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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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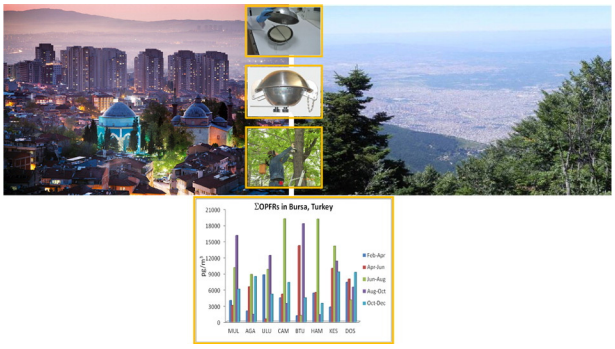
HIGHLIGHTS

- 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(2-chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP), triphenyl phosphate (TPHP), tris(2-butoxyethyl) 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^3. 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 (Cequier 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 Σ_{12}NBFRs (Kurt-Karakus et al., 2017) in indoor air ranged from 0.180–42.4 ng/m^3, in indoor dust from 0.320–97.9 ng/g and in outdoor air from 0.720–2.80 ng/m^3; and levels of Σ_{13}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 side-industries 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 × 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

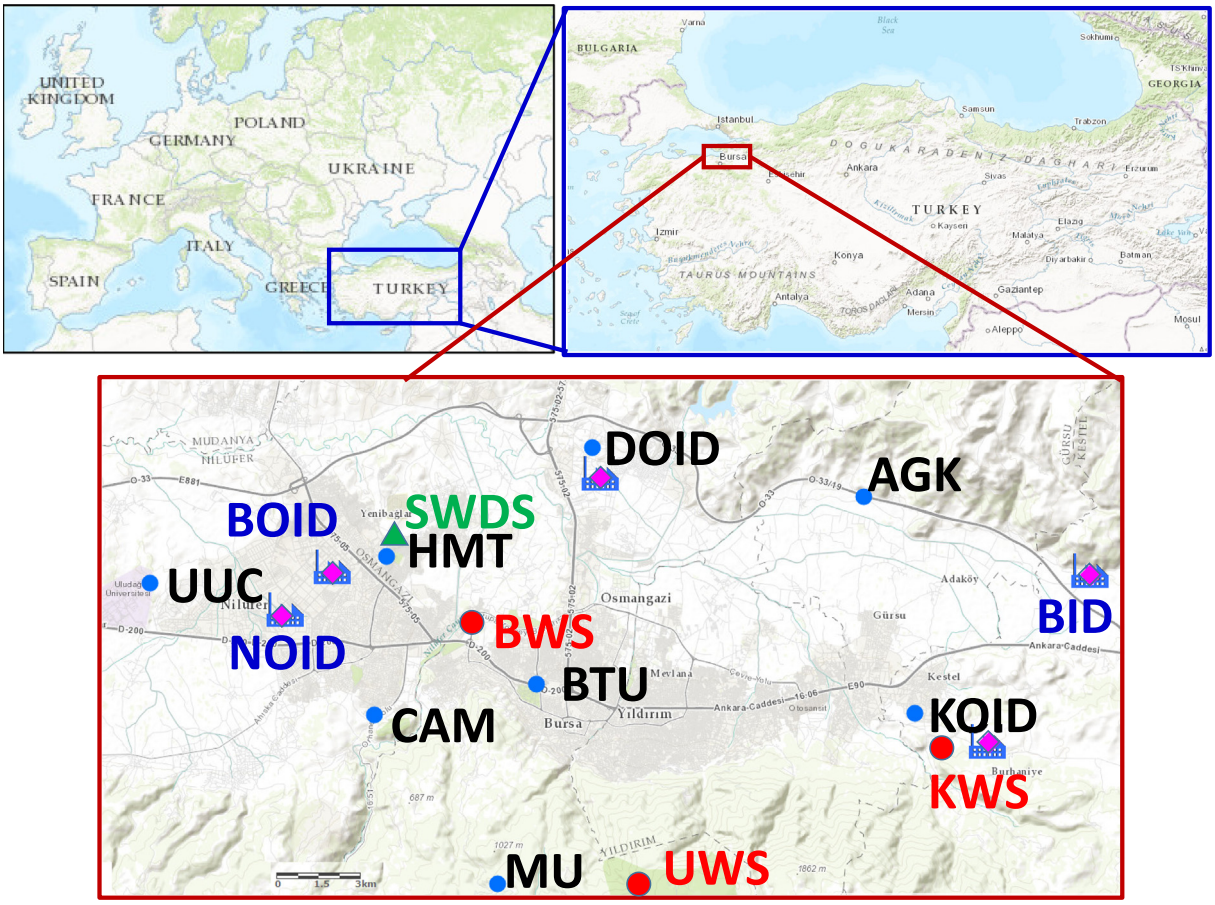

Fig. 1. Sampling sites (blue dots), weather forecast/monitoring stations (red dots; BWS: Bursa Weather Forecasting Station; KWS: Kestel Weather Forecasting Station; UWS: Uludag Weather Forecasting Station), organised industrial districts (pink diamonds; BOID: Bursa Organised Industrial District, NOID: Nilufer Organised Industrial District, BID: Barakfakih Organised Industrial District, KOID: Kestel Organised Industrial District, DOID: Demirtas Organised Industrial District) and Bursa city solid waste disposal site (SWDS; green triangle).

were exposed for about the same amount of days at each site per period and ranged from 43 to 75 days per sampling period, for a total of 40 samples (see Table 1).

PUF-PAS were spiked with a depuration chemicals mixture consisting of three PCB congeners not found in technical mixtures (PCB-34, 62 and 204) at least 3 days prior to deployment. Air volumes for passive sampling were estimated using the depuration rates of these performance reference compounds according to published protocols (Gouin et al., 2005; Pozo et al., 2004; Harner et al., 2004; Shoeib and Harner, 2002) and using the template provided by GAPS Network (Harner, 2016; Parnis et al., 2016) for calculations. A recent PUF-PAS calibration study for OPEs (Abdollahi et al., 2017) showed that these compounds did not reach equilibrium over the first 90 days which is much longer than our deployment period. Sampling rates for individual events were used to derive total air volumes; these rates ranged from 3.33 to 11.15 $m^3\ d^{-1}$ with a mean of 6.21 ± 1.69 $m^3\ d^{-1}$. Abdollahi et al. (2017) reported PUF-PAS sampling rate (m^3/day) for selected OPEs to be between 2.2 and 6.1 m^3/day. Final concentrations were calculated by dividing total amounts of chemicals accumulated in the sampler by the air volumes during the sampling period.

