

Source apportionment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in ambient air of an industrial region in Turkey

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HIGHLIGHTS

- Ambient air samples of PAHs and PCBs were collected at 40 sites during four seasons.
- The main PAHs sources were combustion, iron–steel production and petroleum products.
- PCBs sources were iron–steel production, combustion, and evaporative emissions.
- Iron–steel plants were the most considerable sources for PAH and PCB emissions.
- This study is the first one investigating the sources of PAHs and PCBs in Turkey.

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ABSTRACT

Source apportionment is generally applied to a time series of data collected at a single site. However, in a complex airshed containing several different sources, it may be helpful to collect samples from multiple sites to ensure that some of them have low contributions from specific sources, thus the boundaries can be properly defined. Ambient air polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyls (PCB) samples ($n = 160$) were collected at 40 sites during four seasons (summer, fall, winter, and spring) between July 2009 and April 2010 in the heavily industrialized Aliaga region in Turkey to investigate their spatial, seasonal variations and to identify possible PAH and PCB sources. The newest version of EPA PMF (V5.0) having the capability of handling multiple site data was used for source apportionment. Five PAH sources were identified as biomass and coal combustion, iron–steel production, unburned crude oil and petroleum products, and diesel and gasoline exhaust emissions with contributions of 40, 27, 27, 3, and 3%, respectively. The sources of PCBs were identified as iron–steel production (consisting of steel-making and ship breaking activities), coal and wood combustion, and evaporative emissions from technical PCB mixtures with contributions of 57, 31, and 12%, respectively.

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1. Introduction

Persistent organic pollutants (POPs) are dangerous for human health due to their low water and high fat solubility, low vapor pressure, persistence, and toxicity (Willett et al., 1998; Kim and Smith, 2001). Emissions and occurrence of POPs in the environment are very often limited by regulations (Dmitruk et al., 2008). The United Nations Economics for Europe (UNECE) and Convention on Long-Range Transboundary Air Pollution (CLRTAP) defined the

criteria of POPs as: they possess toxic characteristics, persistent in the environment, tend to bioaccumulate in higher trophic levels, and undergo long-range atmospheric transport (UNECE, 1979).

Polycyclic aromatic hydrocarbons (PAHs) are unintentionally produced by-products. They are widespread throughout environmental compartments including air, water, sediment and soil (Odabasi, 1998; Motelay-Massei et al., 2003; Stanimirova et al., 2011; Kaya et al., 2012). PAHs have natural (forest fires and volcanic activities) and anthropogenic sources (motor vehicles, waste incineration plants, domestic heating, oil refining, liquefying plants, coal gasification, asphalt production, coke and aluminum production, activities in petroleum refineries and other industrial processes) (Pelkonen and Nebert, 1982; Nagpal, 1993).

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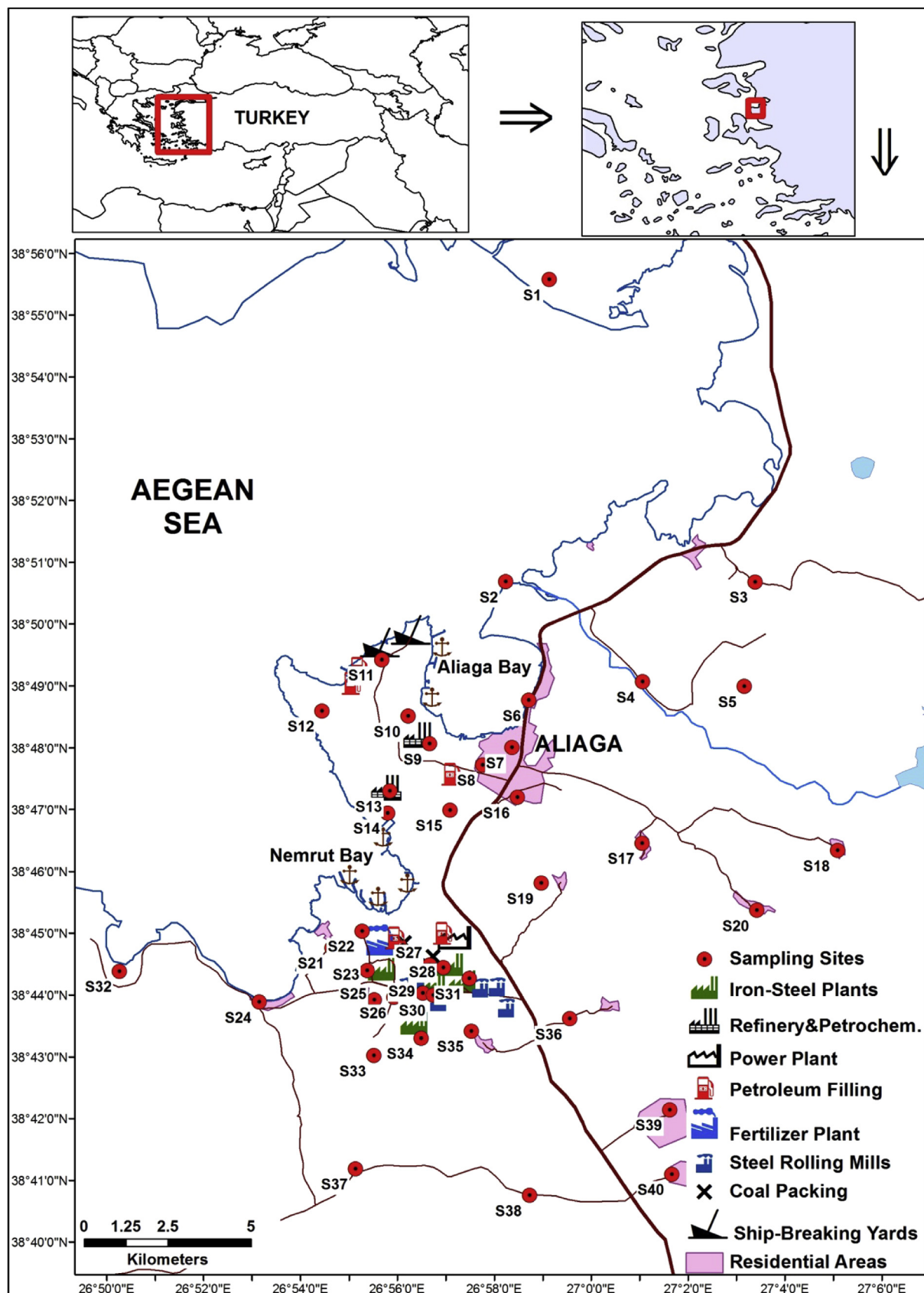


Fig. 1. Locations of the sampling sites ($n = 40$) and industrial activities in the study area.

Polychlorinated biphenyls (PCBs) were primarily used in capacitors, transformers, paints, and in many industrial applications (Hedgcock, 1994; Badawy et al., 2010). However, the production and use of PCBs have been banned in many countries for decades due to their hazardous properties. PCBs are released into the environment from illegal or improper dumping of PCB containing wastes into landfills, open burning, incineration of industrial and municipal wastes (e.g. refuse, sewage sludge), vaporization from contaminated surfaces and products containing PCBs, accidental spills and leakage from products to soil, direct entry or leakage into sewers and streams, leakage from older electrical equipment in use, and the repair and maintenance of PCB containing equipment (Vallack et al., 1998; UNEP, 1999; Breivik et al., 2002; U.S. EPA and DEQ, 2005).

Source identification of POPs is an important step in air quality management (Masunaga et al., 2003). Therefore, two basic methods have been used to identify and apportion sources of POPs; source-oriented models and receptor models (Li et al., 2003). Source-oriented models are not easily applicable for PCBs since it is difficult to acquire their source profiles. However, receptor models can determine contributions from all sources based on ambient air measurements (Gordon, 1988). Factor Analysis with Non-negative Constraints (FA-NNC) and Positive Matrix Factorization (PMF) have been used successfully to identify the sources of POPs in atmospheric particulates (Rachdawong and Christensen, 1997; Uchimiya et al., 2007). PAHs sources have been determined in several studies carried out in different industrial regions (Khalili et al., 1995; Harrison et al., 1996; Vardar et al., 2008; Odabasi et al., 2009; Tian et al., 2009). However, source apportionment of atmospheric PCBs has been scarce (Rodenburg and Meng, 2013).

