Science of the Total Environment 633 (2018) 30–41

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Source apportionment and carcinogenic risk assessment of passive air sampler-derived PAHs and PCBs in a heavily industrialized region

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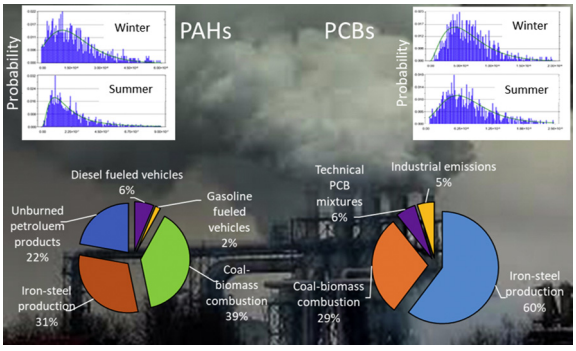
HIGHLIGHTS

- Possible sources and carcinogenic health risks of PAHs and PCBs were investigated in Dilovasi.
- Major anthropogenic origins; traffic, combustion, iron-steel production, were revealed.
- Probabilistic assessment showed that a majority of population face significant health risks.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 December 2017
Received in revised form 22 February 2018
Accepted 14 March 2018
Available online xxxx

Editor: Adrian Covaci

Keywords:
PAHs
PCBs
Source apportionment
Positive Matrix Factorization
Carcinogenic risk
Dilovasi

ABSTRACT

Cancer has become the primary reason of deaths in Dilovasi probably due to its location with unique topography under the influence of heavy industrialization and traffic. In this study, possible sources and carcinogenic health risks of PAHs and PCBs were investigated in Dilovasi region by Positive Matrix Factorization (PMF) and the USEPA approach, respectively. PAHs and PCBs were measured monthly for a whole year at 23 sampling sites using PUF disk passive samplers. Average ambient air concentrations were found as 285 ± 431 ng/m^3 and 4152 ± 6072 pg/m^3, for Σ_{15}PAH and Σ_{41}PCB, respectively. PAH concentrations increased with decreasing temperature especially at urban sites, indicating the impact of residential heating in addition to industrial activities and traffic. On the other hand, PCB concentrations mostly increased with temperature probably due to enhanced volatilization from their sources. Possible sources of PAHs were found as emissions of diesel and gasoline vehicles, biomass and coal combustion, iron and steel industry, and unburned petroleum/petroleum products, whereas iron-steel production, coal and biomass burning, technical PCB mixtures, and industrial emissions were identified for PCBs. The mean carcinogenic risk associated with inhalation exposure to PAHs and PCBs were estimated to be >10^{-6} and >10^{-5}, respectively, at all sampling points, while the 95th percentile was >10^{-5} at 15 of 23 and >10^{-4} at 8 of 23 sampling locations, respectively. Probabilistic assessment showed, especially for PCBs, that a majority of Dilovasi population face significant health risks. The higher risks due to PCBs further indicated that PCBs and possibly other pollutants originating from the same sources such as PBDEs and PCNs may be an important issue for the region.

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https://doi.org/10.1016/j.scitotenv.2018.03.145
0048-9697/

1. Introduction

Dilovasi, a district of Kocaeli City, is a heavily industrialized region in Turkey with many companies working in different sectors next to two motorways, many seaports, and railway lines. Eighty of the 500 largest manufacturing companies in Turkey are located in the industrial regions of Kocaeli. They could be classified into various sectors, which are food, wood, paper, chemical, pharmaceutical, rubber, plastic, cement, metal, and coke coals and refined petroleum products (KSO, 2016). In Dilovasi district, with a population of >50,000, the residential areas are located within these potential air pollutant emitters. Thus, air pollution problem threatens public health and cancer has become the primary reason of deaths in the region (Arslan et al., 2013). Moreover, its unique bowl-like topography has additional adverse impacts on air quality of the district. In parallel with the inversion, decrease of dispersion and lower mixing height were frequently observed in the region (Cetin et al., 2017a).

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are known as persistent, possible toxic and carcinogenic/mutagenic pollutants. The major anthropogenic sources of PAHs were reported as motor vehicle exhaust, coke and aluminum production, coal gasification and liquefying plants, carbon black, coal-tar pitch and asphalt production, catalytic cracking towers and related activities in petroleum refineries (Ravindra and Grieken, 2008; Wang et al., 2015; Wild and Jones, 1995). Benzo(a)pyrene is listed as a human carcinogen by the International Agency for Research on Cancer (IARC) and other PAHs are converted to its equivalents to estimate risks. Primary sources of PCBs are the industrial by-product of thermal processes such as uncontrolled waste incineration, metal smelting and refining processes, thermal power generation, cement kilns, the burning of wood and other biomass fuels used in transport vehicles with combustion or industrial processes such as iron and steel production, paper manufacturing processes, and chlorine bleaching of pulp and paper (Acara, 2006; Breivik et al., 2002). In air quality management, source identification is an important step for better understanding and controlling the pollutants. Positive Matrix Factorization (PMF) is a receptor model that is widely used to identify the sources of persistent organic pollutants (POPs). Last version of PMF (EPA PMF v5.0 program) enables users to successfully handle multiple site data (USEPA, 2014) obtained by means of passive sampling. Recently, Cetin (2016) applied Factor Analysis (FA) to identify the sources of PAHs and PCBs in Dilovasi soil, while Chemical Mass Balance (CMB) was performed for sediment PCBs by Gedik et al. (2010) in Izmit Bay including Dil Creek located in Dilovasi. On the other hand, health risks of PAHs were estimated by Gaga et al. (2012) at only one point in City of Kocaeli but far from Dilovasi, and based on unit risk. Therefore, to date, there is not any study on sources or carcinogenic health risks of atmospheric PAHs and PCBs in Dilovasi region, a unique place where such large and variety of sources, and residential area are conglomerated in a relatively small area. Considering the population living in this polluted area, it is vital to monitor and control the POP contamination, and to assess health risks and possible sources of pollutants for creating a reliable basis for risk management and decision-making by the local government. With these purposes, the possible sources of passive sampler-derived PAHs and PCBs were analyzed using PMF and carcinogenic health risks associated with inhalation exposure were assessed.