2.2.2. Soil sampling

Surface soil was collected at each of the air sampling sites on the day of first deployment of PUF-PAS. For this purpose, the closest feasible site for soil collection was identified and 3–5 samples of bare soil (plant material discarded) were collected with a metal trowel from the surface to 5–10 cm. These were pooled and sieved through a 2-mm stainless steel mesh to provide one homogeneous composite sample for that site. This resulted in a total of 8 pooled soil samples representing each of the sampling sites. For each pooled sample, several subsamples were dried at 105 °C for moisture (ASTM, 2000a) content determination and the percent organic carbon was determined by ignition loss on combustion at 440 °C (ASTM, 2000b).

2.3. Chemical analysis

2.3.1. Sources of chemicals

Solvents and reagents used were chromatographic or analytical quality and purchased from Merck (Merck EMD Millipore, USA). Previously used abbreviations (PUAB) and practical abbreviations (PRAB) (Bergman et al., 2012) of chemicals of interest are shown in SI Table 2. PRABs of labeled or deuterated chemicals are given in bolded in parenthesis and only PRABs have been used in the main text of the current study. Tricresyl phosphate (TMPP), triphenyl phosphate (TPHP), tris(1-chloro-2-propyl) phosphate (TCPP = tris(1-chloro-2-propyl) phosphate (TCIPP) + Bis(2-chloro-1-methylethyl) (2-chloropropyl) phosphate), Tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl) phosphate (TCEP), Tris(2-ethylhexyl) phosphate (TEHP) and tris(2-isopropylphenyl) phosphate (T2IPPP) were purchased from Wellington Laboratories Guelph, Ontario, Canada). Labeled recovery surrogate chemicals (d_{27}- tris butyl phosphate (TBP or TNBP,), d_{21}- tris propyl phosphate (TPrP or TPP,), d_{12}- tris chloroethyl phosphate (TCEP), [$^{13}C_{18}$]- tris phenyl phosphate (TPhP or TPHP;), [$^{13}C_2$]- tris(2-butoxyethyl) phosphate (TBEP or TBOEP) and [$^{13}C_{12}$]-PCB105 (internal standard)) were obtained from Cambridge Isotope Laboratories (Andover, MA, U.S.A.). Supelclean™ ENVI™-Florisil®

Table 1
Concentrations of OPEs in air (pg/m^3): background site: MU; rural/agricultural: AGK; suburban: UUC, CAM; urban: BTU, HMT; industrial: KOID, DOID.

	Sampling	Deployment								Total	alkylated	halogenated	aryl
Site	Phase	time (days)	TCEP	TCPP	TPHP	TBOEP	TEHP	T2iPPP	TDCPP	ΣOPEs	ΣOPEs	ΣOPEs	ΣOPEs
MU	Phase 1[a]	66	45	114	77	3601	62	74	BD	3973	3663	159	152
AGK	Phase 1	65	125	1213	173	BD	340	113	BD	1963	340	1338	285
UUC	Phase 1	65	102	452	173	7726	273	BD	BD	8726	7999	554	173
CAM	Phase 1	66	79	530	142	3674	26	BD	BD	4451	3700	609	142
BTU	Phase 1	66	109	770	155	BD	41	BD	BD	1075	41	879	155
HMT	Phase 1	66	143	503	320	4270	101	BD	BD	5336	4371	646	320
KOID	Phase 1	62	37	794	130	1671	63	80	BD	2775	1734	831	211
DOID	Phase 1	65	BD	853	263	5868	222	122	BD	7327	6090	853	384
MU	Phase 2[b]	58	53	100	66	2781	37	BD	BD	3035	2817	152	66
AGK	Phase 2	61	115	180	136	6033	BD	BD	BD	6464	6033	295	136
UUC	Phase 2	60	61	249	113	BD	51	BD	BD	474	51	310	113
CAM	Phase 2	61	BD	292	98	4659	BD	BD	BD	5049	4659	292	98
BTU	Phase 2	62	71	4097	206	9690	86	BD	BD	14,151	9776	4168	206
HMT	Phase 2	61	BD	195	183	4818	BD	192	BD	5387	4818	195	374
KOID	Phase 2	68	BD	730	287	8808	69	BD	BD	9895	8878	730	287
DOID	Phase 2	61	136	851	148	6790	9	BD	BD	7934	6798	987	148
MU	Phase 3[c]	66	73	144	99	9696	BD	BD	BD	10,013	9696	218	99
AGK	Phase 3	65	102	2647	93	5958	11	BD	BD	8810	5969	2749	93
UUC	Phase 3	76	58	196	96	9231	155	BD	BD	9736	9386	254	96
CAM	Phase 3	68	110	810	209	17,820	189	BD	BD	19,139.	18,009	921	209
BTU	Phase 3	67	39	220	54	802	BD	BD	BD	1115	802	259	54
HMT	Phase 3	67	68	855	227	17,921	34	BD	BD	19,104	17,955	923	227
KOID	Phase 3	66	78	214	302	13,432	BD	BD	BD	14,026	13,432	293	302
DOID	Phase 3	65	BD	256	237	3413	112	BD	BD	4019	3525	256	237
MU	Phase 4[d]	64	112	385	147	15,391	23	BD	BD	16,057	15,413	497	147
AGK	Phase 4	64	76	1142	111	BD	9	BD	BD	1339	9	1218	111
UUC	Phase 4	64	BD	528	127	11,553	87	BD	BD	12,294	11,639	528	127
CAM	Phase 4	64	55	169	81	3032	BD	BD	BD	3336	3032	223	81
BTU	Phase 4	64	140	1203	208	16,533	138	BD	BD	18,222	16,671	1343	208
HMT	Phase 4	65	69	1021	168	BD	12	BD	BD	1270	12	1090	168
KOID	Phase 4	64	89	1103	263	9773	55	BD	BD	11,283	9828	1192	263
DOID	Phase 4	64	69	2737	171	3416	53	BD	BD	6446	3468	2806	171
MU	Phase 5[e]	49	78	123	104	5742	8	BD	BD	6054	5749	201	104
AGK	Phase 5	49	84	407	114	7761	BD	BD	BD	8365	7761	490	114
UUC	Phase 5	43	110	808	175	3901	65	88	BD	5146	3966	918	263
CAM	Phase 5	49	61	793	123	6225	BD	64	BD	7266	6225	854	187
BTU	Phase 5	49	124	1332	162	2288	493	85	BD	4484	2781	1456	247
HMT	Phase 5	49	141	1354	202	1674	46	BD	BD	3416	1720	1495	202
KOID	Phase 5	60	107	335	146	8593	77	BD	BD	9258	8671	442	146
DOID	Phase 5	49	128	4918	246	3823	75	BD	BD	9189	3897	5046	245
Annual	Average		90	891	163	7096	97	102		7435	6285	967	184
	Std Dev		31	1034	67	4652	108	41		50,445	4951	1047	82
	Geomean		84	552	150	5670	58	97		5577	3071	644	166
	Median		81	630	152	5958	63	86		6455	5284	688	170
	Range		BD-143	100–4918	54–320	BD-17,921	BD-493	BD-192		474–19,139	9.2–18,009	159–4168	54–303

[a] Feb-Apr.
[b] Apr-Jun.
[c] Jun-Aug.
[d] Aug-Oct.
[e] Oct-Dec.