Recent studies based on soil, ambient air, and stack-gas sampling have shown that the scrap processing iron–steel plants with electric arc furnaces (EAFs) are important local sources of PAHs, PCBs, several other organic compounds, and trace elements in the Aliaga heavily industrialized region (Cetin et al., 2007; Cetin and Odabasi, 2007; Bayram et al., 2008; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009). Ship breaking activities, petroleum refinery, and petrochemical complex are the other POP emitters in the area.

The objectives of this study were (1) to determine the spatial and seasonal variations of PAH and PCB concentrations in Aliaga region in Turkey and (2) to identify the possible sources of atmospheric PAHs and PCBs.

2. Materials and methods

2.1. Study area and sampling program

The Aliaga region (38°42′–38°55′N and 26°50′–27°04′E) is located in the western part of Turkey on the coast of the Aegean Sea and contains a large petroleum refinery, a petrochemical complex, five ferrous scrap processing iron–steel plants with electric arc furnaces (EAFs), steel rolling mills, a natural gas-fired power plant, a pulp and paper plant, a fertilizer plant, ship breaking yards, scrap storage and classification sites, a very intense transportation activities of ferrous scrap trucks, heavy road traffic, and busy ports used for product and raw material transportation. Aliaga town with a population of ~60,000, several villages, and agricultural areas are also located within the region (Fig. 1).

Ambient air samples ($n = 160$) were collected during four seasons (summer, fall, winter, and spring) at forty sites (17 industrial and 23 non-industrial, Fig. 1). The sampling periods were: July–August 2009 (summer), October–November 2009 (fall), January–February 2010 (winter), and April–May 2010 (spring). Average air temperatures were 27.1, 19.9, 9.3, and 15.9 °C for summer, fall, winter, and spring sampling periods, respectively. Generally

northwesterly winds prevailed during the sampling periods. Southeast (SE) and South (S) winds observed especially in fall.

2.2. Sampling

Ambient air samples were collected using polyurethane foam (PUF) disk passive air samplers (PAS). PUF disks (14 cm diameter, 1.35 cm thick, 365 cm² surface area, 0.0213 g cm⁻³ density, 4.40 g mass, 207 cm³ volume) were placed inside a stainless steel chamber consisted of two stainless steel bowls, one with a diameter of 30 cm and the other of 20 cm. The design of the sampler protects the foam disk from precipitation, coarse particle deposition, and ultraviolet radiation, and minimizes the effects of wind speed on the uptake rate. Before sampling, depuration compounds (DCs) (¹³C-PCB 3, ¹³C-PCB 9, ¹³C-PCB 15, PCB 30, PCB 107, and PCB 198), 17.5–20 ng per sample dissolved in 20 mL hexane were spiked evenly onto PUF disks. Then, solvent was evaporated using a gentle stream of N₂ and PUFs were kept for 1 week in their containers in a freezer. Passive samplers were placed at 2.5–3.5 m above the ground and samples were collected after 30–31 days exposure periods.

2.3. Sample preparation and analysis

All samples were spiked with PAH (naphthalene-d10, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) (Esen et al., 2008; Demircioglu et al., 2011; Lin et al., 2013a; Yang et al., 2013) and PCB (PCB-14, PCB-65, and PCB-166) (Crecelius and Lefkovitz, 1994; Basu, 1995; Odabasi et al., 2009) surrogate standards prior to extraction. PUFs were Soxhlet extracted for 12 h with a mixture of 1:1 acetone:hexane. The extract volumes were reduced and transferred into hexane (2 mL) using a rotary evaporator and a high purity N₂ stream. Then, extracts were cleaned up and fractionated on an alumina-silicic acid column containing 3 g silicic acid (deactivated with 4.5% DI water) and 2 g alumina (deactivated with 6% DI water). The column was pre-washed with 20 mL dichloromethane (DCM) and 20 mL petroleum ether (PE). Then, the sample in 2 mL hexane was added to the column and PCBs were eluted with 35 mL PE (Fraction 1) while PAHs were eluted with 20 mL DCM (Fraction 2). The final extracts were solvent exchanged into hexane and were concentrated to 1 mL under a stream of N₂.

Samples were analyzed for 14 PAHs (acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[a]pyrene (BaP), indeno [1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo [g,h,i]perylene (BghiP)) and 35 PCBs (18, 17, 31, 28, 33, 52, 49, 44, 74, 70, 95, 101, 99, 87, 110, 82, 151, 149, 118, 153, 132, 105, 138, 158, 187, 183, 128, 177, 171, 156, 180, 170, 199, 194, 206) with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) using electron impact ionization. The capillary column used was HP5-MS (30 m, 0.25 mm, 0.25 μm) and the carrier gas was helium. Fraction 1 was analyzed for PCBs in selected ion monitoring mode (SIM). Then, equal volumes of Fraction 1 and 2 were combined and analyzed for PAHs since some lighter PAHs are eluted partly with Fraction 1. Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. Further details for sample preparation and instrumental analysis could be found elsewhere (Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009).

Average recoveries for the surrogate standards of were 84 ± 20% (ACT-d₁₀), 107 ± 23% (PHE-d₁₀), 98 ± 24% (CHR-d₁₂), 92 ± 23% (perylene-d₁₂), 86 ± 12% (PCB-14), 93 ± 13% (PCB-65), 89 ± 11%

