Pollution characteristics and health risk assessment of phthalate esters in urban soil in the typical semi-arid city of Xi’an, Northwest China

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HIGHLIGHTS
• Priority phthalate esters (PAEs) in urban soil of a semi-arid city were investigated.
• PAEs contents exceeded soil allowable concentrations and environmental risk levels.
• Magnetic susceptibility and soil texture were controlling factors of PAEs in soil.
• Soil PAEs were dominated by di-n-butyl phthalate and di(2-ethylhexyl) phthalate.
• Health risks of human exposure to PAEs in urban soil were relatively low.

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ABSTRACT
A total of 62 urban soil samples were collected in the city of Xi’an in Northwest China, and analyzed for six U.S. Environmental Protection Agency priority phthalate esters (PAEs). Unlike earlier studies on PAEs in agricultural soil as well as urban soil in humid climates, this paper for the first time comprehensively assessed pollution characteristics and health risks of human exposure to PAEs in urban soil in a typical semi-arid climate. The total concentrations of the six PAEs (Σ6PAEs) in the urban soil varied between 193.0 and 19146.4 μg kg⁻¹ with a mean of 1369.3 μg kg⁻¹. The PAEs were dominated by di-n-butyl phthalate and di(2-ethylhexyl) phthalate. Magnetic susceptibility and soil texture were controlling factors influencing the concentrations of PAEs in the urban soil. The concentrations of benzyl butyl phthalate, di(2-ethylhexyl) phthalate, and Σ6PAEs increased from the first to third ring roads, while the concentrations of di-n-octyl phthalate decreased. Relatively higher levels of PAEs were observed in industrial, traffic, and residential areas. The PAEs in the urban soil originated mainly from the application of plasticizers or additives, use of cosmetics and personal care products, emissions of construction materials and home furnishings, industrial processes, and atmospheric deposition. The concentrations of some PAEs in the urban soil exceeded soil allowable concentrations and environmental risk levels. The non-cancer and carcinogenic risks of human exposure to the PAEs were relatively low.

1. Introduction

Urban soil, mainly composed of minerals and organic matter, is an important part of urban ecosystems. However, urban soil has been suffering from serious contamination with various pollutants, such as heavy metals, polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs), and phthalate esters/phthalic acid esters (PAEs), due to industrialization, urbanization, and agricultural modernization. These toxic pollutants accumulated in urban soil can be carried into surface and ground water through precipitation and urban runoff, and emitted into atmosphere by volatilization, which indirectly contribute to water and atmosphere pollution (Zeng et al., 2009). They can also be transferred to human body via
ingestion, inhalation and dermal adsorption of soil dust, thus leading to impacts on the health of human beings, especially children and elderly people who are physiologically more vulnerable to environmental pollution (Xia et al., 2011). Therefore, urban soil has been a major reservoir of diverse pollutants and a transmitter of pollutants to water bodies, atmosphere, and human beings. Meanwhile, the quality of urban soil is an important indicator of pollution and environmental risks (Zeng et al., 2009).