SPE cartridges with Teflon frits (500 mg/3 mL) were purchased from Sigma Aldrich (St Louis, MO, USA).

2.3.2. Extraction and cleanup of air and soil samples

The PUF-PAS were spiked with surrogate compounds (50 ng each) to monitor recoveries, then Soxhlet extracted for 16 h with 200 mL of 1:1 dichloromethane:hexane. Extracts were concentrated by rotary evaporation and nitrogen blow-down to 1 mL and solvent-exchanged into isooctane.

Table 2
Pearson correlation coefficients for measured OPEs in air.

	TCEP	TCPP	TPHP	TBOEP	TEHP
TCEP	–	0.29	0.27	0.11	0.23
TCPP	0.29	–	0.27	0.04	0.05
TPHP	0.27	0.27	–	***0.32***	0.19
TBOEP	0.11	0.04	***0.32***	–	0.01
TEHP	0.23	0.05	–	0.01	–

Bold, italicized values indicate that the correlation was statistically significant ($p < 0.05$).

Soil samples (30 g wet weight) were mixed with sodium sulfate, spiked with the surrogate mixture and homogenized with a mortar and pestle. The mixture was Soxhlet extracted for 16 h with 1:1 dichloromethane: hexane mixture. Extracts were concentrated and transferred to isooctane by rotary evaporation and nitrogen blow-down to 1 mL.

Cleanup of extracts was done by solid phase extraction (SPE) using Florisil SPE cartridges by a modification of method reported by Van den Eede et al. (2012) and Hoffman et al. (2015). The cartridge was cleaned with 8 mL methanol followed by 4 mL hexane, the sample was added in a 1-mL volume and the cartridge was eluted with 8 mL hexane followed by 10 mL ethyl acetate. Both eluates were combined, volume was reduced to 1 mL on a rotary evaporator and transferred to isooctane by nitrogen blow-down. 50 ng of [$^{13}C_{12}$]-PCB 105 was added as the internal standard.

2.3.3. Quantitative analysis

All analyses were done by gas chromatography-mass selective detector operating in electron impact (GC-EI-MS) using an Agilent 6890

GC-5973 and 5975 Mass Selective Detector (MSD). Quantitative analysis was done on a DB-5 column (J&W, Agilent Technologies, 30 m, 0.25 mm i.d., 0.25 μm film thickness) with an injector temperature of 200 °C. The temperature program was: initial temperature 70 °C (1.0 min hold); 10 °C min^{-1} to 170 °C, hold for 3 min; then 10 °C min^{-1} to 230 °C, hold for 5.0 min; 5 °C min^{-1} to 250 °C, no hold; and 10 °C min^{-1} to 310 °C, hold for 3 min. Samples were injected splitless (2 μL, split opened after 2.0 min). Other instrument conditions were: the helium carrier gas at 1.0 mL min^{-1}transfer line temperature 280 °C, ion source 230 °C and quadrupole 150 °C. Target peaks were accepted if the target/qualifying ion ratio was within 20% of standards.

2.4. Quality assurance/quality control

Instrumental detection limits (IDLs) were estimated by injecting low concentrations of target analytes until a small peak at ~3:1 signal: noise ratio was obtained. These IDLs are expressed in pg g^{-1} (dw) soil and pg m^{-3} air. The latter calculation was done assuming extract volumes of 1.0 mL, air volume of 500 m^3 and 20 g (dw) of soil.

Laboratory blank samples were run every 10 samples for PUF-PAS ($n = 5$) whereas a total of 3 field blank samples were prepared by taking a clean PUF-PAS sample to the field, exposing to the air for approx. 1 min and taking back to the laboratory in a sealed jar. A total of 5 laboratory blank samples were prepared for soils, consisting of pre-cleaned anhydrous sodium sulfate. All blank samples were treated in the same manner as PUF-PAS and soil samples. The limits of detection (LOD) for 500 m^3 of air and 20 g (dw) soil for the target OPEs were calculated as the mean blank + 3 x S.D. LODs in air and soil for target compounds are shown in Table S1. Sample amounts were compared to LODs and IDLs and if a peak was observed for a sample constituent but the quantity was <LOD, one half of the LOD was used for statistical purposes. If no peak was observed for a sample constituent (<IDL), the air or soil concentration was considered zero (nd = not detected).

To check the performance of the entire method and to control recovery rates, passive air samples, blank PUF-PAS and soils were spiked before extraction with the recovery solution described above. Mean recoveries were: d_{27}-TNBP (80–103%), d_{21}-TPP (81–101%), d_{12}-TCEP (85–108%), [$^{13}C_{18}$]-TPHP (84–106%), and [$^{13}C_2$]-TBOEP (65–89%), with RSD all below 10%. Target chemical recovery test was conducted by spiking known amount of target chemicals on a PUF-PAS disk ($n = 3$) and processing for the entire method. Recovery of all target chemicals was >80%.

2.5. Meteorological data

Daily wind direction data for the period between February and November 2014 was obtained from General Directorate of Bursa District Weather Forecast and Monitoring. There were only 3 weather forecast stations, namely Kestel Weather Station (KWS), Bursa Weather Station (BWS) and Uludag Weather Station (UWS) with available data on wind direction. The sampling stations are grouped based on the distances of sampling sites to these weather forecast stations (Fig. S1). We have calculated dominant wind direction for each month of the periods (Fig. S2a, b and c) and for the period of February–November (overall course of the study). Based on overall course of the study dominant wind directions, we prepared Fig. S3 which shows dominant wind direction of the air masses that each sampling station received.