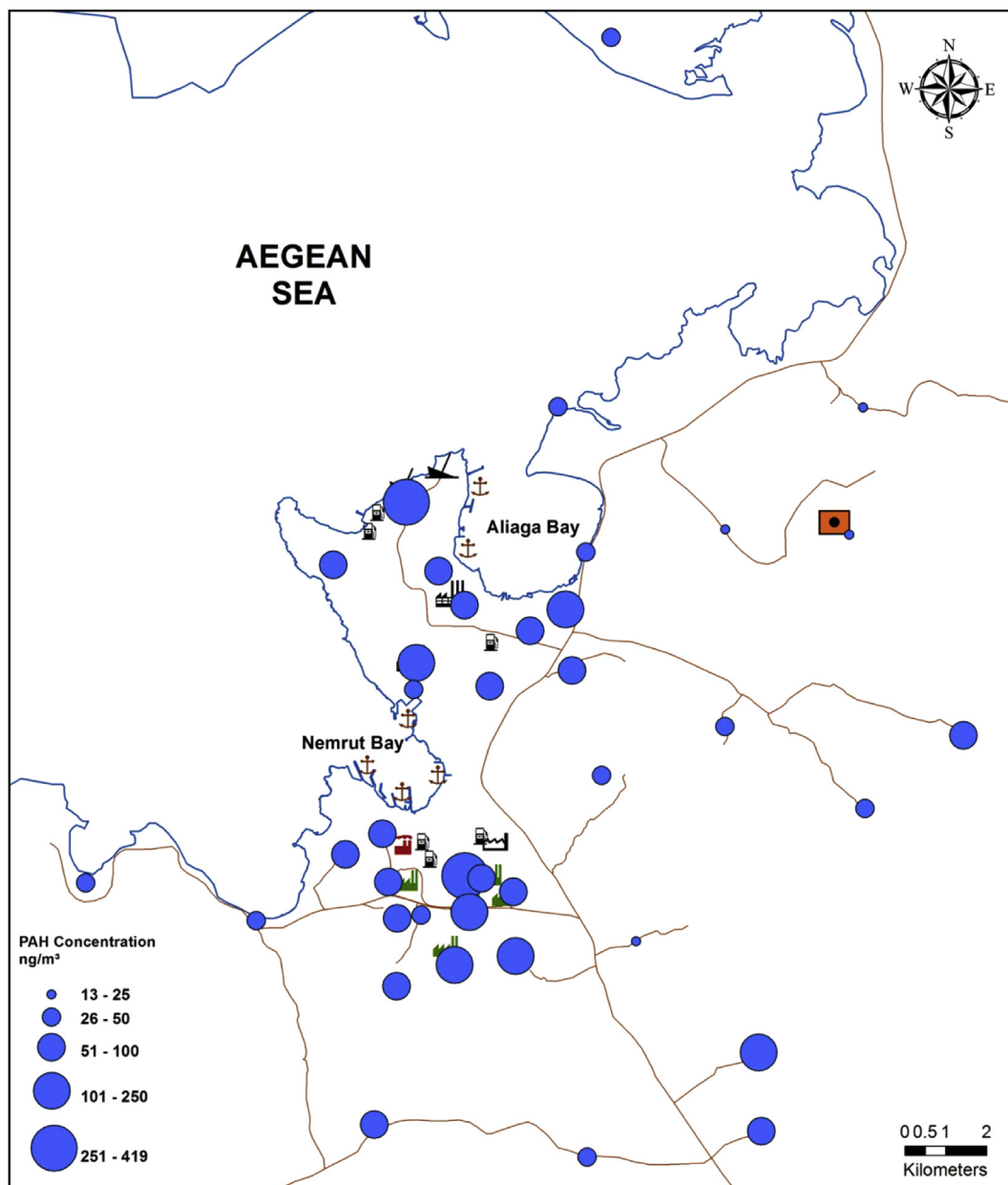


Fig. 2. Spatial distribution of $\Sigma_{14}\text{PAH}$ concentrations (ng m^{-3}) in Aliaga region.

(PCB-166). Instrumental detection limits (IDL) 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 and 0.10 pg for PAHs and PCBs, respectively. Blank PUF disks were also analyzed. The method detection limit (MDL, ng) was defined as the mean blank mass plus three standard deviations ($\text{MDL} = \text{Mean blank value} + 3\text{SD}$). Instrumental detection limit was used for the compounds that were not detected in blanks. Using the MDL values and average sampling volumes determined for different compounds, calculated method detection limit ranged between 0.001 and 0.074 ng m^{-3} and 0.7–6.4 pg m^{-3} for PAHs and PCBs, respectively. Average analyte amounts in blanks were generally <5% of the amounts found in samples. Sample quantities exceeding the MDL were quantified and blank-corrected by subtracting the average blank amounts from sample amounts.

Sampling rates (R , $\text{m}^3 \text{day}^{-1}$) were determined using the depuration compounds (DCs). The effective sampling air volumes (V_{air} , m^3) for PAHs and PCBs for a 1-month sampling period were calculated using the relationship developed by [Shoeib and Harner \(2002\)](#) for the non-polar hydrophobic chemicals. The calculation of effective air sampling volumes was detailed in the [Supplementary Data](#) and was reported by [Kaya et al. \(2012\)](#) and [Aydin \(2013\)](#).

2.4. Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) method has been used to identify the possible sources of PAHs and PCBs ([Tian et al., 2008](#); [Jin et al., 2012](#); [Zhang et al., 2012](#); [Lin et al., 2013a](#); [Wang et al., 2013](#)). PMF is a model for solving a receptor-only, bilinear unmixing model which assumes that a measured dataset conforms to a mass-

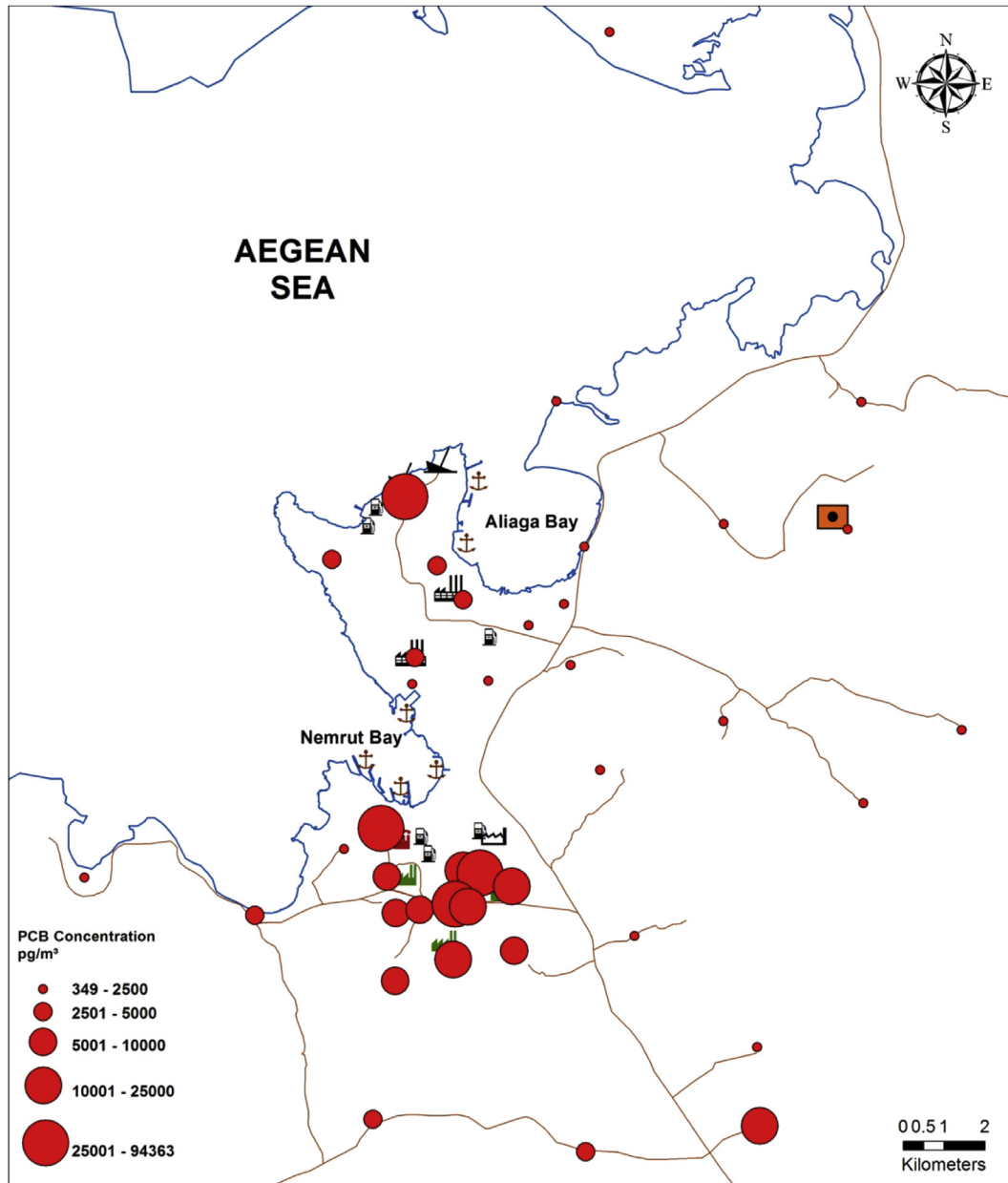


Fig. 3. Spatial distribution of $\Sigma_{35}\text{PCB}$ concentrations (pg m^{-3}) in Aliaga region.

balance of a number of constant source profiles contributing varying concentrations over the time of dataset. Basic information related to PMF has been discussed by Hopke (2003). PMF has some advantages over the principal component analysis (PCA). The main difference is the uncertainty-weighting of each data point in PMF, as opposed to the implicit assumption made in traditional PCA settings that each data point has an equal weight. Second difference is that the factors in PMF are not necessarily orthogonal to each other. This meets the observation of real-source signatures which are also not orthogonal to each other. Furthermore, the non-negativity constraint in PMF is an additional advantage.

