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POPs in a major conurbation in Turkey: ambient air concentrations, seasonal variation, inhalation and dermal exposure, and associated carcinogenic risks

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Abstract Semi-volatile organic compounds were monitored over a whole year, by collection of gas and particle phases every sixth day at a suburban site in Izmir, Turkey. Annual mean concentrations of 32 polychlorinated biphenyls ($\sum_{32}$PCBs) and 14 polycyclic aromatic hydrocarbons ($\sum_{14}$PAHs) were 348 pg/m^3 and 36 ng/m^3, respectively, while it was 273 pg/m^3 for endosulfan, the dominant compound among 23 organochlorine pesticides (OCPs). Monte Carlo simulation was applied to the USEPA exposure-risk models for the estimation of the population exposure and carcinogenic risk probability distributions for heating and non-heating periods. The estimated population risks associated with dermal contact and inhalation routes to $\sum_{32}$PCBs, $\sum_{14}$PAHs, and some of the targeted OCPs (α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), heptachlor, heptachlor epoxide, α-chlordane (α-CHL), γ-chlordane (γ-CHL), and p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT)) were in the ranges of 1.86×10^{-16}–7.29×10^{-9} and 1.38×10^{-10}–4.07×10^{-6}, respectively. The inhalation 95th percentile risks for $\sum_{32}$PCBs, $\sum_{14}$PAHs, and OCPs were about 6, 3, and 4–7 orders of magnitude higher than those of dermal route, respectively. The 95th percentile inhalation risk for $\sum_{32}$PCBs and OCPs in the non-heating period were 1.8- and 1.2–4.6 folds higher than in the heating period, respectively. In contrast, the 95th percentile risk levels for $\sum_{14}$PAHs in the heating period were 4.3 times greater than that of non-heating period for inhalation, respectively. While risk levels associated with exposure to PCBs and OCPs did not exceed the acceptable level of 1×10^{-6}, it was exceeded for 47 % of the population associated with inhalation of PAHs with a maximum value of about 4×10^{-6}.

Keywords Persistent organic pollutants · PCBs · PAHs · OCPs · Exposure · Carcinogenic risk

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Introduction

Semi-volatile organic compounds are considered as one of the significant groups of pollutants because of their wide presence in the environment. Especially the persistent ones, called as persistent organic pollutants (POPs), are of concern because of their characteristics, i.e., being bioaccumulative, capability of long-range atmospheric transport (LRAT) (Halse et al. 2011; Hogarth et al. 2012), low aqueous solubilities, and moderate vapor pressures (Castro-Jiménez et al. 2008; Wick et al. 2011). Although use of these chemicals was restricted/banned in the countries who signed the Stockholm Convention, they can still be detected in the environment because of their persistence, long-range transport, current use, and unintentional emissions (Pozo et al. 2006; MoEF 2010).

The main sources of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are nowadays, decades after peak emissions, volatilization from contaminated sites, and long-range atmospheric transport (LRAT; Lammel and Stemmler 2012; Lohmann et al. 2007). Additional sources may be unintentional emissions from industrial applications and contaminated materials such as capacitors and transformers (Breivik et al. 2002). Polycyclic aromatic hydrocarbons (PAHs) can be released from natural and anthropogenic sources. Natural sources are volcanoes and forest fires, whereas the main anthropogenic sources are combustion of fossil fuels, e.g., traffic, residential heating, industry, and electricity production. After the emissions, partitioning processes take place in the environment. POP concentrations in air and partitioning between gas and particle phases are determined by many factors such as meteorology, primary and secondary emissions, deposition processes, oxidant availability, and their compartmental distribution (in turn dependent on physicochemical properties).

Exposure to POPs may have adverse health effects on the endocrine, immune, and nervous systems (Li et al. 2006), and may cause toxic, mutagenic, and carcinogenic effects (IARC 2013; He et al. 2014). Due to their effects on human health and the environment, production of most of these chemicals has been banned, and the Stockholm Convention (UNEP 2013) was signed to determine their levels and sources, and to prevent their use on a global scale. The Convention was signed and ratified by Turkey in 2001 and 2009, respectively. The national implementation encourages monitoring in air (MoEF 2010; MoEU 2015), which is not in place yet. Additionally, some of the PAHs (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene) are targeted to be reduced back to their levels in the 1990s by the member states of the European Union in 2010 (EC 2001). The effectiveness of international chemical policy was indeed reflected as a decrease in POP levels in air (Dvorská et al. 2009; Pozo et al. 2012). POPs in air have been monitored in central and northern Europe, central parts of North America, as well as in the Arctic (e.g., Holoubek et al. 2007; Hung et al. 2010). Other understudied regions have recently been studied using passive air sampling, which comes with a factor of ≈2 uncertainty (e.g., Pozo et al. 2009, 2012; Klánová et al. 2009; Halse et al. 2011), and also in Turkey (no results published; MoEU 2015). In some parts of the world, including Turkey, our knowledge of POP levels is very sparse and mainly relies on campaign-based (short-term) observations (Lohmann et al. 2007; Klánová et al. 2011). POPs were measured at polluted sites in Turkey reaching an average total (gas and particle phase) concentration of 3370 pg/m³ at an industrial site in summer for PCBs (Bozlaker et al. 2008), 1164 pg/m³ (chlorpyrifos) at an urban site in winter for OCPs (Odabasi et al. 2008), and 645 ng/m³ in winter (Esen et al. 2006) at an urban site for PAHs. POPs levels reported for the region are presented in Table 1.

Environmental human health risk assessment studies are limited for PCBs and OCPs compared to those for PAHs. Zhang et al. (2013) estimated inhalation carcinogenic risk for exposure to PCBs and OCPs in the Yangtze River Delta, China. The mean lifetime cancer risk for sum of some OCPs and $\sum_6$PCBs were 0.77×10^{-6}, 0.83×10^{-6}, and 0.54×10^{-6} for urban, urban-rural transition, and rural areas, respectively. Dermal and inhalation carcinogenic risks for PCBs reported for Catalonia, Spain, did not exceed 1×10^{-5} (Vilavert et al. 2014). While no risk assessment has been conducted for PCBs and OCPs in Turkey, two studies are found for PAHs. Gaga et al. (2012) reported average inhalation risks for heating (2.92×10^{-3}) and non-heating periods (1.15×10^{-3}) in Kocaeli. Gungormus et al. (2014) estimated inhalation risk as 4.12×10^{-5} and dermal risk as 1.63×10^{-6} in Balikesir, a relatively small city.

The aim of this study was to determine ambient air PCB, OCP, and PAH concentrations throughout a full year using active air sampling, investigate their seasonal variation, and estimate associated carcinogenic risks for inhalation and dermal exposures in Izmir, the third largest metropolis in Turkey. This is the first such study and, so far, the most comprehensive POPs-related air monitoring activity in the country (MoEF 2010; MoEU 2015), which can establish a benchmark for assessing historical trends. Monte Carlo simulation was performed to determine the population carcinogenic risks, for which sensitivity and uncertainty analyses were also conducted.

Materials and methods

Sampling, sample processing, and analysis

Air samples were collected at Kaynaklar Campus of Dokuz Eylul University (38° 22′ N, 27° 12′ E) located in a suburban area in Izmir. Izmir is the third largest city in Turkey with a population of 4,061,074 (TUIK 2013). Daytime (8:00 a.m. to sunset) sampling was conducted once every 6 days from May 2003 to April 2004. A total of 51 samples, 30 in the non-heating period (April to September) and 21 in the heating period (October to March), were collected. Meteorological data were obtained from a 10-m-high tower located at the sampling site. The average temperature was 23.6 and 12.2 °C for non-heating and heating periods, respectively.