3. Results and discussion

3.1. OPEs in air

Concentrations of OPEs in ambient air at the eight sampling locations for each sampling phase are shown in Table 1. TCEP, TCPP, TPHP, TBOEP, TEHP, and T2iPPP were detected while TDCPP was below detection limit. Frequency of detection was TCPP and TPHP (100%) > TBOEP (88%) > TCEP (85%) > TEHP (78%) > T2iPPP (20%), and concentrations were in the order TBOEP ≫ TCPP > TPHP > TEHP > TCEP. Annual geometric means of concentrations at all sites over all five sampling periods and ranges (excluding non-detects) were (pg/m^3): TBOEP 5670 (802–17,900) > TCPP 552 (100–4900) > TPHP 150 (54–320) > TEHP 58 (9–493) > TCEP 84 (37–143). T2IPPP was detected at the lowest frequency (20%) so the same statistical treatment was not applied to it to calculate an annual average. For the 20% of cases where it was detected, its mean concentration was 102 pg/m^3 and the range for those 8 samples was 64–192 pg/m^3. In terms of percentage of total OPEs, TBOEP was the dominant flame retardant in 34 of 40 individual samples, ranging in those cases from 40% to 96% of the total. When averaged annually per site, the percent of TBOEP relative to total OPEs ranged from 67% (DOID) to 95% (MU) while for TCPP the range was 2.2% (MU) to 28% (DOID). Fig. 2, which shows the annual mean of each OPE per site (based on the concentrations of each of the five sampling phases), illustrates the predominance of TBOEP in the air in the study region.

OPEs can be categorized by whether they are halogenated, alkylated or aryl OPEs. Of the OPEs measured in this study, TCEP and TCPP are halogenated, TBOEP and TEHP are alkylated, and TPHP and T2iPPP are aryl OPEs. OPEs in air at all sites are dominated by the alkylated compounds, with much lower quantities of halogenated and aryl OPEs. Annual average concentrations of alkylated OPEs as a percentage of total OPEs ranged from 68% (DOID) to 95% (MU), for halogenated OPEs the percentage ranged from 3.1% (MU) to 29% (DOID), while for aryl OPEs the range was 1.4% (MU) to 3.7% (HMT). Interestingly, the rural/agricultural site (AGK) which was expected to be similar to the background site had relative contributions more similar to the industrial and urban sites. Our results are different from those of Salamova et al. (2014a) who reported that air concentrations of OPEs were dominated in urban sites by chlorinated OPEs while in rural sites the predominant OPEs were the non-chlorinated ones. In our study, non-chlorinated OPEs were dominant in every type of environment.

Fig. 3 compares the annual median concentrations of OPEs (total and by type) measured in air in this study. Annual median concentrations of total OPEs were fairly uniform and influenced mainly by the alkylated OPEs, namely TBEOP. Interestingly, the annual median of total OPEs at the background site was not the lowest as might be expected and is instead similar to most other sites. The background site, while removed from the city, was at a high elevation. The atmospheric transport of organic pollutants to and deposition in higher elevations has been shown in other locations (Shunthirasingham et al., 2011; LeNoir et al., 1999). Thus, OPEs from the urban and industrial areas of Bursa may be undergoing transport to higher elevations (see discussion below on wind direction). Also, although this site was located away from the city, there is considerable vehicular traffic in the vicinity from people traveling to Mount Uludag skiing area located farther up the mountain. This may also partly account for the high levels at this site. Higher concentrations of OPEs have also been observed in samples from higher elevations, and these have been attributed to higher sampling rates due to higher wind speeds. Wind speeds were not available in this study but the higher concentrations at the background site may be partly due to this. The annual median of total OPEs at the rural/agricultural site (AGK) was likewise similar to, or even higher than, some urban and suburban sites, again indicating the likelihood of input via atmospheric transport from urban and suburban areas.

Concentrations of halogenated and aryl OPEs are not as uniform as the alkylated OPEs. For halogenated OPEs, concentrations were higher at DOID, BTU and AGK compared to the other sites while for aryl OPEs there seems to be a general trend of increasing median concentrations from the background to the industrial sites. *t*-test calculations were carried out to determine if there were statistically significant differences between sites. There were no statistically significant differences ($p > 0.05$) between sites when comparing total OPEs and alkylated OPEs. There were statistically significant differences ($p < 0.05$) for aryl-OPEs only between MU (background site) and HMT (urban), KOID

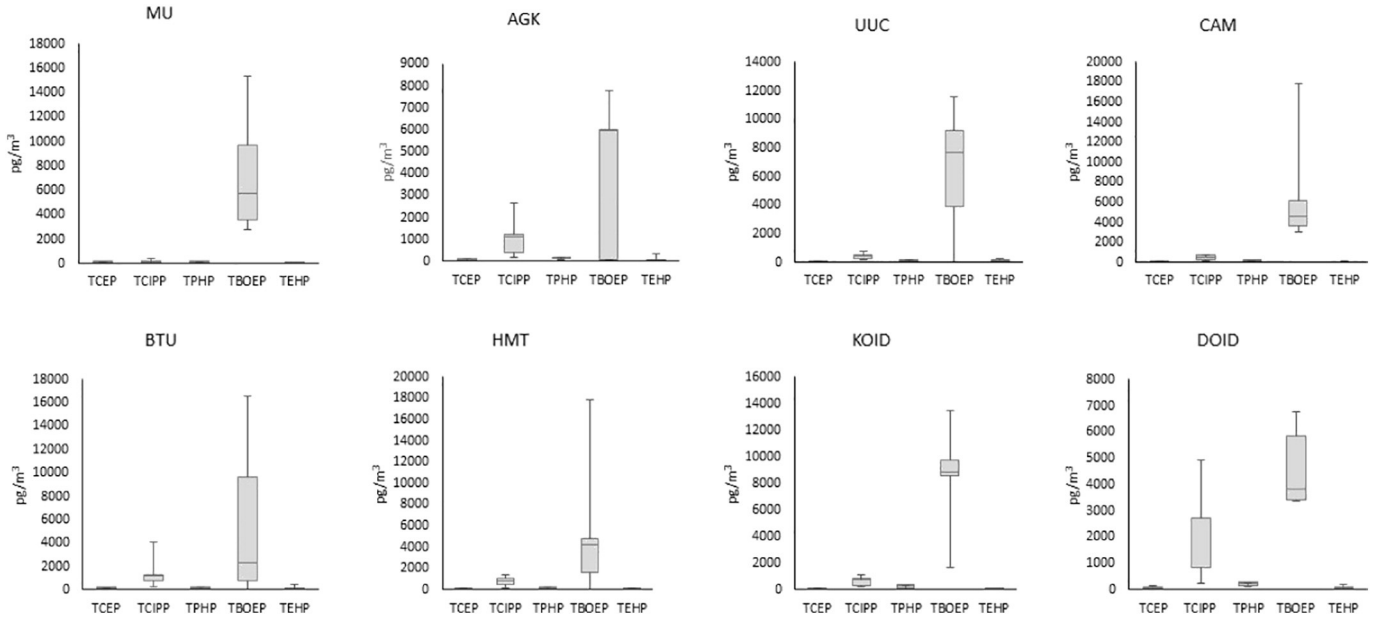

Fig. 2. Annual mean of OPEs in air -the center box is bounded by the quartile 1 and quartile 3, horizontal black line in the box depicts median value, the capped vertical line represents the range of the data (background site: MU; rural/agricultural: AGK; suburban: UUC, CAM; urban: BTU, HMT; industrial: KOID, DOID).

