al. 2014; Li et al. 2016a). Pearson's correlation was performed between the concentrations of each PAE compound and the basic soil properties (Table S4). There was no significant positive correlation between the soil properties and PAE concentrations ($p < 0.05$). However, there were relatively low positive correlations between pH and three PAE compounds (DMP, D*n*BP and D*n*OP), and between TOC and three compounds (D*n*BP, DEHP, D*n*OP) ($p > 0.05$). TOC

and pH play an important role in the behavior of hydrophobic contaminants in soil (Yang et al. 2015). Weak positive correlations between pH and PAEs were reported in the agricultural soil of Guangzhou (Zeng et al. 2008) and of Shandong Peninsula (Li et al. 2016b). Likewise, weak positive correlations between organic matter and PAEs were observed in the agricultural soil across China (Niu et al. 2014) and the soil in the Shandong Peninsula (Li et al. 2016b). The reason for those weak positive correlations was reported in the study of Li et al. (2016a), which is the frequent usage of plastic films hindering the equilibrium achievement between PAEs and organic matter. It is also noticeable that there was a significant negative correlation between TOC and D*n*BP ($r = -0.444$, $p > 0.05$). Negative correlations were also found between basic soil properties (pH and organic matter) and PAE levels in greenhouse soil of Beijing (Li et al. 2016a).

Since extensive and long-term exposure to PAEs could pose high risks to human health, PAE contamination in soil is an important environmental/health factor. Further, PAEs could accumulate from soil into agricultural products or foodstuff, especially the food directly grown onto the soil, volatate to the atmosphere or permeate and penetrate the groundwater, which would lead to more serious contamination and exposure, and in turn negatively affect human health. PAEs in the soil can also directly enter human body via multiple pathways, such as ingestion, dermal contact and inhalation (Li et al. 2016b). Although PAEs are well known as widespread environmental contaminants and endocrine disruptors, their carcinogenic activity has not been well established as only DEHP has been announced as a potential carcinogen (USEPA 2013; Li et al. 2016b). Risk calculation has been widely adopted to reflect quickly and efficiently the potential risks that soil contamination could pose to human health (Niu et al. 2014; Li et al. 2016b). In this study, the risk via the dietary pathway was estimated taking 18 soil samples collected from AF and BG into account, whereas the risk via the non-dietary pathways was performed with the total 24 soil samples. Associated non-cancer and carcinogenic risks of dietary (intake) and non-dietary (ingestion, dermal contact and inhalation) exposure to soil PAEs estimated for adults and children were shown in Table S5. All the HI values were below 1, indicating that there should be no potential non-cancer risks from exposure to soil PAEs. The results of carcinogenic risk calculation were generally below $10^{-6}$. However, there was a value calculated for children (non-dietary pathway) falling in between $10^{-6}$ and $10^{-4}$, which should be categorized as "moderate" risk. Compared to the calculated risk values for the adults, those for children were higher, suggesting that children were more vulnerable and sensitive toward PAE contamination in soil. Risk calculation is considered an efficient tool to decision-making process and the results of risk calculation in this study could
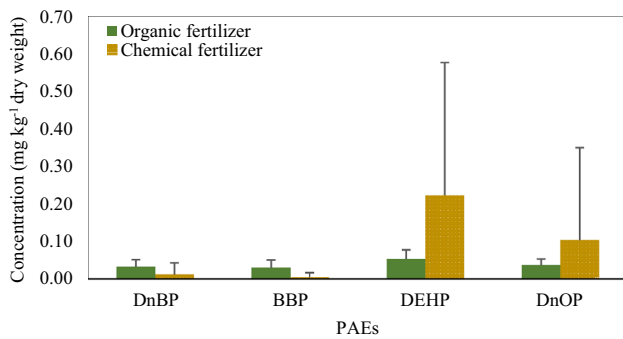
**Fig. 3** PAE concentrations in organic and chemical fertilizer samples taken in AF and BG sites

serve as a baseline for devising future land-use development and environmental management plans in Kaohsiung City.

## PAE contamination in chemical and organic fertilizers

Figure 3 shows PAE concentrations in chemical and organic fertilizer samples. This sampling design was dedicated to measure differences between these two commonly used categories of fertilizer, which in turn should help to investigate the main source of PAE contamination in soil. In this study, six samples of organic (compost) and seven samples of chemical fertilizer were collected in different AF and BG sites. The results showed that the content of BBP in organic fertilizer ($0.03 \pm 0.02$ mg kg$^{-1}$) was higher than that in chemical fertilizer ($0.005 \pm 0.01$ mg kg$^{-1}$) ($p < 0.05$). DEHP and D$n$OP concentrations in organic fertilizer ($0.05 \pm 0.02$ and $0.04 \pm 0.02$ mg kg$^{-1}$, respectively), on the other hand, were far lower than those in chemical fertilizer ($0.22 \pm 0.35$ and $0.1 \pm 0.25$ mg kg$^{-1}$, respectively) ($p < 0.05$). The total PAE concentrations in chemical fertilizer were higher than that in organic fertilizer ($p < 0.05$). Therefore, it is still reasonable to conclude that organic fertilizer was less PAE-contaminated than chemical fertilizer. Our finding was similar to that of Mo et al. (2008) when PAE concentrations in the organic fertilizer were one to two orders of magnitude lower than those in the most commonly used commercial chemical fertilizer in China (Table 2). Likewise, in the study of Vikelsoe et al. (2002), PAE content in chemical fertilizer ($0.34 \pm 0.64$) was 2–40 times higher than that in organic fertilizer ($0.15 \pm 0.08$). The production of chemical fertilizer could be plastic-involved in multiple sections, not to mention the packaging of this type of fertilizer (Vikelsoe et al. 2002). Organic fertilizer, however, is often produced naturally, making it less contaminated with hydrophobic contaminants (Mo et al. 2008). Therefore, future pollution management and human-wellbeing improvement plans should take into account the use of organic fertilizer in farming.

