DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SOURCE APPORTIONMENT OF PERSISTENT ORGANIC POLLUTANTS IN ALIAGA INDUSTRIAL REGION

by

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İZMİR

SOURCE APPORTIONMENT OF PERSISTENT ORGANIC POLLUTANTS IN ALIAGA INDUSTRIAL REGION

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M.Sc THESIS EXAMINATION RESULT FORM

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SOURCE APPORTIONMENT OF PERSISTENT ORGANIC POLLUTANTS IN ALIAGA INDUSTRIAL REGION

ABSTRACT

Ambient air samples of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were collected during four seasons (winter, spring, summer, and fall) at forty different sites in Aliaga that is one of major industrial areas in Turkey including several pollutant sources such as a large petroleum refinery and a petrochemical complex, scrap processing iron–steel plants with electric arc furnaces (EAFs), scrap storage and classification sites, steel rolling mills, a natural gas–fired power plant, a very dense transportation activity of ferrous scrap trucks, heavy road and rail traffic, a ship dismantling area, and busy ports with scrap iron dockyards. Spatial and seasonal variations of PAHs and PCBs were determined by passive sampling in 2009 and 2010. Source apportionment of PAHs and PCBs in the region were determined using Positive Matrix Factorization (PMF) method. Three different factors were identified for both PAHs and PCBs. Sources of PAHs were identified as combustion (residential coal and wood combustion, industrial coal combustion), iron-steel production, and vehicular exhaust emissions while PCBs sources were iron-steel production (consisting of steel-making and ship dismantling) emissions, combustion (coal and wood), and evaporative emissions from technical PCB mixtures.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), Positive Matrix Factorization (PMF), source apportionment, Aliaga.

ALİAĞA SANAYİ BÖLGESİNDE KALICI ORGANIK KİRLETİCİLERİN KAYNAKLARININ BELİRLENMESİ

ÖZ

Türkiye'de en önemli sanayi bölgelerinden birisi olan Aliağa'da ve yakın çevresinde 40 farklı noktadan dört mevsimde (kış, ilkbahar, yaz ve sonbahar) dış havada polisiklik aromatik hidrokarbonlar (PAH'lar) ve klorlu bifenillerin (PCB'ler) örnekleri toplanmıştır. Birçok kirlilik kaynağının bir arada bulunduğu bu bölgede, bir büyük petrol rafinerisi, bir petrokimya tesisi, elektrikli ark ocakları ile çalışan çok sayıda demir-çelik tesisi, hurda metal ve cüruf depolama alanları, çelik haddehaneleri, doğal gaz çevrim santrali, demir hurda taşıyan kamyonların ulaşımdaki aktivitesi, kara ve demiryolu trafiği, gemi söküm tesisleri ve ithal hurda demirin geldiği, indirildiği ve depolandığı limanlar bulunmaktadır. PAH ve PCB konsantrasyonlarının yerel ve mevsimsel değişimleri pasif örnekleme yöntemi ile 2009-2010 yıllarında belirlenmiştir. Bölgedeki PAH'lar ve PCB'lerin kaynak dağılımı Pozitif Matris Faktörizasyonu (PMF) yöntemi kullanılarak belirlenmiştir. Hem PAH'lar hem de PCB'ler için üçer farklı faktör tanımlanmıştır. PAH'ların kaynakları yanma (evsel ısınma amaçlı kömür ve odun yakılması ve endüstriyel amaçlı kömür kullanımı), demir-çelik üretimi ve araç eksozlarının emisyonları iken PCB'lerin kaynakları ise demir-çelik üretimi (gemi söküm faaliyetleri ile birlikte bölgedeki hurda işleyen diğer tesislerin demir-çelik üretimi faaliyetleri), yanma (kömür ve odun) ve ticari PCB karışımlarının buharlaşmasından oluşmaktadır.

Anahtar Kelimeler: Polisiklik aromatik hidrokarbonlar (PAH), poliklorlu bifeniller (PCB), Pozitif Matris Faktörizasyonu (PMF), kaynak dağılımı, Aliağa.

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, and chlorophenols are discharged to the environment by anthropogenic activities. POPs have been used in industrial products (e.g. pesticides, insecticides, dielectric and hydraulic fluids in industrial machinery, transformers and capacitors). They are also generated in industrial processes involving combustion such as food (fertilizers, pesticides, packaging, and food additives), clothing (synthetic fibers, dyestuffs, textile auxiliaries), hygiene (soaps, detergents, cosmetics, insecticides), health (pharmaceuticals, disinfectants, etc.) (Blanchard et al., 2001; Blanchard, Teil, Ollivon, Legenti, & Chevreuil, 2004).

POPs are dangerous for human health due to their low water and high fat solubility, low vapor pressure, persistence, and toxicity (Kim & Smith, 2001; Willett, Ulrich, & Hites, 1998). Many of these compounds could cause pathologic changes to the spleen and the skin. They can also damage the nervous, digestive, and reproductive systems, and promote the generation of tumors (Petrovic, Eljarrat, Lopez de Alda, & Barcelo, 2001).

Emissions and occurrence of POPs in the environment are very often limited by regulations (Dmitruk, Piascik, Taboryska, & Dojlido, 2008). The United Nations Economics for Europe (UNECE) and Convention on Long-Range Transboundary Air Pollution (CLRTAP) defined criteria of POPs as follows (United Nations Economic Commission for Europe [UNECE], 1979):

- possess toxic characteristics
- persistent in the environment
- tend to bioaccumulate in higher trophic levels

- undergo long-range atmospheric transport

In May 2001, the Stockholm Convention on POPs was adopted with the objective of protecting the environment and human health from damages of POPs. The convention was attended on May 17, 2004. The United Nations Environment Program (UNEP) is also proposed to reduce the discharges of POPs emissions (Motelay-Massei et al., 2005).

It is the combination of bioaccumulation, persistence, transport and toxicity that makes these compounds and their decomposition products/metabolites an important concern (Ozfatura, 2009). Although several POPs exist, they are organic compounds of mainly anthropogenic origin characterized by their lipophilicity, long environmental persistence and long-range transport (Cok et al., 2012). Intentionally and unintentionally produced POPs include two important compound groups: PAHs and PCBs.

PAHs are unintentionally produced by-products of POPs family. They have been found to be widespread distributed throughout environmental medium including air, water, sediment and soil (Kaya et al., 2012; Motelay-Massei, Ollivon, Garban, & Chevreuil, 2003; Odabasi, 1998; Stanimirova, Tauler, & Walczak, 2011). Some PAHs are byproducts of natural activities such as forest fires and volcanic activities (Pelkonen & Nebert, 1982). Major anthropogenic sources in the atmosphere include PAH emissions from 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 (Nagpal, 1993; Pelkonen & Nebert, 1982). Humans might be easily exposed to PAHs by inhalation, ingestion or dermal contact (Agency for Toxic Substances and Disease Registry [ATSDR], 2012; Boffetta, Jourenkova, & Gustavsson, 1997). Thus, there has been increasing concerns on PAHs ubiquity due to their health risks as potential carcinogens and mutagens (Jansson, Lundin, & Grabic, 2011; Kim, Hirai, Kato, Urano, & Masunaga, 2004).

PCBs were primarily used in capacitors, transformers, paints, and also in many other industrial applications. They are the industrial chemicals banned and included in the list of priority contaminants to be monitored regularly (Badawy, El-Wahaab, Moawad, & Ali, 2010; Hedgecott, 1994). They have been reported to cause variety of effects including teratogenic, carcinogenic, immunologic, reproductive and neurological problems (Badawy et al., 2010; Dabestani & Ivanov, 1999). The major source of PCBs to the atmosphere is incineration of PCB-containing materials and volatilization from sites where they have been disposed (Mari, Schuhmacher, Feliubadalo, & Domingo, 2008). Even though PCBs production and use were banned in most countries, PCBs are still routinely detected around the world and become global pollutants (Arctic Monitoring and Assessment Program [AMAP], 1998; Bengtson Nash, Poulsen, Kawaguchi, Vetter, & Schlabach, 2008; Porta & Zumeta, 2002; U.S. EPA, 2002a; Wang et al., 2012).

The concentrations of atmospheric organic pollutants are traditionally measured by active sampling using high-volume samplers. Active sampling used for semi-volatile organic compounds (SVOCs) e.g., PCBs and PBDEs is the most accurate method to monitor ambient air concentrations since a pump is used to draw known volumes of air through filters and sorbents. However, the cost and logistical limitations of high-volume samplers do not allow deployment of samples at a large number of sites concurrently. Recently, several different types of passive air samplers (PAS) have been used to measure the atmospheric concentrations of POPs (Ishikawa, Noma, Mori, & Sakai, 2007; Santiago & Cayetano, 2007; Takasuga, Senthilkumar, Matsumura, Shiozaki, & Sakai, 2006; Tian et al., 2008). Polyurethane foam (PUF) passive air samplers are one of the most widely used ones for monitoring POPs (Harner et al., 2006; Takasuga, Kumar, Noma, & Sakai, 2005). PUF disk passive samplers are operated without aid of a pump, and are very hydrophobic and have high retention capacity for target organic compounds in the gas-phase (Harner et al., 2006). PUF disk passive samplers were also used for measurement of ambient PAHs and PCBs concentrations in this study.

Identifying sources of POPs is very important for controlling their emissions (Masunaga, Yao, Ogura, Sakurai, & Nakanishi, 2003). Generally two basic have been used for identification and apportionment of pollutant sources, source-oriented models and receptor models (Li, Jang, & Scheff, 2003). Source-oriented models are not applicable for PCBs, because it is difficult to acquire their source profiles. Receptor models determine contributions from all the major sources based on measurements at sampling sites (Gordon, 1988). Factor Analysis with Nonnegative Constraints (FA-NNC) and Positive Matrix Factorization (PMF) have been used successfully for identification of sources of POPs in atmospheric particulates (Rachdawong & Christensen, 1997; Song et al., 2007; Uchimiya, Arai, & Masunaga, 2007). PAHs and PCBs sources have been determined within numbers of studies in industrial areas (Khalili, Scheff, & Holsen, 1995; Odabasi et al., 2009; Rodenburg & Meng, 2013; Vardar, Esen, & Tasdemir, 2008).

The main objective of this study was to determine the sources of PAHs and PCBs in Aliaga that is one of major industrial areas in Turkey. In order to identify the source profiles of PAHs and PCBs in the region, positive matrix factorization (PMF) method was applied to a dataset of 160 ambient air measurements.

This thesis consists of five chapters. An overview and objectives of the study were presented in Chapter 1. Chapter 2 reviews the concepts and previous studies related to this work. Experimental work is summarized in Chapter 3. Results and discussions are presented in Chapter 4. Chapter 5 includes the conclusions and recommendations drawn from this study.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents information on chemical structures, general properties, health effects, and sources of PAHs and PCBs. Previous studies on PAHs and PCBs in the ambient air were also discussed in this chapter.

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that are generated primarily during the incomplete combustion of organic materials including wood and fossil fuels such as coal, oil, and gasoline (Vallack et al., 1998). There are hundreds of PAH compounds in the environment. However, only 16 of them are included in the priority pollutants list of U.S. EPA based on a number of factors including their toxicity, extent of information available, source specificity, frequency of occurrence at hazardous waste sites, and potential for human exposure (ATSDR, 1995).

PAHs can be divided into two groups based on their physico-chemical, and biological properties: (i) the low molecular weight PAHs with 2- to 3-rings, and (ii) the high molecular weight PAHs with 4- to 7-rings (Nagpal, 1993). Because of their semi-volatile nature, PAH compounds may exist in the atmosphere both in gas and particle-phases. Atmospheric residence time and transport distance depend on the meteorological conditions, reactivity of PAHs, and their particle size distribution (ATSDR, 1995).

During their transport in the atmosphere, PAHs undergo photo-chemical oxidation in the presence of sunlight. This photo-oxidation occurs much faster in gas-phase than particle-phase. The most important mechanism for PAHs is the reaction with hydroxyl radicals. PAHs can also be oxidized by atmospheric pollutants such as ozone, nitrogen oxides, and sulfur dioxide in the air to be transformed into diones,

nitro- and dinitro-derivatives, and sulfonic acids, respectively (Dabestani & Ivanov, 1999; Halsall, Sweetman, Barrie, & Jones, 2001; Possanzini et al., 2004).

2.1.1 Chemical Structures, Properties, and Health Effects of PAHs

Chemical structures of the studied PAH compounds (U.S. EPA 16 priority compounds and carbazole) are illustrated in Figure 2.1. PAHs are composed of two or more fused aromatic (benzene) rings when a pair of carbon atoms is shared. The resulting structure is a molecule where the benzene rings are fused together in a linear fashion (e.g. anthracene) or in an angular arrangement (e.g. acenaphtylene) (Dabestani & Ivanov, 1999). In some PAHs, named as heterocyclic aromatic hydrocarbons, one carbon atom is substituted by an atom of another element, such as nitrogen, oxygen, sulfur, or chlorine (Toxic Organic Compounds in the Environment [TOCOEN], 2007).

The environmentally significant PAHs are the compounds which contain two (e.g. naphthalene with a chemical formula of $C_{10}H_8$) to seven benzene rings (e.g. coronene with a chemical formula of $C_{24}H_{12}$). Within this range, there is a large number of PAHs which differ in number of aromatic rings; position at which aromatic rings are fused to each other; and number, chemistry, and position of substituents on the basic ring system (Nagpal, 1993). Trivial names are used for some of the simple PAHs such as anthracene, phenanthrene, pyrene, fluoranthene, and perylene. More complicated compounds are named by their substitution on their basic structure, such as by benzo- dibenzo-, or naptho- groups (Odabasi, 1998).
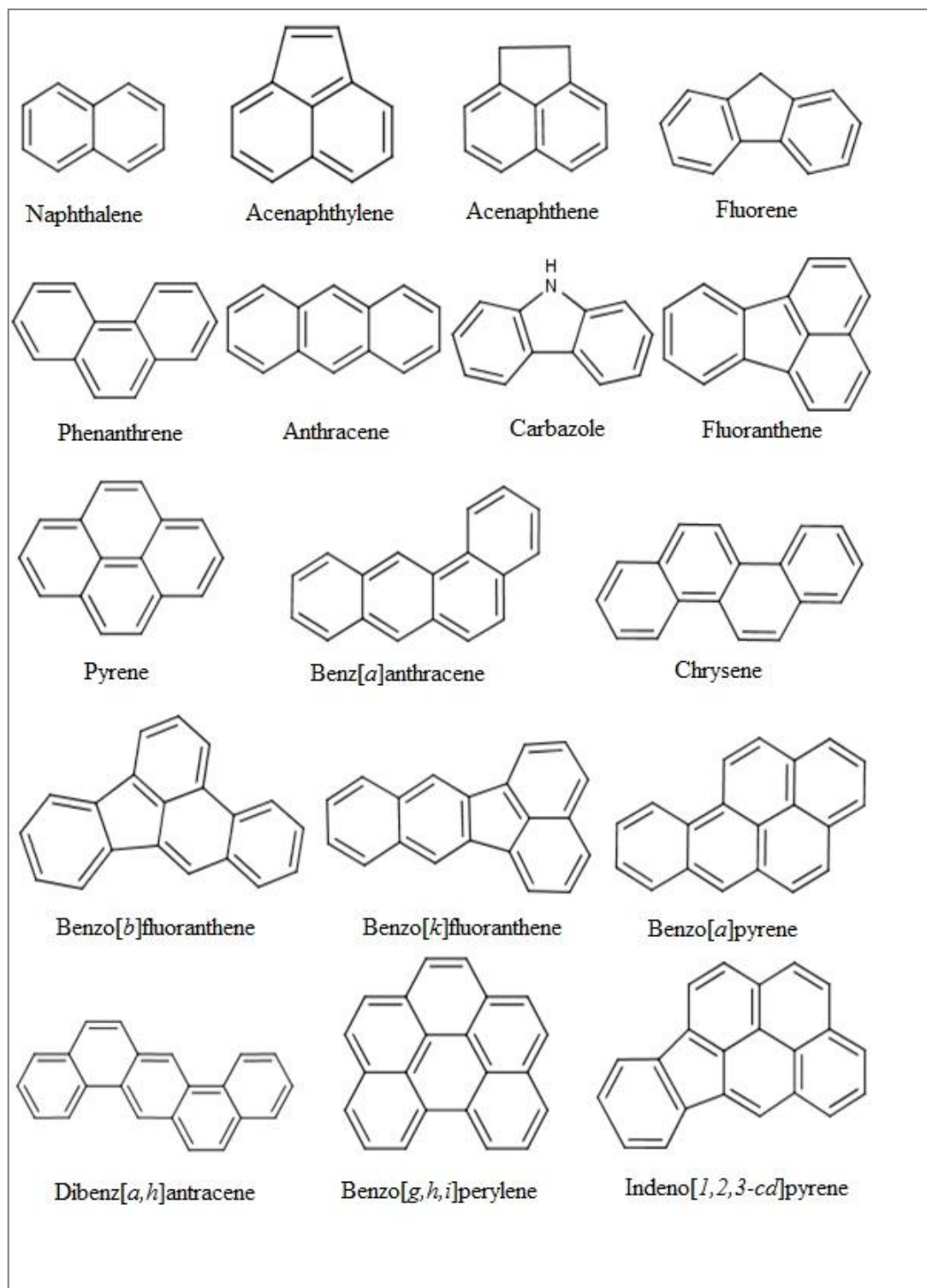
Figure 2.1 Chemical structures of the studied PAHs (National Library of Medicine [NLM], 2008a).

The distribution and partitioning of organic pollutants in various compartments of the environment (e.g. air, water, soil/sediment, and biota) is determined by their physical-chemical properties such as water solubility, vapor pressure, Henry's law

constant, octanol-water partition coefficient (K_{OW}), octanol-air partition coefficient (K_{OA}), and organic carbon partition coefficient (K_{OC}) (ATSDR, 1995). Table 2.1 shows some of the important properties of the studied PAHs. The physical-chemical properties of PAHs vary with molecular weight. For instance, PAH resistance to oxidation, reduction, and vaporization increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases (Nagpal, 1993). Pure PAHs generally exist as colorless, white, or pale yellow-green solids at room temperature and most of them have high melting and boiling points (ATSDR, 1995).

Since PAHs are non-polar and hydrophobic compounds, they are poorly soluble in aqueous environments, but they are soluble in organic solvents or organic acids. This means that they are generally found adsorbed on particulates and on humic matter in aqueous environments, or dissolved in any oily matter which may co-exist in water, sediments and soil as contaminants (Dabestani & Ivanov, 1999). Temperature and dissolved/colloidal organic fractions of water enhance the solubility of the PAHs in water (Nagpal, 1993), and solubility decreases as the molecular weight and number of rings increases. Thus, the high molecular weight PAHs (≥ 4 rings) are almost exclusively bound to particulate matter, while the lower molecular weight ones (≤ 3 rings) can also be found dissolved in water (ATSDR, 1995).

PAHs tend to have low vapor pressures. As their molecular weight and the number of rings increase, their vapor pressure decreases. At a given temperature, substances with higher vapor pressures vaporize more readily than substances with a lower vapor pressure. As a result, the high molecular weight PAHs (≥ 4 rings) are found predominantly in particle-phase, while the lower molecular weight ones (≤ 3 rings) are present predominantly in gas-phase in the air (Dabestani & Ivanov, 1999).

