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Analysis of phthalate esters in soils near an electronics manufacturing facility and from a non-industrialized area by gas purge microsyringe extraction and gas chromatography

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HIGHLIGHTS

- A new method for determining phthalate esters in soil samples was developed.
- Investigate six phthalates near an industry and a non-industrialized area.
- Discuss the congener profiles of the electronics industry on PAE accumulation.

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ABSTRACT

Here, a novel technique is described for the extraction and quantitative determination of six phthalate esters (PAEs) from soils by gas purge microsyringe extraction and gas chromatography. Recovery of PAEs ranged from 81.4% to 120.3%, and the relative standard deviation ($n = 6$) ranged from 5.3% to 10.5%. Soil samples were collected from roadsides, farmlands, residential areas, and non-cultivated areas in a non-industrialized region, and from the same land-use types within 1 km of an electronics manufacturing facility ($n = 142$). Total PAEs varied from 2.21 to 157.62 mg kg^{-1} in non-industrialized areas and from 8.63 to 171.64 mg kg^{-1} in the electronics manufacturing area. PAE concentrations in the non-industrialized area were highest in farmland, followed (in decreasing order) by roadsides, residential areas, and non-cultivated soil. In the electronics manufacturing area, PAE concentrations were highest in roadside soils, followed by residential areas, farmland, and non-cultivated soils. Concentrations of dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-*n*-butyl phthalate (DnBP) differed significantly ($P < 0.01$) between the industrial and non-industrialized areas. Principal component analysis indicated that the strongest explanatory factor was related to DMP and DnBP in non-industrialized soils and to butyl benzyl phthalate (BBP) and DMP in soils near the electronics manufacturing facility. Congener-specific analysis confirmed that diethylhexyl phthalate (DEHP) was a predictive indication both in the non-industrialized area ($r^2 = 0.944$, $P < 0.01$) and the industrialized area ($r^2 = 0.860$, $P < 0.01$). The higher PAE contents in soils near the electronics manufacturing facility are of concern, considering the large quantities of electronic wastes generated with ongoing industrialization.

1. Introduction

Phthalate esters (PAEs) are among the most common industrial chemicals that are widely applied in different manufacturing processes (Dodson et al., 2012; Heudorf et al., 2007; Koniecki et al., 2011). High-molecular-weight (HMW) phthalate compounds, such as diethylhexyl phthalate (DEHP), butyl benzyl phthalate (BBP), and di-*n*-octyl phthalate (DnOP), are primarily used in the production of polyvinylchloride (PVC) plastics (Guo et al., 2014). Low-molecular-weight phthalates, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-*n*-butyl phthalate (DBP), are most commonly found in cosmetics, varnishes, and coatings (Heudorf et al., 2007; Koniecki et al., 2011; Singh and Li, 2012; Sumner et al., 2009). Because PAEs are physically, rather than chemically, bound to polymer chains, they can be released into the environment by leaching, evaporation, migration, and abrasion, or through application of phthalate-containing personal care products

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Table 1
Results of gas purge microsyringe extraction (GP-MSE) coupled with gas chromatography (GC) with flame ionization detector (FID) used to detect phthalate esters (PAEs) in soils.

PAE compound	DL (mg kg^{-1})	Linear range (mg kg^{-1})	Regression equation	r^2	Recovery (%)	RSD (%, $n = 6$)
DMP	0.02	0.1–100	$y = 41.4 + 101.1x$	0.971	84.2–111.3	7.7–9.9
DEP	0.03	0.1–100	$y = 39.7 + 113x$	0.978	84.2–123.0	7.1–10.0
DBP	0.03	0.1–100	$y = 65 + 111.4x$	0.965	85.5–120.3	7.8–10.3
BBP	0.02	0.1–100	$y = 31.4 + 92.79x$	0.981	81.8–115.6	6.3–9.3
DEHP	0.04	0.1–100	$y = 40.6 + 106x$	0.983	81.4–116.2	5.3–10.5
DnOP	0.04	0.1–100	$y = 34.17 + 97.7x$	0.979	86.5–113.2	7.3–10.4

DL, detection limit; RSD, relative standard deviation; DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, di-*n*-butyl phthalate; BBP, butyl benzyl phthalate; DEHP, diethylhexyl phthalate; DnOP, di-*n*-octyl phthalate.

(Darbre and Harvey, 2008; Guo and Kannan, 2013). As a result, The United States Environmental Protection Agency (EPA) and its counterparts in several other countries have classified the most commonly occurring PAEs as priority pollutants and as endocrine-disrupting compounds (Kamrin, 2009).

Soils, which consist primarily of mineral particles and organic matter, are important indicators of pollution and environmental risk. Urban soils, particularly those near industrial areas, are a major reservoir for PAEs (Singh and Li, 2012; Wang et al., 2013a). Previous studies identified a high diversity of materials and contaminants, including heavy metals, diphenyl ethers (PBDE), and PAEs, in waste electrical and electronic equipment (C. Yang et al., 2013). In eastern China, DBP, DEHP, and DnOP are the most frequently detected PAEs near sites that recycle electronic waste (Guo et al., 2012; Zhang et al., 2010). The presence of PAEs in soils can lead to atmospheric or water pollution by evaporation, leaching, deposition, and drainage, and these compounds can contaminate agricultural crops and lead to direct or indirect human exposure. Numerous studies have revealed contamination of agricultural soils by PAEs (Wang et al., 2013a; Zeng et al., 2008a), and some investigators have found that the plastic industry is the major source of PAEs in soils (Ma et al., 2014; Xia et al., 2011); however, few studies have analyzed phthalate esters in soils near electronic waste sites compared to soils from non-industrialized areas.

