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# Organophosphate ester (OPEs) flame retardants and plasticizers in air and soil from a highly industrialized city in Turkey



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#### HIGHLIGHTS

#### Organophosphate ester flame retardants and plasticizers (OPEs) were measured in air and soil in Bursa, Turkey.

- Seasonal air patterns differed between total and alkylated versus halogenated and aryl OPEs, with differences among sites
- Annual air concentrations were dominated by alkylated OPEs with lower levels of halogenated and aryl OPEs at all 8 sites.
- OPE levels were similar to or higher than PBDE air levels reported for Turkey and other locations globally.

#### GRAPHICAL ABSTRACT



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### ABSTRACT

Passive air samples were collected at eight sites in Bursa, Turkey during five sampling periods between February-December 2014. Locations encompassed urban, suburban, industrial, rural and background environments. Soil samples (n = 8) were collected at each site during February 2014. Six OPEs were detected in samples: tris(2chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP), triphenyl phosphate (TPHP), tris(2butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), and tris(2-isopropylphenyl) phosphate (T2iPPP). Frequency of detection in air samples was TCPP and TPHP (100%) > TBOEP (88%) > TCEP (85%) > TEHP (78%) > T2iPPP (20%). Total OPEs in air per site by sampling period (excluding non-detects) ranged from 529 to 19,139 pg/m<sup>3</sup>. In soil, total OPEs ranged from 38 to 468 ng/g dw. In air, alkylated OPEs dominated followed by halogenated and aryl OPEs. In air, annual mean concentrations were TBOEP > TCPP > TPHP > T2iPPP > TEHP > TCEP. In soils, alkylated OPEs were dominant at six sites and chlorinated OPEs at two sites. A comparison of OPE profiles between air and soil suggests that soils may be partly a source of OPEs to air. Mean concentrations in air were not directly proportional to temperature, and there were differences between alkylated compared to halogenated and aryl OPEs. In air, total and alkylated OPEs levels were fairly uniform, whereas more variability was found for the halogenated and aryl compounds. The relative contribution to total OPEs decreases for alkylated OPEs and increases for halogenated OPEs in samples going from background to suburban to urban and industrial sites. Levels of individual OPEs were all positively correlated between air and soils. In air,

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correlations between individual compounds were weak to moderate and were only statistically significant for TBOEP and TPHP. In soils, correlations were generally stronger and statistically significant only for TPHP and T2iPPP

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#### 1. Introduction

Flame retardants are chemicals that are added to many consumer products such as plastics, electronics, textiles, foams for furniture, automobile interiors and many others. The most widely used flame retardants have been polybrominated diphenyl ethers (PBDEs) until commercial mixtures of these chemicals were banned, and then alternative chemicals including organophosphate flame retardants (OPEs) and non-PBDE brominated new flame retardants (NBFRs) became available as replacements.

OPEs are used as flame retardants and plasticizers in a variety of consumer and industrial products such as plastics, electronic equipment, furniture, textiles and building materials and plasticizers and antifoaming agent in various products such as lacquers, hydraulic fluids and floor polishes (Van der Veen and de Boer, 2012; Marklund et al., 2003, 2005; Reemtsma et al., 2008; Abdallah and Covaci, 2014). In 2013, the market volume of OPEs usage as flame retardant was approximately 620 kt, accounting for 30% of the global total (China Market Research Reports, 2016). Generally, halogenated OPEs are FRs (for example TCPP is added to spray foam insulation and TDCPP to polyurethane foam) whereas aryl and alkylated OPEs are plasticizers, although there are some compounds used for both (for example, TPhP is a plasticizer but is also a component of FireMaster 550).

OPEs were reported in river water, seawater and sediment (Tachikawa et al., 1975; Meijers and van der Leer, 1976; Sheldon and Hites, 1978) as early as 1970s. Although OPEs have been widely used for decades, after some studies in the 1980s indicated that these chemicals degrade quickly in the environment interest waned. Studies on environmental samples such as ambient air (Salamova et al., 2014a; Luo et al., 2016), biota (Muir et al., 1980; Greaves et al., 2016; Guo et al., 2017); freshwater ecosystems (Iqbal et al., 2017); precipitation (Laniewski et al., 1998; Regnery and Püttmann, 2009; Regnery and Püttmann, 2010), indoor air and dust (Ceguier et al., 2014; Hoffman et al., 2015; Tajima et al., 2014); remote arctic air (Salamova et al., 2014b; Sühring et al., 2016), food stuff (Poma et al., 2017) as well as human blood, breast milk and urine (Kim et al., 2014; Zhao et al., 2016; Carignan et al., 2013; Sundkvist et al., 2010; Van den Eede et al., 2015) reported the presence and occurrence of these chemicals, including their metabolites. Hoffman et al. (2017) also showed an increasing exposure trend to some OPEs based on urinary metabolite concentrations (Hoffman et al., 2017).