Table 2.1 Selected physical-chemical properties of individual PAH compounds

PAHs[*]	CAS-No[a]	Molecular Formula[a]	MW[a] (g mol^{-1})	T_M[a] (°C)	T_B[a] (°C)	S_W[a] (25°C) (mg L^{-1})	VP[a] (25°C) (mm Hg)	H[a] (25°C) (atm m^3 mol^{-1})	log K_{OA}[c] (25°C)	log K_{OW}[a]
NAP	91-20-3	$C_{10}H_8$	128	80	218	31	8.50E-02	4.40E-04	-	3.36
ACL	208-96-8	$C_{12}H_8$	152	93	280	16.1	6.68E-03	1.14E-04	6.34	3.94
ACT	83-32-9	$C_{12}H_{10}$	154	93	279	3.9	2.15E-03	1.84E-04	6.52	3.92
FLN	86-73-7	$C_{13}H_{10}$	166	115	295	1.69	6.00E-04	9.62E-05	6.9	4.18
PHE	85-01-8	$C_{14}H_{10}$	178	99	340	1.15	1.21E-04	3.35E-05[b]	7.68[b]	4.46
ANT	120-12-7	$C_{14}H_{10}$	178	215	340	0.0434[*]	2.67E-06[d]	5.56E-05	7.71	4.45
CRB	86-74-8	$C_{12}H_9N$	167	246	355	1.8	7.50E-07[e]	1.16E-07[b]	8.03[b]	3.72
FL	206-44-0	$C_{16}H_{10}$	202	108	384	0.26	9.22E-06	8.86E-06	8.76	5.16
PY	129-00-0	$C_{16}H_{10}$	202	151	404	0.135	4.50E-06	1.19E-05	8.81	4.88
BaA	56-55-3	$C_{18}H_{12}$	228	84	438	0.0094	2.10E-07	1.20E-05	10.28	5.76
CHR	218-01-9	$C_{18}H_{12}$	228	258	448	0.002	6.23E-09	5.23E-06	10.30	5.81
BbF	205-99-2	$C_{20}H_{12}$	252	168	-	0.0015	5.00E-07	6.57E-07	11.34	5.78
BkF	207-08-9	$C_{20}H_{12}$	252	217	480	0.0008	9.70E-10[d]	5.84E-07	11.37	6.11
BaP	50-32-8	$C_{20}H_{12}$	252	177	495[f]	0.00162	5.49E-09[d]	4.57E-07	11.56	6.13
IcdP	193-39-5	$C_{22}H_{12}$	276	164	536	0.00019	1.25E-10	3.48E-07	12.43	6.7
DahA	53-70-3	$C_{22}H_{14}$	278	270	524	0.00249	1.00E-10	1.23E-07	12.59	6.75
BghiP	191-24-2	$C_{22}H_{12}$	276	278	>500	0.00026	1.00E-10	3.31E-07	12.55	6.63

[*] Naphthalene (NAP), acenaphthylene (ACL), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP).

MW: Molecular weight, T_M: Melting point, T_B: Boiling point, S_W: Solubility in water, VP: Vapor pressure, H: Henry's law constant, log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient, [*] at 24°C.

[a] NLM, 2008a, [b] Odabasi, Cetin, & Sofuoglu, 2006a, [c] Odabasi, Cetin, & Sofuoglu, 2006b, [d] NLM, 2008b, [e] Virtual Computational Chemistry Laboratory [VCCL], 2007, [f] Estimation Program Interface [EPI], 2007.

The ratio of a chemical's concentration in air and water at equilibrium can be expressed by Henry's law constant. This partition coefficient is used as a measure of a compound's volatilization. Henry's law constants for low molecular weight PAHs are in the range of 10^{-3}-10^{-5} atm m^3 mol^{-1} and for the high molecular weight PAHs they are in the range of 10^{-5}-10^{-8} atm m^3 mol^{-1}. Thus, significant volatilization can take place for compounds with Henry's law constant values ranging from 10^{-3}-10^{-5} while PAHs with values $<10^{-5}$ do not volatilize much (ATSDR, 1995; Dabestani & Ivanov, 1999).

The K_{OW} is used to estimate the potential for an organic chemical to move from water into lipid, and has been correlated with bio-concentration in aquatic organisms. For PAHs, the values of log K_{OW} increase with increasing number of rings. K_{OW} values for PAHs are relatively high indicating a relatively high potential for adsorption to suspended particulates in air and water, and for bio-concentration in organisms (ATSDR, 1995).

The K_{OC} indicates the chemical's potential to bind to organic carbon in soil and sediment. The log K_{OC} values for PAHs increase with increasing number of rings. The low molecular weight PAHs have K_{OC} values in the range of 10^3-10^4 indicating a moderate potential to be adsorbed to organic carbon in the soil and sediments. High molecular weight PAHs have K_{OC} values in the range of 10^5-10^6 indicating stronger tendencies to adsorb to organic carbon (ATSDR, 1995). Persistence of the PAHs also varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported half-lives of naphthalene, anthracene, and benzo[*e*]pyrene in sediment are 9, 43, and 83 hours, respectively, while for higher molecular weight PAHs, their half-lives are up to several years in soils/sediments (The United Nations Environmental Programme [UNEP], 2002).

In human beings, systemic, immunological, neurological, reproductive, developmental, genotoxic, and carcinogenic adverse health effects have been linked to several PAHs (ATSDR, 1995). The International Agency for Research

on Cancer (IARC) has reported that benz[*a*]anthracene and benzo[*a*]pyrene are probably carcinogenic to human (Group B2); benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno[1,2,3-*c,d*]pyrene are possibly carcinogenic to human (Group 2A). In the U.S. EPA list, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*c,d*]pyrene are classified as Group B2, probable human carcinogens (ATSDR, 1995).

2.1.2 Production and Uses of PAHs

Among a large number of compounds, only a few PAHs (e.g. acenaphthene, anthracene, fluorene, fluoranthene, naphthalene, and phenanthrene) are produced for commercial use. They are mostly used as intermediaries in pharmaceutical, photographic, and chemical industries. Limited uses in the production of fungicides, insecticides, moth repellent, and surfactants have been also reported (ATSDR, 1995; Nagpal, 1993).

Acenaphthene is used as a chemical intermediate in pharmaceutical and photographic industries, and to a limited extent, in the production of soaps, pigments and dyes, insecticides, fungicides, plastics, and processing of certain foods (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003a).

Anthracene is used as a raw material for the manufacture of fast dyes, pigments, and coating materials; as a chemical intermediate for dyes; and as a diluent for wood preservatives. It is used in the manufacture of synthetic fibers, plastics, mono-crystals, and scintillation counter crystals. It is used in insecticides, smoke screens and organic semiconductor researches have been also reported (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003b).

Fluorene is used as a chemical intermediate in many chemical processes, in the formation of poly-radicals for resins, and in the manufacture of resinous products and

dyestuffs. Derivatives of fluorene show activity as herbicides and growth regulators (ATSDR, 1995; Spectrum, 2003d).

Fluoranthene is a constituent of coal tar and petroleum derived asphalt. This compound is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (ATSDR, 1995; Spectrum, 2003c).

Naphthalene is the most abundant distillate of coal tar. Its most common use is as a household fumigant against moths. In the past, it was used in the manufacture of carbaryl insecticide and vermicide. Naphthalene is also an important hydrocarbon raw material used in the manufacture of phthalic anhydride (intermediate for polyvinyl chloride, PCV, plasticizers), celluloid and hydronapthalenes (used in lubricants), and motor fuels. Naphthalene is also used in the production of beta-naphthol, synthetic tanning agents, leather, resins, dyes, surfactants and dispersants. Some uses as an antiseptic and as a soil fumigant have also been reported (ATSDR, 1995; Nagpal, 1993; Spectrum, 2003e; U.S. EPA, 2002b).

Phenanthrene is used in the manufacture of dyestuffs, explosives, and phenanthrenequinone which is an intermediate for pesticides. It is also an important starting material for phenanthrene based drugs. This leads directly to use in biochemical research for the pharmaceutical industry. A mixture of phenanthrene and anthracene tar is used to coat water storage tanks to keep them from rusting (ATSDR, 1995; Spectrum, 2003f).

There are no known commercial uses for acenaphthylene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*e*]pyrene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]erylene, benzo[*a*]pyrene, chrysene, dibenz[*a,h*]anthracene, indeno[1,2,3-*c,d*]pyrene, and pyrene except as research chemicals (ATSDR, 1995).

2.1.3 Sources of PAHs

The sources of PAHs can be divided into two categories: natural and anthropogenic sources. Emissions from anthropogenic activities predominate, but some PAHs in the environment originate from natural sources.

2.1.3.1 Natural Sources

In nature, PAHs may be formed by three ways: (i) high temperature pyrolysis of organic materials, (ii) low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel, and (iii) direct biosynthesis by microorganisms and plants (Nagpal, 1993).

Emissions from agricultural burning, forest and prairie fires are the largest contributors of PAHs from natural sources. Volcanic activity and biosynthesis by plants, algae/phytoplankton, and microorganisms are other natural sources of PAHs. But compared to fires, these sources emit smaller amounts (Nagpal, 1993; Odabasi, 1998). PAHs occur naturally in bituminous fossil fuels, such as coal and crude oil deposits, as a result of diagenesis (i.e. the low temperature, 100-150 °C, decomposition of organic material over a significant span of time) (Nagpal, 1993). Slow transformation of organic materials in lake sediments by diagenesis is another minor natural source of PAHs to the environment (Dabestani & Ivanov, 1999). They also form as significant components of petroleum products such as some paints, creosote (used in wood preservation), and asphalt (used for road paving) (U.S. EPA, 2002a).

2.1.3.2 Anthropogenic Sources

Anthropogenic sources include combustion and industrial production. Incomplete combustion of organic matter at high temperature is one of the major anthropogenic sources of environmental PAHs. Emissions into the atmosphere during the

production of some PAHs for commercial uses are not considered as significant (ATSDR, 1995).

Atmospheric PAH emissions from anthropogenic sources fall into two groups: (i) stationary sources and (ii) non-stationary sources. Stationary sources include coal and gas-fired boilers, coal gasification and liquefaction plants, carbon black, coal tar pitch and asphalt production, aluminum production, coke-ovens, the iron-steel industries, catalytic cracking towers, petroleum refineries and related activities, power plants, industrial and municipal incinerators (waste burning), residential heating, and any other industry that uses wood, petroleum or coal to generate heat and power (Nagpal, 1993; Dabestani & Ivanov, 1999).

Non-stationary sources of PAHs refer to automobiles or other vehicles which use petroleum derived fuels. Temperatures within an internal combustion engine are often sufficient enough to convert a fraction of the fuel or oil into PAHs via incomplete combustion. These compounds are then emitted to the atmosphere through exhaust (Nagpal, 1993).

2.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) have no natural sources and have been commercially prepared by chlorination of biphenyl (Park, 2000). Due to their thermal stability, excellent dielectric properties, and resistance to oxidation, acids, and bases, they were widely used in electrical equipment (mostly in capacitors and transformers) and other industrial applications where chemical stability has been required for safety, operation and durability until recently (UNEP, 1999).

Because of their toxicity and resistance to degradation into the environment, the production and use of PCBs have been banned in many countries for decades. However, due to their persistence, PCB levels in the environmental matrices are declining slowly, and this makes them ubiquitous. Breivik, Sweetman, Pacyna, &

Jones (2007) have estimated that PCB emissions during 2005 were approximately 10% of what was released in 1970.

In the atmosphere, PCBs may exist in both gas- and particle-phases and are capable of long-range transport. Low molecular weight PCBs are predominantly in the gas-phase, and thus are easily transported further away from the sources compared to the particle-phase ones. The heavier PCBs tend to be particle-phase and more readily removed from the atmosphere by deposition (ATSDR, 2000).

Commercial PCBs consist of a mixture of PCB congeners. However, after release into the environment, the composition of PCB mixtures changes over time through processes such as volatilization, partitioning, chemical and biological transformation, and preferential bioaccumulation (U.S. EPA, 1996). Generally, biodegradability decreases with increasing degree of chlorination. Congeners with 3 or fewer chlorine atoms are significantly biodegradable and are also more likely to evaporate to air. However, PCBs having more than 5 chlorine atoms tend to sorb to suspended particles, sediments and soil, and resist to biodegradation (Nagpal, 1992). In the air, reaction with hydroxyl radicals is the dominant transformation process for gaseous PCBs, but this mechanism is not important for particle-phase ones (ATSDR, 2000).

2.2.1 Chemical Structures, Properties, and Health Effects of PCBs

PCBs is a group of aromatic, synthetic compounds formed by the addition of chlorine atoms (Cl_2) to biphenyl molecule ($C_{12}H_{10}$) which is a dual-ring structure comprising two benzene rings (Nagpal, 1992). The general formula for PCBs is $C_{12}H_{10-n}Cl_n$, where n ranges from 1 to 10 (UNEP, 1999).

Figure 2.2 shows the basic structure of a PCB molecule where the numbers 2-6 and 2'-6' represent possible substitution locations for chlorine. Positions 2, 2', 6, and 6' are called *ortho* positions, positions 3, 3', 5, and 5' are called *meta* positions, and positions 4 and 4' are called *para* positions. The benzene rings can rotate around the bond connecting them. Their two extreme configurations are planar (i.e. two benzene

rings in the same plane) and non-planar (the benzene rings are at a 90° angle to each other). The benzene rings of non-*ortho* substituted PCBs, as well as mono-*ortho* substituted PCBs, may assume a planar configuration, referred to as planar or coplanar congeners (ATSDR, 2000). There are 20 non-*ortho* substituted PCB congeners that are often called "dioxin-like compounds" in terms of their toxicity (World Health Organization [WHO], 2000).
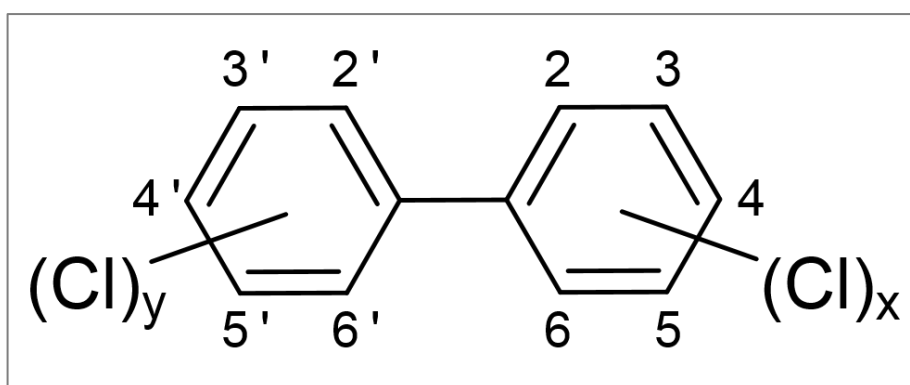
Figure 2.2 Basic molecular structure of a biphenyl molecule (UNEP, 1999).

The nature of an aromatic ring allows a single attachment to each carbon. This means that there are 10 possible positions for chlorine substitution by replacing the hydrogen atoms in the biphenyl. There are, thus, 10 different PCB homologues depending on the number of chlorines (Nagpal, 1992). Species with a single chlorine substituent are called mono-chlorobiphenyl (mono-CBs). Species with two through ten chlorines are called di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-CBs (ATSDR, 2000).

Congener is a single, unique, well-defined chemical compound in the PCB category. The name of the congener specifies the total number of chlorine substituents and the position of each chlorine atoms (ATSDR, 2000). For example, 4,4'-dichlorobiphenyl is a congener comprising the biphenyl structure with two chlorine substituents, one on each of the two carbons at the *para* positions of the two rings. Theoretically, 209 different congeners are possible, but only about 130 of these have been identified in commercial products (UNEP, 1999).

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Table 2.2 shows some physical-chemical properties of the studied PCB congeners that vary widely depending on the degree of chlorination and the position of chlorine atoms. Although most PCB congeners are solids at room temperature, the commercial mixtures are mobile oils, viscous fluids, or sticky resins (Nagpal, 1992). Pure individual PCB congeners are colorless to light yellow and have no known smell or taste (ATSDR, 2000). They have extremely high boiling points and are practically nonflammable. The important characteristics of PCBs that have led to their widespread use are (i) thermal stability, (ii) high degree of chemical stability, (iii) resistance to oxidation, acids, bases, and other chemical agents, and (iv) excellent dielectric properties (i.e. low electrical conductivity) (UNEP, 1999).

PCBs exhibit low vapor pressure (Nagpal, 1992) and their vapor pressures and Henry's law constants tend to decrease with increased chlorination. Thus, the more chlorinated congeners are relatively non-volatile. PCBs with vapor pressures $>10^{-4}$ mm Hg (mono- and di-CBs) appear to exist in the atmosphere almost entirely in the gas-phase, while PCBs with vapor pressures $<10^{-8}$ mm Hg exist substantially in the particle-phase, and PCBs with vapor pressures between 10^{-4} and 10^{-8} mm Hg (tri- to hepta-CBs) are distributed in both phases (ATSDR, 2000).

PCBs are non-polar compounds. This makes them only slightly water soluble, but they dissolve easily in fats, oils, and most organic solvents (UNEP, 1999). Generally, water solubility of PCBs decreases as with degree of chlorine substitution. Within a homologue group, the solubility depends on the positions of the chlorine atoms on the biphenyl structure (Nagpal, 1992).

Table 2.2 Selected physical-chemical properties of PCB congener

PCBs	CAS-No[a]	Molecular Formula[a]	Molecular Structure[a]	MW[a] (g mol^{-1})	T_M[a] (°C)	T_B[a] (°C)	S_W[b] (25°C) (mg L^{-1})	VP[b] (25°C) (mm Hg)	H[c] (at 25°C) (atm m^3 mol^{-1})	log K_{OA}[d] (at 20°C)	log K_{OW}[g]
PCB-18	37680-65-2	$C_{12}H_7Cl_3$	2,2',5	258	101	341	0.4	1.05E-03	2.52E-04	7.79	5.19
PCB-17	37680-66-3	$C_{12}H_7Cl_3$	2,2',4	258	101	341	0.0833	4.00E-05	6.02E-04	7.74	5.33
PCB-31	16606-02-3	$C_{12}H_7Cl_3$	2,4',5	258	101	341	0.143	4.00E-04	2.68E-04	8.4	5.66
PCB-28	7012-37-5	$C_{12}H_7Cl_3$	2,4,4'	258	101	341	0.27	1.95E-04	3.63E-04	8.4	5.63
PCB-33	38444-86-9	$C_{12}H_7Cl_3$	2',3,4	258	101	341	0.133[*]	1.03E-04	5.97E-04	8.52	5.46[h]
PCB-52	35693-99-3	$C_{12}H_6Cl_4$	2,2',5,5'	292	122	360	0.0153	8.45E-06	3.11E-04	8.49	5.74
PCB-49	41464-40-8	$C_{12}H_6Cl_4$	2,2',4,5'	292	122	360	0.0781[*]	8.48E-06	4.17E-04	8.63	5.91
PCB-44	41464-39-5	$C_{12}H_6Cl_4$	2,2',3,5'	292	122	360	0.10[*]	8.45E-06	2.68E-04	8.71	5.62
PCB-74	32690-93-0	$C_{12}H_6Cl_4$	2,4,4',5	292	122	360	0.00496	8.45E-06	4.17E-04	9.14	6.2
PCB-70	32598-11-1	$C_{12}H_6Cl_4$	2,3',4',5	292	122	360	0.041	4.08E-05	2.77E-04	9.22	6.2
PCB-95	38379-99-6	$C_{12}H_5Cl_5$	2,2',3,5',6	326	135	378	0.0211[*]	2.22E-06	6.29E-04	9.06	6.15
PCB-101	37680-73-2	$C_{12}H_5Cl_5$	2,2',4,5,5'	326	135	378	0.0154	2.52E-05	4.29E-04	9.28	6.26
PCB-99	38380-01-7	$C_{12}H_5Cl_5$	2,2',4,4',5	326	135	378	0.00366	2.20E-05	4.27E-04	9.38[f]	6.4
PCB-87	38380-02-8	$C_{12}H_5Cl_5$	2,2',3,4,5'	326	135	378	0.0294[*]	1.70E-05	3.63E-04	9.25[f]	6.12
PCB-110	38380-03-9	$C_{12}H_5Cl_5$	2,3,3',4',6	326	135	378	0.00731	2.22E-06	3.99E-04	9.58	6.22
PCB-82	52663-62-4	$C_{12}H_5Cl_5$	2,2',3,3',4	326	135	378	0.0291[*]	2.22E-06	5.97E-04	9.16[f]	6.11
PCB-151	52663-63-5	$C_{12}H_4Cl_6$	2,2',3,5,5',6	361	146	397	0.0136[*]	2.29E-06	1.35E-03	9.58	6.57
PCB-149	38380-04-0	$C_{12}H_4Cl_6$	2,2',3,4',5',6	361	146	397	0.00424	8.43E-06	3.96E-04	9.74	6.46
PCB-118	31508-00-6	$C_{12}H_5Cl_5$	2,3',4,4',5	326	135	378	0.0134[*]	8.97E-06	3.62E-04	10.04	6.72
PCB-153	35065-27-1	$C_{12}H_4Cl_6$	2,2',4,4',5,5'	361	146	397	0.00095[**]	3.43E-06	5.40E-04	9.99	6.76
PCB-132	38380-05-1	$C_{12}H_4Cl_6$	2,2',3,3',4,6'	361	146	397	0.00808	5.81E-07	2.83E-04	10.07	6.42
PCB-105	32598-14-4	$C_{12}H_5Cl_5$	2,3,3',4,4'	326	135	378	0.0034	6.53E-06	3.39E-04	10.20	6.59
PCB-138	35065-28-2	$C_{12}H_4Cl_6$	2,2',3,4,4',5'	361	146	397	0.0015[*]	3.80E-06	4.55E-04	10.20	6.68
PCB-158	74472-42-7	$C_{12}H_4Cl_6$	2,3,3',4,4',6	361	146, 107[b]	397	0.00807[*]	1.55E-06[a]	8.11E-04	10.14	6.74