In PMF model a matrix X of data of dimension n rows and m columns, where n and m are the number of samples and the number of species, can be factorized into two matrixes, namely $G(n \times p)$ and $F(p \times m)$, and the residual matrix, E , where p is the number of factors.

$$X = GF + E \quad (1)$$

The product of G and F explains the systematic variations in X . The residuals, E_{ij} can be expressed as:

$$E_{ij} = X_{ij} - \sum_{h=1}^p G_{ih} \cdot F_{hj} \quad (2)$$

The object function Q that has to be minimized is defined as:

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left[\frac{E_{ij}}{S_{ij}} \right]^2 \quad (3)$$

where S_{ij} is the uncertainty in X_{ij} . The next step of the process is to minimize Q as a function of G and F with the constraints of all

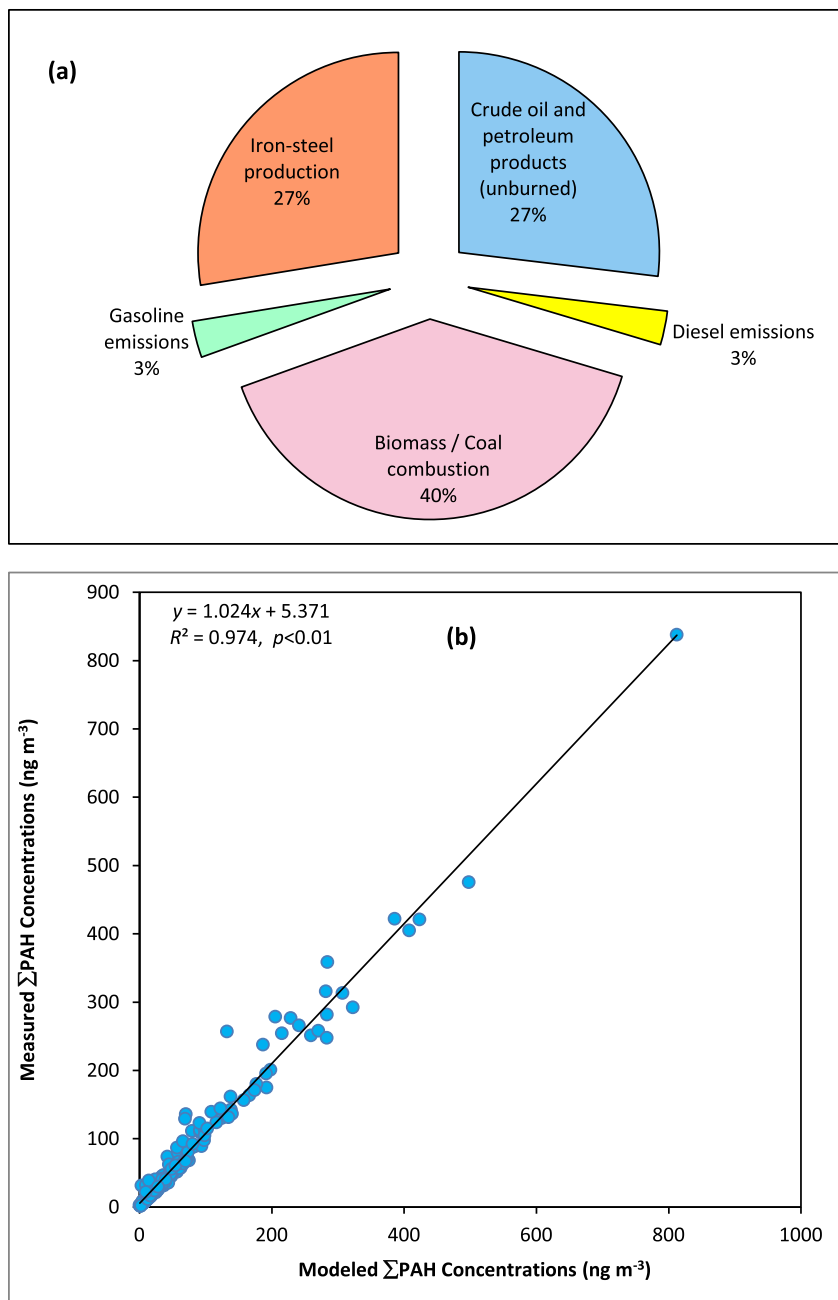


Fig. 4. (a) Source contributions to the total PAH concentrations, (b) relationship between the measured and modeled PAH concentrations.

elements of G and F to be non-negative. The solution of Equation (3) is obtained using the program of PMF (Paatero, 1997).

As each sample is associated with its own inherent uncertainty, PMF generally requires a large number of samples to make stable and reliable source identification. Therefore, data collected in the present study at all sampling sites and in all seasons were lumped together for PMF source apportionment analysis, similar to the approach that has been used by recent studies (Lau et al., 2010; Civan et al., 2011; Lin et al., 2013b; Yuan et al., 2013).

Data was resolved using the EPA PMF (V5.0) (U.S. EPA, 2014). The input data file consisted of receptor concentration (C) and uncertainty (U) matrices. U for each variable was calculated using C and the method detection limit (MDL). If C was above the MDL, U was

assumed to be $(0.1C + \text{MDL}/3)$, and if else C replaced by $\text{MDL}/2$ and U was assumed to be $(0.2C + \text{MDL}/3)$ (Tauler et al., 2009; Jang et al., 2013).

To determine the optimal number of sources, the model was tested for 3–7 factors by running 20 times with a random seed to determine the stability of Q values; Q values were stable and all runs converged. In addition, extra modeling uncertainty (10% for both PAHs and PCBs) was imposed to account for changes in the source profiles and other sources of variability. The Q values, the resulting source profiles, and the scaled residuals distributions were studied and the optimum solutions were obtained as five and three factors for PAHs and PCBs, respectively. Then, one hundred bootstrap runs were conducted with minimum correlation R -value