Air samples were collected using a modified high-volume sampler model GPS-11 (Thermo-Andersen Inc.). Particles (total suspended particles) were collected on 10.5-cm-diameter quartz filters and the gas-phase compounds were collected in a modified cartridge containing 30 g XAD-2 resin placed between layers of polyurethane foam (PUF) (6-cm diameter, 5-cm length each) at an average sampling flow rate of 0.262 m³/min. The average sampling volume was 173 ± 44 m³ while the

Table 1 Overview of the gas-phase mean concentrations observed in near-ground air in the region (PAHs: ng/m³, all other: pg/m³). Limited number of individual substances included for the sake of comparability

Study	Sampling Time	Sampling Site	ΣPAH_5 [a]	ΣPCB_7 [b]	ΣHCH [c]	$\Sigma DDTs$ [d]
Rural, residential						
Lammel et al. 2015	Summer 2012	Thessaloniki area, residential site	2.33–3.64	26.7–47.5	9.3–10.4	8.4–51/0.56–1.12
Lammel et al. 2015	Summer 2012	Athens/Greece, suburban site	0.25	50.2	9.7	4.7
Lammel et al. 2015	Summer 2012	C Greece, rural site	0.58	9.0	4.8	7.0
Lammel et al. 2015	Summer 2012	NW Turkey, semi-residential site	0.23	25.6	5.7	7.9
Lammel et al. 2015	Summer 2012	Gulbahce/Izmir/W Turkey, rural/coastal site	0.27	55.3	13.8	12.8
Yolsal et al. 2014	Whole year 2008-09	NW Turkey, rural and coastal sites		80		
Birgül and Taşdemir 2011	Whole year 2008-09	NW Turkey, semi-rural site		74		
Halse et al. 2011	Summer 2006	Aliartos/C Greece, rural site	23.7	13.6	54.0	228
Stafilov et al. 2011	Summer 2007	Macedonia, 2 rural sites		24–174	101–182	36–126
Terzi and Samara 2004	Whole year 2000-01	W Greece, 2 rural sites	2.9-13.8			
This study	Whole year 2003-04 Heating/non-heating season	Izmir, suburban site	37.6/13.9[e]	49.4/107	17.1/43.7	33.9/55.3
Urban, industrial						
Lammel et al. 2015	Summer 2012	Thessaloniki area, urban site	2.38	85.7	14.9	42.5/6.96
Odabasi et al. 2015	Fall 2011	Aliaga/ Izmir/W Turkey	24.6–553 (105±105)	65.7–2011 (672±524)		
Birgül et al. 2011; Yolsal et al. 2014	Whole year 2008-09	Bursa/NW Turkey	117[f]	67		
Kaya et al. 2012	All seasons 2009-10	Aliaga/ Izmir/W Turkey	78	2560		
Akyüz and Çabuk 2010	Winter/summer 2007-08	Zonguldak/N Turkey	260/21			
Ozcan and Aydin 2009	Whole year 2006-07	Konya/S Turkey	93	78	520	130
Pozo et al. 2009	Winter/summer 2005	Izmir/W Turkey		644/287	29/48	51/60
Vasilakos et al. 2007	June and November 2003	Athens/Greece, 2 sites in suburban area	17.5-20.1[f]			
Taşdemir and Esen 2007	All seasons 2004-05	Bursa/NW Turkey	20			
Terzi and Samara 2004	Whole year 2000-01	W Greece, urban site	21.7[f]			

[a] sum of ACE, FLN, PHE, FLT, and PYR

[b] PCB-28, -52, -101, -118, -138, -153, -180

[c] sum of α- and γ-HCH

[d] sum of DDT and DDE isomers

[e] without ACE

[f] without ACE, FLN

average sampling time was 11 ± 1 h. Before sampling, quartz filters were conditioned at 450 °C and cooled down to room temperature in a desiccator. Soxhlet extraction was applied for cleaning of the PUF cartridges with acetone/hexane mixture (1:1) for 12 h, and then the cartridges were covered in aluminum foil and dried at 70 °C , and replaced into a glass container with a Teflon lid until sampling. Gas and particle samples were extracted by soxhlet extraction for 12 h with dichloromethane (DCM)/petroleum ether (PE) (1:4). Prior to extraction, PCB (PCB-14, 65, and 166; each 10.5 ng/sample) and PAH (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12; each 8000 ng/sample) surrogate standards were spiked to the samples to determine the recovery efficiencies. Volumes of extracts were reduced to 2 ml and solvent was exchanged to hexane using a rotary evaporator. Then, samples were introduced into columns packed with 3 g of silicic acid (deactivated with 3 % deionized water) and 2 g of alumina (deactivated with 6 % deionized water) which were pre-washed with 20 ml DCM followed by 20 ml PE. Samples were eluted with 25 ml PE (fraction 1 containing PCBs) followed by 25 ml DCM (fraction 2

containing PAHs and OCPs). Finally, solvent was changed into hexane and final volume was reduced to 1 ml with a gentle N_2 stream. All samples were analyzed for PAHs, PCBs, and OCPs in separate runs for each POP group with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). PAHs and PCBs were analyzed using electron impact ionization (EI) while negative chemical ionization (NCI) was used for OCPs. The capillary column used was HP5-MS (30 m, 0.25 mm, 0.25 μm). Helium was the carrier gas (at a flow rate of 1.5 ml/min for PAHs and PCBs and 1.0 ml/min for OCPs) and high purity methane was the reagent gas for NCI. For PAHs, the initial oven temperature was held at 50 °C for 1 min and raised to 200 °C at 25 °C/min, to 300 °C at 8 °C/min, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were 295, 300, and 180 °C, respectively. For PCBs, the same temperature program was used except the final hold time was 3 min. The injector, ion source, and quadrupole temperatures were 250, 230, and 150 °C, respectively. Prior to analysis, OCP samples were spiked with internal standard (BDE-77,3,3′,4,4′-tetrabromodiphenyl ether,

20 ng/sample). The initial oven temperature was held at 50 °C for 1 min, was raised to 100 °C at 25 °C/min, to 260 °C at 5 °C/min, to 300 °C at 10 °C/min, and was held for 2 min. The injector, ion source, and quadrupole temperatures were 250, 150, and 150 °C, respectively. Compounds were identified based on their retention times and target and qualifier ions, and were quantified using the internal standard calibration procedure. Additional details can be found elsewhere for PCBs, OCPs (Sofuoglu et al. 2004; Odabasi et al. 2008), and PAHs (Demircioglu et al. 2011). Concentrations of 32 PCBs (PCB-17, PCB-18, PCB-28, PCB-31, PCB-33, PCB-44, PCB-49, PCB-52, PCB-70, PCB-74, PCB-82, PCB-87, PCB-95, PCB-99, PCB-101, PCB-105, PCB-110, PCB-118, PCB-128, PCB-132, PCB-138, PCB-149, PCB-151, PCB-153, PCB-158, PCB-170, PCB-171, PCB-177, PCB-180, PCB-183, PCB-187, PCB-199); 23 OCPs (those that were legally in use as pesticides and their metabolites: chlorpyripos (CHLPYR), endosulfan I (ESLF I), endosulfan II (ESLF II), endosulfan sulfate (ESLF SUL) and those that were banned around the 1980s in Turkey: methoxychlor (MEOCL), heptachlor (HEPCHL), heptachlor epoxide (HEP EPOX), aldrin (ALD), α-chlordane (α-CHL), γ-chlordane (γ-CHL), c-nonachlor (c-NONA), t-nonachlor (t-NONA), endrin aldehyde (END AL), endrin ketone (END KET), endrin (END), dieldrin (DIELD), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), γ-hexachlorocyclohexane (γ-HCH), δ-hexachlorocyclohexane (δ-HCH)); and 14 PAHs (fluorene (Flu), phenanthrene (PHE), anthracene (Ant), carbazole (Carb), fluoranthene(FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]flouranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenzo[a,h]anthracene (DahA), and benzo[ghi]pyrene (BghiP)) were quantified.