Table 2.2 Continued

PCBs	CAS-No[a]	Molecular Formula[a]	Molecular Structure[a]	MW[a] (g mol^{-1})	T_M[a] (°C)	T_B[a] (°C)	S_W[b] (25°C) (mg L^{-1})	VP[b] (25°C) (mm Hg)	H[c] (at 25°C) (atm m^3 mol^{-1})	log K_{OA}[d] (at 20°C)	log K_{OW}[g]
PCB-187	52663-68-0	$C_{12}H_3Cl_7$	2,2',3,4',5,5',6	395	164	416	0.00451[*]	1.30E-07	6.64E-04	10.22	7.04
PCB-183	52663-69-1	$C_{12}H_3Cl_7$	2,2',3,4,4',5',6	395	164, 83[b]	416	0.0049[*]	9.66E-07[a]	3.46E-04	10.26	7.04
PCB-128	38380-07-3	$C_{12}H_4Cl_6$	2,2',3,3',4,4'	361	146	397	0.00035	2.56E-06	3.31E-04	9.93[f]	7.24[e]
PCB-177	52663-70-4	$C_{12}H_3Cl_7$	2,2',3,3',4',5,6	395	164	416	0.0015	1.30E-07[a]	3.36E-04	10.58	6.92[h]
PCB-171	52663-71-5	$C_{12}H_3Cl_7$	2,2',3,3',4,4',6	395	164	416	0.00217	1.40E-06	2.38E-04[a]	10.51	7.06
PCB-156	38380-08-4	$C_{12}H_4Cl_6$	2,3,3',4,4',5	361	146	397	0.00533[*]	1.61E-06	3.36E-04	10.87	7.12
PCB-180	35065-29-3	$C_{12}H_3Cl_7$	2,2',3,4,4',5,5'	395	164	416	0.00385[*]	9.77E-07	3.79E-04	10.72	7.18
PCB-191	74472-50-7	$C_{12}H_3Cl_7$	2,3,3',4,4',5',6	395	164	416	0.000314	1.30E-07[a]	2.38E-04[a]	10.91	7.24
PCB-169	32774-16-6	$C_{12}H_4Cl_6$	3,3',4,4',5,5'	361	146	397	0.00051	5.81E-07	4.43E-04	11.32	7.49
PCB-170	35065-30-6	$C_{12}H_3Cl_7$	2,2',3,3',4,4',5	395	164	416	0.00347[*]	6.28E-07	1.98E-04	11.07	7.07
PCB-199	52663-75-9	$C_{12}H_2Cl_8$	2,2',3,3',4,5,6,6'	430	181	434	0.00022	2.87E-08	9.91E-04	11.05	7.31
PCB-208	52663-77-1	$C_{12}HCl_9$	2,2',3,3',4,5,5',6,6'	464	191	453	0.000018	7.60E-09	3.56E-05[a]	11.26	7.71
PCB-195	52663-78-2	$C_{12}H_2Cl_8$	2,2',3,3',4,4',5,6	430	181	434	0.00022	2.87E-08	1.54E-04	11.44	7.52
PCB-194	35694-08-7	$C_{12}H_2Cl_8$	2,2',3,3',4,4',5,5'	430	181	434	0.000272	2.87E-08	8.76E-05	11.59	7.54
PCB-205	74472-53-0	$C_{12}H_2Cl_8$	2,3,3',4,4',5,5',6	430	181	434	0.0000858	2.87E-08[a]	3.23E-04[a]	11.62	7.68
PCB-206	40186-72-9	$C_{12}HCl_9$	2,2',3,3',4,4',5,5',6	464	191	453	0.000025	7.60E-09	2.45E-04[a]	11.79	7.86
PCB-209	2051-24-3	$C_{12}Cl_{10}$	2,2',3,3',4,4',5,5',6,6'	499	199, 306[b]	472	0.00000743	1.06E-07	1.06E-06[a]	11.96	8.09

MW: Molecular weight, T_M: Melting point, T_B: Boiling point, S_W: Solubility in water, VP: Vapor pressure, H: Henry's law constant, log K_{OW}: Octanol-water coefficient, log K_{OA}: Octanol-air coefficient, [*] at 20 °C, [**] at 24 °C.

[a] EPI, 2007, [b] NLM, 2008a, [c] Bamford, Poster, & Baker, 2000; Bamford, Poster, Huie, & Baker, 2002, [d] Zhang et al., 1999, [e] Jabusch & Swackhamer, 2005, [f] Chen et al., 2002, [g] Zhou, Zhai, Wang, & Wang, 2005, [h] Padmanabhan, Partasarathi, Subramanian, & Chattaraj, 2006.

PCBs are often associated with the solid fraction (e.g. particulate matter, sediment, soil) of the aquatic and terrestrial environments. In general, sorption tendency of PCBs increases with increasing degree of chlorination, the surface area and the organic carbon content of the sorbents (Nagpal, 1992). The higher chlorinated PCBs with lower water solubility and higher K_{OW} values have a greater tendency to bind to solids. In contrast, the low molecular weight PCBs with higher water solubility and lower K_{OW} values sorb to a lesser extent on solids and remain largely in dissolved-phase in aquatic environments. Therefore, in comparison with the lower chlorinated PCBs, volatilization of highly chlorinated ones in the aquatic and terrestrial environments is reduced significantly by binding these compounds to solids (ATSDR, 2000).

Most PCB congeners are extremely persistent in the environment. Their estimated half-lives range from three weeks to two years in air and more than six years in aerobic soils and sediments, with the exception of mono- and di-chlorobiphenyls (UNEP, 2002). Due to their stability and lipophilicity, PCBs bio-accumulate in food chains and are stored in fatty tissues of exposed animals and humans (ATSDR, 2000).

In people, some acute (e.g. skin conditions, spasms, hearing and vision problems) and chronic (e.g. irritation of nose and lungs, gastrointestinal discomfort, changes in blood and liver, depression, fatigue, and possibly cancer) adverse health effects have been linked to PCBs. The U.S. EPA and the IARC have determined that certain PCB mixtures including Aroclor-1016, -1242, -1254 and -1260 are probably carcinogenic (Group B2) to humans (U.S. EPA, 2002b).

2.2.2 Production and Uses of PCBs

PCBs are synthetic chemical compounds and their production involves the chlorination of biphenyl in the presence of a catalyst. Depending on the reaction conditions, the degree of chlorination varies between 21 and 68% chlorine on a weight-by-weight basis (Breivik, Sweetman, Pacyna, & Jones, 2002a).

Commercially produced PCBs are a complex mixture of individual PCB congeners, and they were marketed under several trade names including Aroclor, Askarel, Pyroclor, Santotherm, Kanechlor, Hyvol, Chlorextol, and Pyranol (Nagpal, 1992). The most common trade name is Aroclor.

There are many types of Aroclors and each of them is characterized by a four digit number that indicates the degree of chlorination. The first two digits generally refer to the number of carbon atoms in the phenyl rings. For PCBs, this is 12. The last two digits indicate the percentage of chlorine by mass in the mixture. For example, the name Aroclor 1254 means that the mixture contains approximately 54% chlorine by weight. Therefore, higher Aroclor numbers reflect higher chlorine content (ATSDR, 2000; UNEP, 1999).

The industrial and commercial uses of PCBs (ATSDR, 2000; Breivik et al., 2002a; UNEP, 1999; U.S. EPA & Oregon Department of Environmental Quality [DEQ], 2005; Vallack et al., 1998) can be classified based on their presence in closed, partially closed, and open systems as follows:

- Closed system applications (as coolants and dielectric fluids in transformers, capacitors, electric motors, and electrical household appliances such as television sets, refrigerators, air conditioners, microwave ovens; in fluorescent light ballast, and electromagnets),
- Partially closed system applications (as heat transfer fluids in mechanical operations at the inorganic/organic chemicals, plastics and synthetics, and petroleum refining industries; as hydraulic fluids in mining equipment, aluminum, copper, steel, and iron forming industries; in gas turbines and vacuum pumps; in electrical equipment such as voltage regulators, switches, circuit breakers; as stabilizing additives in flexible PVC coatings of electrical wiring and electronic components, in cable insulation materials),
- Open system applications (as ink solvents in carbonless copy paper; as plasticizers in polyvinyl chloride (PVC) plastics, rubber, synthetic resins, and sealants; as additives in cement and plaster; in casting waxes; in paints, textiles,

surface coatings, de-dusting agents, asphalt, natural gas pipelines, flame retardants; adhesives; in insulating materials; pesticide extenders; in lubricating and cutting oils; in dyes and printing inks).

Products such as oil, carbonless copy paper and plastics made with recycled PCB materials, and automobiles with PCB containing oil, fluids and cables have been also reported (UNEP, 1999; U.S. EPA & DEQ, 2005).

The production and use of PCBs have been banned for decades in many countries. In Turkey, the uses of PCBs were banned in 1995, except for the closed system uses such as capacitors and transformers that are already in-use (Acara et al., 2006).

2.2.3 Sources of PCBs

Generally, closed and partially closed systems contain PCB oils and fluids. PCBs in closed systems can not readily be emitted into the environment. However, they may be released during equipment servicing, repairing, or as a result of damaged equipment. Also, the reclamation process for used out instruments and wasted material is a possible source. PCBs in partially closed systems are not directly exposed to the environment, but may be released periodically during typical use or discharge. The PCBs in open systems take on the form of the product used in as a component. Open systems are applications in which PCBs are in direct contact with their surroundings and thereby, they may be easily transferred to the environment (UNEP, 1999).

Because their hazardous nature has only recently been understood, PCBs have been routinely disposed of over the years without any precautions being taken. As a result, large volumes of PCBs have been released into the environment from illegal or improper dumping of PCB wastes into landfills; open burning; incineration of industrial and municipal wastes (e.g. refuse, sewage sludge, products containing PCBs); vaporization from contaminated surfaces and products

containing PCBs; accidental spills and leakage from products to soils; direct entry or leakage into sewers and streams; leakage from older electrical equipment in use; the repair and maintenance of PCB containing equipment (Breivik et al., 2002b; UNEP, 1999; U.S. EPA & DEQ, 2005; Vallack et al., 1998).

Recycling operations of PCB containing materials (e.g. oil, carbonless copy paper, PVC plastic, and scrap metal) are the other PCB source to the environment. In scrap metal recycling operation, PCBs are emitted from transformer shell salvaging; heat transfer and hydraulic equipment; and shredding and smelting of waste materials such as cars, electrical household appliances (e.g. refrigerators, air conditioners, television sets, and microwave ovens) and other appliances used for upholstery, padding, and insulation. In iron-steel industries, PCBs are also released from non-ferrous metal salvaging as parts from PCB containing electrical equipment, and oil/grease insulated electrical cable (UNEP, 1999; U.S. EPA & DEQ, 2005).

PCBs emissions may be generated from various thermal processes in the production of organic pigments, pesticides, chemicals (such as PVC manufacturing and petroleum refining industries), cement, copper, iron-steel, and aluminum refining industries. In these processes, they may be formed by de-novo synthesis, similar to polychlorinated dioxins and benzofurans. The forming of PCBs as a by-product is possible when chlorine, hydrocarbons and elevated temperatures along with catalysts are present (UNEP, 1999).

PCBs are combustible at high temperatures. However, the products of combustion may be more hazardous than the original compounds. Combustion by-products include hydrogen chloride and polychlorinated dibenzodioxins/dibenzofurans (PCDD/DFs). The pyrolysis of commercial PCB mixtures produces several PCDFs. PCDFs are also produced as a by-product during the commercial production and handling of PCBs, and as impurities in various commercial PCB mixtures (ATSDR, 2000).

2.3 Source Apportionment Techniques Applied to PAHs and PCBs

Source apportionment is the assessment of the contributions to the airborne species that are emitted from natural and anthropogenic sources. In order to identify sources, data analysis tools are applied to derive information on the sources of species from the measured concentrations.

There are two main receptor modeling approaches that are widely used for source apportionment. The first one is receptor oriented models. These models use the chemical composition measured at the receptor. In such cases, the outcome is the identification of the pollution source types and estimates of the contribution of each source type to the observed concentrations (Hopke, 2009). The second modeling approach is a source oriented model called Chemical Mass Balance (CMB). The CMB model is applicable to cases when reliable local source profiles and some ambient samples measured at receptors are available (Watson, Chow, & Fujita, 2001).

2.3.1 Receptor Oriented Models

If the number and the profiles of the sources in the region are not exactly known, then receptor oriented models are useful for source apportionment studies. Receptor oriented methods are multivariate models that analyze a series of observations simultaneously in an attempt to determine the number of sources, their chemical compositions and their contributions to each observations (Guo, Wang, & Louie, 2004a). Source identification depends upon the prior knowledge on the tracers. In some cases, additional source identification techniques such as pollution rose, conditional probability function and potential source contribution function can be used with the source contribution output of the model.

2.3.1.1 Principle Component Analysis

In Principle Component Analysis (PCA), source apportionment of a data set is performed under orthogonal constraints for both source contribution and source profile (loading).Additionally, loadings are also normalized and forced to be in the direction of explaining maximum variance. Under such restrictions, PCA provides a unique solution (Tauler et al., 2008).

In order to quantify the contributions of all sources to measured pollutants, the Absolute Principle Component Score (APCS) method is used (Thurston & Spengler, 1985). To estimate each identified source's mass contribution, APCS values were used for the regression of sample mass concentrations (Guo et al., 2004b).

2.3.1.2 Unmix

The Unmix model is a newer version of PCA that is geometrically constrained to generate source profiles and contributions with the physically meaningful attribute of non-negativity (Hopke, 2009; Jorquera & Rappenglück, 2004). If there are N sources, the data space can be reduced to an N-1 dimensional space. In Unmix, it is assumed that for each source there are some data points where the contribution of a source is not present or negligible compared to the other sources. These data points are called edge points. Each edge defines the points where a single source is not contributing. If there are N sources, then the intersection of N-1 of these edges defines a point that has only one source contributing. Thus, this point gives the source composition. In this way, the profiles of the N sources are found, and then the source contributions of each data point are calculated (U.S. EPA, 2007).

2.3.1.3 Positive Matrix Factorization

Positive Matrix Factorization (PMF) uses the least square approach by integrating non-negative constraints into the optimization process and using the error estimates for each data value. The main advantage of PMF over other source apportionment

tools is that in PMF, missing data and below-detection limit data can be handled more effectively by assigning them higher error estimates. Although replacements in the data file give the corresponding data a lower weight, this gives an opportunity to use more samples in the analysis. Quantitatively, the mass profile factors produced by the PMF model are better at describing the source structure than those derived by the other receptor oriented methods (Pekey & Dogan, 2013).

2.3.2 Source Oriented Models (Chemical Mass Balance)

When the number the sources and their profiles are known in the region, then the only unknown is the mass contribution of each source to each sample. CMB model is useful for primary emissions. Secondary pollutants are difficult to identify as they are formed in the atmosphere (Hopke, 2009).

The essentials of CMB modeling are identification of the contributing source types; selection of chemical species to be involved in the modeling; estimation of source profile of in each source type; and estimation of the uncertainty in source profiles and ambient concentrations (Watson, Chow, & Fujita, 2001).

Assumptions of CMB model, other than those listed in general assumptions for source apportionment models are that:

- all sources are identified, and
- the emission profiles of the sources are significantly different from each other (Watson, Chow, & Fujita, 2001).

2.4 Source Markers for PAHs and PCBs

2.4.1 PAH Source Markers

There are some commonly referred compounds in literature for the identification of certain sources. In this section, these commonly referred PAH compounds are summarized.

Lin et al. (2013) has reported benzo[*g,h,i*]perylene, indeno[1,2,3-*c,d*]pyrene and Benzo[*a*]pyrene as the dominant PAHs in exhaust emissions, while Sofowote, McCarry, & Marvin (2008) have reported that benzo[*g,h,i*]perylene, benzo[*a*]pyrene, benzo[*b*]fluoranthene were markers of vehicular emissions. The use of benzo[*g,h,i*]perylene as a marker for traffic-related emissions has been reported by several works (Harrison, Smith, & Luhana, 1996; Nielsen, 1996). Khalili, Scheff, & Holsen (1995) has reported that benz[*a*]anthracene was a marker for diesel engine. Both benzo[*g,h,i*]perylene and indeno[1,2,3-*c,d*]pyrene have been identified as typical tracers of vehicular emissions (Harrison, Smith, & Luhana, 1996; Larsen & Baker, 2003; Simcik, Eisenreich, & Lioy, 1999).

High emissions of phenanthrene, fluoranthene, and pyrene were observed in particulate matter of wood burning (Freeman & Cattell, 1990). Also Harrison, Smith, & Luhana (1996) have reported that anthracene could be used as the marker of wood combustion. Acenaphthylene was often used to indicate wood/firewood combustion (Khalili, Scheff, & Holsen 1995; Lee, Coleman, Jones, Jones, & Lohmann, 2005).

Phenanthrene, fluoranthene, benzo[*b*]fluoranthene and pyrene are representative of residential emissions (Tian et al., 2009).The residential emissions referred to combustion process mainly for residential heating or cooking by usage of coal, wood, and natural gas.

Fluoranthene and pyrene were usually used as markers for coal combustion (Tian et al., 2009; Wang, Tian, Yang, Liu, & Li, 2009). A similar profile was provided for

the coal combustion in power plants. High emissions of fluoranthene, phenanthrene and pyrene were also observed from coke ovens. Sofowote, McCarry, & Marvin (2008) have reported that phenanthrene could be identified as a coal combustion marker. In addition to phenanthrene, anthracene, fluoranthene, and pyrene; benzo[*k*]fluoranthene, benz[*a*]anthracene and chrysene were identified in emissions from coal combustion (Harrison, Smith, & Luhana, 1996; Kannan, Johnson-Restrepo, Youhn, Giesy, & Long, 2005; Larsen & Baker, 2003;). Esen, Tasdemir, & Vardar (2008) have reported that fluoranthene, chrysene, pyrene and benz[*a*]anthracene were typical markers of coal combustion for residential heating.

Acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene were predominant components of PAHs in commercial creosotes (Kohler et al., 2000). Fluorene and phenanthrene were used as indicators for coke oven sources in some cases (Simcik, Eisenreich, & Lioy, 1999). Khalili, Scheff, & Holsen (1995) have reported that fluorene was the dominant PAH in the coke oven emissions.

Benz[*a*]anthracene, chrysene and benzo[*a*]pyrene were associated with combustion of natural gas (Kulkarni & Venkataraman, 2000; Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1993; Simcik, Eisenreich, & Lioy, 1999) and Benz[*a*]anthracene has been considered as a tracer for this source (Simcik, Eisenreich, & Lioy, 1999). Ciaparra et al. (2009) have reported that anthracene, benz[*a*]anthracene and derivatives of pyrene (benzo[*a*]pyrene and indeno[1,2,3-*c,d*]pyrene) were reflected the steel industry profile.