2. Material and methods

2.1. Sampling program, preparation, and analysis

The ambient air sampling was conducted monthly using polyurethane foam (PUF) disks for a whole year at 23 sites from February 2015 to February 2016. The samples were collected each month (12 samples for each site) and the average sampling duration was 30.5 days. Totally, 276 samples were collected and analyzed for PAHs and PCBs. During the sampling period, the average ambient air temperatures fluctuated from 5.1 to 26.7 °C, and generally northerly and southwesterly winds were observed in the region. Before sampling, all the PUF disks were spiked with depuration compounds (DCs) (^{13}C–PCB 3, ^{13}C–PCB 9, ^{13}C–PCB 15, PCB 30, PCB 107, and PCB 198) and they were stored in the freezer until field study, about 1 week. After sampling, PUF disks were spiked with surrogate standards and were extracted with equal volumes of acetone-hexane mixture for 24 h in Soxhlet system. After extraction, sampling preparation procedure was carried out with various steps in order of solvent exchange and concentrating using rotary evaporator, clean-up and fractionation with alumina-silicic acid column, and final concentrating to 1 ml with a gentle stream of N_2. The details of procedure can be found in Supplementary Material (SM1).

USEPA priority PAHs and 41 PCBs (please see SM1 for details of target compounds) were analyzed with Agilent 6890 N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5975 inert MSD) in electron impact ionization mode. An HP-5 ms (30 m, 0.25 mm, 0.25 μm) capillary column was utilized for the separation of chemicals in selected ion-monitoring mode (SIM). Chemicals were identified based on their retention times, target and qualifier ions. Further details can be found elsewhere (Cetin et al., 2017a, 2017b; Cetin et al., 2007; Cetin, 2016). The average recoveries of the surrogate standards were 69 ± 10% (acenaphthene–d10), 74 ± 12% (phenanthrene–d10), 77 ± 16% (chrysene–d12), 69 ± 13% (perylene–d12), 94 ± 13% (PCB–14), 90 ± 11% (PCB–65) and 87 ± 14% (PCB–166). Due to low recoveries of naphthalene, its concentrations are not reported herein. The instrumental detection limits were determined by linear extrapolation from the lowest standard in the calibration curve and the area of a peak that has a signal/noise ratio of 3. The quantifiable amounts of the PCB and PAH were found to be 0.10 and 0.15 pg for 1 μl injection, respectively. In addition, blanks were analyzed along with the samples, and the results were reported as blank corrected. For the estimation of the method detection limit (ng), three times the standard deviation was added to the mean blank mass (MDL = mean blank value + 3SD).

The effective sampling air volumes, V_{air} (m^3) were determined using the equation developed by Shoeib and Harner (2002) and the sampling rates, R (m^3 day^{-1}) were calculated using the recovery of depuration compounds (Shoeib and Harner, 2002). For all the sampling periods, the average sampling rate was found between 1.75 and 4.07 m^3 day^{-1} (AVG ± SD; 2.76 ± 0.47 m^3 day^{-1}). Details of the calculation of ambient air concentrations can be found in SM2 and was reported by Cetin et al. (2017a).

2.2. Positive Matrix Factorization (PMF)

EPA PMF v5.0 program, developed by the US Environmental Protection Agency which enables users to handle multiple site data, was used to infer on the sources of PAHs and PCBs measured in the Dilovasi atmosphere. Two types of data sets (input parameters) belonging to the measured pollutants; concentration and uncertainty must be entered into the model. Before applying PMF analysis, the dataset of measured pollutant concentrations was examined, and both the pollutants and samples with <80% occupancy were removed from the dataset.

The methodology developed by Polissar et al. (2001) was followed for the calculation of the uncertainty of each pollutant. Accordingly, values below detection limit were replaced with the half of the detection limit values. For the uncertainty, the values above the detection limit were replaced with "the value x 0.05 + detection limit" whereas the values below the detection limit were replaced with 5/6 of the detection limit. Concentration values of the missing data were replaced with their geometric means and their accompanying uncertainties were replaced with four times of their geometric means. The PAH dataset consisted of 89 samples × 15 compounds while the PCB dataset consisted of 90 samples × 31 compounds, because seasonal average values were used for the analysis. According to the model results, both