Average recoveries (determined from the response ratios from calibration and sample analysis runs) of PCB surrogate standards including filters and PUFs were 97 ± 17 % for PCB-14, 107 ± 18 % for PCB-65, and 93 ± 31 % for PCB-166 ($n = 102$). The recoveries of target compounds were also determined externally by matrix spike experiments. Average external recoveries of targeted PCB congeners ($n = 12$ replicates) were in the range of 69 ± 15 % (PCB-18) and 115 ± 5 % (PCB-49) with a general exceedance of 85 %. Average external recovery of OCPs ($n = 6$ replicates) was 85 ± 21 % with a range of 40 ± 11 % (endosulfan II) and 128 ± 22 % (endosulfan sulfate), which were generally higher than 70 %. Since the recoveries were generally high, sample amounts were not corrected for external recoveries. Average recoveries of PAH surrogate standards were found as 68 ± 14 % for PHE-d$_{12}$, 82 ± 14 % for CHR-d$_{12}$, and 77 ± 19 % for perylene-d$_{12}$ ($n = 102$). The spike recoveries ($n = 6$ replicates) of the targeted PAH species were found between 88 ± 22 % (DahA) and 121 ± 6 % IcdP with the average of 107 ± 16 %. Instrumental detection limits (IDLs) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. For 1-μl injection, the quantifiable amounts were 0.15, 0.10, and 0.01–0.35 pg for PAHs, PCBs, and OCPs, respectively. Blank filters and cartridges columns ($n = 6$ for each) were also analyzed to determine if there was contamination during sampling and sample preparation. Method detection limit (MDL, ng) was defined as the mean blank mass plus three standard deviations (MDL = mean blank value + 3 SD). IDLs were used for the compounds that were not detected in blanks. Method detection limits were also expressed in terms of air concentrations by dividing them by the average sampling volume. Gas-phase MDLs ranged between 0.01 (BaP) and 0.9 (PHE) ng/m³, 0.6 (PCB-70) and 5.4 (PCB-18) pg/m³, and 0.1 (α-CHL) and 7.2 (p,p'-DDE) pg/m³ for PAHs, PCBs, and OCPs, respectively. Particle-phase MDLs ranged between 0.01 (BaA) and 0.5 (PHE) ng/m³, 0.6 (PCB-70) and 3.3 (PCB-18) pg/m³, and 0.1 (α-CHL) and 5.0 (p,p'-DDE) pg/m³ for PAHs, PCBs, and OCPs, respectively. Average analyte amounts in blanks were generally <10 % of the amounts found in samples. Sample quantities exceeding the MDLs were quantified and blank-corrected by subtracting the mean blank amount from the sample amount. Additional QA/QC information can be found in Sofuoglu et al. (2004), Odabasi et al. (2008), and Demircioglu et al. (2011).

Exposure and risk assessment

Exposure assessment was conducted for the routes of inhalation and dermal contact, and associated health risks were assessed. Chronic daily intake (CDI) was used as the measure of exposure for PCB, OCP, and PAH compounds. Equations 1 and 2 were used for inhalation and dermal exposures, respectively (USEPA 1992a).

$$\sum_{j=1}^{J} \text{iCDI} = \frac{C_i \times IR \times ED \times EF}{BW \times AT} \tag{1}$$

where iCDI is the inhalation chronic daily intake (pg/kg/day for PCBs and OCPs, ng/kg/day for PAHs); C is the pollutant concentration (pg/m³ for PCBs and OCPs, ng/m³ for PAHs); IR is the average daily intake rate of air (m³/day); ED is the exposure duration and equal to 70 years for lifetime exposure assessment; EF is the exposure frequency (180 days/year for heating and non-heating periods), BW is the body weight (kg), AT is the averaging time (70 years), i is the compound, and j is the heating and non-heating periods ($j = 2$). In this case, indoor pollutant concentrations were assumed as equal to those

measured outdoors. PAH concentrations were converted to BaP equivalent (BaP$_{eq}$) concentrations by using toxic equivalency factor (TEF) values given in Supplementary Material (SM) Table S1.

$$\sum_{j=1}^{J} \mathrm{dCDI} = \frac{C_{pi} \times Kp \times SA \times ED \times EF}{BW \times AT} \qquad (2)$$

where dCDI is the dermal chronic daily intake (pg/kg/day for PCBs and OCPs, ng/kg/day for PAHs); C_p is the particle-phase pollutant concentration (pg/m^3 for PCBs and OCPs, ng/m^3 for PAHs); Kp is the permeability coefficient (m/day); and SA is the body surface area exposed to the contaminant (m^2). Kp values for PCBs, OCPs, and PAHs were obtained from RAIS (2013). SA was calculated using Eq. 3 which relates the body weight to the body surface area (Livingston and Lee 2001), where SA is in square meters and BW is in kilograms.

$$SA = 0.1173 \times BW^{0.6466} \qquad (3)$$

Since exposed surface area changes depending on the seasons, hands (2.7 % of SA) and head (4.0 % of SA) were considered for the heating period while arms (12.6 % SA) were added for the non-heating period.

Lifetime cancer risk associated with inhalation and dermal exposures to OCPs, Σ_{14}PAHs, dioxin-like PCBs, and non-dioxin-like PCBs were calculated using Eq. 4. Dioxin-like PCBs were considered separately because they are attributed with potency of dioxin which can be converted with the use of a TEF (i.e., 0.00003 (USEPA 2010) for the only detected dioxin-like congener PCB-118 among the PCBs that exposure could be estimated). Then, the total carcinogenic risk for PCBs was calculated by summation of risk values of dioxin-like PCB and non-dioxin-like PCBs.

$$R = CDI \times SF \qquad (4)$$

where R is the estimated lifetime cancer risk, CDI is the chronic daily intake (pg/kg/day for PCBs and OCPs, ng/kg/day for PAHs), and SF is the slope factor of the subject pollutant (1/(pg/kg/day) for PCBs and OCPs, and 1/(ng/kg/day) for PAHs).

There was no available dermal slope factor for OCPs. However, it can be estimated by dividing oral SF by gastrointestinal adsorption factor (USEPA 1992b) which can be assumed as one conservatively for all OCPs (RAIS 2013). All SF values were taken from IRIS (2015) except for dioxin and dermal SF of γ-HCH obtained from USEPA (1997), and inhalation SF values of BaP and γ-HCH taken from CalEPA (2005). All data used in the calculations are given in SM, Table S2.