Carbazole is one of the major nitrogen containing polycyclic aromatic hydrocarbons in fossil fuels (i.e., coal, crude oil, oils derived from the pyrolysis of oil shales) (Benedik, Gibbs, Riddle, & Willson, 1998; Odabasi, Cetin, & Sofuoglu, 2006a; Williams & Nazzal, 1998). Carbazole is emitted from coal and wood combustion and it is also found in cigarette smoke (Liang & Pankow, 1996; Odabasi, Cetin, & Sofuoglu, 2006a; Smith & Hansch, 2000).

Motelay-Massei et al. (2005) have reported that anthracene was indicated petrogenic origins (unburned) and also acenaphthylene, acenaphthene, fluorene, phenanthrene could be used as indicators of unburned petroleum products (Wang et al., 2013). Odabasi et al. (2009) measured steel-making plant emissions and determined PAH profiles emitted by electric arc furnaces.

2.4.2 PCB Source Markers

There are a few commonly referred compounds in literature for the identification of certain PCB sources. In this section, these commonly referred PCB compounds are summarized.

Kim et al. (2004) have reported that PCB-38, 40/57, 77, 85, 107/108, 126, 129, 128, 157, 169, 171, 172/192, 170, 189, 203/196, 194, 206, etc. were the PCB congeners originated from combustion. They also specified that characteristic congeners in Kanechlor especially KC300 and 400, KC500 and 600. PCB77 and PCB126 were also reported to be formed in combustion process also by Ishikawa et al. (2007).

Emissions from house coal and hardwood had diverse PCB congeners. Major PCBs emitted from both coal and wood were PCB49, 41/64. Emission factors for coplanar PCB77, 126 and 169 were also determined and decreased from PCB77 (4 Cl) to PCB169 (6 Cl) (Lee et al., 2005). Jin, Park, Park, & Kim (2012) have reported that PCBs 11, 12/13, 15 and 17 were identified in incineration emissions. Odabasi et al. (2009) measured steel-making plant emissions and determined PCB congener profiles emitted by electric arc furnaces in these plants. There are several studies that identified characteristic congeners in both Kaneclor and Aroclor mixtures (Du & Rodenburg, 2007; Ishikawa et al., 2007; Jin et al., 2012; Takasuga et al., 2005; Takasuga et al., 2006).

CHAPTER THREE
MATERIALS AND METHODS

Study area, sampling program, sampling methods, laboratory analysis, and data analysis methods used in this study are explained in the following sections.

3.1 Study Area

Izmir metropolitan city with a population of 3.7 million people is the center of a highly industrialized area by the Aegean shoreline of Turkey (Turkish Statistical Institute [TSI], 2012). Aliaga is a town of Izmir and is located around 50 km north of the city. The town is surrounded by the several mountains and located along D550 Canakkale - Izmir highway. Aliaga's municipal land area is 412.5 km^2. Typical Mediterranean climate is observed in the town and almost all of the precipitation events occur during winter. Northwesterly winds dominate during winter whereas local sea breezes are particularly effective on summer afternoons. South and southeasterly winds were also observed. Average daily temperatures are 24-27 °C and 7 °C in summer and winter, respectively (Municipality of Aliaga, 2009).

Until early 1960's, the economy of Aliaga region was based on mainly agriculture; after the 1970's, it has gained an industrial character as the region was declared as a "heavy industrial zone" in the first five year development plan of the government (Municipality of Aliaga, 2009). Aliaga Organized Industrial Zone (AOIZ) was established in 1977 and the region became an industrial center. Today, Aliaga produces 1-1.3% of Turkey's gross national product per capita (Aliaga Chamber of Commerce, 2011). The population of Aliaga town according to 2012 statistics is 59124 (TUIK, 2012).

Various industrial facilities in different production sectors have established in the region, after the AOIZ was established. The region includes currently a refinery (TUPRAS), a petrochemical complex (PETKIM), petroleum products

storage and filling facilities, several iron-steel industries, several power plants, ship-breaking facilities, a pulp and paper plant, and a fertilizer plant. Locations of these major industrial facilities are given in Figure 3.1.

The crude oil demand of Turkey is about 694000 tons and one third of this demand is processed by the refinery. A natural gas fired thermal power plant, with a capacity of 1520 MWh was built in 2002. Another major industry in the region is the petrochemical complex, which became operational in 1985. It has production capacity of 3.2 million tons of petrochemical products. Aside from these three major plants, several harbors, including petrochemical complex port, Nemrut Port, Refinery Port, Port of Aliaga, and ship breaking facilities played significant roles in the development of the area. These harbors are especially important for the transportation of crude oil, distilled products, petrochemical products and various chemicals to and from the region. The scrap for iron steel industry, ammonia and phosphoric acid for fertilizer factory, pulp for paper industry and raw materials for petroleum coke industry are also supplied from these harbors. There are 25 ship breaking units located in the shoreline of the Nemrut area. Approximately 10 iron-steel plants are located in the Horozgedigi area. These plants use the ferrous scrap recovered from ships and from metal recovery facilities. Major pollution sources in the Aliaga region, their capacities and types of pollutants in their emissions are summarized in Table 3.1 (Dogan, 2013; Muezzinoglu, 2000).
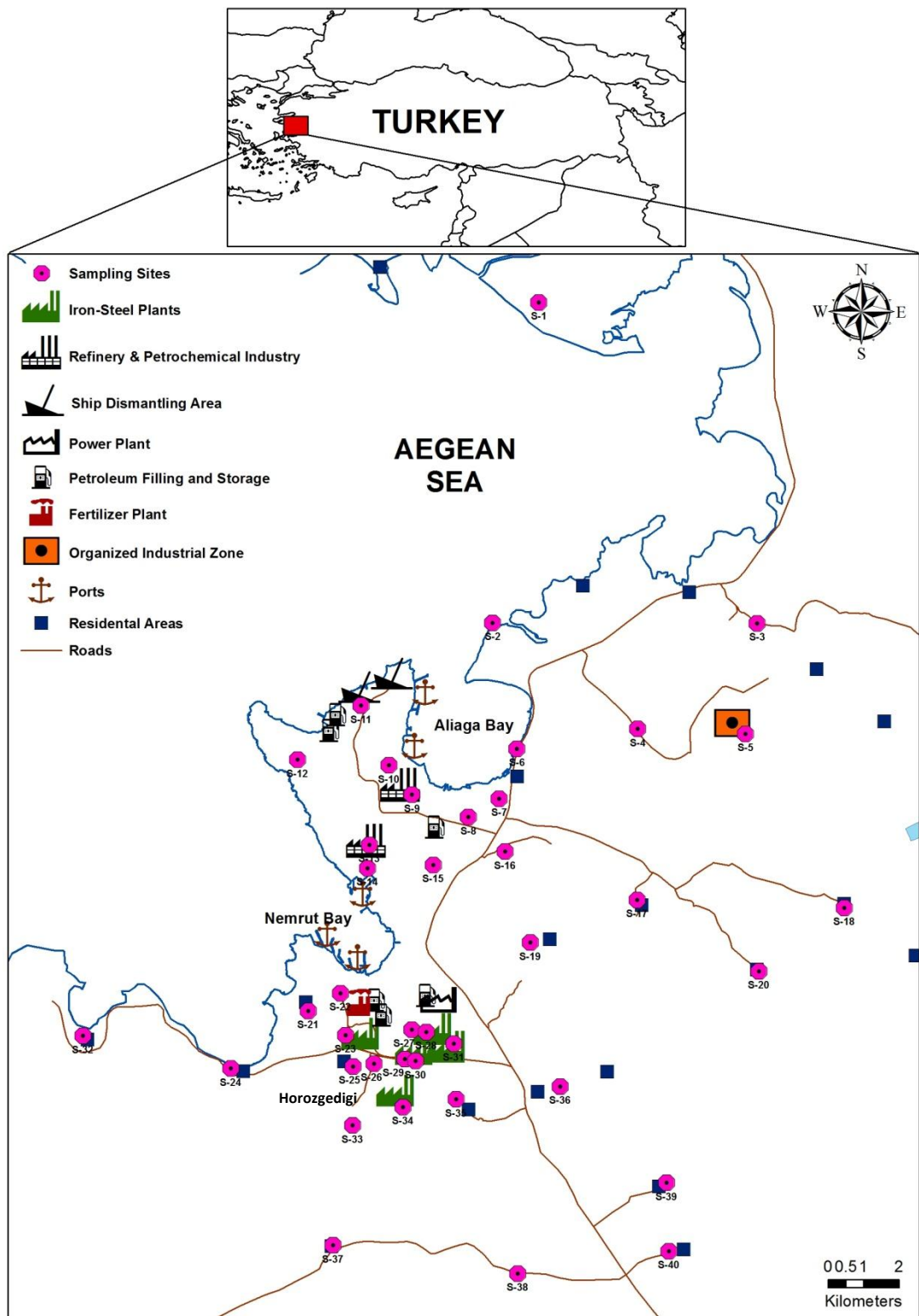
Figure 3.1 Locations of the sampling sites (*n*=40) and industrial activities in the study area.

Table 3.1 Major pollutant sources in the Aliaga region (modified from Muezzinoglu, 2000 and Dogan, 2013)

Type	Production	Annual Capacity	Pollution type
Steel mills	Various	8.5 million tons[*]	PM, SO_x, NO_x, CO, **PAHs, PCBs**, PCDD-PCDF, trace elements, VOCs
Rolling mills	Various	7.35 million tons[*]	PM, CO, SO_x, NO_x
Petroleum refinery	Various	8.9 million tons	Mercaptanes, H_2S, SO_x, NO_x, VOCs, PM, CO, trace elements, PCDD/Fs, **PAHs, PCBs**
Petrochemicals	Various	3.2 million tons	SO_x, NO_x, PM, CO, VOCs, trace elements, PCDD/Fs, **PAHs, PCBs**
Metal foundry	Special alloy casting	1.2 million tons	CO, PM, VOCs, **PAHs**
Petroleum coke	Drying imported petroleum coke	25600 tons dry coke[*]	CO, PM, VOCs, SO_x, NO_x, **PAHs**
Solvent distillers	Various chemicals	450000 tons[*]	VOCs
Petrochemical storage	Storage	79000 tons[*]	VOCs
Concrete production	Concrete	24000 m^3 tons	PM
Pulp and paper mill	Paper	23000 tons	PM, NO_x, SO_x, CO
Fertilizer	Chemical fertilizer	330000 tons	PM, acid, CO, NO_x, SO_x, NH_3
Ship breaking	Iron and steel	195000 tons	PM, NO_x, So_x, CO, VOCs, asbestos, PCDD/Fs, trace elements, **PAHs, PCBs**
Natural gas-fired power plant	Electricity	12.4 billion KWh	PM, VOCs, CO, NO_x, SO_x, **PAHs**
Harbors	Transportation and storage	34 million tons	PM, VOCs, CO, NO_x, SO_x
Highway	Transportation	6.54 million vehicle	PM, VOCs, **PAHs**, CO, NO_x, SO_x
Coal storage and packing	Coal	580000tons	**PM, PAHs**
Metal recovery	Iron, steel and aluminum	Not reported	PM, trace elements,
Solvent recovery	Various	Not reported	PM, VOCs, CO, NO_x, SO_x

[*]Data does not include productions of all facilities in the region.

3.2 Sampling Program

Ambient air samples were collected during the four seasons at 40 different sampling sites. Locations of the sampling sites are shown in Figure 3.1. Several sampling sites (N=17) were located in industrial areas and some were located in residential and rural areas (N=23).

The first sampling period was summer (July to August 2009) and the following sampling months were October to November 2009, January to February and April to May 2010, respectively. Sampling program is summarized in Table 3.2.

Table 3.2 Summary of the sampling information

Sampling Period	Duration	Number of sites	Sampling Time (min)		Temperature (°C)
			Average±SD	Days	Average±SD
Summer	02.07.2009 03.08.2009	40	45977±110	31.9	27.1±1.1
Fall	02.10.2009 02.11.2009		44572±120	31.0	19.9±1.1
Winter	04.01.2010 04.02.2010		44510±650	30.9	9.3±1.3
Spring	01.04.2010 01.05.2010		43159±117	30.0	15.9±0.9

SD: Standard Deviation

Meteorological data was provided from three meteorological stations located in the study area such as Aliaga (station 1), Horozgedigi (station 4) and petrochemical complex (station 5) and from two meteorological stations outside the study area such as Foca (station 2) and Menemen (station 3) (Figure 3.2). Average air temperatures of sampling periods were 27 °C for summer, 20 °C for fall, 9 °C for winter and 16 °C for spring. Wind roses of sampling periods were plotted in Figure 3.3. Meteorological data for wind roses were obtained from Horozgedigi station. Generally northwesterly winds (WNW) prevailed during the sampling periods. Southeast (SE) and South (S) winds observed especially in fall. Meteorological parameters, i.e., temperature, wind speed and wind direction measured during the sampling campaigns were not significantly different than the overall seasonal averages.
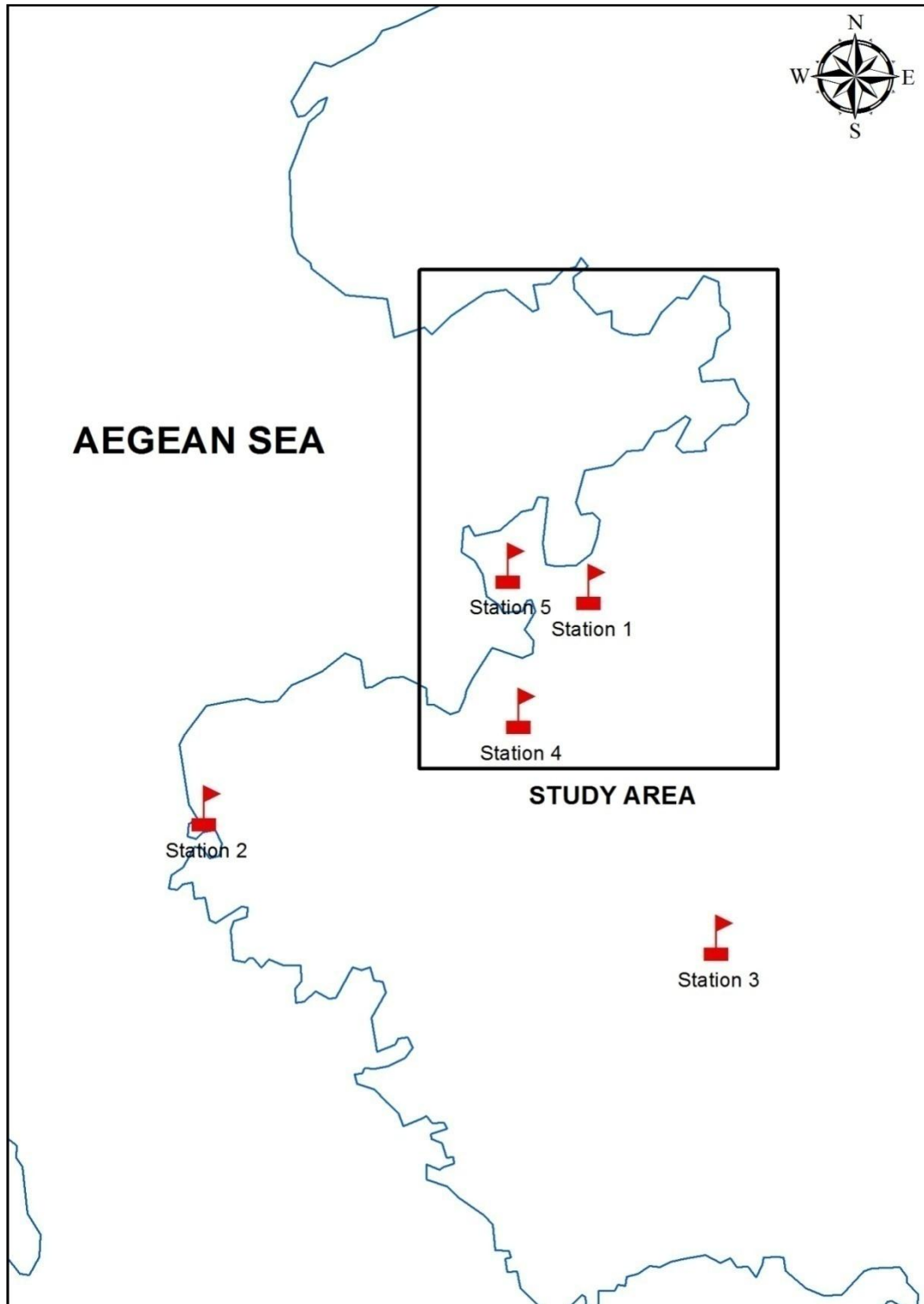
Figure 3.2 Meteorological stations in the region.

Table 3.3 shows the details of individual sampling sites in the study area. Sites were classified as industrial and residential/rural to investigate their possible differences.

Table 3.3 The list of sampling sites

Sites	X Coordinate (UTM 35N)	Y Coordinate (UTM 35N)	Site category
S1	498808	4308686	Residential/Rural
S2	497501	4299642	Residential/Rural
S3	504976	4299630	Industrial
S4	501597	4296643	Industrial
S5	504639	4296509	Industrial
S6	498189	4296088	Residential/Rural
S7	497104	4290884	Residential/Rural
S8	496817	4294154	Residential/Rural
S9	495217	4294787	Industrial
S10	494577	4295615	Industrial
S11	493794	4297302	Industrial
S12	492000	4295774	Industrial
S13	494031	4293373	Industrial
S14	493970	4292715	Industrial
S15	495830	4292800	Residential/Rural
S16	497852	4293181	Residential/Rural
S17	501591	4291814	Residential/Rural
S18	507436	4291593	Residential/Rural
S19	498571	4290612	Residential/Rural
S20	505025	4299802	Residential/Rural
S21	492300	4288680	Residential/Rural
S22	493205	4289180	Industrial
S23	493350	4288000	Industrial
S24	490115	4287055	Residential/Rural
S25	493570	4287115	Residential/Rural
S26	494150	4287192	Industrial
S27	495225	4288157	Industrial
S28	495630	4288090	Industrial
S29	495024	4287327	Industrial
S30	495330	4287264	Industrial
S31	496410	4287760	Industrial
S32	485935	4287975	Residential/Rural
S33	493550	4285450	Industrial
S34	494942	4285941	Industrial
S35	496470	4286185	Residential/Rural
S36	499418	4286552	Residential/Rural
S37	493002	4282062	Residential/Rural
S38	498215	4281265	Residential/Rural
S39	502356	4283756	Residential/Rural
S40	501421	4281829	Residential/Rural
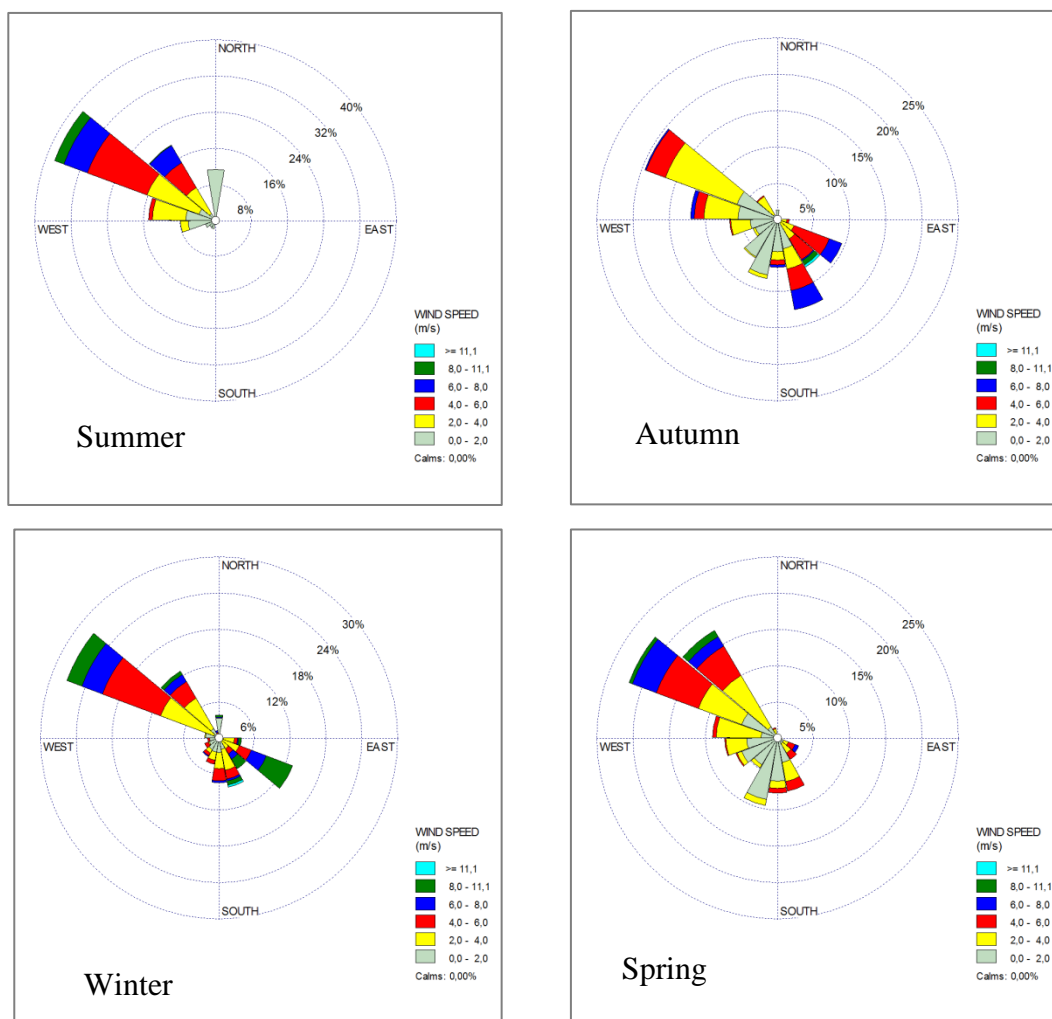
Figure 3.3 Wind-roses showing the frequency (%) of prevailing wind directions during the sampling periods.