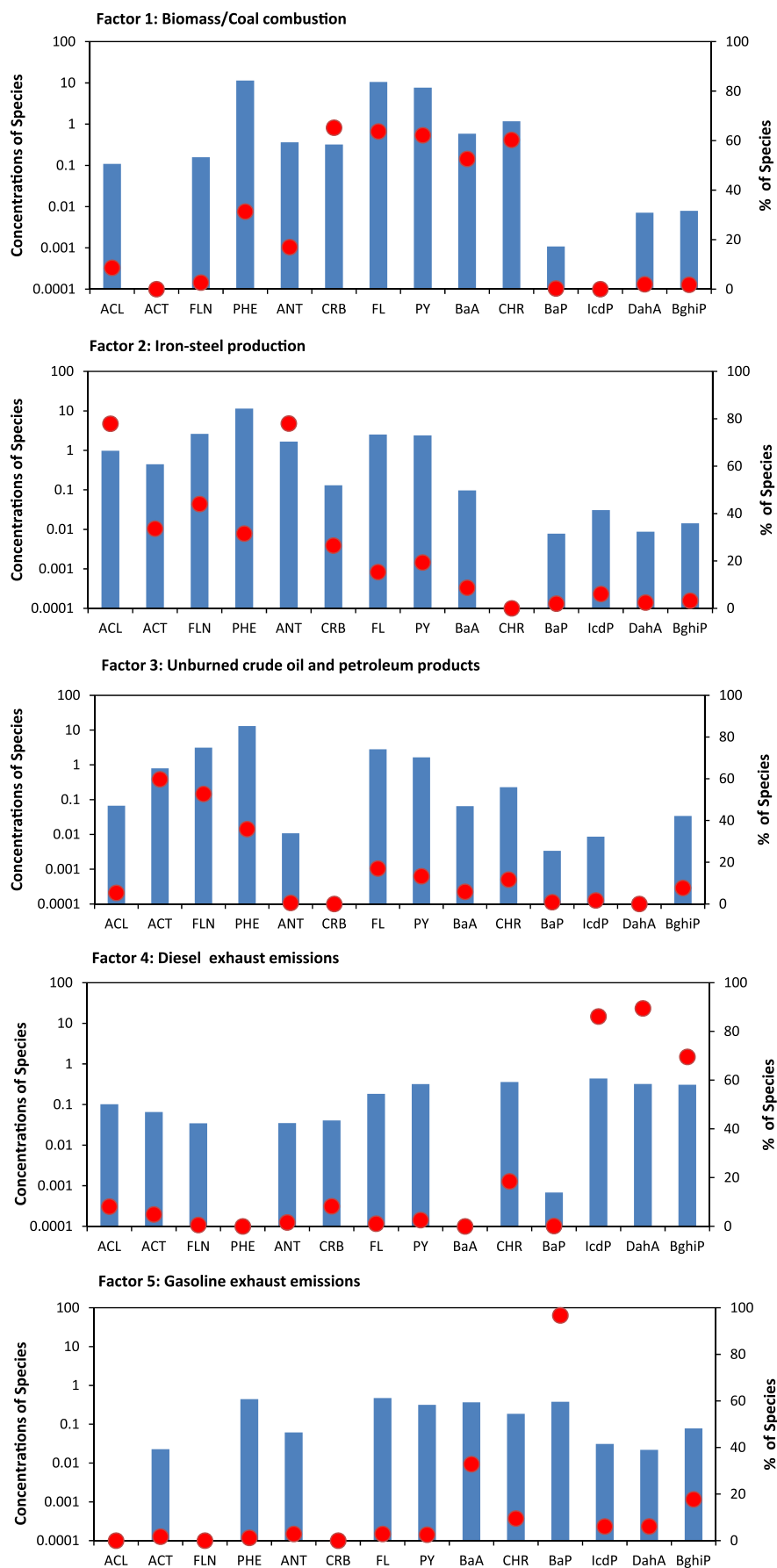


Fig. 5. PMF source profiles of PAHs. Acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA).

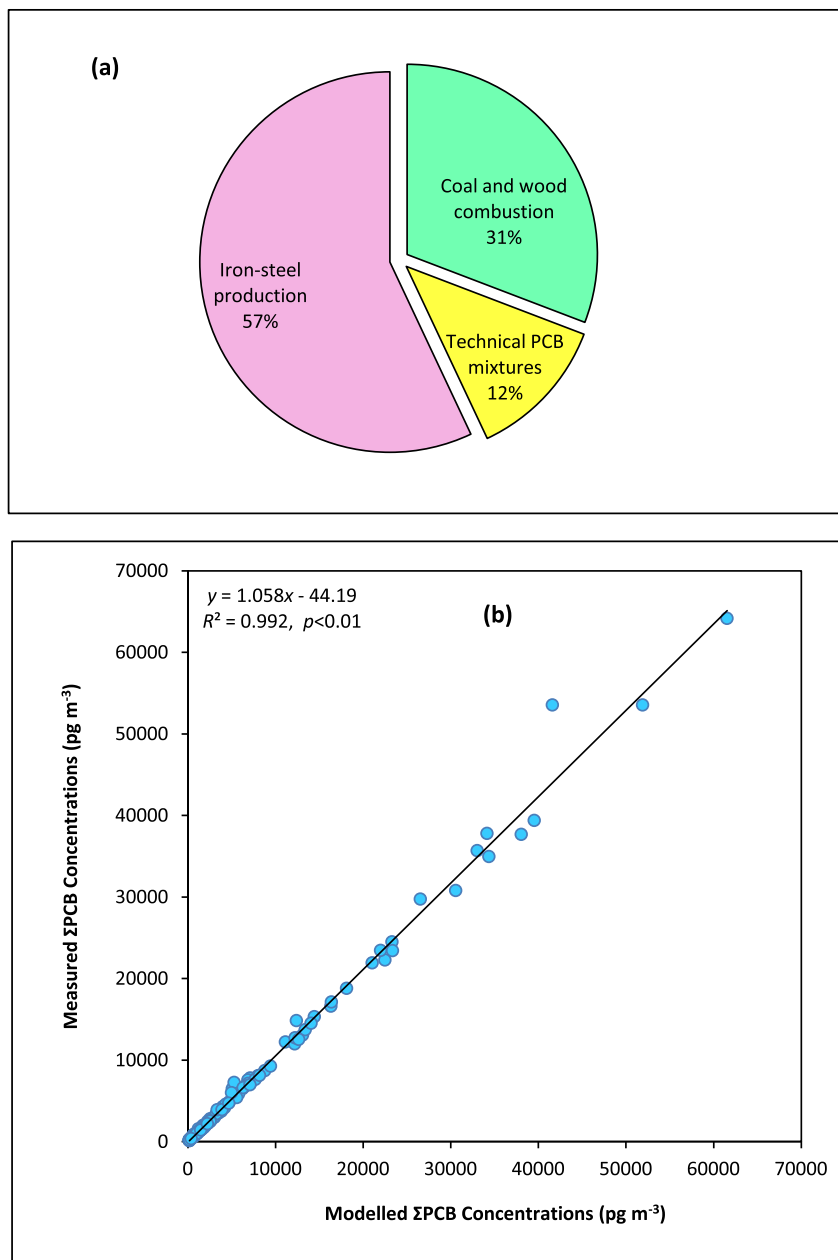


Fig. 6. (a) Source contributions to the total PCB concentrations, (b) relationship between the measured and modeled PCB concentrations.

of 0.6 to examine the stability and to estimate the uncertainty of the base run solution. All of the bootstrapped factors were uniquely matched with a factor from the base solution.

3. Results

3.1. PAH and PCB concentrations

The concentrations of Σ_{14} PAHs ranged from 1.6 to 838 ng m^{-3} (Table S1). PAH concentrations showed a substantial increase in the industrial sites, especially around the iron–steel plants and ship breaking yards (Fig. 2). For all periods, site-averaged Σ_{14} PAH concentrations were 2–5 times higher in industrial sites compared to non-residential sites (Table S1).

Except three sampling sites, the highest PAH concentrations were measured during winter period. A recent study has reported

that combustion-derived PAH emissions may be elevated during the colder months (Pozo et al., 2012). Higher PAH concentrations in winter were also reported in several studies (Bae et al., 2002; Gevao et al., 1998; Kiss et al., 2001; Odabasi et al., 2006a; Vardar et al., 2008). Therefore, high PAH concentrations measured in the present study during winter could be attributed to coal and wood combustion for residential heating at the settlements in the region. The lowest PAH concentrations were detected during the summer sampling period (July–August) in the study area. On the other hand, in three sites located the vicinity of iron–steel plants (see Fig. 1, Sites 29, 30, and 34), the highest PAH concentrations were observed in summer. Kaya et al. (2012) have recently calculated the soil to air fugacity ratios (f_s/f_a) in the sampling sites of the present study. During summer, at Sites 29, 30, and 34 fugacity ratios for ACL, ACT, and FLN were generally >1.0 indicating net volatilization from soil. This suggests that the highest PAH concentrations measured in

Sites 29, 30, and 34 in summer may have been affected by increased volatilization from their sources at higher temperatures.

Σ_{14} PAHs were dominated by PHE followed by FL, PY and FLN in the region (Fig. S2). PHE was also the dominant compound in several regions (Cumbria, UK; Chicago, USA; Philippines; Aliaga, Turkey) as reported by Gevaio et al. (1998), Odabasi et al. (1999); and Santiago and Cayetano (2007), and Bozlaker et al. (2008a).

Site-averaged Σ_{35} PCB concentrations in the air ranged from 349 to 94,363 pg m⁻³. Low molecular weight congeners (PCB-18, 28, 31, 33, 52, and 49) dominated the Σ_{35} PCB concentrations (Fig. S3). During all seasons, PCB concentrations showed a strong increase in the industrial sites compared to the non-industrial sites, confirming the continuing role of industries in Aliaga as PCB sources (Fig. 3). High PCB concentrations were measured at the sampling sites in the vicinity of the iron–steel plants and ship breaking facilities, where all kind of scrap iron steel materials are stored, classified, cut into parts, and melted (Table S2). Highest atmospheric PCB concentrations were observed in summer (Table S2). Kaya et al. (2012) have recently investigated soil–air exchange of PCBs in the same area of the present study. During summer, fugacity ratios (f_s/f_a) for low molecular weight PCBs (PCB 17, 18, and 28) were generally >1.0 indicating net volatilization while the ratios for the remaining congeners indicated deposition. During winter, most of the PCBs deposited. These results suggest that the highest PCB concentrations observed in the present study during summer may be due to increased volatilization from their sources at higher temperatures.