Statistical methods

Risk assessment was performed for compounds that were detected ≥50 % of the samples, for which the missing data were generated by fitting a distribution to the measured concentrations (Helsel 1990). Detection frequencies are shown in SM, Table S3. Most of the data were below detection limit (BDL) for particle phase dioxin-like PCB-118 (MDL = 0.6 pg/m^3 for both gas and particle phases). However, due to its presence in the gas phase, we opted to include this compound in the assessment. Therefore, half of instrumental detection limit was assigned as concentration for these days. The average concentration was used for health risk assessment instead of fitting a distribution since it would have been distorted.

Monte Carlo Simulation was conducted using Crystal Ball (v 4.0e) software. Monte Carlo is a simulation program acquiring a probabilistic approximation by using statistical sampling techniques to the output of a mathematical equation or a model. The best probability distribution to describe input and output variables was determined based on the Kolmogorov-Smirnov and Anderson-Darling tests. Distribution of body weight was taken from Kavcar et al. (2006) to represent Izmir population (lognormal distribution; mean = 65.56, standard deviation = 13.02 kg). Inhalation rate was assumed to have a uniform distribution with minimum and maximum values 0.21 and 0.74 m^3/h, respectively, as reported by Gephart et al. (1994). For each simulation, 10,000 trials were performed, and this many forecasts were obtained to fit the population distribution. Seasonal differences were tested using Mann-Whitney non-parametric hypothesis test using a significance level of 0.05. Kolmogorov-Smirnov test was also applied for confirmation. The results were in agreement with each other and p values obtained from Mann-Whitney tests are presented.

Results and discussion

Ambient air concentrations

POP concentrations in this section are presented as total concentrations (gas + particle − phase) unless specified otherwise.

PCBs

The mean, median, and 95th percentile concentrations of $\sum_{32}$PCBs were 348, 276, and 861 pg/m^3, respectively. There was a seasonal variation in the concentrations of homolog groups of PCBs as shown in Fig. 1. The mean, median, and 95th percentile of gas-phase $\sum_{32}$PCB concentrations in the non-heating period were 377, 275, and 1521 pg/m^3, respectively, whereas lower concentrations were measured (184, 163, and 567 pg/m^3, respectively) in the heating period

Fig. 1 Seasonal variation in the average PCB concentrations. **a** Gas phase in non-heating period. **b** Particle phase in non-heating period. **c** Gas phase in heating period. **d** Particle-phase in heating period (*error bars* indicate one standard deviation)
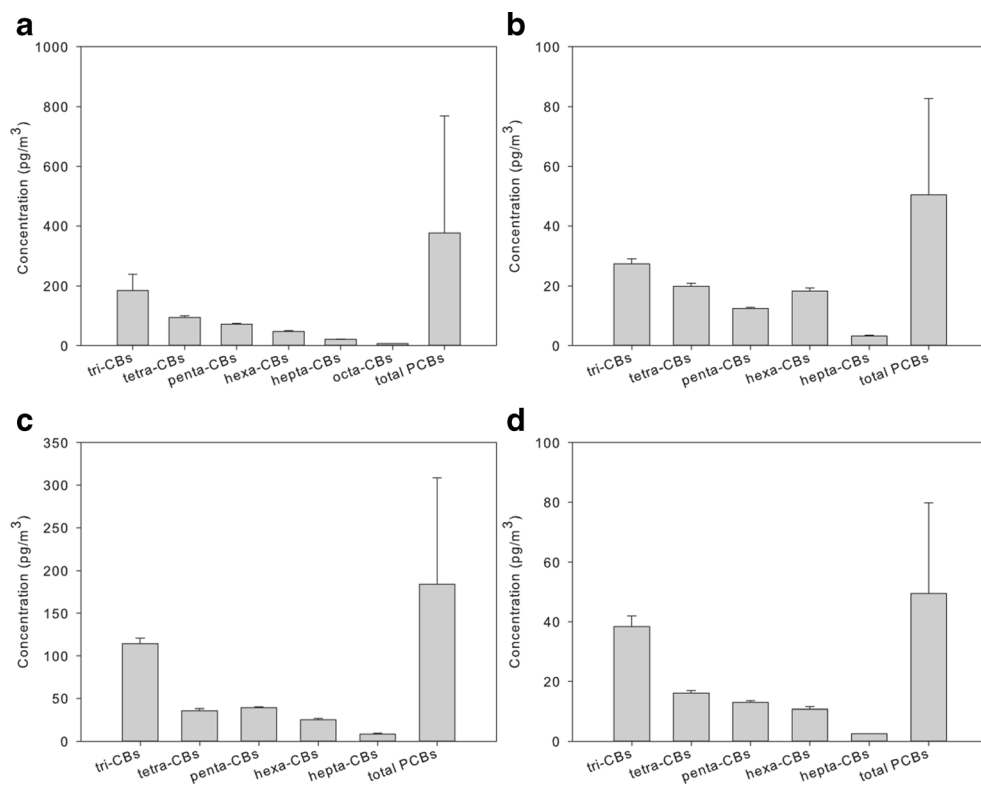
($p = 0.001$). Particle-phase concentrations in the non-heating period was similar to the measured concentrations in the heating period ($p = 0.74$) (Fig. 1). Tri-CBs dominated the homolog pattern, in agreement with those reported in the literature (Stern et al. 1997; Choi et al. 2008). Fractions of tri-, tetra-, penta, hexa-, hepta-, and octa-CBs in $\sum_{32}$PCBs were 52.6, 23.2, 14.2, 8.1, 1.7, and 0.2 %, respectively. PCB concentrations in the non-heating period were generally greater than the heating period concentrations probably because increasing temperature increases volatilization from contaminated terrestrial surfaces (Sofuoglu et al. 2001). In general, 86 % of the detected PCBs were in the gas phase. Cetin et al. (2007) measured the average $\sum_{36}$PCB concentrations as 847 and 314 pg/m^3 in March–April 2005 and June 2005, respectively, on the shore of Aegean Sea in urban Izmir. The average heating period-$\sum_{32}$PCBs concentration measured in this study is much lower than the winter concentration reported by Cetin et al. (2007) while the opposite is observed for the non-heating period compared to the reported summer concentration. Higher concentrations measured in winter were explained by the southerly winds carrying pollutants from the industrial area located SW of the urban area. The ferrous scrap processing steel plants with electric furnaces were found to be hot spots for POPs in the area (Bozlaker et al. 2009). Aliaga industrial area is located north of the sampling site of the present study. Therefore, northerly winds may carry POPs from the Aliaga industrial region where reported mean concentrations were as high as 8727 pg/m^3 (Kaya et al. 2012).