3.3 Sampling Methods

Ambient air samples were collected using Polyurethane foam (PUF) disks as passive air samplers (PAS). These samplers consist of a foam disk (14 cm diameter, 1.35 cm thick, surface area 365 cm^2, density 0.0213 g cm^{-3}, mass, 4.40 g, volume, 207 cm^3) were placed inside a stainless steel chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm. Figure 3.4 shows a typical PAS used in this study. Sampler design protects the foam disk from direct precipitation and coarse particle deposition and also eliminates ultraviolet radiation and minimizes the effects of wind speed on the uptake rate.

In this study, sampling rates were determined using depuration compounds (DCs). The losses of DCs depend on their physicochemical properties, exposure time, and wind speed.
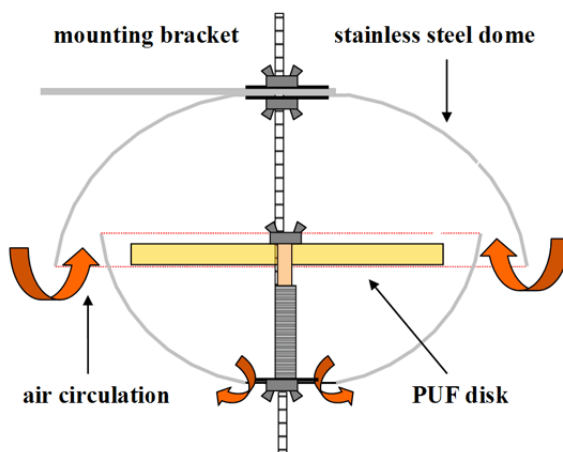
Figure 3.4 A PUF passive air sampler used in this study.

3.4 Preparation for Sampling

PUF disks were cleaned by Soxhlet extraction using an acetone:hexane mixture (50:50 by volume) for 24 h. After extraction, they were wrapped loosely with aluminum foil, dried in an oven at 70 °C overnight, and stored in a freezer in glass jars capped with Teflon-lined lids. Prior to sampling (about 10 days), 25 µL of a DC standard spiked to approximately 15 ml of hexane and this solution was

homogeneously spiked on PUF disks using a Pasteur pipette. Each PUF contained 1.7-20 ng of DCs. After the solvent was evaporated using pure N_2, spiked disks were stored in glass jars in freezer until deployment. Then, passive samplers were transported to the field. PUF disk passive samplers were placed approximately 2 meters from the ground, and sampling was ended after one month.

3.5 Laboratory Analysis

Samples were analyzed in two steps in the laboratory. First step is sample extraction and concentration and the second one is clean-up and fractionation. These sampling stages were explained in this section.

3.5.1 Sample Extraction and Concentration

All samples were Soxhlet extracted with a volumetric mixture of ACE:HEX (50:50 by volume) for 12 h.

Prior to extraction, all samples were spiked with 0.5 ml internal standard mixtures of PAHs and PCBs to monitor their analytical recovery efficiencies. The extracts were concentrated and transferred into hexane using a rotary evaporator. The temperature of water bath was maintained at 30 °C. After volume reduction to 5 ml, the extract was transferred into hexane by adding 10 ml of hexane. Then, the mixture was evaporated again down to 5 ml, and 10 ml of hexane were added to the flask. After volume reduction to 5 ml, the sample was transferred into a 40 ml amber vial. The concentrated sample was reduced to 2 ml by a gentle flow of pure N_2.

3.5.2 Clean Up and Fractionation

The samples were cleaned up and fractionated on an alumina-silicic acid column. Before use, Na_2SO_4 and alumina were placed in ceramic plates covered with aluminum foil, and then they were baked in a muffle furnace at 450 °C for 4 h. Silicic acid was placed in a flask covered with aluminum foil, dried in an oven at

105 °C overnight for activation. Then, they were allowed to cool to room temperature in a desiccator.

In an amber vial, three grams of silicic acid was deactivated by adding 140 μL of deionized (DI) water, and then the mixture was shaken until homogenized. Similarly, two grams of alumina was deactivated by adding of 120 μL of DI water and the mixture was homogenized by shaking.

Alumina-silicic acid column was prepared by adding a piece of glass wool, 3 g of silicic acid, 2 g of alumina, and 1 cm of Na_2SO_4 in series. The column was pre-washed with 20 ml of dichloromethane (DCM) followed by 20 ml of petroleum ether (PE). Then, the sample in 2 ml of hexane was added to the top of the column. After letting the sample pass through the column, 35 ml of PE was added to the column (fraction 1). Fraction 1 contained the PCBs. Then the vial was changed, 20 ml of DCM was added into the column, (fraction 2). Fraction 2 contained PAHs and OCPs. For both fractions, the sample volume was reduced, and the solvent was exchanged into hexane using a high purity stream of nitrogen. The sample was blown-down to 5 ml, and 10 ml of hexane was added to the vial. After volume reduction to 5 ml, again 5 ml of hexane was added into the sample. Then, the final sample volume was adjusted to exactly 1 ml by N_2 blow-down. All samples were stored in a freezer until they were analyzed.

3.6 Analysis of Samples

All the sample and blank extracts were analyzed for PAHs and PCBs with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). They were analyzed with the same capillary column (HP-5ms, 30 m, 0.25 mm, 0.25 μm).

For PAH analysis, the initial oven temperature was held at 50 °C for 1 min, was raised to 200 °C at 25 °C min⁻¹ and from 200 to 300 °C at 8 °C min⁻¹, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were

295, 300, and 180 °C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 ml min^{-1}, 45 cm s^{-1} linear velocity).

PCBs were also analyzed at electron impact ionization mode. The initial oven temperature was held at 50 °C for 1 min and was raised to 200 ºC at 25 ºC min^{-1}, to 300 ºC at 8 ºC min^{-1}, and was held for 3 min. The injector, ion source, and quadrupole temperatures were 250, 230, and 150 °C, respectively.

3.7 Quality Assurance/Quality Control

3.7.1 Procedural Recoveries

Prior to extraction and clean-up, all samples and blanks were spiked with surrogate standard mixtures of PAHs (naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-d$_{12}$ and perylene-d$_{12}$) and PCBs (PCB-14, 65, and 166) to determine the analytical recoveries. Each sample was checked for the surrogate standard recovery efficiencies if they were in the range of 50-120%. The recoveries of the surrogate standards were used to correct the amounts of the specific PAHs and PCBs found in the samples, correspondingly.

Average recoveries of PAH and PCB surrogate standards in all blank and sample matrices are given in Table 3.4.

Table 3.4 Average recovery efficiencies (%) of PAH and PCB surrogate standards (avg±SD) in blanks and samples

Surrogate Standards	Recovery (%)
Acenaphthene-d10	84±20
Phenanthrene-d10	107±23
Chrysene-d12	98±24
Perylene-d12	92±23
PCB-14	86±12
PCB-65	93±13
PCB-166	89±11

3.7.2 Blanks

Blanks were analyzed to determine the amount of contamination from sample collection and preparation. To determine the contribution of PAHs and PCBs from the sample preparation, solvent blanks were processed for the samples. All blanks were extracted and analyzed in the same manner as the samples to determine if there was any contamination during sample handling and preparation. Average PAH and PCB amounts mostly detected in the blank matrices are presented in Table 3.5.

Table 3.5 Average PAH & PCB amounts (ng, avg±SD) in blanks

PAHs[a]	avg±SD (ng)	PCBs	avg±SD (ng)
ACL	10±5	PCB-18	1.4±1.1
ACT	15±5	PCB-17	1.1±0.5
FLN	34±9	PCB-31	1.0±0.4
PHE	108±21	PCB-28	1.4±1.3
ANT	6±2	PCB-33	0.3±0.4
CRB	2±1	PCB-52	0.5±0.6
FL	15±4	PCB-49	0.2±0.2
PY	15±4	PCB-70	0.2±0.3
BaA	1±1	PCB-99	0.3±0.3
CHR	2±1	PCB-87	0.5±0.5
BaP	0.2±0.5	PCB-101	0.1±0.2
IcdP	*nd*	PCB-110	0.1±0.2
DahA	0.3±0.5	PCB-118	0.1±0.3
BghiP	0.3±0.6	PCB-149	*nd*

[a] 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).

3.7.3 Detection Limits

The lower limit of quantification is based on the sensitivity of the analytical equipment. Instrumental detection limits (IDL) were determined from liner extrapolation from the lowest standard in calibration curve using the area of a peak having a signal/noise ratio of 3. This ratio was used because peaks with smaller ratios cannot be reliably integrated. The quantifiable PAH and PCB amounts were approximately 0.15 and 0.10 pg for 1 µl injection, individually. For the compounds detected in blanks the limit of method detection limits (MDL) was

defined as the mean blank mass plus three standard deviations. Instrumental detection limit was used for the compounds that were not detected in blanks. MDL for individual PAH and PCB compounds are presented Table 3.6 and Table 3.7, respectively.

Generally, the amounts of the target compounds in the samples were substantially higher than MDLs. Sample quantities exceeding the MDL were quantified and blank-corrected by subtracting the mean blank amount from the sample amount for all samples.

Table 3.6 MDLs for individual PAHs

PAHs[a]	MDLs (ng) for individual PAHs	MDLs for air concentrations of individual PAHs (ng/m^3)
ACL	13.9	0.329
ACT	19.6	0.375
FLN	53.1	0.700
PHE	164.7	1.450
ANT	8.50	0.074
CRB	3.59	0.029
FL	24.3	0.183
PY	21.8	0.163
BaA	3.67	0.027
CHR	3.13	0.023
BaP	0.15	0.001
IcdP	1.05	0.008
DahA	0.15	0.001
BghiP	1.31	0.009

[a] 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).

Table 3.7 MDLs for individual PCBs

PCB congeners	MDLs (ng) for individual PCBs	MDLs for air concentrations of individual PCBs (ng/m^3)
PCB-18	1.47	13.2
PCB-17	1.92	17.1
PCB-31	1.55	12.6
PCB-28	1.56	12.7
PCB-33	0.531	4.25
PCB-52	1.28	9.91
PCB-49	1.17	9.07
PCB-44	0.100	0.763
PCB-74	0.100	0.747
PCB-70	0.465	3.47
PCB-95	0.181	1.35
PCB-101	0.658	4.86
PCB-99	0.507	3.74
PCB-87	0.873	6.40
PCB-110	0.620	4.54
PCB-82	0.100	0.730
PCB-151	0.100	0.730
PCB-149	0.100	0.729
PCB-118	0.573	4.16
PCB-153	0.100	0.727
PCB-132	0.100	0.727
PCB-105	0.100	0.725
PCB-138	0.100	0.725
PCB-158	0.100	0.725
PCB-187	0.100	0.724
PCB-183	0.100	0.724
PCB-128	0.100	0.724
PCB-177	0.100	0.723
PCB-171	0.100	0.723
PCB-156	0.100	0.722
PCB-180	0.100	0.723
PCB-170	0.100	0.722
PCB-199	0.100	0.722
PCB-194	0.100	0.721
PCB-206	0.100	0.721

3.7.4 Calibration Standards

The PAH calibration standard solution contained 16 PAHs, carbazole, and five deuterated PAHs (naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-

d$_{12}$, and perylene-d$_{12}$) that were used to determine the analytical recoveries. Six levels of calibration standards (0.04, 0.4, 1, 4, 6, 10 µg ml^{-1} for PAHs, and deuterated PAHs at a fixed concentration of 8 µg ml^{-1}) were used to calibrate the GC/MS system.

The PCB calibration standard solution contained 41 PCB congeners and internal standard mix (PCB-14, -65, and -166). Five point of calibration standards were used to prepare the calibration curves for analytical system. In every case, the linear fit was good with $r^2 \geq 0.999$.

3.8 Calculation of Effective Air Sampling Volume

The effective sampling air volumes for PAHs and PCBs for a 1-month sampling period were calculated using relationship developed by Shoeib & Harner (2002) for the non-polar hydrophobic chemicals. PUF disk effective air volume (V_{air}) is calculated as:

$$V_{air} = (K'_{PSM-A}) \times (V_{PSM}) \times \left[1 - exp \left(-\frac{k_A}{K'_{PSM-A}} \times \frac{t}{D_{film}} \right) \right] \tag{1}$$

$$K'_{PSM-A} = K_{PSM-A} \times \rho_{PSM} \tag{2}$$

where, V_{PSM} is the volume (cm^3) of the PUF disk, ρ_{PSM} is the density (g cm^{-3}) of the disk, t is the exposure time (day), k_A is the air-side mass transfer coefficient (MTC) (cm d^{-1}), and D_{film} (m) is the effective film thickness (Pozo et al., 2004). K_{PSM-A} is the passive sampling medium (PSM)-air partition coefficient but differs from the K'_{PSM-A} (dimensionless). For PUF disk:

$$logK_{PSM-A} = logK_{PUF-A} = 0.6366 \, logK_{OA} - 3.1774 \tag{3}$$

where, K_{OA} is the octanol-air partition coefficient (Shoeib & Harner, 2002). k_A was calculated using the recovery of depuration compounds initially spiked into the PUF disk:

$$k_A = ln\left(\frac{C_t}{C_0}\right) D_{film} \; K'_{PSM-A} \left(\frac{1}{t}\right) \tag{4}$$

where, C_t and C_o (mass cm^{-3}) are the concentrations in the disk at the end and beginning of the sampling, respectively. Sampling rate (R, m^3 day^{-1}) is calculated by Shoeib & Harner (2002):

$$R = k_A \; A_{PSM} \tag{5}$$

where, A_{PSM} is the planar surface area (m^2) of the PUF disk.

Average sampling rates (R, m^3 d^{-1}) calculated using the loss of depuration compounds (Equation 5) ranged from 4.21±1.37 to 4.93±1.50 m^3 d^{-1} for all sampling periods. Then, the air-side MTCs were calculated from these sampling rates were used along with compound-specific K_{PSM-A} values (Equation 1) to determine the effective sampling volumes (V_{air}) for individual PCBs and PAHs. Concentrations in the air $C_{i,air}$ (ng m^{-3}) were calculated as:

$$C_{i,air} = \frac{m_i}{V_{air}} \tag{6}$$

where, m_i is the mass of a target compound (i) in the passive samples (ng sample^{-1}).

3.9 Positive Matrix Factorization

Positive Matrix Factorization (PMF) is a receptor modeling tool developed in the early 1990s by Paatero & Tapper (1994) and utilized non-negativity constraints for obtaining physically realistic meanings. PMF has two very significant 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 equal weight. Second difference is that the factors in PMF are not necessarily orthogonal to each other, which represent another advantage; this meets the observation of real-source signatures which are also not orthogonal to each other.

Furthermore, the non-negativity constraints in PMF are an advantage. The PMF method is described elsewhere (Paatero & Tapper, 1994; Paatero, 1997; U.S. EPA, 2008) and the model principle is only briefly explained here. U.S. EPA (2008) reported, although other source apportionment models include Unmix and CMB have aims similar to that of PMF, they have different mechanisms. Unmix does not allow individual weighting of data points as does PMF and not resolve as many factors as PMF. In CMB analysis, source profiles are provided whereas in PMF, the source profiles are estimated. According to several studies compared PMF and CMB, major factors were correlated well and were similar in magnitude; additionaly, PMF-resolved source profiles were generally same with measured source profiles (Jaeckels et al., 2007; Rizzo & Scheff, 2007).

In PMF model any 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×p) and F(p×m), and the residual matrix, E, where p is the number of factors.

$$X = GF + E \tag{7}$$

The product of G and F can explain the systematic variations in X.

The residuals, E_{ij} can be expressed as:

$$E_{ij} = X_{ij} - h = 1pG_{ih} \cdot F_{kj} \tag{8}$$

The residuals, E_{ij} are espressed as:

$$E_{ij} = X_{ij} - \sum_{h=1}^{p} G_{ih} \cdot F_{kj} \tag{9}$$

The objective function (Q) related to the residual and uncertainty is minimized using weighted least-squares by PMF, which is defined as:

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{E_{ij}}{U_{ij}}\right]^2 \qquad (10)$$

where, U_{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 elements of G and F to be non-negative. The PMF solution minimizes the object function Q based on the given uncertainty U (Paatero, 1999). The uncertainties for each sample were calculated using measurement uncertainties ($MU\%$) and method detection limits (MDL). If the concentration$\leq$MDL, the uncertainty U is calculated as:

$$U = \frac{5}{6} \times MDL \qquad (11)$$

When the concentration$>$ MDL, U is calculated as:

$$U = \sqrt{(MU \times concentration)^2 + (MDL)^2} \qquad (12)$$

Before the analysis, undetected values are replaced with half the MDL. Uncertainty file should be provided to give the model an estimate of the confidence the user has in each value.

In this study, PMF analysis was conducted using the EPA-PMF 3.0 model (U.S. EPA, 2008). EPA-PMF 3.0 has some advantages according to other versions. The initial version, 1.0, contained no tools for processing input data or performing rotations. Version 2.0 added a suite of tools for processing input data and model results. Version 3.0 includes additional tools and the capability to perform F_{peak} and constrain elements of the contribution matrix (U.S EPA, 2009).

Principal Factor Analysis (PFA) is used as a method to simplify the complex data set, aiming to identify relationships between variables and possible sources of air pollution. Before the application of PMF, PFA was applied as a screening method in the present study (Appendix A). Principal component analysis (PCA) was used as the extraction method, and the raw calculated factor loading

coefficients were rotated by Varimax with Kaiser Normalization (Kaiser, 1958). Only components with Eigenvalues greater than 1.0 after rotation were retained. IBM® SPSS® Statistics, Version 20 (IBM Corporation, USA), was used for the multivariate statistical analysis, and for descriptive and correlation analyses.

Measured PAH and PCB concentrations at 40 sampling sites for four seasons in Aliaga industrial region were used in PMF to identify their sources. Species were measured below method detection limits (MDL) were replaced by 1/2 MDL and assigned an uncertainty equal to 5/6 DL as suggested by U.S. EPA (2008). Missing data were approximated as the geometric mean of the corresponding species concentrations with an uncertainty of four times the geometric mean. According to the uncertainty statistics and knowledge of the dataset, all variables were categorized as "strong", i.e., not to be down-weighted in the analysis (signal-to-noise ratio > 2) (Paatero & Hopke, 2003).