(industrial) and DOID (industrial) and between CAM (suburban) and the same three sites; and for halogenated OPEs between MU and HMT and KOID. This is in agreement with *t*-test calculations carried out to determine if there were any statistically significant differences ($p < 0.05$) in annual concentrations of each individual OPE between sites. This was the case only for TPHP (the dominant aryl-OPE) between the same sites (MU and HMT/KOID/DOID and CAM and HMT/KOID/DOID) and as well as AGK (rural/agricultural) and HMT/KOID/DOID and UUC (suburban) and two of those sites (HMT/DOID); and for TCPP between MU and HMT/KOID.

As noted previously, Bursa is an important industrial centre in Turkey. It has also experienced a major construction boom for many years. Therefore, the OPEs measured in this study are likely due to their use in these activities (construction, automobile and associated industries, textile industry, metallurgy, etc.), some of which are widespread in the Bursa metropolitan area. The similarity in OPE profiles (as indicated by the lack of statistically significant differences between most two-site comparisons) suggests similar sources of these chemicals at all sites. It also suggests the possibility that air circulation patterns in the Bursa region may mix OPEs released by all the sources and make the

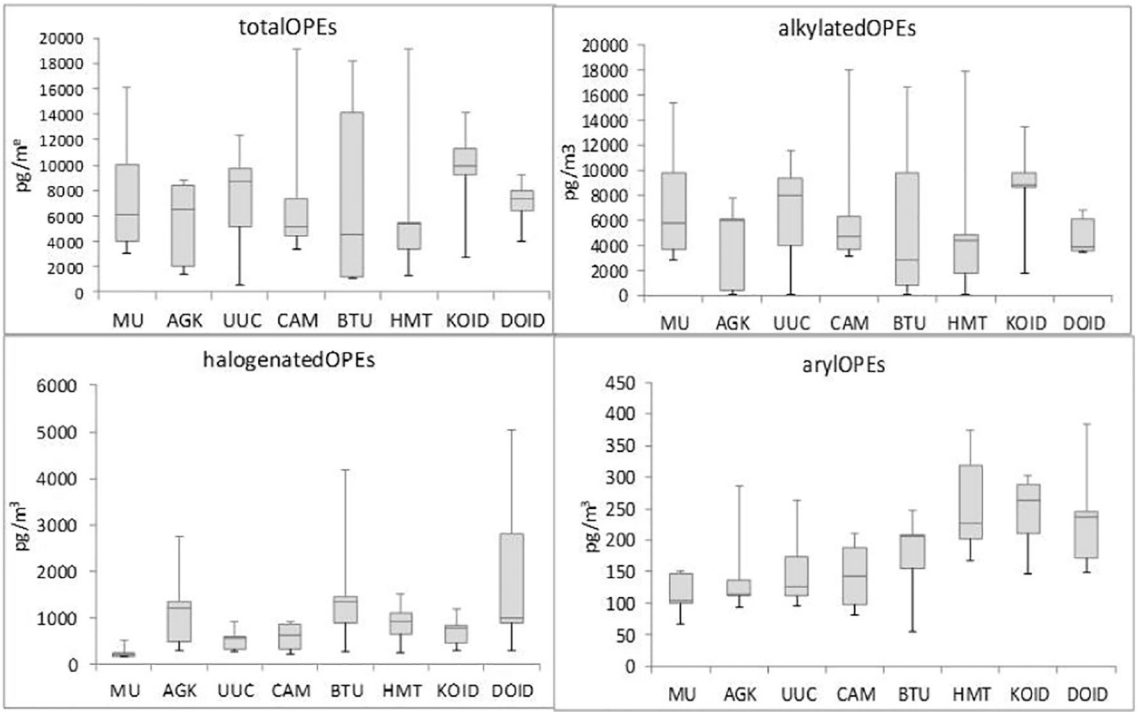

Fig. 3. Comparison of annual averages of OPEs by site - the center box is bounded by the quartile 1 and quartile 3, horizontal black line in the box depicts median value, the capped vertical line represents the range of the data (background: MU; rural/agricultural: AGK;suburban: UUC, CAM; urban: BTU, HMT; industrial: KOID,DOID).

concentrations more homogeneous. The statistically significant difference in levels of TPHP between the industrial sites (KOID and DOID) and one urban site (HMT) and 4 of the other 5 sites (background, agricultural, and suburban) may be due to higher quantities of this OPE being used at industrial and urban areas near to the sampling sites. In general, there is a trend of decreasing levels of TPHP from the industrial sites through the background site, supporting the hypothesis that the industrial and urban sites were close to point sources of aryl OFRs. The statistically significant differences in levels of the chlorinated TCPP between the background site (MU) and the urban HMT and industrial (KOID) may be due to the same factor. The levels of OPEs at the background and rural sites suggest atmospheric transport of these chemicals from sources to the surrounding areas.

As noted above, the high levels of OPEs at the background site may be explained by atmospheric transport from urban and industrial sites. To determine this, wind direction data was obtained from the Bursa District Weather Forecast and Monitoring Office. Only three weather forecast stations had available wind direction data – Kestel Weather Station (KWS), Bursa Weather Station (BWS) and Uludag Weather Station (UWS). Therefore, we grouped the sampling stations based on the distances of sampling sites to these weather forecast stations (Fig. S1). We calculated dominant wind direction for each month of the sampling phases and for the overall February – November period at each of the weather forecast stations (Fig. S2a–c). As seen in Figs. S2a–c and S3, wind direction supports the hypothesis that OPEs undergo atmospheric transport from urban to rural sites (assuming that predominant wind direction at each sampling site is reflected by the predominant wind direction of the nearest weather forecast station). MU, the background sampling site, was affected by winds predominantly from north and north-west. Bursa City and its districts are located north and north-west of MU and could be the source of the elevated levels of OPEs measured at this site. As noted previously, median levels of total OPEs and relative contributions of each type of OPEs at AGK (the rural/agricultural site) were similar to levels at urban and suburban sites. Figs. S2a–c and S3 show that the predominant wind direction at AGK and KOID was from the south-east. KOID is south-east of AGK, indicating that OPEs are likely undergoing atmospheric transport from the former to the latter.