## PAE contamination in plastic mulching films and other types of plastic materials used in agricultural and gardening activities

Figure 4 shows PAE concentrations in plastic samples of mulching films and other types of plastic materials used in agricultural and gardening activities taken from AF and BG sites. Initially, plastic mulching films were collected because they were reported to be the main source of PAE contamination to agricultural soil (Li et al. 2016a). However, during the sampling, we noticed that there were other types of plastic materials that were frequently used in agricultural and gardening activities, such as water hose, plastic bags used to cover the ripening fruit, plastic gloves, plastic boots and some other plastic gardening tools. These plastic materials occurred diffusely on the agricultural fields and the gardens. Although the amount of these plastic materials was not as high as that of mulching films, they could also add up to the PAE contamination in soil given that they contain higher PAE levels. The analytical results of 19 plastic mulching film samples and 8 samples of other types of plastic materials showed that PAE concentrations in plastic mulching films were much lower than those of the other types of plastic materials, especially in the case DEHP ($67.06 \pm 32.78$ vs $302 \pm 208.58$ mg kg$^{-1}$) and D$n$OP ($157.76 \pm 96.23$ vs $862.28 \pm 599.05$ mg kg$^{-1}$) ($p < 0.05$). As for D$n$BP (ND vs $7.73 \pm 6.2$ mg kg$^{-1}$) and BBP ($3.2 \pm 1.8$ vs $13.1 \pm 9.17$ mg kg$^{-1}$), although the results were less different between the two plastic groups, high discrepancies between plastic mulching films and the other types of plastic materials occurred ($p < 0.05$). The finding of PAE content in
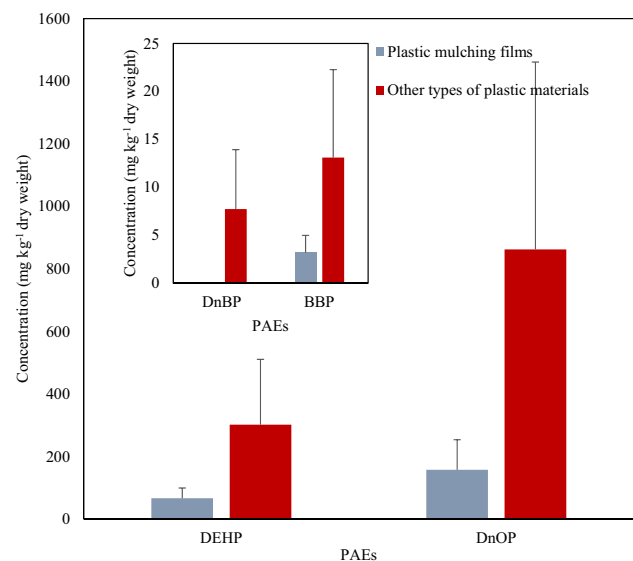


**Fig. 4** PAE concentrations in plastic mulching films and other types of plastic materials used in farming and gardening activities taken in AF and BG sites

plastic mulching films in this study was comparable to that in the studies conducted in Nanjing (Wang et al. 2016) and across China (Zhou et al. 2012), but was far higher than that in the study conducted in Beijing (Li et al. 2016a) (Table 2). Besides, we could not make a similar comparison to PAE content in the mulching films for our finding for the other types of plastic materials used in farming and gardening activities since they have not been studied in the literature. The results of this study suggest that in addition to the pollution control for PAE levels in plastic mulching films, other plastics-related materials employed in agricultural and gardening activities should also be taken into consideration.

## Conclusions

This study reports the status of PAE contamination in soil, fertilizer and plastic materials taken around the major industrial area in Kaohsiung City. In soil samples, DEHP, which accounts for over 60% of total PAEs, was the most popular compound among six PAEs studied. In fact, DEHP was present in all soil samples with very high concentrations ($0.26 \pm 0.34$ mg kg$^{-1}$), indicating the popular use of this compound in agricultural and industrial activities. Soil samples collected from AF sites (0.1–1.61 mg kg$^{-1}$) were more PAE-contaminated than those collected from BG (0.07–0.44 mg kg$^{-1}$) and RS sites (0.1–0.66 mg kg$^{-1}$), suggesting that PAE contamination in Kaohsiung City's soil is mainly due to the use of plastic mulching film, chemicals and fertilizers containing PAEs, and other plastic materials and equipment used for farming practices rather than industrial activities. The risk calculation for soil PAE exposure for adults and children resulted in values mostly within "acceptable" range, apart from a "moderate risk" value (2.06E-06) for carcinogenic risk calculated for children (non-dietary pathway). Also, PAE content in organic fertilizer ($0.15 \pm 0.07$ mg kg$^{-1}$) was much lower than that in chemical fertilizer ($0.34 \pm 0.56$ mg kg$^{-1}$). PAE content in plastic mulching films ($58.56 \pm 103.44$ mg kg$^{-1}$), supposedly the main source of PAE contamination in soil, was far lower than that in other types of plastic materials used in farming and gardening activities ($350.56 \pm 817.96$ mg kg$^{-1}$). The findings of this study should serve as a reference for future environmental management plans regarding the industrial operation and discharge as well as the farming and gardening practices.

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