In the PMF analysis, extra modeling uncertainty (20% and 15% for PAHs and PCBs, respectively) was imposed to account for changes in the source profiles and other sources of variability. PMF was performed on a matrix made up of 14 columns (number of PAHs species) and 160 rows (number of air samples for four seasons) for PAHs while the matrix for PCBs consisted of 35 columns and 160 rows. Models were tested with 3-5 factors. According to the results from PCA analysis and PMF results, a three factor model was selected as the optimal solution fitting the dataset. Appendix B includes the some model outputs (input data statistics and base run summary for three factor models). Twenty base runs were performed and the run with the minimum Q value was selected as the base run solution. Q values (Q_{true}, Q_{robust}, $Q_{theoretical}$) of both PAH and PCB compounds for 3-5 factor models are presented in Appendix C. One hundred bootstrap runs were conducted with minimum correlation R-value 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. The high correlations between measured and modeled concentrations validated the choice of the selected factors.

The EPA-PMF 3.0 model also provides the rotational freedom parameter (F_{peak}) function that can control whether more extreme values are assumed for the factor loadings (by assigning positive F_{peak} values) or the factor scores (by assigning negative F_{peak} values). In this study, altering the F_{peak} value was not found to result in subsequently better source profiles. Consequently base run results (F_{peak}=0) were selected.

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the results of ambient air concentrations, spatial and seasonal distributions of concentrations, and source apportionment of PAHs and PCBs.

4.1 Spatial and Seasonal Distributions of Atmospheric PAH and PCB Concentrations

4.1.1 PAH Concentrations

Atmospheric PAH concentrations in the sampling sites are given in Table 4.1. The concentrations of Σ_{14}PAHs ranged from 1.6 to 838 ng m^{-3}. PAH concentrations showed a strong increase in the industrial areas, especially around the iron-steel plants and ship dismantling areas. For all periods, site average PAH concentrations in all sites showed a distinct residential and industrial contributions indicating total concentrations were 2-5 times higher in industrial sites than in the residential ones (Figure 4.1).

Σ_{14}PAH concentrations in the air ranged from 1.6 to 838 ng m^{-3} for the summer sampling period, from 5.5 to 282 ng m^{-3} for the fall period, from 28 to 422 ng m^{-3} for the winter period and from 6.1 to 476 ng m^{-3} for the spring period.

Table 4.1 Atmospheric concentrations (ng m^{-3}) of Σ_{14}PAHs measured four seasons at the air sampling sites

Sampling Sites	Minimum	Maximum	Geometric Mean	Median	Average	Standard Deviation
S1	2.0	136.2	20.7	27.3	48.2	60.3
S2	2.9	161.9	17.9	16.7	50.0	75.5
S3	3.2	35.0	8.0	6.0	12.6	15.0
S4	5.9	38.2	12.0	9.5	15.8	15.0
S5	1.6	74.0	8.88	7.3	22.6	34.4
S6	6.5	80.8	26.5	31.6	37.6	31.7
S7	13.5	358.9	49.6	35.6	111	166
S8	11.3	254.6	37.3	26.5	79.7	117
S9	40.2	141.1	71.5	68.8	79.7	44.1
S10	45.0	130.5	62.2	50.7	69.2	41.1
S11	252.0	475.9	349	357	361	106
S12	24.9	111.6	55.7	70.6	69.4	47.5
S13	68.5	405.2	168	185	211	153
S14	16.2	66.4	34.4	36.4	38.9	21.1
S15	7.4	175.1	35.1	34.3	62.8	76.0
S16	12.1	278.9	40.7	37.8	91.6	127
S17	12.9	87.8	32.1	30.7	40.5	32.7
S18	7.5	138.5	29.2	29,0	51.0	60.0
S19	5.5	129.4	22.2	18.4	43.0	58.0
S20	7.9	88.5	24.6	23.4	35.8	36.1
S21	21.6	163.8	53.5	50.9	71.8	64.3
S22	31.7	113.7	51.6	46.1	59.4	38.2
S23	21.7	124.1	38.0	28.0	50.5	49.2
S24	12.1	87.2	23.1	16.4	33.0	36.2
S25	34.3	123.2	56.0	48.4	63.6	40.4
S26	12.2	71.5	35.8	44.3	43.1	25.2
S27	180	421.2	277.5	279	290	99.1
S28	58.4	142.7	79.1	68.6	84.6	39.2
S29	258	838.2	367	290	419	281
S30	89.3	316.0	139	117	160	106
S31	27.1	105.1	58.3	65.4	65.8	34.2
S32	15.1	131.6	31.0	22.8	48.1	56.2
S33	32.5	96.6	47.2	39.9	52.2	29.8
S34	92.6	247.9	159	170	170	68.2
S35	48.4	237.9	106	126	135	96.4
S36	2.25	28.0	10.6	14.5	14.8	10.8
S37	39.0	115.2	63.3	60.0	68.5	32.8
S38	17.1	40.6	23.5	21.2	25.0	10.9
S39	40.7	156.7	86.6	103	101	58.4
S40	22.2	171.3	52.6	48.6	72.7	68.7
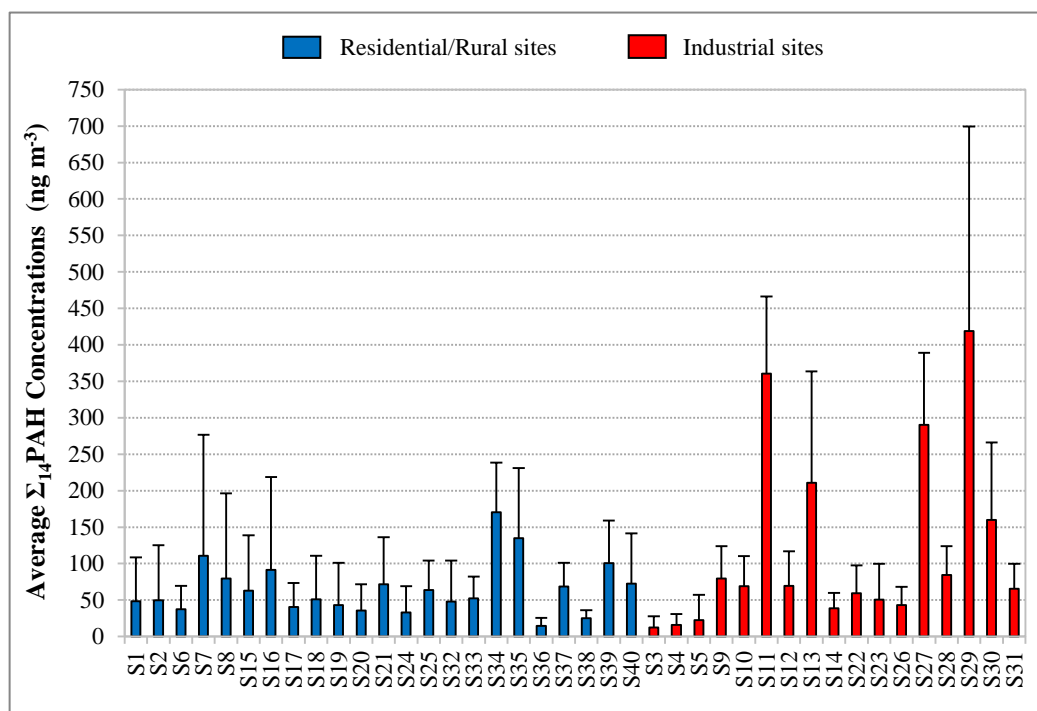
Figure 4.1 Average Σ_{14}PAH concentrations (ng m^{-3}) at the residential/rural and industrial sites. Error bars indicate 1 SD.

For all sites, the highest PAH concentrations except for three sampling sites were found during the winter period due to residential heating activities at the settlements in the region. These tree sampling sites are around the iron-steel plants, therefore, evaporative emissions due to increased temperature and combustion process in the plants during the summer may be the reasons for these highest PAH concentrations. A study reported that combustion-derived PAH emissions may be elevated during the colder months (Pozo et al., 2009). Higher PAH concentrations in winter were also reported recently (Bae, Yi, & Kim, 2002; Gevao, Hamilton-Taylor, & Jones, 1998; Kiss et al., 2001; Odabasi, Cetin, & Sofuoglu, 2006b; Vardar, Esen, & Tasdemir, 2008). In agreement with the literature, the lowest PAH concentrations were detected during the summer sampling period (July-August) in the study area.

Figure 4.2 shows the overall average concentrations of individual PAHs in air including all sites and seasons. Σ_{14}PAHs were dominated by phenanthrene followed by fluoranthene, pyrene and fluorene in the region. In several regions, phenanthrene was also found as the dominant compound as reported by Gevao, Hamilton-Taylor,

& Jones (1998), Odabasi, Vardar, Sofuoglu, Tasdemir, & Holsen (1999) and Santiago & Cayetano (2007), even in Aliaga region (Bozlaker, 2008).
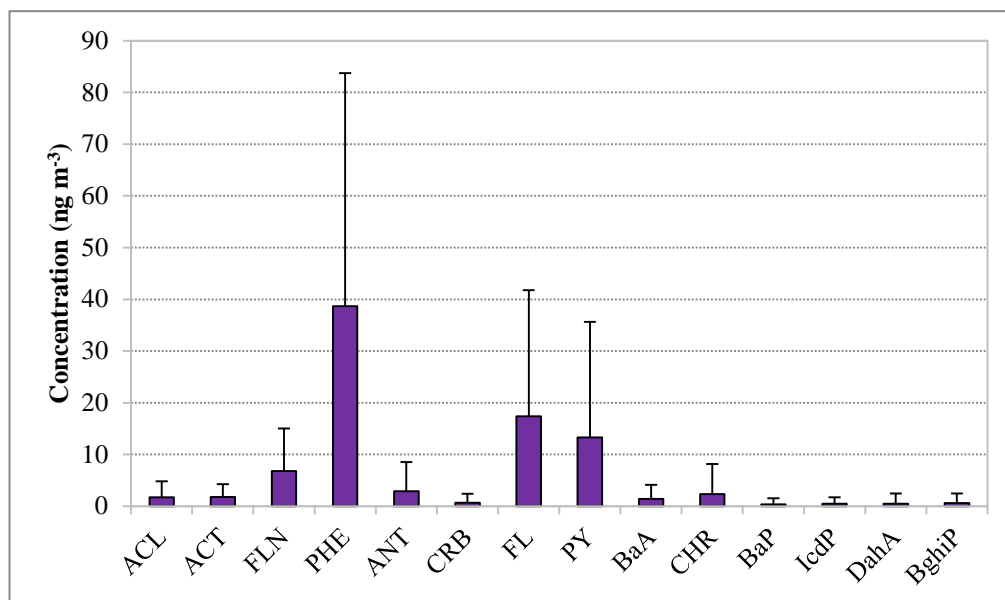
Figure 4.2 Overall average concentrations (ng m^{-3}) of individual PAHs including all sites and seasons. Error bars indicate 1 SD.

The spatial distribution of annual average PAH concentrations in the air ranged from 13 to 419 ng m^{-3} and at 25 sites concentrations were higher than 50 ng m^{-3}. These concentrations are higher than the reported values (25-35 ng m^{-3}) of 12 PAHs in London and Manchester (Jaward, Farrar, Harner, Santiago & Cayetano, 2007; Sweetman, & Jones, 2004). The highest concentration of 419 ng m^{-3} measured in this study is lower than the highest total PAHs concentration of 881 ng m^{-3} reported in Taiwan by Fang, Chang, Lu, & Bai (2004). On the other hand, this value is already higher than the reported by several studies (Harner et al., 2006; Santiago & Cayetano, 2007). $\sum_{16}$PAH concentrations measured in the present study were highly variable (Table 4.1). 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, Turkey (Demircioglu, Sofuoglu, & Odabasi, 2011).

Figures 4.3 - 4.6 show that the spatial distributions of ambient air PAH concentrations (ng m^{-3}) during summer, fall, winter and spring, respectively.
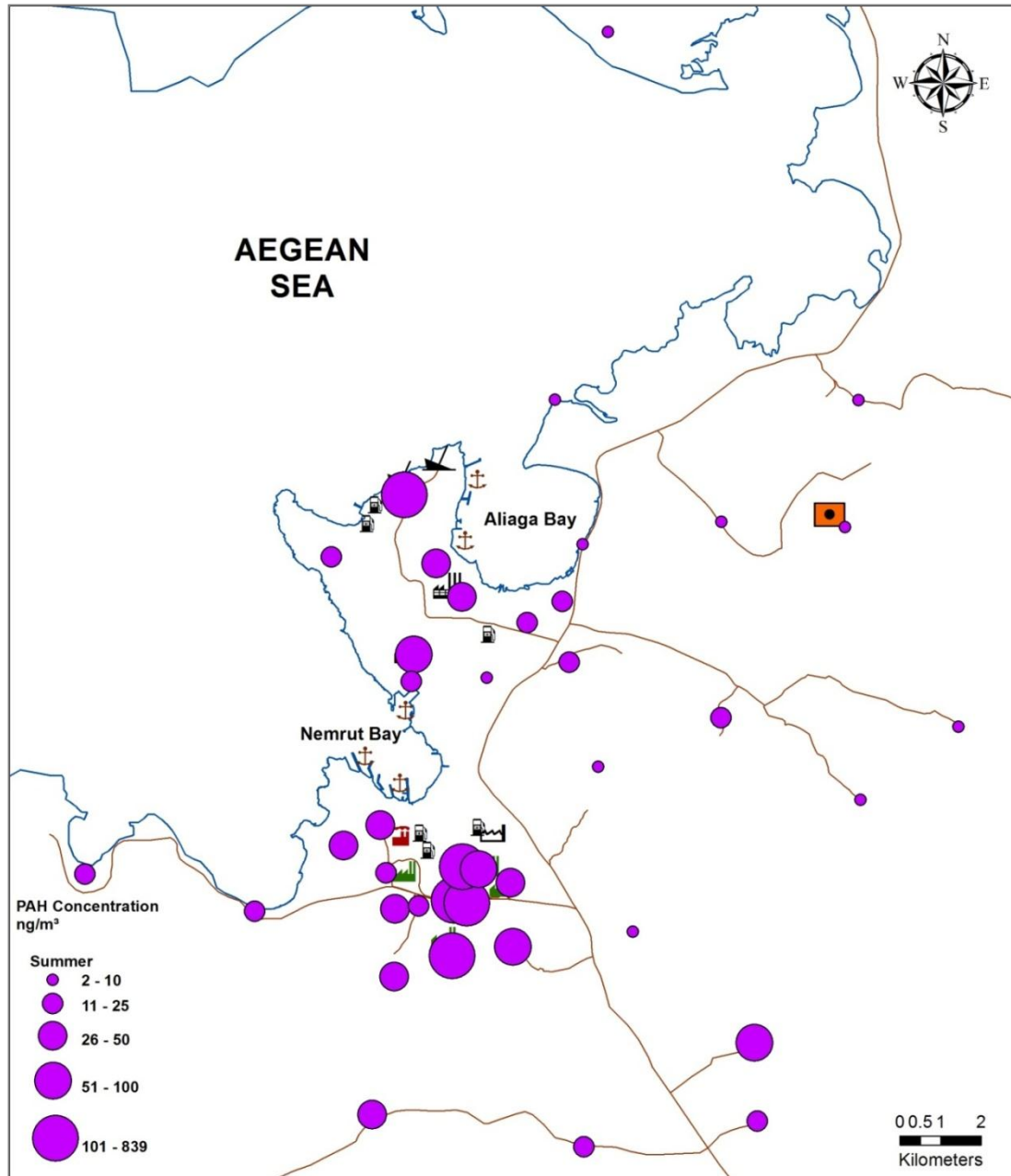
Figure 4.3 The spatial distribution of total ambient air PAH concentrations (ng m^{-3}) for summer.
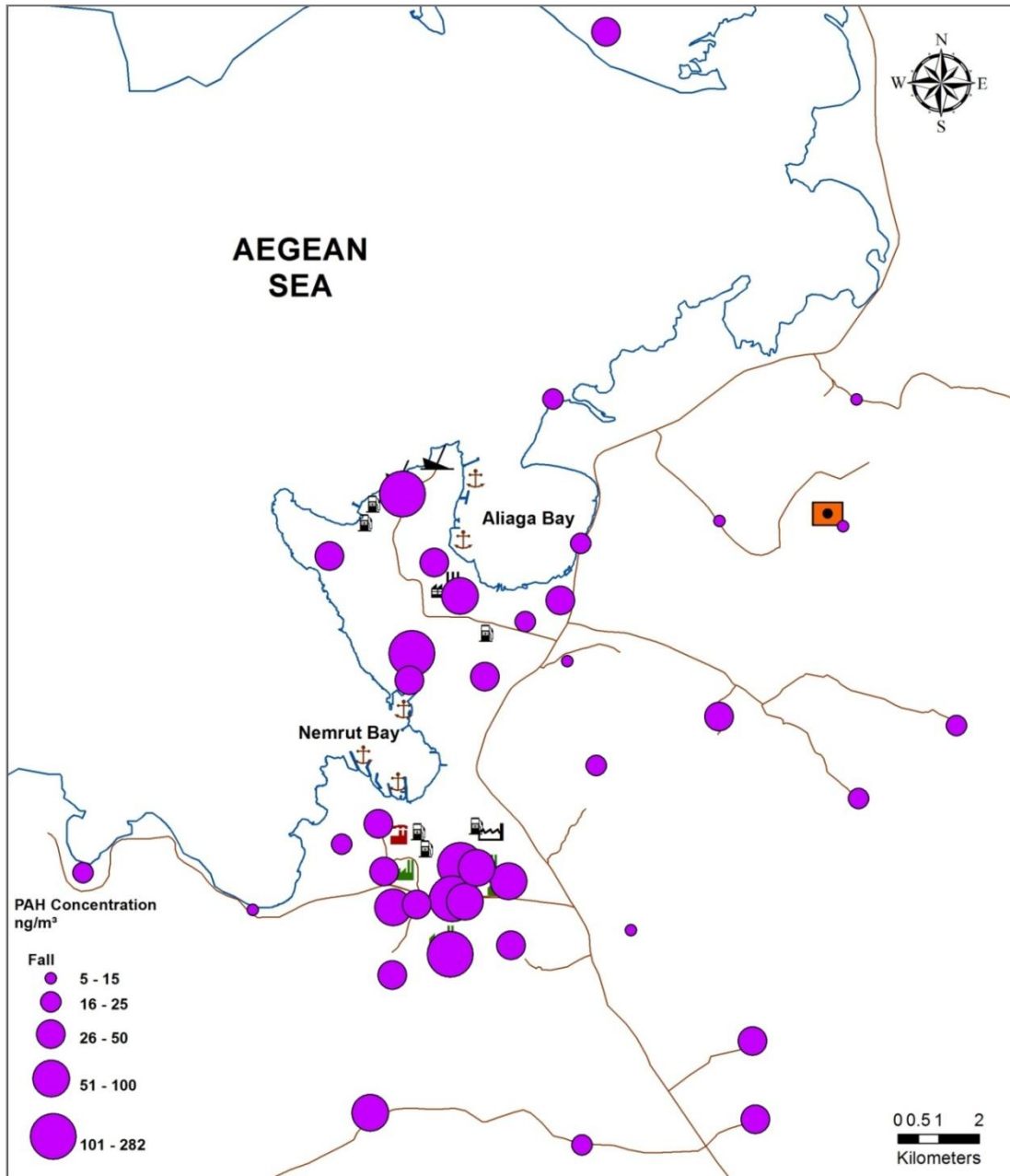
Figure 4.4 The spatial distribution of total ambient air PAH concentrations (ng m^{-3}) for fall.
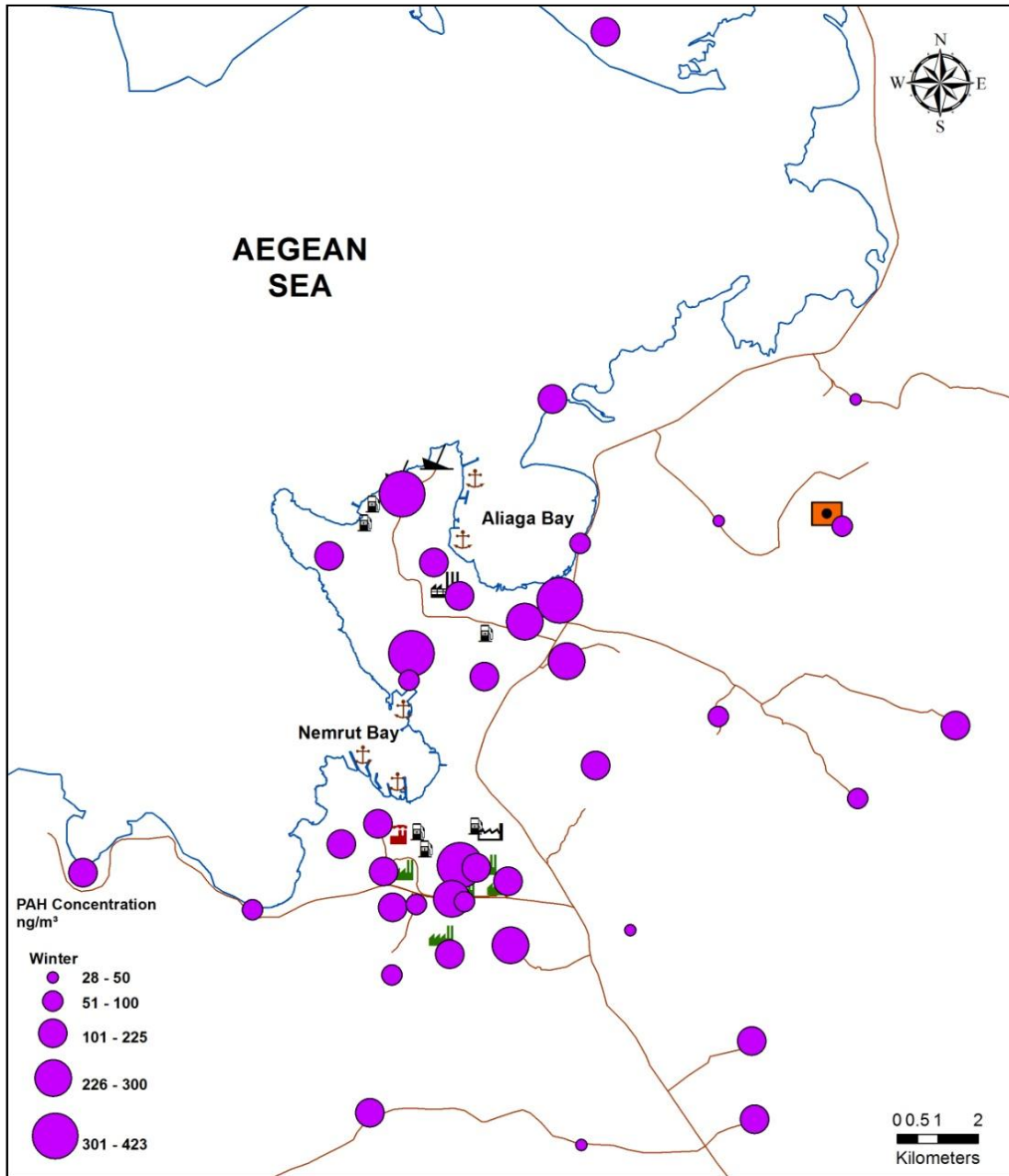
Figure 4.5 The spatial distribution of total ambient air PAH concentrations (ng m^{-3}) for winter.
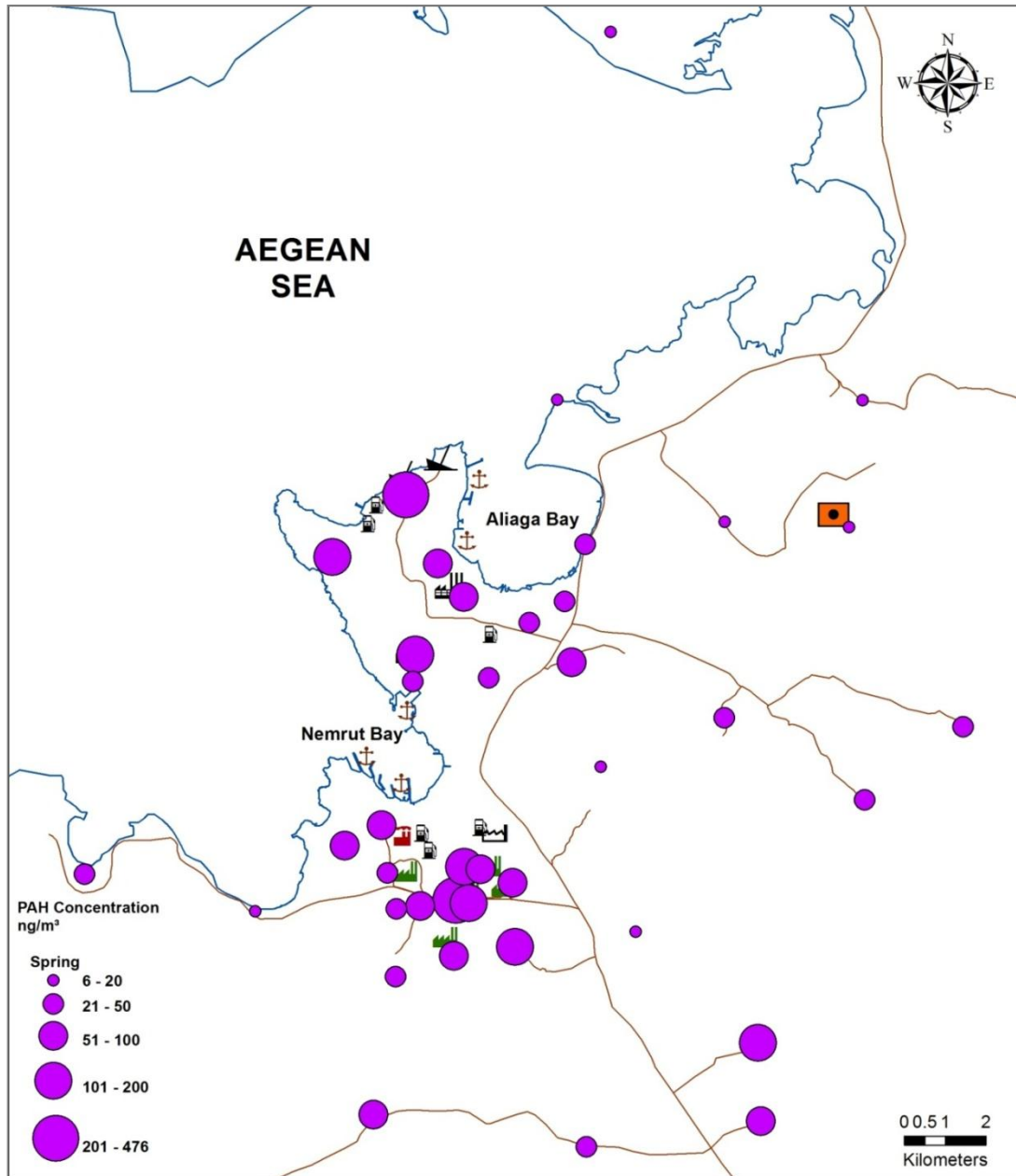
Figure 4.6 The spatial distribution of total ambient air PAH concentrations (ng m^{-3}) for spring.