OCPs

Seasonal variation in individual OCPs in gas and particle phases are shown in Fig. 2. The dominating OCP was endosulfan I (52 % of the total OCPs) with mean, median, and 95 % percentile concentrations of 273, 96.6, and 1155 pg/m^3, respectively. The compound having the lowest level was *t*-nonachlor (0.14 % of the total OCPs) with the mean, median, and 95 % percentile concentrations of 0.75, 0.27, and 8.08 pg/m^3, respectively. Among the remaining OCPs, chlorpyrifos, endosulfan I, and endosulfan II had higher concentrations probably because these compounds were legally in use during the sampling period. This is also reflected in high endosulfan levels in biota in Turkey (MoEF 2010). The mean concentration ratios of α-CHL/γ-CHL and α-HCH/γ-HCH were 1.96 and 1.07, respectively, suggesting past emissions (Haugen et al. 1998). The respective ratios of 0.83 and 0.80 were reported for the Aliaga industrial region, also indicating past use (Bozlaker et al. 2008). Gas-phase average concentrations of OCPs in the non-heating period were in the range of 1.10 (*c*-nonachlor) to 26.4 pg/m^3 (endosulfan I), and of BDL to 42.5 pg/m^3 (endosulfan I) in the heating period. Gaseous phase concentrations of heptachlor and *p,p'*-DDE in the heating period were similar to those measured in the non-heating period ($p = 0.965$ and $p = 0.314$, respectively), whereas all the others were significantly different. Particle-phase average concentrations of OCPs were in the range of BDL to 25.4 pg/m^3 (endosulfan II) in the non-heating period and of BDL to 16.8 pg/m^3 (chlorpyrifos) in the heating period. The levels of *p,p'*-DDT,
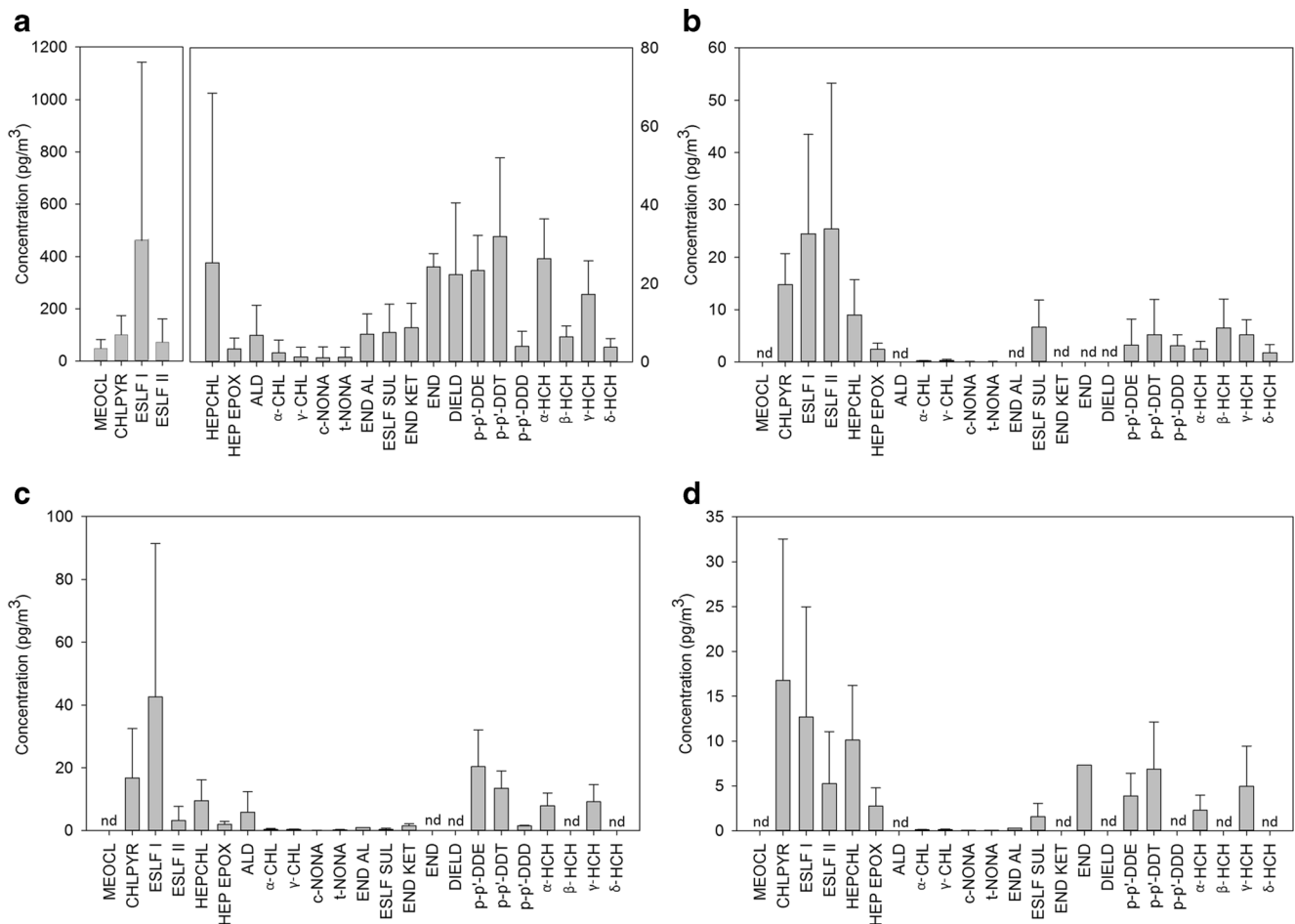
Fig. 2 Seasonal variation in the average OCP concentrations **a** Gas phase in non-heating period. **b** Particle phase in non-heating period. **c** Gas phase in heating period. **d** Particle phase in heating period (*error bars* indicate one standard deviation)

endosulfan II, *p,p′*-DDE, and endosulfan sulfate in the non-heating period were significantly higher than those in the heating period (*p* = 0.035, *p* = 0.001, *p* = 0.033, and *p* < 0.0001, respectively). The remaining OCPs were either not detected in one of the periods or the difference was not significant. Higher particle-phase concentrations of some OCPs in winter were reported by Yenisoy-Karakas et al. (2012) with some exceptions in Bolu in relation to the difference in the winter- and summer-dominant wind sectors. High particle-phase levels in winter may be related to transport of particles to the sampling site with accumulated chemicals on particle surfaces by dominant winds. Higher levels of gas-phase α-HCH were reported as 71.9 pg/m³ for summer and 17.1 pg/m³ for winter than those of particle phase (0.6 for summer and 0.2 pg/m³ for winter) in Aliaga industrial region (Odabasi and Cetin 2012). Heptachlor epoxide, α-CHL, and γ-CHL concentrations were similar to the concentrations observed in the present study. Particle-phase *p,p′*-DDT concentrations measured in this study were one order of magnitude higher in the non-heating period and 3.6 times higher in heating period compared to Aliaga. All γ-HCH concentrations were reported to be higher in Aliaga compared to this study except for summer.