There are relatively few measurements of OPEs in the environment. Salamova et al. (2014a) recently reported values for these compounds in air on the U.S. side of the Great Lakes. Concentrations of ΣOPEs (12 compounds) ranged from 120 ± 18 pg/m^3 to 2100 ± 400 pg/m^3 in airborne particulates collected with high-volume air samplers. These values are lower than the values in Bursa air, which ranged from 451 to 19,139 pg/m^3. Concentrations in Bursa are also higher than those reported by Möller et al. (2012) for airborne particulates over the polar regions (with particulate air concentrations of individual OPEs ranging from 10 pg/m^3–2900 pg/m^3). Ohura et al. (2006) reported a median concentration of TCEP of 9.39 ng/m^3, higher than the values for this compound in Bursa. Mihajlovic and Fries (2012) reported calculated average air levels of TCEP of 5.4 pg/m^3 and TCPP of 990 pg/m^3 in the city centre of Osnabrueck, Germany. In Bursa, the annual average of TCEP was higher at 84 pg/m^3 and the TCPP levels were similar at 888 pg/m^3. Total OPEs measured in air in Bursa are similar to a recent report of OPEs in air measured in ship- and land-based samples from the Canadian Arctic (Sühring et al., 2016).

Salamova et al. (2014a) reported air concentrations of OPEs were dominated in urban sites by chlorinated OPEs while in rural sites the predominant OPEs were the non-chlorinated ones, contrary to our results in which air concentrations are dominated by non-chlorinated OPEs at all sites. Sühring et al. (2016) reported that in both ship- and land-based samples from the Canadian Arctic chlorinated OPEs were dominant in almost all samples and Möller et al. (2012) also reported the predominance of chlorinated OPEs over polar regions, contrary to the results in this study. These differences may be due to differences in usage patterns in Turkey compared to other locations.

3.2. Seasonal variations of OPEs in air

Since there are not large spatial differences, the seasonal patterns were determined using the geometric means (combining all 8 sites) of total, alkylated, halogenated and aryl OPEs concentrations plotted against average temperature of that sampling period. Fig. 4 shows the results. The relationship between concentrations and temperature is not directly proportional. For total OPEs the mean concentrations during the warmer months (April through October) were higher than the colder February–April period, but mean concentration was higher in October–December (average temperature 11.8 °C) than in April–June (average temperature 18.7 °C) and August–October (average temperature 19.5 °C). The pattern for alkylated OPEs was most similar to total OPEs, except for much lower mean concentration of the former in August–October. In the case of halogenated OPEs, mean concentrations were higher during the colder October–December and February–April periods than the warmer April–June and June–August periods; mean concentration during the warmest August–October period was similar to the October–December value. For aryl OPEs the mean concentrations were higher during the colder sampling periods than the warmer periods. Mean concentrations were only significantly different ($p < 0.05$) only between February–April and June–August for total OPEs and alkylated OPEs. Halogenated and aryl OPEs concentrations are not significantly proportional to temperature ($p > 0.05$). These results suggest that emission from sources may not be driven by the vapour pressures of these chemicals. The levels in air may be a factor of quantities of each type used near the sampling sites.

Fig. 5a and b show the seasonal levels of total, alkylated, halogenated, and aryl OPEs at each sampling site. There are clear differences between the sites for all cases. In general, there is more uniformity between the sites for aryl OPEs than for alkylated or halogenated OPEs. For alkylated OPEs, while in general (with the exception of AGK) higher levels were measured in the warmer months, the patterns were markedly different for different sites. Levels of alkylated OPEs were much higher during June–August and August–October at MU; June–August, August–October and February–April at UUC; June–August at CAM and HMT; and April–June and August–October at BTU. At the two industrial sites there was more uniformity. Levels were higher (and similar) during February–April and April–June and lower (and quite uniform) during the three other periods at DOID; at KOID levels were much lower during February–April and fairly uniform during the other months (with the highest levels during June–August). In the case of halogenated OPEs, levels were higher during the warmer months for five sites, with highest levels during August October at MU and KOID, during June–August at AGK and CAM, and April–June at BTU. Levels were higher during the colder months, with highest levels during October–December at HMT, DOID, and UUC (with levels during these months nearly similar to the highest values during June–August at CAM).

3.3. OPEs in soil

Concentrations (in ng/g dw) of total OPEs in soils are shown in Fig. 6. Total OPEs were in the order BTU (468 ng/g) > MU (379 ng/g) > KOID (186 ng/g) > UUC (169 ng/g) > DOID (149 ng/g) > HMT (74 ng/g) > AGK (41 ng/g) > CAM (37 ng/g). The reasons for the high levels of OPEs at the background site are unclear. However, this site, while removed from the city was at a high elevation. As noted previously, OPEs from the urban and industrial areas of Bursa may be undergoing transport to higher elevations. This, coupled with vehicular traffic in the vicinity from people traveling to Mount Uludag skiing area located farther up the mountain may result in deposition and high levels at this site. Table 3 in SI shows the organic carbon content in each soil sample. Levels of OPEs do not correlate with organic carbon content of soils.

Alkylated OPEs were the dominant type at 5 of the 8 sites (MU, UUC, BTU, KOID and DOID), ranging from 88% (KOID) to 97% (MU);