Many studies of PAEs in soil have focused on simple, rapid, and automatic methods for extraction and cleanup of complex samples before determination by gas or liquid chromatography coupled to mass spectrometry (GC–MS or LC–MS). Soxhlet extraction is commonly used but is time-consuming and requires the use of organic solvents (Liu et al., 2010; Zeng et al., 2008b). A gas-purge microsyringe extraction (GP-MSE) technique was developed by Li and co-workers for volatile and semi-volatile chemicals and has been used for quantitative GC determination of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCP) in plants (Piao et al., 2011; Wang et al., 2013b; X. Yang et al., 2013). GP-MSE integrates sampling, extraction, and concentration. In this system, samples are automatically or semi-automatically introduced into the instrument, analytes are evaporated from the solid or semi-solid matrix to the gas phase, and then the analytes are enriched from the gas phase to a microliter solvent drop on the microsyringe tip. This method is fast, simple, and inexpensive, requires little solvent, and produces little waste.

Our study was performed in Xiangyang (112°00′N, 31°54′E), western Hubei Province, central China. Xiangyang (population approximately 5.5 million) covers 197,000 km^2 and is a typical urbanized area with extensive road networks and heavy industrialization, agricultural production, and commercial activity. Developing industries (particularly electronics manufacturing) might significantly contribute to elevated PAE deposition in this area. The objectives of this work were to (a) introduce a new GP-MSE/GC method for determining phthalate esters in soil samples; (b) investigate the concentration, composition, and distribution of six phthalates (DMP, DEP, DBP, BBP, DEHP, and DnOP) in soils near an electronics industry and in a non-industrialized area; and (c) discuss the congener profiles and the influence of the electronics industry on PAE accumulation in soils.

2. Materials and methods

2.1. Reagents and chemicals

We used six PAE standard solutions containing 2000 mg L^{-1} DMP, DEP, DnBP, DEHP, BBP, and DnOP in methanol (Supelco, USA). Benzyl benzoate was used as an internal standard and was acquired as a solid (99% purity; Aldrich Chemicals, USA), and water was triple-distilled using a Milli-Q purification system (Millipore, USA). Stock solutions (100 mg L^{-1}) of the six phthalates and the internal standard were prepared in dichloromethane. All solutions were used within 6 months. All solvents (dichloromethane, methanol, acetone) were of HPLC grade.

To avoid contamination, no plastic equipment was used during sampling or processing. All glassware was initially soaked in a mixture of potassium dichromate and sulfuric acid for 12 h, rinsed with Milli-Q water, baked at 400 °C for 8 h, and sealed with a glass stopper in aluminum foil. Neutral silica gel and alumina (100 mesh) were cleaned with dichloromethane for 72 h using a Soxhlet extractor, activated at 180 °C, maintained at 250 °C for 12 h, and then deactivated with 3% (w/w) deionized water. Filter paper was also extracted with dichloromethane using a Soxhlet extractor for 72 h prior to use.

2.2. Sampling protocol

Soil samples ($n = 142$) were collected in December 2013 within 1 km of an electronics factory in Xiangyang. The factory (approximately

Table 2a
Concentrations of phthalate esters (PAEs, mg kg^{-1}) in soils sampled from different land-use types in a non-industrialized area.

PAE	Residential ($n = 44$)			Roadside ($n = 36$)			Farmland ($n = 32$)			Non-cultivated ($n = 33$)		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Mean ± SD	Median
DMP	0.19–2.07	0.67 ± 0.49	0.51	0.15–2.26	0.83 ± 0.58	0.45	0.15–8.04	1.10 ± 1.38	0.85	ND–1.37	0.53 ± 0.37	0.42
DEP	0.15–11.31	1.08 ± 1.70	0.59	0.25–10.23	1.37 ± 1.77	0.87	0.13–14.09	1.76 ± 2.90	1.21	0.1–1.59	0.91 ± 0.45	1.08
DBP	0.18–15.11	1.66 ± 2.41	1.22	0.34–7.18	1.77 ± 1.50	1.22	0.69–18.24	2.22 ± 3.01	1.35	0.34–4.24	1.23 ± 0.77	1.21
BBP	0.21–12.35	1.25 ± 1.79	1.03	0.21–10.23	1.48 ± 1.66	1.07	ND–9.16	1.86 ± 1.70	1.25	0.23–2.69	1.30 ± 0.52	1.26
DEHP	0.59–42.04	11.12 ± 13.32	2.36	0.36–35.04	14.50 ± 10.20	10.5	3.26–153.4	16.59 ± 25.74	12.21	4.2–26.31	11.4 ± 5.83	12.07
DnOP	ND–1.34	0.65 ± 0.39	0.50	0.28–2.41	0.76 ± 0.59	0.45	ND–2.31	0.67 ± 0.50	0.47	ND–1.51	0.56 ± 0.36	0.41
∑PAEs	2.21–54.15	15.97 ± 14.28	8.78	2.84–51.05	20.63 ± 12.96	16.76	9.11–157.62	23.99 ± 26.16	15.87	5.63–31.58	15.87 ± 6.18	15.25

DMP, dimethyl phthalate; DEP, diethyl phthalate; DBP, di-*n*-butyl phthalate; BBP, butyl benzyl phthalate; DEHP, diethylhexyl phthalate; DnOP, di-*n*-octyl phthalate.