PAHs

Concentrations of PAHs are briefly presented here because they were previously discussed in detail elsewhere (Demircioglu et al. 2011). The mean concentrations of targeted 14 PAH compounds in gas and particle phases in the two periods are shown in Fig. 3. Annual mean concentration of $\sum_{14}$PAHs was 35.7 ng/m³. Dominant compounds in gas phase were PHE and Flu, followed by FL and Pyr in both seasons. The most abundant compound in particle phase was PHE in the non-heating period; FL, Chry, PHE, and Pyr in the heating period. Gas- and particle-phase PAH concentrations were significantly lower in non-heating period but the contribution of gas phase to $\sum_{14}$PAHs (gas + particle) were 62 and 71 % in the heating and non-heating periods, respectively, for which the difference was significant (*p* < 0.0001). The higher contribution may be attributed to the effect of higher temperatures increasing the volatilization from contaminated surfaces, shifting the gas-particle partitioning to gas phase. Ambient air standard in Turkey for annual average PM₁₀-bound BaP concentration was published to come into effect as 1 ng/m³ in January 2020 (Official Gazette, 2008). The annual average
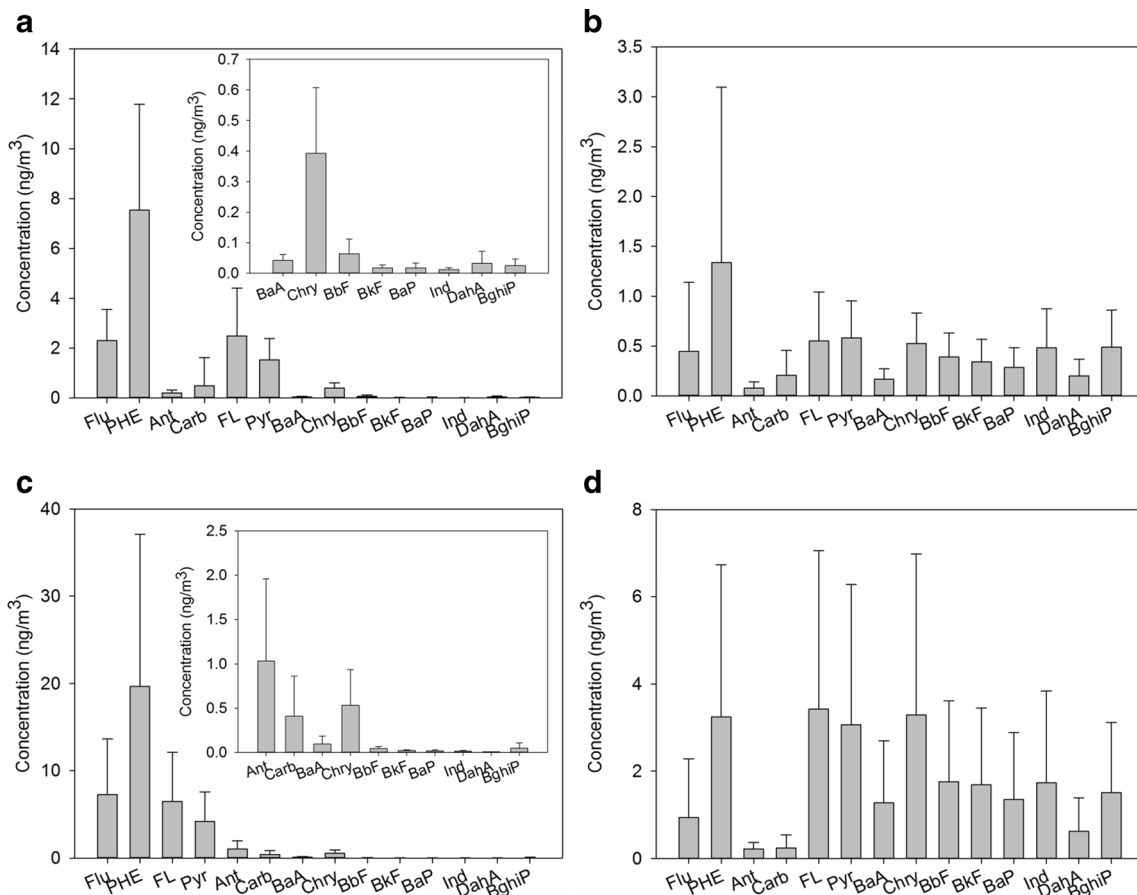
Fig. 3 Seasonal variation in the average PAH concentrations. **a** Gas phase in non-heating period. **b** Particle phase in non-heating period. **c** Gas phase in heating period. **d** Particle phase in heating period (*error bars* indicate one standard deviation)

TSP-bound BaP measured in this study (0.7 ng/m^3) is less than the standard level.

Exposure and risk assessment

Monte Carlo simulation was implemented to estimate population exposure and risk distributions for inhalation and dermal exposure routes. Fitted distributions to model parameters are given in SM, Tables S4 and S5. The 95th percentile exposure to $\sum_{32}$PCBs was found as 1.83×10^{-3} and 121 pg/kg/day for dermal and inhalation routes, respectively, which were translated into the 95th percentile risks of 3.81×10^{-12} and 2.49×10^{-7}, respectively. Ding et al. (2013) determined the highest inhalation exposure to $\sum_{25}$PCBs for adults as 8.69×10^{-3} non-I-TEQ pg/kg/day at a background area in Tianjin, China. The average exposure via inhalation route in this study was almost four orders of magnitude higher than the corresponding value in Tianjin, China. Overall, heating and non-heating period 95th percentile risk levels associated with inhalation and dermal exposures for $\sum_{32}$PCBs, OCPs, and $\sum_{14}$PAHs are given in Table 2. The overall risks, ranked from high to low, were $\sum_{14}$PAHs, $\sum_{32}$PCBs, and $\sum_{7}$OCPs. The 95th percentile inhalation exposure and risk for individual OCPs

ranged from 0.16 to 11.85 pg/kg/day, and from 1.38×10^{-10} to 5.71×10^{-8}, respectively. The minimum and maximum levels were for γ-CHL and heptachlor, respectively. The 95th percentile dermal exposure and risk ranged from 5.30×10^{-7} to 5.55×10^{-4} pg/kg/day and from 1.86×10^{-16} to 5.55×10^{-13}, respectively. The lowest level compound among OCPs was γ-CHL, whereas the highest was heptachlor. The 95th percentile exposure to $\sum_{14}$PAHs was 0.90 ng/kg/day for inhalation and 1×10^{-3} ng/kg/day for dermal routes. The 95th percentile inhalation and dermal risks for $\sum_{14}$PAHs are 4.07×10^{-6} and 7.29×10^{-9}, respectively.

The risks are dominated by the PAHs with the highest in the heating period. Overall, the other addressed pollutants, led by PCBs, account for ≈10 % of the risk (≈20 % in the non-heating period). Similarly, high PAH levels have been observed in Turkish cities in the recent years (Table 1). Therefore, significant decreasing trends can not be expected for PAHs in Turkey during the last decade. In Europe (EU-28), PAH levels have been declining from 1990 until ≈2002 but were leveling off, even slightly increasing thereafter (EEA 2014). PCB levels in air are believed to slowly fall in all regions (except in the Arctic; Lammel and Stemmler 2012), which is confirmed for central Europe for 1997–2006 (Dvorská et al. 2009), but it could be regionally

Table 2 Overall, heating, and non-heating period 95th percentile carcinogenic risks for inhalation and dermal exposure routes

