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# Occurrence and distribution of organophosphate esters in urban soils of the subtropical city, Guangzhou, China

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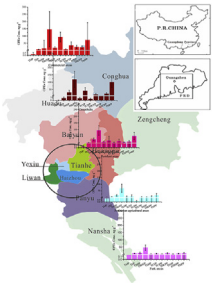
## HIGHLIGHTS

- The OPEs were widely detected in the urban soil.
- TBOEP was the most abundant OPEs.
- The spatial distribution of OPEs was site-specific.
- Human activities influence the distribution of OPEs in the urban soils.

## GRAPHICAL ABSTRACT

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## ABSTRACT

67 soil samples from the road greenbelts, the paddy/vegetable fields, the parks, the commercial and residential areas in the subtropical city, Guangzhou, China, were collected and analyzed for 11 organophosphate esters (OPEs) and triphenylphosphine oxide (TPPO). OPEs were detected in all soil samples analyzed, which indicate that OPEs are ubiquitous environmental contaminants. The $\sum_{11}$OPEs concentrations ranged from 0.041 mg $kg^{-1}$-dry weight (dw) to 1.37 mg $kg^{-1}$-dw, with the mean and median concentrations of 0.25 mg $kg^{-1}$-dw and 0.24 mg $kg^{-1}$-dw, respectively. High concentrations of OPEs were observed in the roadside soils collected from the commercial areas with heavy traffic and extensive anthropogenic activities. Of 11 OPEs, tris(2-butoxyethyl) phosphate (TBOEP), tri-cresyl-phosphate (TMPP), tributyl phosphate (TNBP) and tris(2-chloroethyl) phosphate (TCEP) were the most abundant OPEs, contributing 42.8 ± 15.4%, 17.2 ± 11.9%, 10.9 ± 6.85% and 9.70 ± 9.56% of $\sum_{11}$OPEs, respectively. Principal component analysis (PCA) suggested that OPEs accumulation in the urban soils derived from different sources. As compared to the results for other studies, the urban soils of Guangzhou were moderately polluted by OPEs.



## 1. Introduction

Organophosphate esters (OPEs) are a class of manufactured chemicals widely used as flame retardants (FRs) in industrial and household products. In addition, some OPEs, mainly the nonhalogenated alkyl OPEs, are used as plasticizers, as well as antifoaming agents in lacquers, hydraulic fluids, and floor polishes (van der Veen and de Boer, 2012; Wei et al., 2015). With the bans and restrictions of polybrominated diphenyl ethers (PBDEs), the global consumption of OPEs has increased sharply in recent years (Stapleton et al., 2014; Sühring et al., 2016). In most cases, OPEs are used as additives

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**Table 1**
Summary of the concentrations of OPEs (mg kg$^{-1}$-dw) in urban soils of the tropical city, Guangzhou, China.