Among various pollutants, PAEs are a class of synthetic organic compounds. They are widely used as plasticizers/additives in various plastic products and non-plasticizers in consumer products (Abdeldaiem et al., 2012; Fu et al., 2013; Staples et al., 1997). For instance, PAEs with a lower molecular weight, such as dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-n-butyl phthalate (DnBP), are typically used in cosmetics and personal care products. DnBP is also used in epoxy resins, cellulose esters and special adhesives formulations (IARC, 2000; Abdel daim et al., 2012). Longer/branching alkyl chain PAEs, such as benzyl butyl phthalate (BBP), di-n-octyl phthalate (DnOP) and di(2-ethylhexyl) phthalate (DEHP), have been widely used as plasticizers in the polymer industry to improve flexibility, workability and general handling properties, and about 80% of PAEs are used for this purpose (IARC, 2000; Hens and Caballos, 2003). The content of PAEs in a finished plastic product ranges from 10% to 60% by weight (IARC, 2000; Abdel daim et al., 2012). BBP and DnOP are also used in construction materials and home furnishings such as vinyl flooring, wallpapers, synthetic leather, and adhesives (Hens and Caballos, 2003). It has been estimated that the worldwide production and consumption of PAEs is approximately 6.0 million tons per year (Mackintosh et al., 2006). The consumption of PAEs in China reached 2.2 million tons in 2011 (CPPU, 2011). PAEs can be directly or indirectly released into the environment during the manufacturing of plastics and plastic materials, in the use of plastic products, and after disposal because PAEs are not chemically bound with polymers in such products (Benson, 2009; Staples et al., 1997). Because of the widespread application of products containing PAEs, PAEs are ubiquitous in environmental compartments, such as drinking water and surface water (Wang et al., 2015a; Zhang et al., 2012), indoor/outdoor air and dust (He et al., 2016; Kong et al., 2013; Lan et al., 2012; Wang et al., 2008a, 2014a; Zhang et al., 2014a), sediment (Liu et al., 2010; Wang et al., 2008b), and soil (Kong et al., 2012; Peijnenburg and Struijs, 2006; Tran et al., 2015; Vikelsøea et al., 2002; Yang et al., 2013; Yin et al., 2003). Although PAEs are not as toxic as persistent organic pollutants, their ubiquitous existence poses great threats to the environment and human beings. There was one phthalate pollution incident that DEHP was detected in food additives in Taiwan in 2012. Another incident was that DEHP, DnBP and di-iso-butyl phthalate were detected in a human being’s urine (Yang et al., 2013; Yin et al., 2003). It has been estimated that PAEs in urban soil. Li et al. (2006), Xia et al. (2011), and Zhang et al., 2014b studied the distribution and health risk of PAEs in urban soil in Beijing, China. Zeng et al. (2009) investigated the concentration and sources of PAEs in urban soil in Guangzhou, China. Skrbic et al. (2016) conducted a study on the concentration and human exposure of PAEs in urban soil and street dust in Novi Sad, Serbia. All these study areas are located in humid climates. There is a lack of comprehensive assessment on PAEs in urban soil in semi-arid climates. Xi’an, a typical semi-arid city, is the capital of Shaanxi Province and the largest city in Northwest China. Due to rapid industrialization and urbanization, Xi’an suffers from severe environmental pollution. Therefore, the objectives of this study were to determine the concentration and composition of PAEs in urban soil, identify the distribution and source of the PAEs, and assess the health risk of human exposure to PAEs in urban soil of Xi’an. Such a comprehensive analysis demonstrates a methodology available for worldwide comparative studies on PAEs in urban soil. This study also explored the correlations of PAEs pollution with soil magnetic properties.

2. Materials and methods

2.1. Sample collection and pre-treatment

Xi’an is located on the Guanzhong Plain, which is surrounded by Qinling Mountain in the south and by Loess Plateau in the north. It has an annual air temperature of approximately 13 °C and an annual precipitation of 558–750 mm. It is an important center of economy, education, culture, manufacturing, and high-tech industries in Northwest China. Its urban area spans 1066 km² with an urban population of 5.8 million (XBS and XITNBS, 2014). Sixty-two soil sampling sites were arranged within the third ring road of Xi’an City (Fig. S1), and covered six urban functional districts: industrial areas, traffic areas, mixed commercial and traffic areas, residential areas, educational areas, and parks. At each sampling site, five subsamples (0–20 cm) were collected from the four corners and center of a 2 m × 2 m grid with a stainless steel shovel, and mixed into a composite soil sample of ~1 kg by a quartile method on the spot. Each composite soil sample was stored in a brown glass bottle. All the samples were air-dried in a cool, dark and ventilated place at room temperature (Hu et al., 2003; Li et al., 2006; Liu et al., 2010; Xia et al., 2011; Zhang et al., 2014b). The air-dried topsoil samples were first crushed, then sieved through a 1 mm stainless steel sieve to remove stones, plant debris and other refusals, and stored in brown glass bottles at 4 °C before analysis.

2.2. Analysis of PAEs

PAEs in urban soil were extracted with a Soxhlet extraction apparatus using a mixed solution of n-hexane and acetone (1:1, v:v), purified with a glass chromatography column of silica gel/neutral alumina (2:1, m:m), then separated with a Hypersil ODS2 column (250 mm L × 46 mm I.D., 5 μm, Dalian Elite Analytical Instruments Co., Ltd., China) in a Dionex Ultimate-3000 high performance liquid chromatograph equipped with a diode array detector (HPLC-DAD). The details of extraction, purification, and instrumental analysis as well as quality control and assurance were described in our previous studies (Wang et al., 2015c, 2017a). The process blank experiments showed that only DEHP was detected, though at concentrations lower than the corresponding instrument detection limit (IDL). The IDLs for DMP, DEP, BBP, DnBP, DEHP, and DnOP defined as three times the ratio of signal to noise were 13, 28, 6, 71, 15, and 11 μg L⁻¹, respectively. The method detection limits (MDLs) of DMP, DEP, BBP, DnBP, DEHP and DnOP were 1.6, 3.5, 0.8, 8.9, 19, and 1.4 μg kg⁻¹, respectively. The recovery of a surrogate