Recently, several studies (Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009; Demircioglu et al., 2011)

have reported the ambient air PAH and PCB concentrations in Izmir region. Concentrations measured at those studies covered a range of spatial (urban, suburban, and industrial sites) and a seasonal (winter, summer) variation. Comparisons have indicated that the atmospheric PAH and PCB concentrations measured in the area were within the ranges reported in the literature (Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Demircioglu et al., 2011). In general, the concentrations measured in industrial sites of the present study were substantially higher than those recently reported for the Izmir area. Σ PCB concentrations reported in the literature and measured in Izmir area are in the range of a few hundreds to a few thousands pg m⁻³ (Cetin et al., 2007; Bozlaker et al., 2008a). Comparably high Σ_{27} PCB concentrations (4,230–11,350 pg m⁻³) were measured around an electronic waste dismantling facility in China (Li et al., 2008). Σ_{41} PCB concentrations measured in a recent study near the steel plants in Aliaga (19,000–136,000 pg m⁻³) were among the highest ones measured around the world (Odabasi et al., 2009). Similarly high Σ_{35} PCB concentrations were measured at the industrial sampling sites of the present study (up to 230,818 pg m⁻³) (Table S2). Measured average total (gas + particle) Σ_{14} PAH concentrations were 36 ± 39 and 144 ± 163 ng m⁻³ for suburban and urban sites in Izmir (Demircioglu et al., 2011). Σ_{14} PAH concentrations measured in the present study were highly variable (1.6–838 ng m⁻³, Table S1), however concentrations measured at industrial sites were generally higher than those measured recently at suburban (23.5 ng m⁻³) and urban sites (109.7 ng m⁻³) in Izmir (Demircioglu et al., 2011).

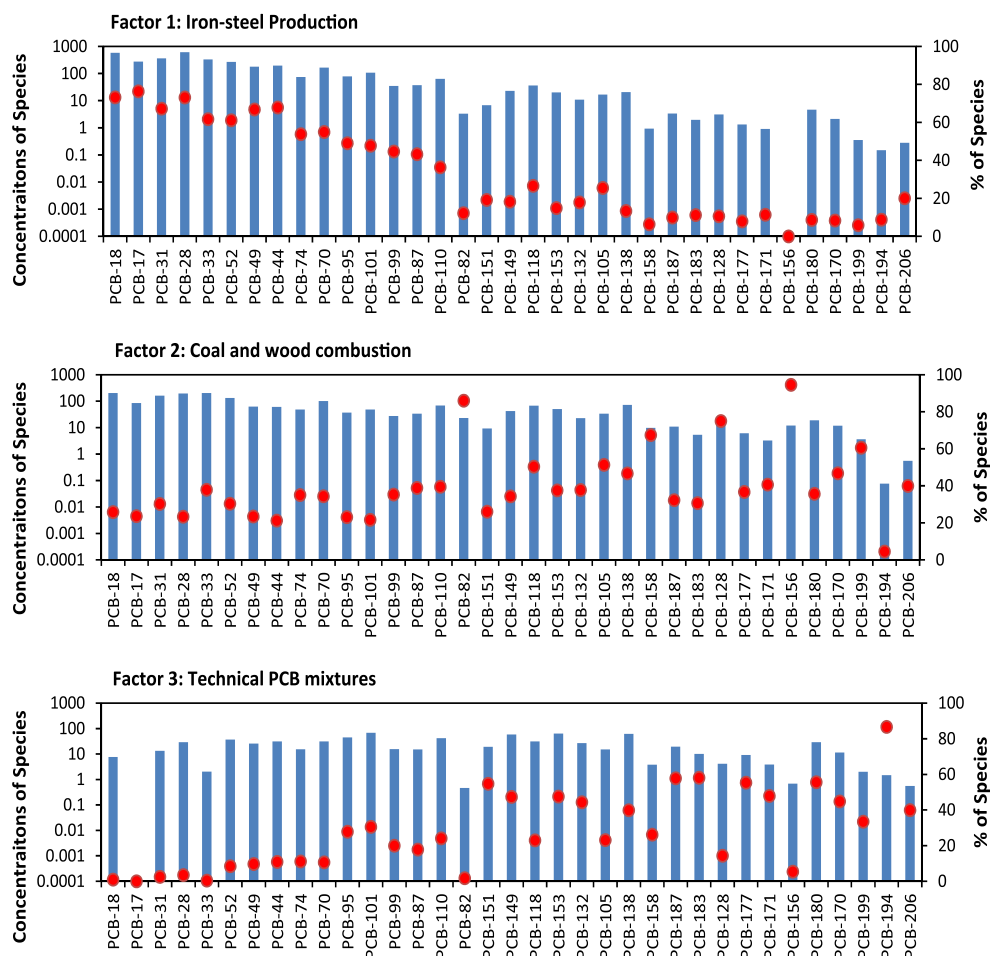


Fig. 7. PMF source profiles of PCBs.

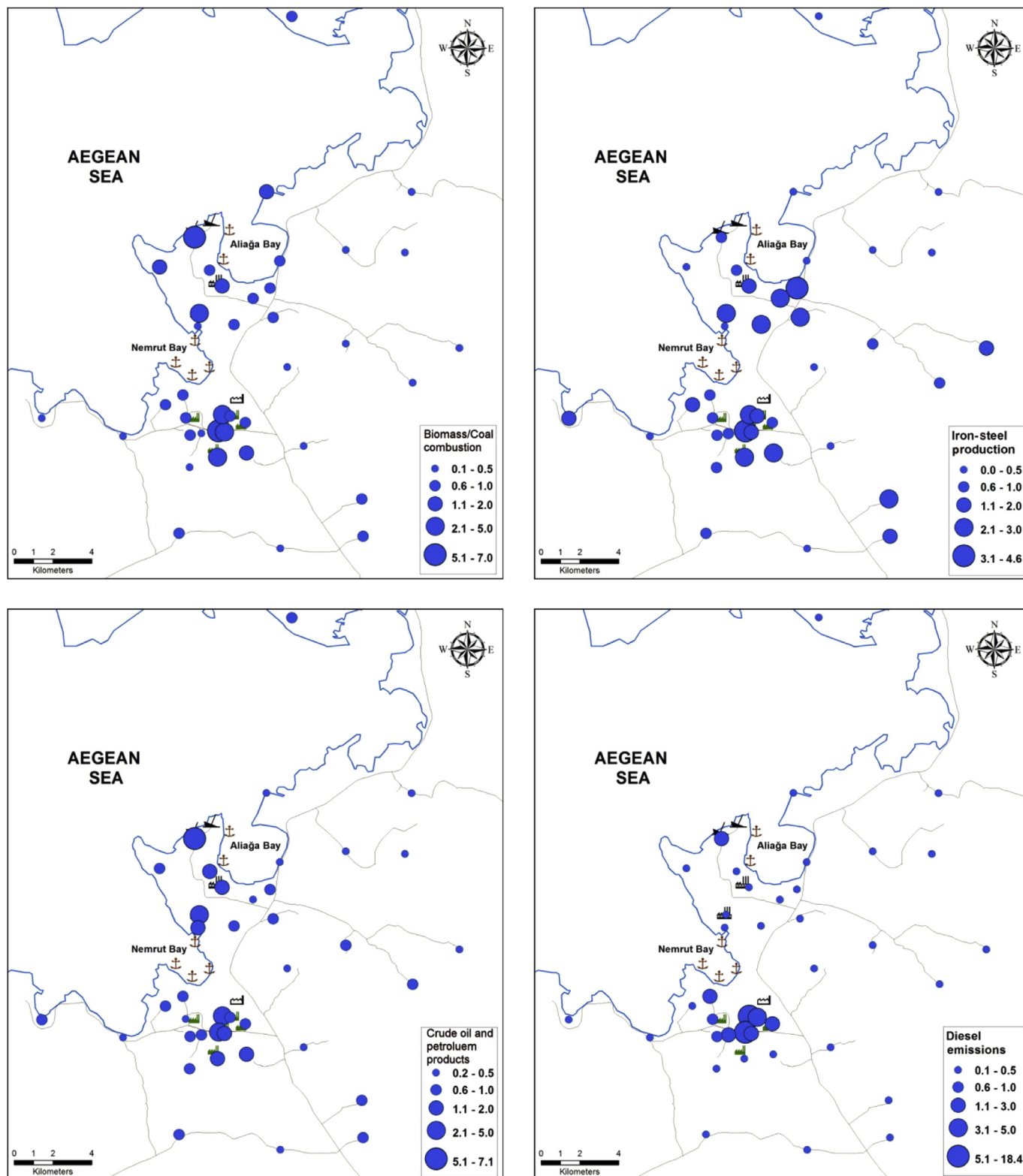


Fig. 8. Spatial distribution of source contributions to the $\Sigma_{14}\text{PAH}$ concentrations (ng m^{-3}) in the study area.

