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Ambient polychlorinated biphenyl levels and their evaluation in a metropolitan city

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HIGHLIGHTS

- PCB concentrations are found to be correlated to mixing height during summer period.
- MLR, PSCF and gas/particle particle partitioning results suggested the same outcome as evaporation of PCBs from sea.
- PSCF input parameters were normalized according to mixing height for the first time.

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ABSTRACT

In this study, summer and autumn ambient PCB concentrations were investigated in metropolitan city of Istanbul. 84 congeners were targeted from di-CBs to nona-CBs on both particle and gaseous phases. Gaseous ambient concentrations were determined to be 372 ± 134 $pg \cdot m^{-3}$, while on the particle phase this value was 49 ± 17 $pg \cdot m^{-3}$, corresponding to an average of 420 $pg \cdot m^{-3}$. About one-tenth of all PCBs lay in ambient aerosols, while 90% of all comprise 2-, 3-, 4-, and 5-CBs.

Measured ambient concentrations of each congener group were tested against meteorological data. The di-CB concentrations were independent of ambient temperature while northerly winds lead to an increase in their concentrations, which was an indicator of considerable contribution to di-CB concentrations from the medical waste incineration plant in Istanbul. In contrast, other congeners' concentrations were found to be correlated with southerly winds. Being an inland sea and having been contaminated, for years, by industrial discharges along the coastline, volatilization from Marmara Sea was considered as the most probable source of other congeners. PSCF analysis was run with 12-hour trajectories to locate possible local sources and check these results.

Gas/particle partitioning was applied using three different models. m_r and b_r values for log P_L^0 model were determined as −0.23 ± 0.09 and −3.25 ± 0.38, respectively. For absorption based log K_{oa} model, m and b values were calculated as 0.23 ± 0.08 and −4.73 ± 0.83, respectively.

1. Introduction

Of the chlorinated benzene rings, PCBs pose a great threat to human health as well as animals, plants and so forth. For this reason, these semi-volatile organic compounds (SVOCs) have attracted much interest especially in the last two decades (Cindoruk and Tasdemir, 2010). Earlier, PCBs were used as dielectric fluids, lubricants, hydraulic and heat transfer fluids until their ban in 1970s. Currently, major sources of atmospheric PCBs are listed as leakage from previously contaminated fluids, open burning, waste incineration, evaporation from contaminated sites, landfills and sludge drying beds (Breivik et al., 2002; Hsu et al., 2003). Apart from these closed or semi closed systems, some production activities and combustion processes produce PCB emissions as by-product. In an inventory study, considering each production type which has PCB emission factor, 920 $kg \cdot yr^{-1}$ of industrial PCB release to atmosphere is estimated within Turkey (Kuzu et al., 2013). Among the production activities, steel production by electric arc furnaces with pre-heating has the highest emission factor (Odabasi et al., 2009).

Once these compounds are emitted from the source, they tend to partition at different media due to their semi-volatile characteristics (Atkinson, 1991). However, equilibrium is never reached and a continuous transfer of PCBs takes place between distinct media due to dynamic structure of the atmosphere and other compartments of the Earth. Thus, researchers inclined to understand the behavior of the compounds in the environment (Carlson and Hites, 2004).

Transport of these compounds in the atmosphere is the major pathway from the point of emission until their deposition (Chen et al., 2009).

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Further, these compounds reach water and soil bodies through atmospheric deposition mechanisms (Birgul and Tasdemir, 2011).

Istanbul is located on both European and Asian sides, separated by the Bosphorus Strait. The city is surrounded by the Black Sea on the northern side and Marmara Sea on the southern side. Istanbul is on the route of dominant atmospheric motion through which contaminants are transported over Europe, Asia and Mediterranean region (Karaca et al., 2009).

The main aims of this study is to i) investigate the ambient PCB levels in this thirteen-million-city with no previous reports on ambient levels of PCBs, ii) identify potential source regions to the ambient PCB levels, iii) determine gas/particle partitioning by present models and discuss their results.

2. Materials and methodology

2.1. Sampling

Sampling was conducted within Davutpasa Campus of Yildiz Technical University in Istanbul, Turkey (41°01′26″ N and 28°53′16″ E). The campus area is surrounded by the main coach station of Istanbul on the northern side, O-1 highway on the southern side where traffic density is more than 100,000 cars per day (Onat and Stakeeva, 2013), and a great number of light and heavy industrial facilities from various sectors on western and eastern sides.

A high volume air sampler (HVAS) was used to collect both particle and gaseous phase pollutants (Tecora ECHO HiVol). HVAS was equipped with a filter holder and cartridge. Ambient air was first drawn through glass fiber filter (GFF) of 10 cm in diameter and then through poly urethane foam (PUF) cartridge consisting of two identical foam layers of 5 cm in diameter and 6 cm in thickness. The foam layers were in series. The sampler was operated at 350 $\mathrm{L \cdot min^{-1}}$ for 24 h which corresponds to approximately 500 $\mathrm{m^3}$ of ambient air sample. The device was calibrated before each sampling campaign.

Samples were collected from May 2012 to October 2012, representing summer and autumn seasons. Davis Vantage 2 Pro online weather station was employed to obtain meteorological data during the sampling. The mixing height data were gathered from Atmospheric Research Laboratory (NOAA, 2012).

Gravimetric measurements were conducted by AND GR-202 analytical microbalance. Before sampling process, GFFs were wrapped with aluminum foil and heated at 450 °C in a furnace for 6 h to remove any organic residuals. Then, the filters were conditioned in a desiccator at a temperature of 20 ± 2 °C and a relative humidity of 50 ± 5%.