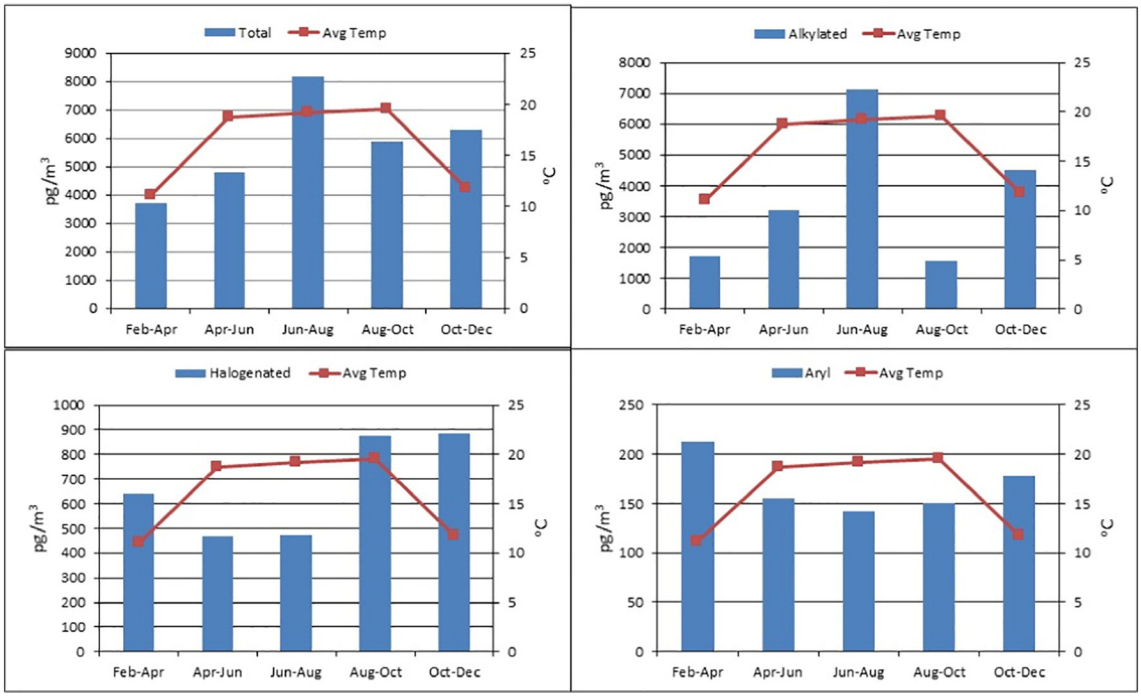

Fig. 4. Comparison of OPEs in air by season.

halogenated OPEs were dominant at 2 sites (87% at HMT and 89% at AGK); and at 1 site (CAM) the two types were approximately equal in relative contribution (45%). It is difficult to explain the difference at these three sites. It may be a reflection of the type of OPEs used in the nearest sources. Halogenated OPEs are generally used to a greater extent as flame retardants compared with alkylated OPEs and the sources nearest these three sites may use these more extensively so their presence in the soils may reflect this. For example, Fig. S4 indicates differences between the two organised industrial areas nearest HMT and CAM (NOID and BOID) compared to the other three (BID, KOID and DOID). In the latter three, the textile industry was the overwhelmingly dominant industry, accounting for over 50%. In NOID and BOID, however, textiles account for <50%, and instead automotive parts, machinery, and metals are significant industries and it is possible that halogenated OPEs are used more extensively in these industries. However, an analysis of the exact type of OPEs used in each type of industry is difficult because these can change based on factors such as availability.

OPEs profiles were compared between soil and air in February – April (since soils were collected at the beginning of this sampling period). They were similar at 5 sites. At MU, UUC, KOID and DOID alkylated OPEs dominated total levels (with relative contributions being alkylated > halogenated > aryl) and at AGK halogenated OPEs were dominant (with relative contributions being halogenated > alkylated > aryl) in both soil and air. At the two urban sites the profiles in air and soil were different: At BTU, relative contributions were halogenated > aryl > alkylated in air but alkylated > halogenated > aryl in soil while at HMT the profile in air was alkylated > halogenated > aryl while in soil it was halogenated > alkylated > aryl. At CAM relative contributions were in the order alkylated > halogenated > aryl while in soil alkylated and halogenated were virtually identical with aryl OPEs contributing less. Similar profiles in soil and air at some sites may indicate similar or the same sources of OPEs at those sites. However, caution must be exercised in interpreting these results since a more comprehensive study would be needed to study the relationship between air and soil levels.

As with outdoor air levels, there are few reported studies of OPEs in soils. Mihajlovic and Fries (2012) reported values ranging from 5.07–23.48 ng/g dw for TCEP and 5.66–19.82 ng/g dw for TCPP in Osnabrueck, Germany. Matsukami et al. (2017) reported values for TCEP, TCPP and TPHP in soils from Bui Dau, Vietnam from three environments (median, range): TCEP - < 2 ng/g dw in rice raddy soil, <2 ng/g dw in soil from an open burning site and 3.2 (3 − 20) ng/g dw in soils from an e-waste workshop site; TCPP - < 4 ng/g dw, <4 ng/g dw and 28 (<4–300) ng/g dw, respectively; and TPHP - < 3 (<3–8) ng/g dw, <3 (3–55) ng/g dw and 720 (9.9–4100) ng/g dw, respectively. In comparison, in Bursa TCEP levels in soils ranged from 1.03–2.30 ng/g dw (median 1.56), TCPP from 7.11–64.08 ng/g dw (median 17.07), and TPHP from 1.63–2.67 ng/g dw (2.07). Thus, soil levels in Bursa are lower for TCEP and higher for TCPP compared to values in Osnabrueck, Germany. Levels of TCEP in this study were similar to the levels in soils from rice paddies and near open burning sites reported for Vietnam; and they were lower than the levels in soils from an e-waste workshop site in Vietnam. Levels of TCPP were higher than the levels in soils from rice paddies and near open burning sites and lower than levels from the e-waste workshop site in Vietnam. Levels of TPHP were similar the levels from rice paddies and lower than levels in soils from open burning sites and the e-waste workshop site in Vietnam.

3.4. Correlation between target analytes

Pearson correlation coefficients were determined to explore the possibility of common sources. The results for air are presented in Table 2. The results indicate weak positive correlations (Pearson coefficients ranging from 0.04 to 0.32) between all OPEs. Correlations were all non-significant ($p > 0.05$) except for that between TPHP and TBOEP ($p < 0.05$). These results suggest that the OPEs measured in air have some common sources, but these are not necessarily the only or dominant sources in most cases. The weak positive correlations may also be due to differences in environmental fates (e.g. differences in rates of degradation and transport properties). The OPEs have a wide range of character travel distances in air, ranging from 41 km for TBOEP and 2739 km for T2iPPP (Sühring et al., 2016), the lack of correlations between OPE compounds may indicate a mixture of local, regional and long-range transport sources.