OPEs have been found in air in remote locations, indicating they are subject to long-range transport (Möller et al., 2011; Möller et al., 2012; Salamova et al., 2014b; Hallanger et al., 2015; Sühring et al., 2016). McPherson et al. (2004) point out that human and environmental impacts of the phosphate flame retardants (PFRs) cannot be ignored and Van der Veen and de Boer (2012) note there is evidence that some OPEs pose adverse biological effects, including in humans (e.g. hemolytic and reproductive effects of TCP and TCEP). There is now increased interest in understanding their environmental fate and transport (Greaves and Letcher, 2017).

It has been reported that flame retardants were not produced in Turkey (NIP, 2014; Yilmaz Civan, 2016). In Turkey, there are few studies on FRs in environmental compartments, and most focus on PBDEs. In homes and offices in the Istanbul area, levels of  $\Sigma_{12} \text{NBFRs}$  (Kurt-Karakus et al., 2017) in indoor air ranged from 0.180–42.4 ng/m³, in indoor dust from 0.320–97.9 ng/g and in outdoor air from 0.720–2.80 ng/m³; and levels of  $\Sigma_{13} \text{OPEs}$  in indoor dust ranged from 1.45–17.3 ng/g (Kurt-Karakus et al., 2014, 2015). To the best knowledge

of the authors, there are no other studies on the organophosphate flame retardants in Turkish outdoor environmental compartments. This highlights the need to understand the levels, sources, and movement of flame retardants in the Turkish environment. As a developing and industrializing country, it is to be expected that there are significant levels of alternative flame retardants in the environment of Turkey. Therefore, the main aims of this work are a) to determine levels of OPEs in air and soil, b) to assess spatial/temporal differences in air concentrations, c) to assess potential source areas of OPEs in Bursa, an industrial city in Turkey.

#### 2. Materials and methods

#### 2.1. Sampling locations

Target OPEs were analyzed in air and soil samples from 8 sites in and near Bursa (Fig. 1). Bursa is the fourth biggest city of Turkey based on the 2015–2016 address-based population registration (2,901,396 people) of the Turkish Statistical Institute (TUIK, 2017) and the fifth biggest city of the country based on economic and social development index (Gul and Cevik, 2015). Detailed information on industrial zones and types of industries existing in the city is given elsewhere (Birgul et al., 2017) and in Fig. S4. Briefly, industrial production in Bursa has been focused on the textile, automotive, automotive spare parts, ready-to-wear garments, machinery and metal industries, dry-fresh and frozen foods, agriculture and service sectors. Besides the main automotive, textile/upholstery and furniture industry in Bursa, there are several sideindustries providing spare parts, interior design parts and fabrics as well as seats for automotive manufacturers. Air sampling sites were selected to be representative of the local/regional environment, but away from direct sources. The sampling sites were located in rural/background (Mount Uludag (MU)), urban (Bursa Technical University Osmangazi Campus (BTU) and Hamitler Area (HMT)), semiurban (Uludag University Campus (UUC) and Camlica Area (CAM)), industrial (Kestel Organised Industrial District (KOID) and Demirtas Organised Industrial District (DOID)) and agricultural (Ağaköy Village (AGK)) areas. Further details regarding the sampling sites are given in Supplemental Table S1. Soils were collected at each site on the day of first deployment of passive air samplers.

#### 2.2. Sampling methods

#### 2.2.1. Passive air sampling

Passive air samples were collected using a polyurethane foam disk (PUF-PAS) housed in the well characterize double sheltered assembly (Shoeib and Harner, 2002; Harner et al., 2004) which has been used in many field investigations for a variety of semivolatile organic pollutants (Wong et al., 2010, 2009; Jaward et al., 2004; Motelay-Massei et al., 2005; Gouin et al., 2005; Pozo et al., 2004) including OPEs (Abdollahi et al., 2017). These were PUF-PAS disks (5 ½ "Dia  $\times$  ½" Thick Foam Pad (FR-Free), Tisch Environmental Inc., USA) suspended inside two stainless steel bowls, the upper inverted one being slightly larger to allow airflow between the two bowls (Harner et al., 2004. PUF-PAS were washed with water, Soxhlet extracted sequentially for 16-24 h with acetone, 1:1 acetone: hexane, and hexane, and dried in a vacuum desiccator. Cleaned PUF-PAS were stored in amber jars in a freezer. All glassware used was baked at 450 °C and solvent-washed immediately prior to use. Samplers were exposed at each of the eight sites for five sampling periods between February and December 2014, the samplers

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