2.2. Extraction and analysis

Following the sample collection, the samples were taken to the laboratory for gravimetric analysis and extraction. PCB surrogate standard mixture of PCB #14, #65, and #166 (5 $\mathrm{ng \cdot mL^{-1}}$ for each congener) was added to the PUF cartridges and GFFs prior to the extraction procedure.

The PUF cartridges were extracted with 1:1 (v/v) acetone (ACE)/hexane (HX) mixture for 24 h in a Soxhlet extractor (Cetin et al., 2007). GFF contents were extracted in an ultrasonic bath with a mixture of dichloromethane (DCM)/petroleum ether (PE) of 1:4 (v/v) (Cindoruk and Tasdemir, 2010). Following the extraction procedure, filters were soaked in a glass jar capped with Teflon lined lids containing 25 mL of solvent mixture for 30 min. A second aliquot was formed with the same amount of solvent mixture to continue extraction for another 30 min. At the end of 1 h, the solvent mixture was evaporated and the volume was reduced to 5 mL in a rotary evaporator, which is followed by the switching of the solvent mixture to hexane by the addition of 15 mL of hexane. The latter was repeated twice. The final mixture was stripped gently by constant flow of ultra-pure nitrogen gas until its volume reached to 2 mL.

Samples were then cleaned up and fractionated through a column of 3 g silicic acid (3% water), 2 g neutral alumina (6% water), and 2 g $\mathrm{Na_2SO_4}$ (Falconer et al., 1995; Tasdemir et al., 2004), which was prewashed with 20 mL of DCM and 20 mL of PE, respectively. Next, the sample in 2 mL of hexane was poured to the column and PCBs were eluted with 20 mL of PE. The procedure to switch the solvent was repeated and the final extract was taken into hexane again. These extracts were cleaned with $\mathrm{H_2SO_4}$ and concentrated to 1 mL by stripping with ultra pure nitrogen gas. At the last stage internal standard mixtures of PCB#30 and PCB#121 of 5 $\mathrm{ng \cdot ml^{-1}}$ were included for volume correction purpose.

Quantification of PCB concentrations was performed by a GC-ECD system (Perkin Elmer Clarus 500) equipped with a HP-5MS (30 m × 0.25 mm × 0.25 μm), capillary column. The column temperature was kept constant at 70 °C for 2 min and then raised to 150 °C at a rate of 25 $\mathrm{°C \cdot min^{-1}}$, to 200 °C at a rate of 3 $\mathrm{°C \cdot min^{-1}}$, and finally to 280 °C at a rate of 8 $\mathrm{°C \cdot min^{-1}}$. The temperature was kept constant at 280 °C for 10 min. The inlet temperature 250 °C and detector temperature was 320 °C. Ultra pure helium was used as the carrier at a flowrate of 1.2 $\mathrm{mL \cdot min^{-1}}$. The makeup gas (nitrogen) flowrate was 25 $\mathrm{mL \cdot min^{-1}}$. No split flow was used during the analysis. The calibration was accomplished using seven standard solutions with concentrations ranging from 0.1 $\mathrm{ng \cdot \mu L^{-1}}$ to 30 $\mathrm{ng \cdot \mu L^{-1}}$ After each 10 sample injections, stability was checked with the medium standard. The average value of coefficients of determination for distinct PCB congener was approximately 0.995.

The investigated 84 congeners are those presented in Fig. 4 and additionally, PCB#7/9, PCB#6, PCB#12/13, PCB#18, PCB#100, PCB#66/95, PCB#92, PCB#123.

2.3. Quality assurance/quality control (QA/QC)

All samples were spiked with surrogate standards and the recovery efficiencies are shown in Table 1.

Least volatile congeners have higher recovery efficiencies for both PUF plugs and TSP filters. Usually PUF plugs had higher recovery efficiency among the same congener group.

Limit of detection (LOD) for each PCB congener was assumed as its blank signal plus three times its standard deviation (Cindoruk and Tasdemir, 2007; Odabasi et al., 1998). Obtained LOD values for individual PCB congeners varied between 0 and 1.6 pg. Sample concentrations under LOD value were ignored. Blank samples were collected for each set of analysis. All results were blank corrected.

3. Results and discussion

3.1. Ambient PCB concentrations

Both gaseous- and particulate-phase PCB concentrations in ambient air were measured in Istanbul between May 2012 and November 2012. Results are shown in Fig. 1 along with the atmospheric mixing heights during the sampling periods. Average gaseous phase PCB concentrations were found as 372 ± 134 $\mathrm{pg \cdot m^{-3}}$ whereas particle phase PCB concentrations were 49 ± 17 $\mathrm{pg \cdot m^{-3}}$. Total ambient PCB concentration was 420 $\mathrm{pg \cdot m^{-3}}$ on average. About 12% of the total PCB

Table 1
Recoveries of the surrogate standards.

Statistical parameters	Recoveries of TSP filters			Recoveries of PUF plugs		
	PCB#14	PCB#65	PCB#166	PCB#14	PCB#65	PCB#166
Average	78.8	81.2	88.6	79.5	80.2	96.6
Standard deviation	13.3	12.3	14.4	15.4	12.8	14.5
75th percentile	85.6	87.8	95.2	86.9	86.5	106.5
Median	78.3	85	89.4	77.6	83.4	93.5
25th percentile	70.2	75.5	81.7	69.3	73.1	85.8