Pearson correlation coefficients for soils are shown in Table 3. Results indicate positive correlations ranging from weak ($r = 0.01$) to

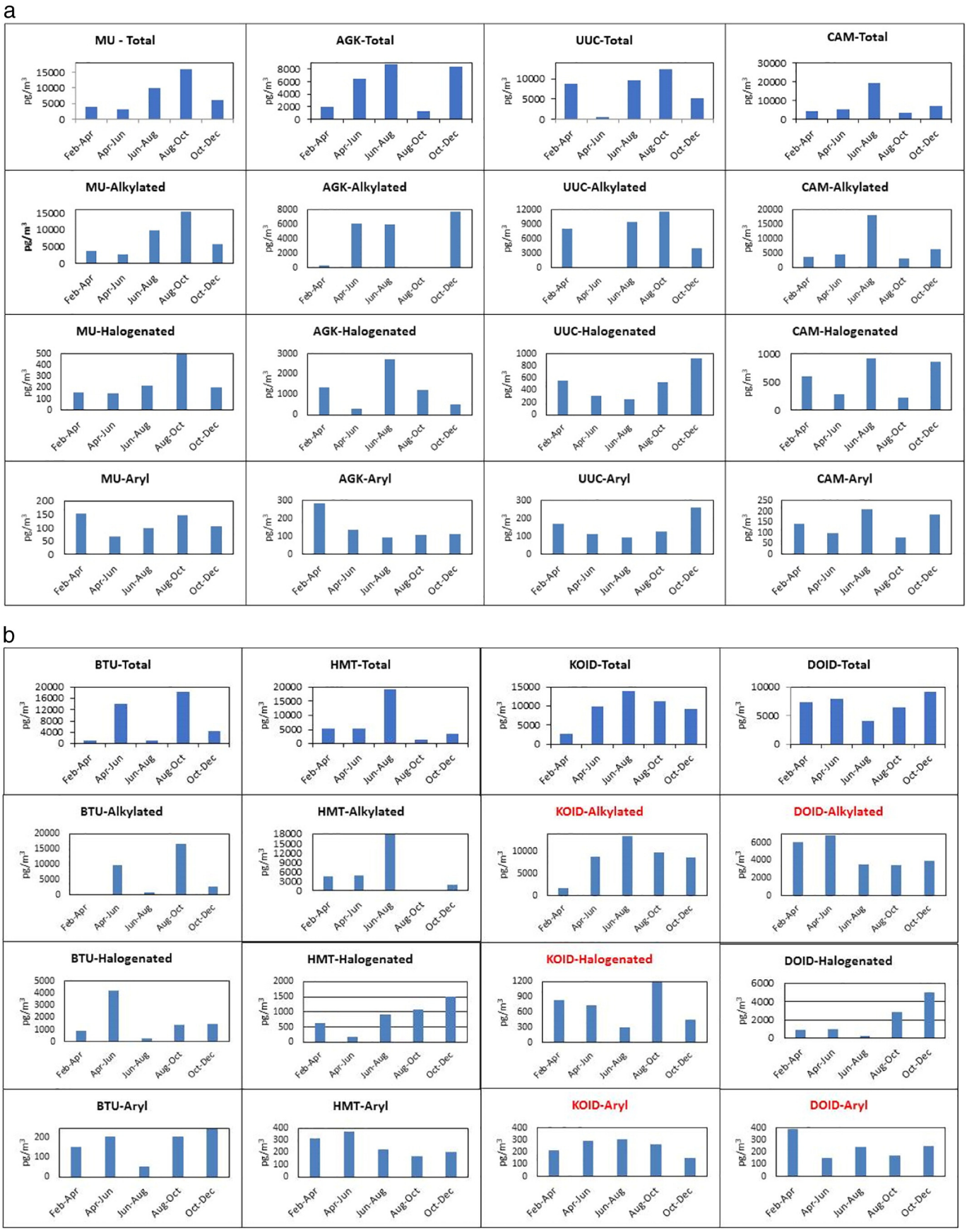

Fig. 5. a,b. Seasonal variation of total OPEs in air at each site.

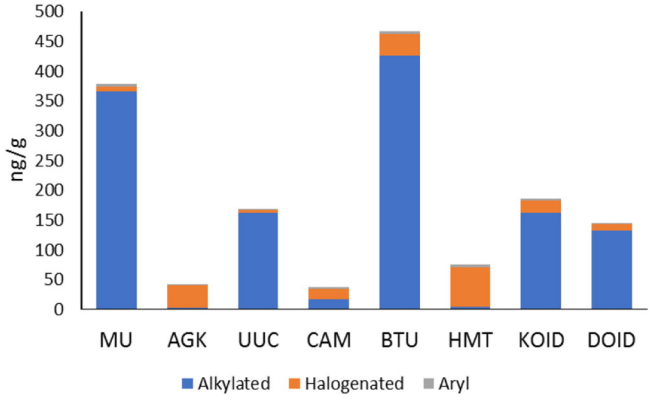

Fig. 6. OPEs in soil.

strong ($r = 0.87$) for all pairs of OPEs tested. Correlations were moderately strong ($r = 0.32$ to $r = 0.61$) between TCEP and TPHP, TBOEP, and T2IPPP; TCPP and TPHP, TBOEP and T2IPPP; and T2IPPP and TBOEP. The correlation was strong ($r = 0.87$) between TPHP and T2IPPP. Only in the case of TPHP and T2IPPP (the aryl OPEs) was the correlation significant ($p < 0.05$). The results suggest that overall, compared with air, the influence of common sources was more important for OPEs in soil.

4. Conclusions

The results of this study indicate ongoing emission of OPEs into ambient air in and around the city of Bursa, Turkey. Levels of OPEs in air measured in this study were generally similar or higher than concentrations of PBDEs in ambient air in different regions of the world, including the UK, Europe, the U.S., Asia and Canada. Compared to levels of PBDEs in air reported for Turkey, the levels of OPEs measured in this study are much higher. This suggests that the use of OPEs as replacements for PBDEs has been significant in Turkey. Levels and profiles in this study indicate that OPEs are undergoing regional transport, including to background areas as indicated by the fact that concentrations in air and soils in the background site were not the lowest. The results indicate that further studies are needed to examine the cycling of OPEs in the environment of Turkey.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.12.307.

Table 3
Pearson correlation coefficients for measured OPEs in soil.

	TCEP	TCPP	TPHP	TBOEP	TEHP	T2IPPP
TCEP	–	0.06	0.61	0.56	0.07	0.59
TCPP	0.06	–	0.32	0.32	0.01	0.49
TPHP	0.61	0.32	–	0.05	0.07	***0.87***
TBOEP	0.56	0.32	0.05	–	0.21	0.45
TEHP	0.07	0.01	0.07	0.21	–	0.03
T2IPPP	0.59	0.49	***0.87***	0.45	0.03	–

Bold, italicized values indicate that the correlation was statistically significant ($p < 0.05$).

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