3.2. Source apportionment

Five sources for PAHs were identified as biomass (including, wood and crop stalks) and coal combustion (residential and industrial), iron–steel production, unburned crude oil and petroleum

products, diesel, and gasoline exhaust emissions. Biomass and coal combustion processes had the largest contribution (40%) to $\Sigma_{14}\text{PAHs}$. It was followed by iron–steel production, unburned crude oil and petroleum products, diesel and, gasoline exhaust emissions that contributed to total mass by 27, 27, 3, and 3%, respectively

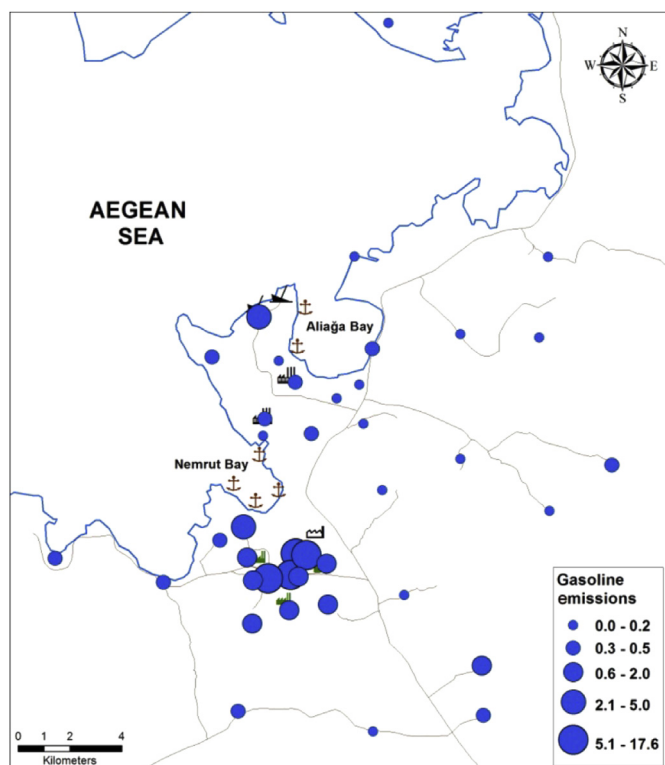


Fig. 8. (continued).

(Fig. 4). The relationship between measured and modeled Σ_{14} PAH concentrations was good and significant ($R^2 = 0.97$, $p < 0.01$) and the slope of the regression line (1.02) was close to unity indicating a close agreement (Fig. 4).

The first factor had high loadings on CRB, FL, PY, CHR, BaA and moderately loadings on PHE and ANT (Fig. 5). CRB is a nitrogen containing PAH found in fossil fuels (i.e., coal, and crude oil) (Benedik et al., 1998; Williams and Nazzal, 1998), and it is also emitted from coal and wood combustion (Liang and Pankow, 1996; Smith and Hansch, 2000; Ross et al., 2002; Odabasi et al., 2006b). FL and PY are usually used as markers for coal combustion (Tian et al., 2009; Wang et al., 2009; Cao et al., 2011; Lin et al., 2013a). CHR is also a marker for residential coal combustion, coke ovens, and biomass/coal related sources (Cao et al., 2011; Wang et al., 2013; Yang et al., 2013). ANT, PHE, FL, PY, and CHR were identified as source fingerprints of wood combustion (Khalili et al., 1995; Cao et al., 2011). ACL has also been commonly used as an indicator of wood combustion (Zuo et al., 2007; Shao et al., 2014). Therefore, this factor represents biomass and coal combustion emissions from residential and industrial sources.

The second factor had high loadings on ACL, ANT, FLN, and moderate loadings on ACT, PHE, FL, PY, BaA, and CRB (Fig. 5). This profile was very similar to that reported by Odabasi et al. (2009) for iron–steel production from ferrous scrap in this study area. ACL, FLN, PHE, PY, BaA were reported as distinctive markers in that study. Therefore, factor 2 was described as iron–steel production from scrap.

The third factor was highly loaded on ACT and FL, and moderately loaded on PHE, ACL, FLN, PY, CHR, BghiP (Fig. 5). The petrogenic sources are characterized by the predominance of 2 and 3-ring PAHs (Yunker et al., 2002). The PAH profile of factor 3 was also similar to those reported for gasoline and diesel (Alkurdi et al., 2013). Considering that there is a large petroleum refinery and a

petrochemical complex in the study area, factor 3 was identified as unburned crude oil and petroleum products.

The fourth factor was dominated by high molecular weight PAHs, i.e., BghiP, IndP, DahA and also moderately loaded on CHR (Fig. 5). The predominance of PAHs with more than four rings has been attributed to a pyrogenic PAH profile (Harrison et al., 1996; Simcik et al., 1999). Motelay-Massei et al. (2005) suggested that IndP and DahA can be indicators for vehicular emissions. Diesel exhaust is known to contain more particulate matter than gasoline exhaust, and heavier PAHs such as BghiP, IndP, and DahA are associated with these particles (Manoli et al., 2004; Ravindra et al., 2008; Umbuzeiro et al., 2008; Callen et al., 2012; Cristale et al., 2012). Tian et al. (2013) assigned CHR as a marker of diesel emissions. Therefore, this factor explained as diesel exhaust emissions.

The last factor was highly loaded on BaP and moderately on BaA, BghiP, DahA, and IndP (Fig. 5). BaP, BaA, BghiP, DahA, IndP are the indicators of exhaust emissions from gasoline-powered vehicles (Esen et al., 2008; Tian et al., 2013). IndP was related to gasoline-powered vehicle emissions also by Guo et al. (2003). Thus, factor 5 resolved in the present study was explained as gasoline exhaust emissions.

Three sources for PCB emissions were identified based on the marker congeners for each source that are exclusively or largely appear in the factor. The emission sources of PCBs were identified as iron–steel production (consisting of steel-making and ship breaking activities), coal and wood combustion, and evaporation from technical PCB mixtures. The major source was iron–steel plant emissions with 57% of contribution to Σ_{35} PCB concentrations. It was followed by coal and wood combustion and technical PCB mixtures that contributed to Σ_{35} PCBs by 31% and 12%, respectively. The relationship between the measured and modeled concentrations was significant ($R^2 = 0.99$, $p < 0.01$) and the slope of the regression line (1.06) was close to unity indicating a close agreement (Fig. 6).

The first factor had high loadings on PCB-17, PCB-18, PCB-28, PCB-31, PCB-33, PCB-44, PCB-49, PCB-52, PCB-70, and PCB-74, moderately loaded on PCB-82, PCB-87, PCB-95, PCB-99, PCB-101, PCB-105, PCB-110, PCB-118, and PCB-206 (Fig. 7). Odabasi et al. (2009) have reported the emissions factors of iron–steel plants (with pre-heating and no pre-heating) and determined that especially low molecular weight congeners (PCB-18, PCB-28, PCB-31, PCB-33) dominated as source fingerprints in iron–steel production plant emissions. PCBs were widely used on ships in 1960–1980s. The ship breaking process is relatively simple and labor-intensive. The ship is stripped entirely and then cut into fragments using oxygen torches. As a result, ship breaking process itself, as well as the fires that burn the non-recyclable waste materials emits PCBs (Basha et al., 2007). Therefore, this factor represents the emissions of scrap processing iron–steel plants with electric arc furnaces (EAFs) and related activities (i.e., scrap storage and classification sites, steel rolling mills, and ship breaking activities).