4.1.2 PCB Concentrations

Table 4.2 shows the ambient air PCBs concentrations measured in the study area. Σ_{35}PCB (sum of the 35 individual congeners) concentrations ranged from 187 to 230818 pg m^{-3} for summer (July-August 2009), from 410 to 86858 pg m^{-3} for fall (October-December 2009), from 140 to 22293 pg m^{-3} for winter (January-February 2010) and from 491 to 44454 pg m^{-3} for spring (April-May 2010). Site-

averaged PCB concentrations in the air ranged from 349 to 94363 pg m^{-3}. Spatial distribution of seasonal concentrations is shown in Figure 4.8.

Average seasonal PCB concentrations were approximately 2-3 times higher during the summer and fall (mean temperatures 27 °C and 20 °C, respectively) than during the winter and spring (9 °C and 16 °C, respectively). Elevated ambient air concentrations during the summer months may be related to the increased volatilization rates of previously deposited PCBs on terrestrial surfaces. Observed seasonal cycling of PCB levels in air is supported by other recent studies (Cousins & Jones, 1998; Currado & Harrad, 2000; Hillery, Basu, Sweet, & Hites, 1997; Montone, Taniguchi, & Weber, 2003; Simcik, Franz, Zhang, & Eisenreich, 1998; Stern et al., 1997; Yeo, Choi, Chun, & Sunwoo, 2003). In a seasonal basis, summer concentrations were higher than the concentrations in winter in industrial sites, while the opposite was observed for some residential sites as observed by Cetin, Yatkin, Bayram, & Odabasi (2007).

During all seasons, PCB concentrations showed a strong increase in the industrial sites compared to the residential/rural sites, confirming the continuing role of industrial areas in Aliaga as PCB emission sources (Bozlaker, 2008). High PCB concentrations were measured at some sampling sites close to the iron-steel plants and ship dismantling plants, where all kind of scrap iron steel materials are stored, classified, cut into parts, and melted.

Table 4.2 Atmospheric concentrations (pg m^{-3}) of Σ_{35}PCBs measured for four seasons at the air sampling sites

Sampling Sites	Minimum	Maximum	Geometric Mean	Median	Average	Standard Deviation
S1	301	1096	670	795	747	353
S2	1041	2824	1423	1185	1559	849
S3	223	713	407	462	465	260
S4	314	1086	670	778	739	335
S5	335	1149	656	702	722	344
S6	1441	2252	1700	1604	1725	360
S7	462	1016	649	639	689	273
S8	610	1312	880	868	915	297
S9	1842	4179	2708	2745	2878	1141
S10	2085	6512	3329	3007	3653	1955
S11	7824	53573	23517	27140	28919	18911
S12	2172	6527	3666	3629	3989	1904
S13	907	8094	2466	2472	3486	3271
S14	956	2497	1534	1550	1638	679
S15	878	2278	1510	1619	1599	585
S16	514	848	667	674	678	140
S17	149	623	417	572	479	221
S18	140	695	360	416	417	226
S19	409	1097	716	816	784	364
S20	185	539	345	390	376	167
S21	1350	2581	2003	2149	2058	514
S22	14860	34982	24754	27127	26024	8842
S23	2438	7233	4705	5286	5061	2000
S24	492	8726	1843	1643	3126	3774
S25	3744	12624	7118	7372	7778	3659
S26	2525	21941	6466	5726	8980	8819
S27	5877	37700	15946	17691	19740	13729
S28	12242	37818	23617	27263	26146	12578
S29	15323	230819	60790	65656	94363	95594
S30	3437	64190	14986	15188	24501	27059
S31	7278	23473	14560	16244	15810	6671
S32	187	531	319	338	349	162
S33	2532	12003	6268	7142	7205	3889
S34	3925	39411	12019	11909	16789	15692
S35	1104	12754	5929	9775	8352	5521
S36	369	2307	1107	1364	1351	831
S37	1451	8147	3987	4682	4740	2801
S38	483	6021	2058	2484	2868	2304
S39	218	1450	764	1037	936	517
S40	384	53571	3831	3472	15225	25626

Figure 4.7 shows the distribution of ambient PCB concentrations. Figure indicates that the industries have a significant contribution to the PCB pollution in the study area. PCBs are mainly found in the scrap. They can be emitted when the material is heated up during steel production or they may also form by de novo synthesis during thermal processes (Odabasi et al., 2009).
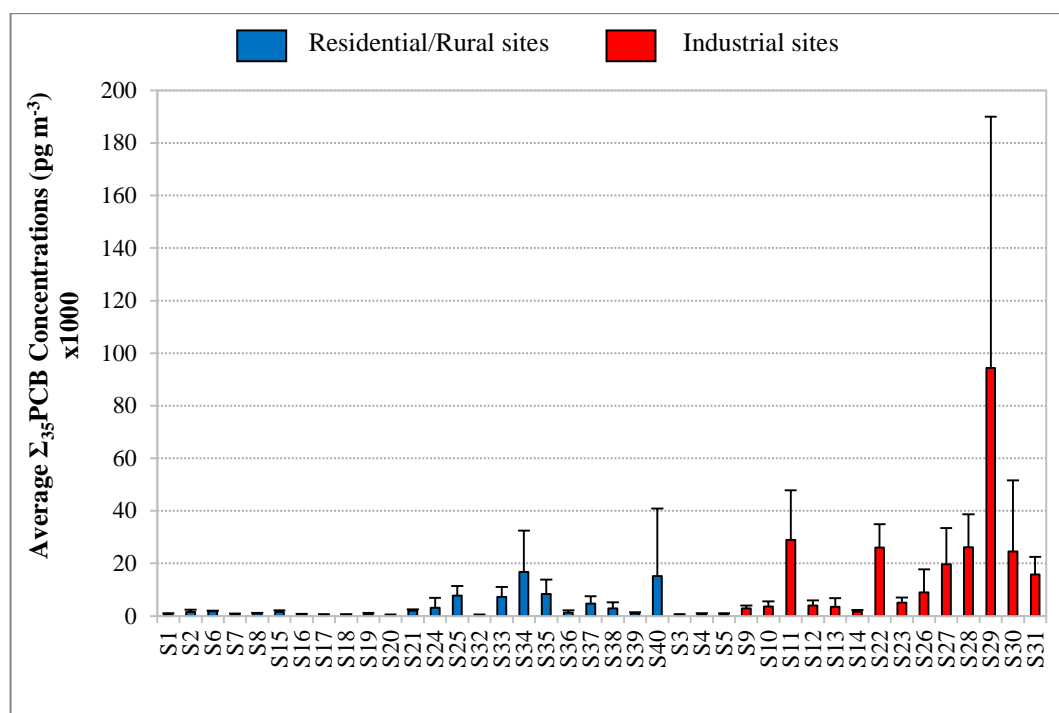
Figure 4.7 Average Σ_{35}PCB concentrations (pg m^{-3}) at the residential/rural and industrial sites. Error bars indicate 1 SD.

Total PCB concentrations in air were dominated by lower chlorinated congeners for all periods. Average gas-phase concentrations of PCB congeners are shown in Figure 4.8. Several studies measuring PCB concentrations are available in the literature. A study (Motelay-Massei et al., 2005) reported that total Σ_{13}PCB concentrations ranged from 72 to 550 pg m^{-3} for July-October, from 66 to 506 pg m^{-3} for November-March and from 129 to 1350 pg m^{-3} for April-June. The highest total concentration of 29 PCBs was approximately measured as 787 pg m^{-3} in an industrial site by Roots & Sweetman (2007). In the same site, the levels for the sum of 29 PCBs ranged from 10 to 787 pg m^{-3}. Σ_{36}PCB concentrations were 3136 ± 824 and 1371 ± 642 pg m^{-3} for an industrial site in Aliaga, and lower total Σ_{36}PCB concentrations as 314 ± 129 and 847 ± 610 pg m^{-3} were reported by Cetin et al.

(2007) at urban Aliaga for summer and winter periods, respectively. For another urban site in Turkey, Cindoruk & Tasdemir (2007) measured annual total Σ_{37}PCB concentrations as 492 ± 189 pg m^{-3}. Average total Σ_{50}PCB concentration for summer-fall period was 1900 ± 1700 pg m^{-3} at urban Chicago (Tasdemir, Vardar, Odabasi, & Holsen, 2004). The concentrations measured in Aliaga town were usually similar to those observed at urban sites in other studies. However, PCB concentrations measured in Aliaga industrial sites were substantially higher than those measured in other studies.
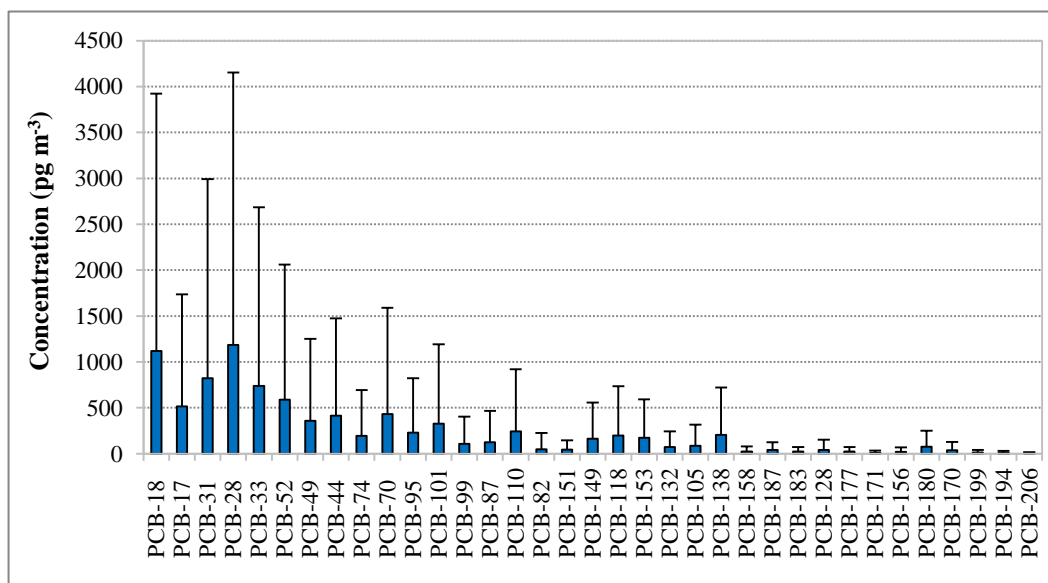
Figure 4.8 Overall average concentrations (for all sites and seasons) of individual PCBs. Error bars indicate 1 SD.