Pollutant	Inhalation			Dermal		
	Non-heating period	Heating period	Overall	Non-heating period	Heating period	Overall
α-HCH	3.35×10^{-8}	1.29×10^{-8}	4.32×10^{-8}	1.66×10^{-14}	8.19×10^{-15}	2.06×10^{-14}
γ-HCH	5.53×10^{-9}	3.95×10^{-9}	8.48×10^{-9}	7.02×10^{-15}	3.72×10^{-15}	8.95×10^{-15}
HEPCHL	5.12×10^{-8}	1.28×10^{-8}	5.71×10^{-8}	4.91×10^{-13}	1.19×10^{-13}	5.55×10^{-13}
HEP EPOX	1.02×10^{-8}	8.67×10^{-9}	1.71×10^{-8}	2.32×10^{-14}	1.17×10^{-14}	2.95×10^{-14}
γ-CHL	1.15×10^{-10}	3.78×10^{-11}	1.38×10^{-10}	1.57×10^{-16}	5.61×10^{-17}	1.86×10^{-16}
α-CHL	1.60×10^{-10}	3.51×10^{-11}	1.78×10^{-10}	–	–	–
p-p'-DDT	1.04×10^{-9}	7.34×10^{-10}	1.54×10^{-9}	1.70×10^{-13}	4.49×10^{-14}	1.89×10^{-13}
$_{32}$PCBs	1.81×10^{-7}	9.64×10^{-8}	2.49×10^{-7}	3.24×10^{-12}	9.52×10^{-13}	3.81×10^{-12}
$_{14}$PAHs	9.08×10^{-7}	3.66×10^{-6}	4.07×10^{-6}	3.47×10^{-9}	5.92×10^{-9}	7.29×10^{-9}

overcompensated by climate variability (mobilization from ground compartments triggered by higher temperatures; Lamon et al. 2009). The decision about the prohibition of PCB usage in Turkey was published in the official gazette in 1993, then entered into force in 1996 (RCHC 1993), but the long-term PCB trend in Turkey is not confirmed. However, PCB concentrations were measured in July 2012 at a rural/coastal site (38° 19′ N, 26° 38′ E) at the campus of Izmir Institute of Technology in Gulbahce, Urla, ≈50 km west (direct distance) of the sampling site (Lammel et al. 2015). Eleven daytime gas and particle-phase samples were collected and analyzed for indicator PCBs (PCB-28, -52, -101, -118, -138, -153, and -180). The average total (gas and particle phases) concentration for the sum of the indicator PCBs (Σ_iPCBs) was 97 ± 50 pg/m^3 (arithmetic mean ± standard deviation). The corresponding Σ_iPCBs concentration of samples collected in this study in Summer 2003 (July ($n = 4$) and August ($n = 4$) samples were compiled to have similar sample sizes) was 107 ± 72 pg/m^3. Obviously, there is no clear long-term downward trend in PCB levels. Moreover, lower levels at Gulbahce than at the suburban Izmir site in this study could be attributed to the rural/coastal character of Gulbahce, i.e., lower density of electrical utilities, open applications, and residential buildings, which are possible PCB sources (MoEF 2010). It can be concluded that PCB levels were not very different in 2012 from 2003 to 2004. This is further supported by a recent study investigating the historical variations of POPs using dated tree cores at 14 industrial and background sites in Izmir region (Odabasi et al. 2015) showing that PAH and PCB concentrations in tree ring samples (that are suggested to be representative of ambient air levels) were stable or slightly increasing during the period of 2001–2011. Therefore, the estimated risk levels associated with inhalation and dermal contact in this study for both PAHs and PCBs are probably reasonable estimates for the current levels, assuming the same values for the other variables (inhalation rate and body weight) in the exposure-risk model.

The ratios of non-heating/heating period for 95th percentile risk due to inhaled total PCBs and individual OCPs were found as 1.87 and 1.18–4.56, while these ratios for dermal exposure were calculated as 3.52 and 1.89–4.12, respectively. An increase in ambient air temperature gives rise to volatilization from atmospheric particles, soil, water, and vegetation (Sofuoglu et al. 2001). Therefore, the main reason for the difference in carcinogenic risks between sampling periods is most probably related to the higher volatilization rates for PCBs and OCPs in the non-heating period. The exposed surface area in the non-heating period is 19.3 % of the total human body whereas this percentage decreases to 6.7 % in the heating period, which contributes to the seasonal differences in risks associated with dermal contact. An assessment of seasonal variation in carcinogenic risk for individual PCB congeners in Catalonia, Spain (Vilavert et al., 2014), showed that dermal contact and inhalation risks in spring and autumn of 2010 and 2011 were very similar. On the other hand, risk associated with dermal exposure to PAHs in the heating period was found 1.70-folds that of in the non-heating period in this study. The main reason for the difference between the periods was the estimated particle BaP$_{eq}$ concentrations, thus the detected particle-phase PAH concentrations. While the mean values of total PAH concentrations and BaP$_{eq}$ concentrations in the heating period were calculated as 12.8 and 2.3 ng/m^3, lower levels were detected as 5.2 ng/m^3 for total PAH concentrations and 0.84 ng/m^3 for BaP$_{eq}$ concentrations in the non-heating period. The similar seasonal trend also occurred for inhalation exposure with the ratio of heating/non-heating period of 4.03. Wu et al. (2014) analyzed PAH samples collected from Quanzhou and Xiamen, Southeast China. The ratios of inhalation risk in winter to summer at three sampling sites ranged from 2.13 to 2.63, whereas this ratio was 23.65 at a fourth site. The seasonal differences are most probably due to increased combustion emissions in heating period and meteorological conditions such as lower mixing height, sunlight intensity, and thermal- and photo-decomposition (Devi et al. 2013; Liu et al. 2014; Wu et al. 2014). Carcinogenic risks due to PAH exposures have been studied extensively compared to

PCBs and OCPs. However, there have been only two reports from Turkey. Gaga et al. (2012) investigated ambient air PAH concentrations and seasonal differences in the estimated inhalation carcinogenic risks in Kocaeli, Turkey, one of the most industrialized regions in the country. Risks via inhalation route were estimated by using the unit risk approach. Results of the assessment showed that cancer risk in heating period (2.92×10^{-3}) was approximately two times higher than that in non-heating period (1.15×10^{-3}). Although risk levels were much higher in Kocaeli, heating to non-heating period ratio was lower than that of this study (2.54 vs. 4.03) which may indicate the effect of industrial emissions and the type of fuel used in residential heating and the industry.

Inhalation risk for $\sum_{32}$PCBs, OCPs, and $\sum_{14}$PAHs was approximately 6, 4–7, and 3 orders of magnitude greater than dermal risk, respectively (Fig. 4). The lower risk levels for dermal exposure can be explained with involvement of only the particle-phase concentrations and low skin permeability. Risk associated with inhalation route was 1.83–4.20 times higher than the dermal route in Spain (Vilavert et al. 2014). The only study considering both of the exposure routes for

assessment in Turkey was conducted by Gungormus et al. (2014) in Balikesir, a relatively small city with a population of about 266,000. The population risks associated with inhalation exposure ranged between 1.32×10^{-7} and 2.23×10^{-4} by using the same SF value used in this study. The dermal exposure was lower compared to those of inhalation, ranging from 6.58×10^{-9} to 2.57×10^{-6}. Although Balikesir is a relatively small city, risk levels were higher than those of this study probably because their sampling site was urban while it was suburban in this study. The risks were also assessed for Taiwan, China (Chen and Liao 2006). The average risk for inhalation route (1.04×10^{-4}) was found as 2.70 times higher than dermal exposure (3.85×10^{-5}), a similar ratio to this study.