The second factor was highly loaded on PCB-82, PCB-87, PCB-105, PCB-110, PCB-118, PCB-128, PCB-156 and also on highly chlorinated congeners (PCB-170, PCB-171, and PCB-206) (Fig. 7). According to Lee et al. (2005), these PCBs can be found in residential coal and hardwood emissions. Kim et al. (2004) have also reported that PCB-128, PCB-170, PCB-171, and PCB-206 are combustion marker congeners. Therefore, this factor was described as coal and wood combustion for residential heating.

The last factor showed high correlations for highly chlorinated biphenyls (PCB-151, PCB-128, PCB-187, PCB-183, PCB-177, PCB-180, PCB-193, PCB-170, PCB-199, PCB-194) and indicated a mixed profile for Aroclor 1254 and 1260 (Jin et al., 2012). Factor 3 also showed similarity to Kanechlor 600 that is consisted predominantly of PCB-

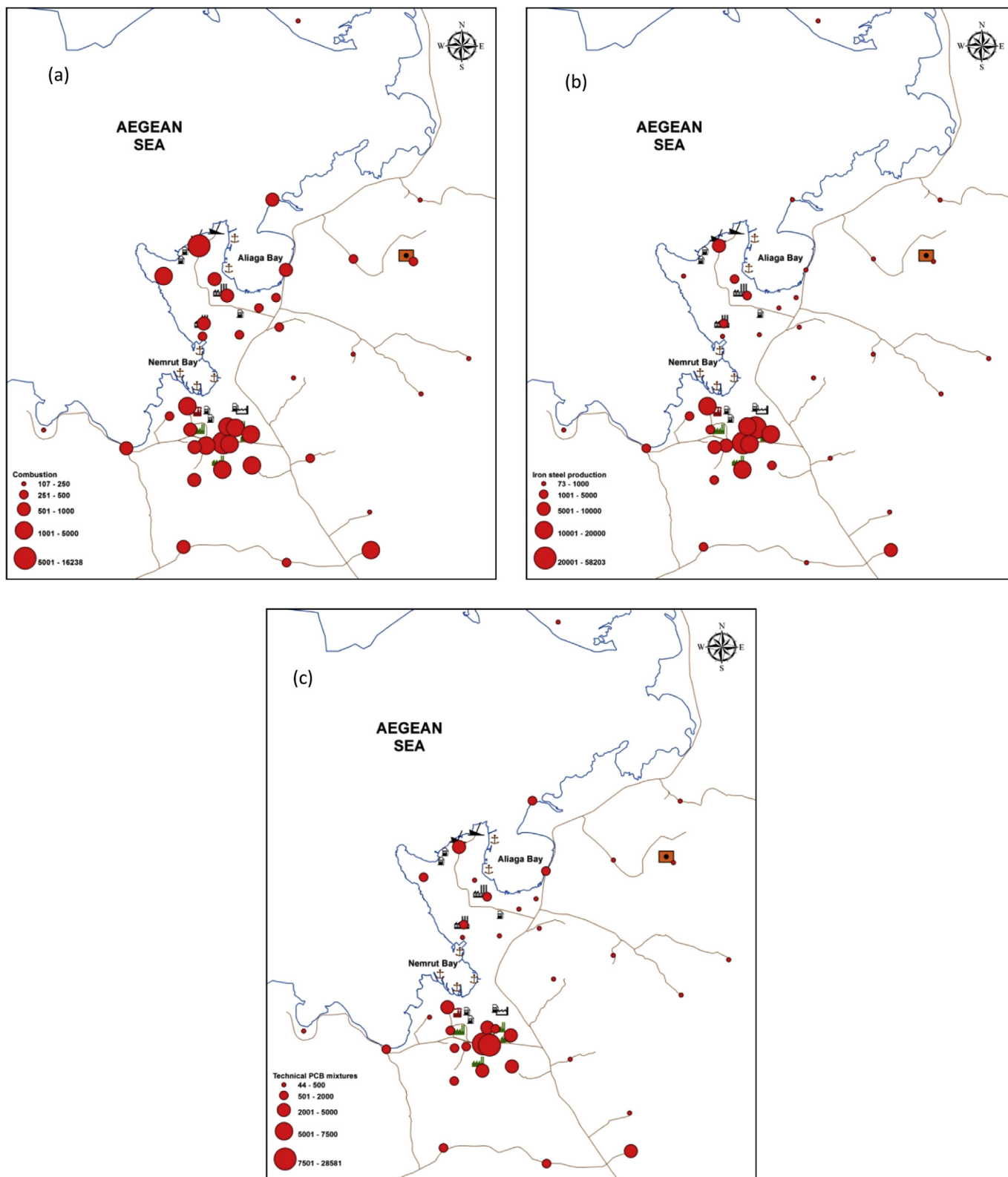


Fig. 9. Spatial distribution of source contributions to the $\Sigma_{35}\text{PCB}$ concentrations (pg m^{-3}) in the study area.

180, PCB-187, and PCB-170 (Takasuga et al., 2005, 2006). Therefore, this factor was ascribed to technical PCB mixtures (Fig. 7).

According to PMF analysis, source contributions at each sampling site and in the region were also determined. Figs. 8 and 9

show the spatial variation of contributions by identified sources. The spatial distributions of the sources were consistent with the outputs of receptor modeling, and identification of the sources. Contribution of biomass and coal combustion to PAHs is

widespread as they are emitted from residential heating and industrial sources. The contributions for iron–steel production were higher in the sites located in the vicinity of iron–steel plants and ship breaking yards since these activities affected the sites to a great extent. Vehicular exhaust emissions (gasoline and diesel) mainly affected sites located near steel plants and ports, due to intense truck traffic on the roads in the area (17,153 passenger cars and 6,610 heavy duty vehicles on the main road shown as the thick brown line in N–S direction and crossing the Aliaga town in Fig. 1, 5,473 passenger cars and 2,834 heavy duty vehicles on the road crossing the iron–steel plant area in E–W direction) (see also Fig. 8). Contribution of wood and coal combustion to atmospheric PCBs is widespread as wood emissions originate from residential heating, burning of crop residues on farmlands, forest fires while coal emissions are from industrial and residential sources. Contribution of iron–steel production emissions to PCBs has a similar profile to PAHs, but it is mainly concentrated in the vicinity of steel plants. However, contribution of technical PCB mixtures mainly affected the sites in the steel production area and those close to the ship breaking activities.

Contribution of sources to PAH and PCB concentrations in different seasons are also indicated in Figs. S4 and S5. Generally highest contributions were observed in winter and in summer for PAHs and PCBs, respectively. This is consistent with the seasonal variability in emissions (i.e., high PAH emissions from residential heating in winter and increased evaporative PCB emissions in summer). Spatial distributions were also similar to those shown in Figs. 8 and 9 with higher contributions in sites near the local sources.

4. Conclusions

Spatial and seasonal distributions of atmospheric polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in Aliaga industrial region were determined by passive sampling. Sources of PAHs and PCBs in the region were identified using EPA PMF (V5.0). Contributions of the pollutant sources were also specified. Five sources were identified as biomass and coal combustion (residential and industrial coal combustion), iron–steel production, unburned crude oil and petroleum products, diesel and gasoline exhaust emissions with contributions of 40, 27, 27, 3, and 3%, respectively. PCB sources were identified as iron–steel production (consisting of steel-making and ship breaking activities), coal and wood combustion, and evaporative emissions from technical PCB mixtures with contributions of 57, 31, and 12% to the measured total PCB concentrations.

According to PMF results especially iron–steel plants are one of the most considerable sources in the region for PAH and PCB emissions. It could be suggested that establishment of new iron–steel plants should not be allowed and control measures should be applied to reduce PAH and PCB emissions in the region.

The results of the present study indicated that PMF can be successfully used for source apportionment of atmospheric PAHs and PCBs. However, the studies on source characterization and identification of marker compounds (especially for PCBs) are relatively scarce. Therefore, it is recommended that future studies should be focused on identification on specific source marker compounds.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.08.032>.

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