| OPEs | Parks areas (n = 11) | | | | Paddy/vegetable fields (n = 13) | | | |
|---|---|---|---|---|---|---|---|---|
| | Min-Max mg kg$^{-1}$ | Mean ± SD mg kg$^{-1}$ | Median mg kg$^{-1}$ | Fr* (%) | Min-Max mg kg$^{-1}$ | Mean ± SD mg kg$^{-1}$ | Median mg kg$^{-1}$ | Fr* (%) |
| TMP | nd*-0.002 | 0.0002 ± 0.0005 | 0.001 | 18.2 | nd* −0.005 | 0.001 ± 0.001 | 0.002 | 38.5 |
| TEP | 0.004–0.011 | 0.006 ± 0.002 | 0.005 | 100 | 0.001–0.007 | 0.004 ± 0.002 | 0.004 | 100 |
| TNBP | 0.002–0.023 | 0.009 ± 0.007 | 0.010 | 100 | 0.002–0.025 | 0.015 ± 0.007 | 0.014 | 100 |
| TBOEP | 0.013–0.067 | 0.046 ± 0.018 | 0.054 | 100 | 0.017–0.114 | 0.069 ± 0.031 | 0.068 | 100 |
| TEHP | 0.001–0.007 | 0.002 ± 0.002 | 0.001 | 100 | nd* −0.015 | 0.004 ± 0.006 | 0.003 | 61.5 |
| TCEP | 0.003–0.008 | 0.004 ± 0.002 | 0.004 | 100 | nd* −0.047 | 0.006 ± 0.013 | 0.003 | 53.8 |
| TCIPP | 0.0002–0.003 | 0.002 ± 0.001 | 0.001 | 100 | nd* −0.001 | 0.0001 ± 0.0002 | 0.0002 | 50.7 |
| TDCIPP | 0.002–0.015 | 0.007 ± 0.004 | 0.005 | 100 | nd* −0.011 | 0.002 ± 0.003 | 0.003 | 38.5 |
| TPHP | 0.0004–0.004 | 0.002 ± 0.001 | 0.002 | 100 | 0.001–0.005 | 0.002 ± 0.002 | 0.001 | 100 |
| EHDPP | 0.002–0.009 | 0.005 ± 0.002 | 0.004 | 100 | nd* −0.022 | 0.005 ± 0.006 | 0.003 | 84.6 |
| TMPP | nd*-0.019 | 0.006 ± 0.007 | 0.012 | 45.5 | nd* −0.048 | 0.014 ± 0.015 | 0.013 | 76.9 |
| Alkyl-OPEs | 0.027–0.095 | 0.062 ± 0.023 | 0.061 | 100 | 0.036–0.137 | 0.092 ± 0.035 | 0.089 | 100 |
| Cl-OPEs | 0.008–0.025 | 0.013 ± 0.005 | 0.010 | 100 | nd* −0.054 | 0.008 ± 0.015 | 0.002 | 100 |
| Aryl-OPEs | 0.003–0.030 | 0.016 ± 0.010 | 0.012 | 100 | 0.003–0.074 | 0.021 ± 0.020 | 0.014 | 100 |
| $\sum_{11}$OPEs | 0.041–0.15 | 0.087 ± 0.034 | 0.075 | 100 | 0.063–0.25 | 0.12 ± 0.054 | 0.11 | 100 |
| TPPO | 0.0003–0.004 | 0.001 ± 0.001 | 0.001 | 100 | nd*-0.006 | 0.002 ± 0.002 | 0.002 | 84.6 |

*nd: Concentration was lower than the MDL. Fr: frequency of detection (%).

that are just mixed and not chemically bonded to the polymer matrix. OPEs could therefore be slowly released into the ambient environment by volatilization, leaching and abrasion (van der Veen and de Boer, 2012; Wei et al., 2015). Widespread use of OPEs-added electronic devices and commercial products have led that elevated levels of OPEs are ubiquitous in urban environmental matrices (Abdallah and Covaci, 2014; Cao et al., 2014; Li et al., 2014; Yang et al., 2014; Kucharska et al., 2015; Ding et al., 2016a,b; Gao et al., 2016; Wu et al., 2016). Additionally, potential adverse effects of OPEs to the ecosystem and human health have also been reported (WHO, 1998, 2000; Meeker and Stapleton, 2010; van der Veen and de Boer, 2012; Araki et al., 2014; Hou et al., 2016). For instance, tri-*n*-butyl phosphate (TNBP), triphenyl phosphate (TPHP), and tris (2-chloroethyl) phosphate (TCEP) showed neurotoxic properties after chronic exposure (van der Veen and de Boer, 2012; Araki et al., 2014). TCEP, tris (1-chloro-2-propyl) phosphate (TCIPP) and tris (1,3-dichloro-2-propyl) phosphate (TDCIPP) are suspected to be carcinogenic (WHO, 1998, 2000; Hou et al., 2016). Moreover, TDCIPP and TPHP levels in house dust were associated with the altered hormone levels and decrease of semen quality (Meeker and Stapleton, 2010). Nowadays, the occurrence, fate and potential for ecological effect of OPEs in the urban environment have raised a global concern (Abdallah and Covaci, 2014; Cao et al., 2014; Li et al., 2014; Yang et al., 2014; Kucharska et al., 2015; Ding et al., 2016a,b; Gao et al., 2016; Hammel et al., 2016; Luo et al., 2016; Wu et al., 2016).