The acceptable carcinogenic risk may be different for different substances and countries, e.g., 10^{-4}–10^{-6} in the USA (USEPA 1991). However, 10^{-6} is considered as the general acceptable risk level for environmental pollutants. All the risk levels estimated in this study are lower than the general acceptable risk level except for PAHs. It should be, however, noted that results are based on ambient air concentrations
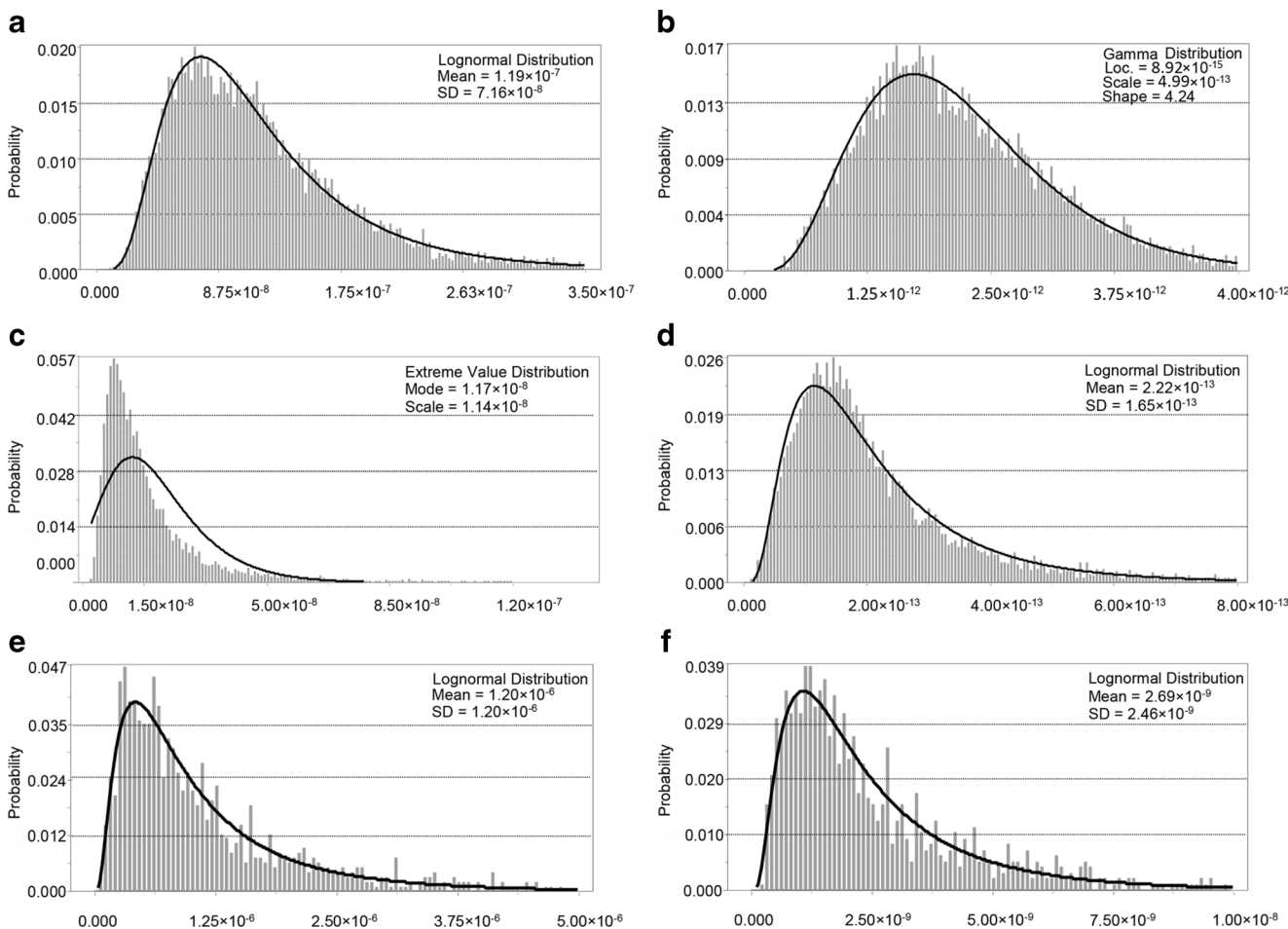

Fig. 4 Fitted probability distributions of carcinogenic risk associated with $\sum_{32}$PCBs **a** inhalation and **b** dermal exposure, to heptachlor **c** inhalation and **d** dermal exposure, and $\sum_{14}$PAHs **e** inhalation and **f** dermal exposure

measured at a suburban site. Higher chronic exposure concentrations may occur in industrial regions, urban locations, and areas around waste disposal/destruction facilities (Hsu et al. 2003). The total PCB concentrations of 3370 pg/m^3 (summer) and 1164 pg/m^3 (winter) were measured at an industrial site in Aliaga industrial area near İzmir (Bozlaker et al. 2008), and 2119 pg/m^3 (summer) and 1716 pg/m^3 (winter) in urban İzmir, (Odabasi et al. 2008). In addition, indoor air concentrations may be higher than those of outdoors depending on the presence of indoor sources (Bohlin et al. 2008). Therefore, exposure and associated risk levels may be higher in those cases. Furthermore, POPs are ubiquitously found in house dust (Frederiksen et al. 2010). Children young enough to have hand-to-mouth behavior are additionally exposed compared to the rest of the population excluding people with high occupational exposures.

Sensitivity and uncertainty analysis

Sensitivity analysis was performed to determine the impact of input variables to the outputs (i.e., exposure and risk). Risk associated with dermal contact of PCBs mainly influenced from the particle-phase concentrations (86.6 %). The gas-phase concentration of PCBs was the main influence with 42.9 % for risk associated with inhalation. Due to having the highest risk levels, heptachlor was chosen as an example OCP for sensitivity analysis. Particle-phase heptachlor concentration was the dominant input variable for dermal risk with 85.7 %. Risk calculated for inhalation exposure was mostly affected from gas-phase heptachlor concentration with 47.6 %. The contribution of BaP$_{eq}$ concentration was the most significant variable with 69.6 % for inhalation risk of PAHs. However, body weight was the most dominant input variable with the value of 99.2 % for dermal risk.

Bootstrapping was implemented with 200 bootstrap samples and 1000 trials to analyze the uncertainties in the estimated carcinogenic risks. The results of the analysis are given in SM, Table S6. Coefficient of variation values (CV) were <7 % for 5th percentile for both of the exposure routes, and 95th percentile of inhalation route for all of the pollutants. CV values for the mean and 50th percentile were <4 %. CV was the largest (21.4 %) for 95th percentile risk of dermal exposure to PCBs, indicating that uncertainties originating from the Monte Carlo simulation were low in general.

Summary and conclusions

Ambient air concentrations were measured for a year at a suburban site in Izmir, Turkey, and carcinogenic risks associated with inhalation and dermal exposure were estimated for 32 PCBs, 7 OCPs, and 14 PAHs from May 2003 to April 2004. Annual mean concentrations of $\sum_{32}$PCBs and

$\sum_{14}$PAHs were determined as 348 ± 334 pg/m^3 and 35.7 ± 39.5 ng/m^3, respectively. Endosulfan I was found at higher levels (273.3 ± 549.9 pg/m^3) than the other target OCPs probably due to being legally in use in the study period. Higher PCB and OCP concentrations were apparent in the non-heating period probably because of the volatilization of the pollutants at higher temperatures. Inverse behavior was observed for PAHs probably because residential heating is one of the main sources of PAH emissions during the heating season. Exposure and risks for inhalation route were higher than dermal route. The 95th percentile risk levels were below the acceptable level except for PAHs. Sensitivity analysis suggested that the gas and particle-phase POP concentrations are the main determinants in the exposure-risk estimation. Comparable PCB and PAH levels measured in this study to those recent ones measured in the region indicate that the risks associated with exposure to the addressed pollutants through inhalation and dermal routes are similar today, i.e., one decade after this study.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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