Soil, comprising of mainly mineral particles and organic matter, is the major terrestrial environmental reservoir and one of the major sinks for hydrophobic organic compounds such as OPEs (van der Veen and de Boer, 2012; Wei et al., 2015). However, limited data is available of OPEs in urban soil (Fries and Mihajlović, 2011; Mihajlović et al., 2011; Mihajlović and Fries, 2012), especially in China, which produced more than 70,000 tons of OPEs in 2007 and was projected to increase 15% annually (Hammel et al., 2016). Guangzhou, a mega-city in South China, is located at the center of the Pearl River Delta region, with a population of over 10 million and an area of 7545 km$^2$. It is one of the most prosperous city of China, and many previous studies conducted in this region revealed the extensive contamination of FRs, including PBDEs, decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), bis(hexachlorocyclopentadieno) cyclooctane (DP) and chlorinated paraffins (CPs) in the environment and biota due to the rapid industrialization and urbanization (Deng et al., 2007; Guo et al., 2014; Zeng et al., 2014a,b; Wang et al., 2015a,b; Zheng et al., 2015; Ding et al., 2016a,b; Huang et al., 2016). High atmospheric particle-bound OPEs concentrations had been reported, implying existence of outdoor OPEs sources (Luo et al., 2016). The aims of the present study were to investigate the contamination levels of OPEs in soil, to obtain information on the spatial distribution, congener profiles and the potential sources.

## 2. Materials and methods

### 2.1. Chemicals and materials

Trimethyl phosphate (TMP, CAS no. 512-56-1), triethyl phosphate (TEP, CAS no. 78-40-0), TNBP (CAS no. 126-73-8), tris(2-butoxyethyl) phosphate (TBOEP, CAS no. 78-51-3), tri(2-ethylhexyl) phosphate (TEHP, CAS no. 78-42-2), trihexyl phosphate (THP, CAS no. 2528-39-4), tricresyl phosphate (TMPP, CAS no. 1330-78-5) (mix of isomers), TPHP (CAS no. 115-86-6), triphenylphosphine oxide (TPPO, CAS no. 791-28-6) were purchased from Sigma-Aldrich (St. Louis, USA). TCEP (CAS no. 115-96-8), TCIPP (CAS no. 13674-84-5), TDCIPP (CAS no. 13674-87-8) and 2-ethylhexyl diphenyl phosphate (EHDPP, CAS no. 1241-94-7) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). TNBP-$d_{27}$ and TPHP-$d_{15}$ were purchased from Cambridge Isotope Laboratories (Andover, USA). Acetone (Ace), dichloromethane (DCM), ethyl acetate (EtAc) and *n*-hexane (n-Hex) were of HPLC-grade and purchased from Fisher Scientific (Waltham, USA). All other organic solvents used were of analytical grade and redistilled using a glass system. Silica gel (60–200 μm) was purchased from Merck (Darmstadt, Germany). Neutral alumina (63–200 μm) was purchased from Sigma-Aldrich (St. Louis, USA). Silica gel and alumina were extracted with DCM and n-Hex, activated at 180 ± 1 °C, 250 ± 1 °C and 300 ± 1 °C for 12 h, and deactivated with deionized water, respectively. Sodium sulfate was baked at 420 °C for 12 h and stored in sealed glass containers. Water was obtained from a Milli-Q purification system (Millipore Corporation, Billerica, MA, USA) and then was double distilled. Laboratory glassware was soaked overnight in a $K_2Cr_2O_7/H_2SO_4$ solution, washed with tap water and redistilled water, baked at 300 °C for 12 h, and then rinsed with Ace, DCM and Hex.