Ambient air Σ_{35}PCB concentrations (pg m^{-3}) measured during the different sampling periods in the study area are shown in Figures 4.9 to 4.12.
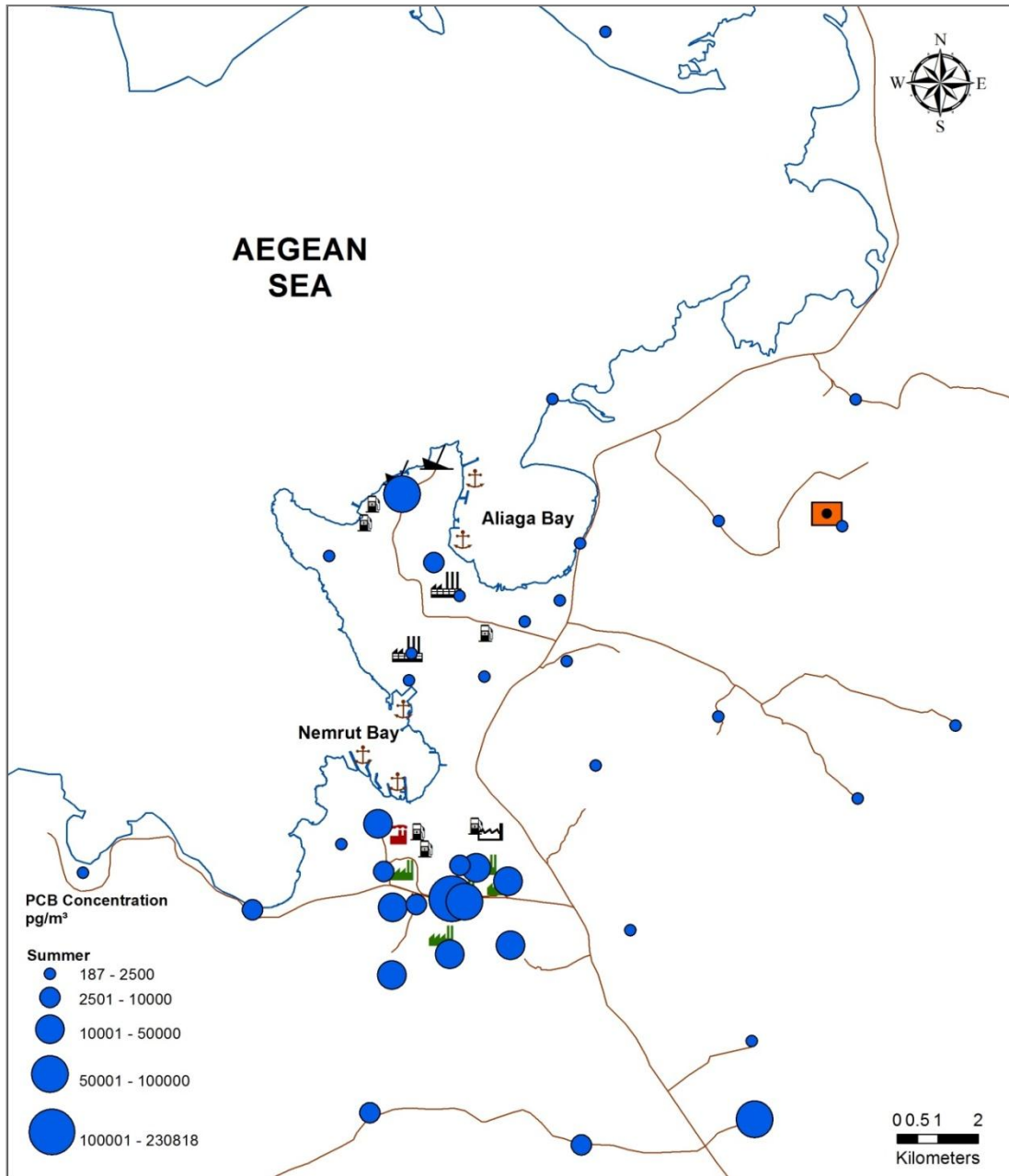
Figure 4.9 The spatial distribution of total ambient air PCB concentrations (pg m^{-3}) for summer.
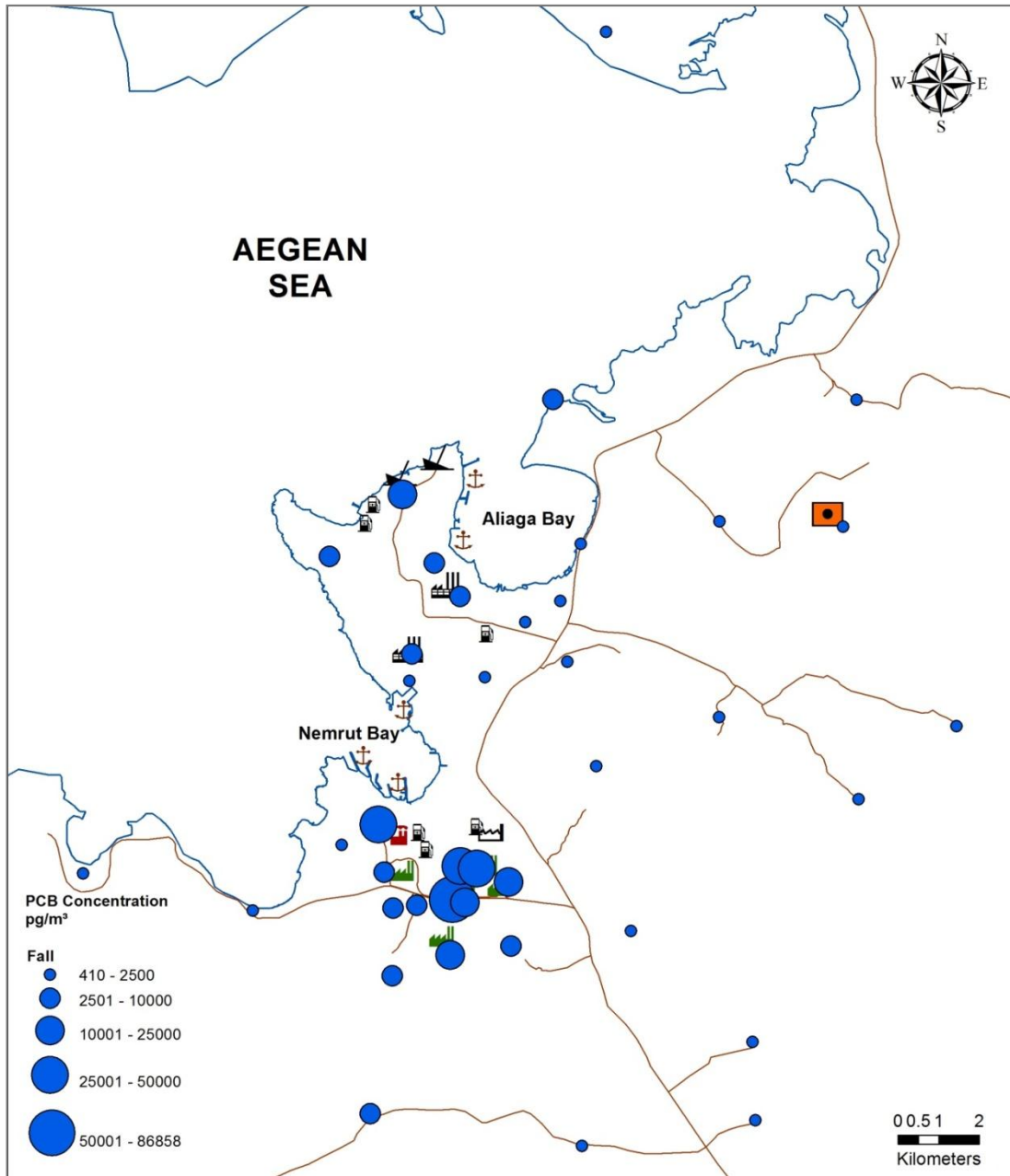
Figure 4.10 The spatial distribution of total ambient air PCB concentrations (pg m^{-3}) for fall.
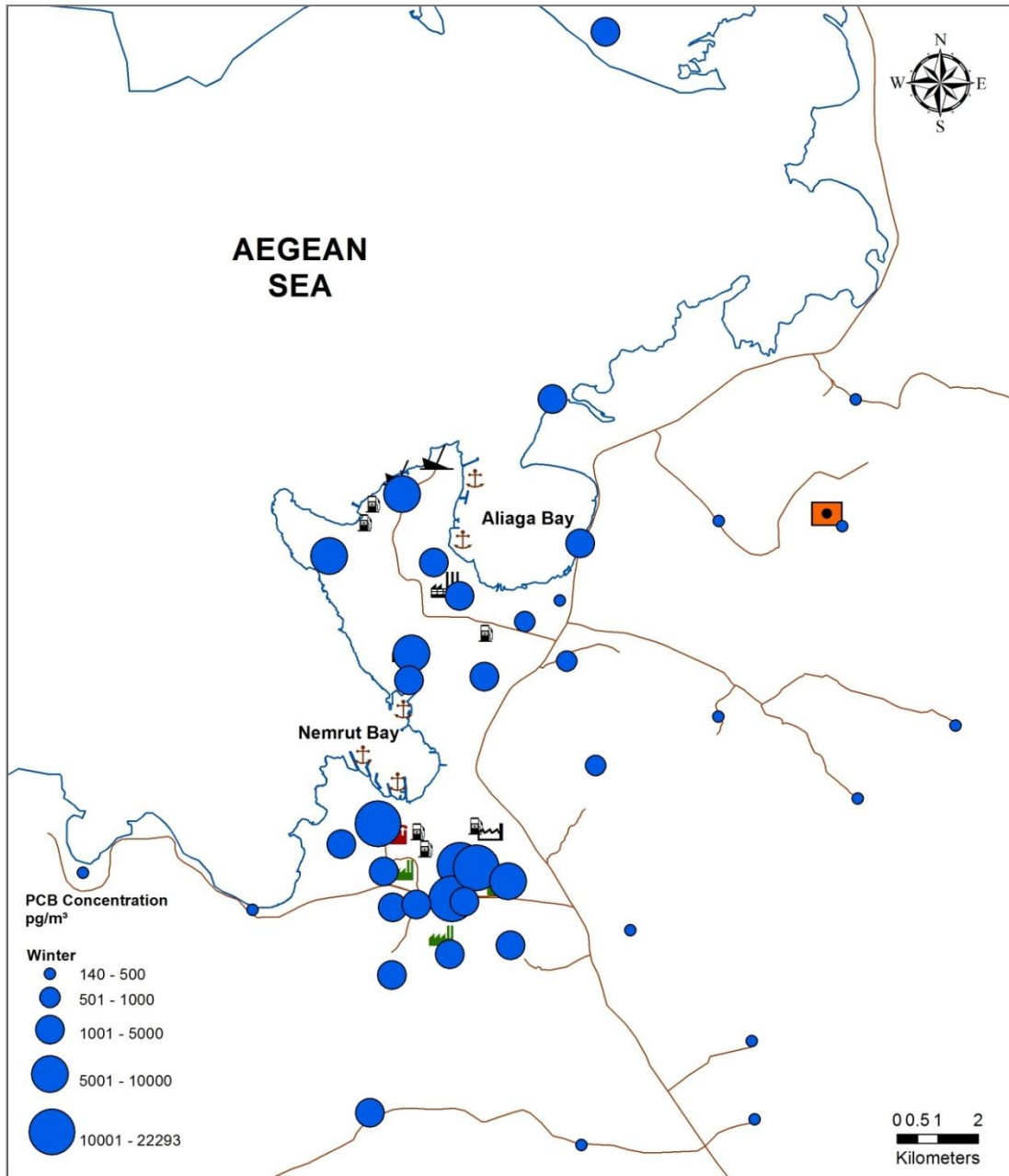
Figure 4.11 The spatial distribution of total ambient air PCB concentrations (pg m^{-3}) for winter.
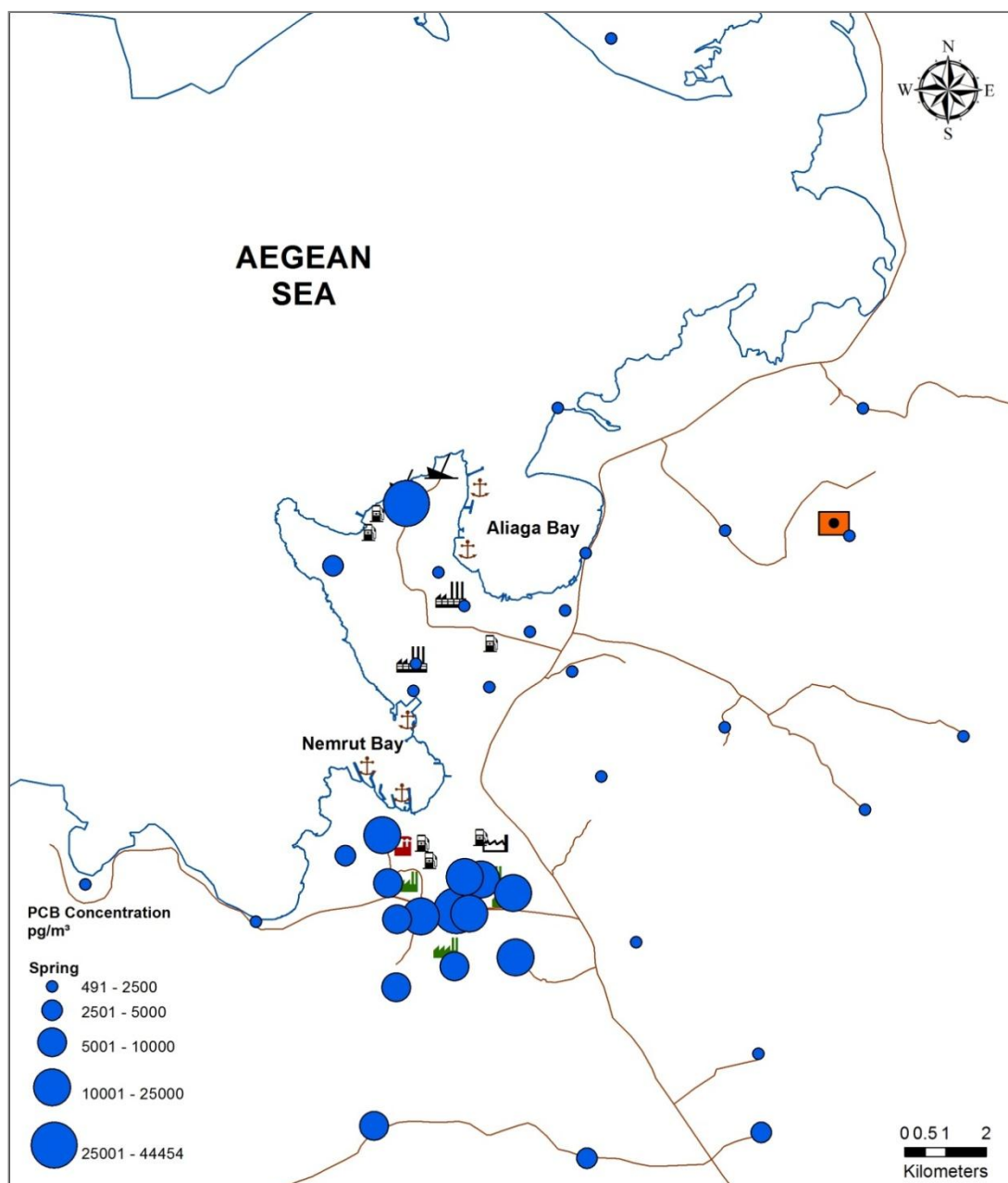
Figure 4.12 The spatial distribution of total ambient air PCB concentrations (pg m^{-3}) for spring.

4.2 Source Apportionment

The PMF method was applied to identify the sources of measured concentrations at 40 sampling sites for four seasons in Aliaga industrial region.

4.2.1 Sources of PAHs

Application of PMF resolved 3 factors for PAHs. PAH emission sources were identified using the markers for each source that are exclusively or largely appear in the factors. A total of three sources were identified by the PMF analysis. The emission sources of PAHs were determined as combustion (residential coal and wood combustion, industrial coal combustion) (factor 1), steel production (factor 2), and vehicular exhaust emissions (factor 3). The largest contribution (48%) to total PAHs was from combustion. It was followed by steel production and vehicular exhaust emissions that contributed to total mass by 47% and 5%, respectively. Figure 4.13 illustrates source contribution percentages of the overall PAH concentrations. To control the coherence of measured PAH concentrations with modeled PAH concentrations by PMF, the scatter-plot (Figure 4.14) was drawn. The relationship was good and significant (R^2=0.89, p<0.01 and the slope of the regression line (1.09) was close to unity indicating a close agreement.
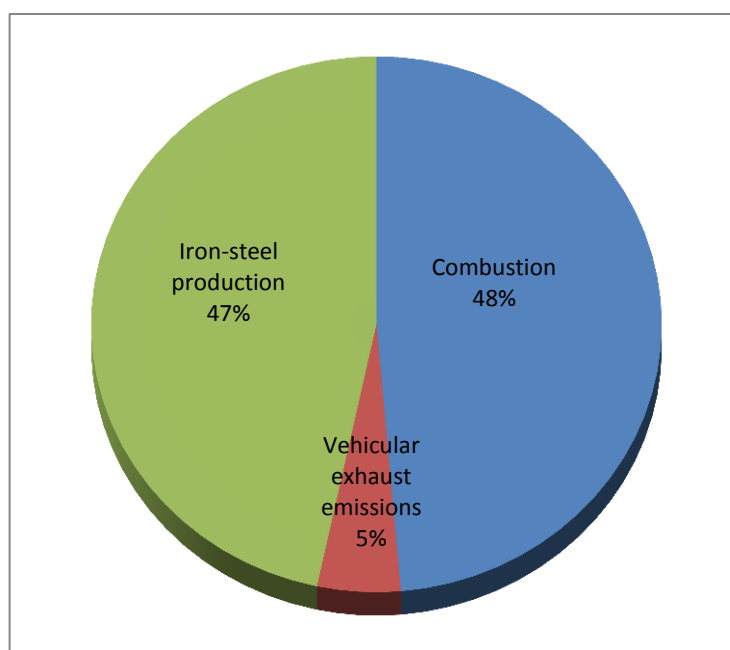
Figure 4.13 Source contributions to the total PAH concentrations.
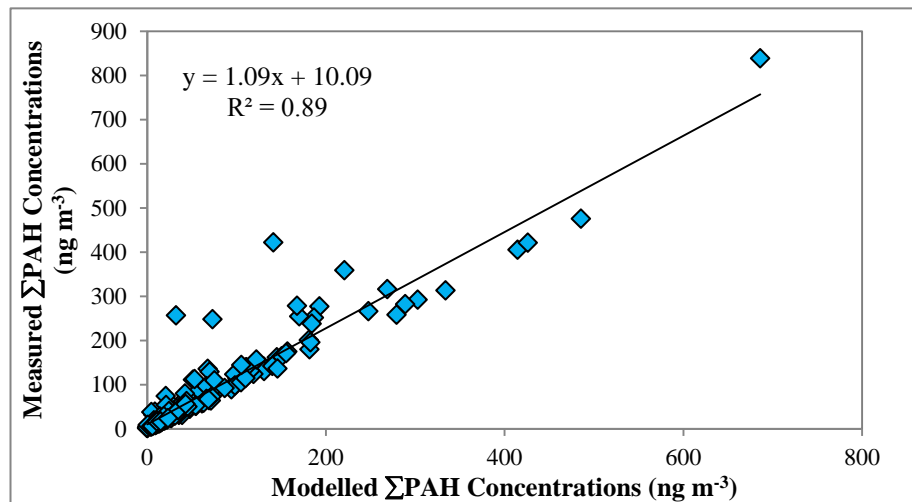
Figure 4.14 Relationship between the measured and modeled PAH concentrations.

The first factor (explaining 48% of the contribution) has high loadings on carbazole, anthracene, fluoranthene, pyrene, phenanthrene, and chrysene (Figure 4.15). Khalili, Scheff, & Holsen (1995) identified that anthracene, phenanthrene, fluoranthene and pyrene were source fingerprints of wood combustion. On the other hand, Carbazole is one of the major nitrogen containing PAHs in fossil fuels (i.e., coal, crude oil, oils derived from the pyrolysis of oil shales) (Benedik et al., 1998; Williams & Nazzal, 1998). Carbazole is also known as a main component emitted from coal and wood combustion (Liang & Pankow, 1996; Odabasi, Cetin, & Sofuoglu, 2006a; Ross et al., 2002; Smith & Hansch, 2000). Fluoranthene and pyrene are usually used as a marker of coal combustion (Tian et al., 2009; Wang et al., 2009). A similar profile was provided for coal combustion in a power plant (Lin et al., 2013). High emissions of fluoranthene, phenanthrene and pyrene were also observed from coke ovens (Lin et al., 2013). Therefore, the factor 1 in this study represents wood and coal burning at residential and industrial sources.

The second factor explained 47% of the total contribution and had high loadings on acenaphthylene, acenaphthene, fluorene, phenanthrene and moderately loadings on fluoranthene, pyrene, benz[*a*]anthracene and chrysene (Figure 4.16). This profile was very similar to that reported by Odabasi et al. (2009) for steel production. Acenaphtylene was reported as a distinctive marker in

that study. Therefore, factor 2 obtained in the present study was described as iron-steel production.

The last factor explained 5% of the total source contribution, highly loaded on higher molecular weight PAHs benzo[*g,h,i*]perylene, dibenz[*a,h*]anthracene, indeno[1,2,3-*c,d*]pyrene, benzo[*a*]pyrene and moderately loaded on benz[*a*]anthracene and chrysene (Figure 4.17). The predominance of PAHs with more than four rings has been attributed to a pyrogenic PAH sources (Harrison, Smith, & Luhana, 1996; Simcik, Eisenreich, & Lioy, 1999). Motelay-Massei et al. (2005) indicated that indeno[1,2,3-*c,d*]pyrene and dibenz[*a,h*]anthracene can be indicators for vehicular emissions. Benzo[*g,h,i*]perylene was reported as a marker for traffic related emissions (Harrison, Smith, & Luhana, 1996; Lin et al., 2013; Nielsen, 1996). Indeno[1,2,3-*c,d*]pyrene was related to gasoline powered vehicle emissions (Guo, Lee, Ho, Wang, & Zou, 2003). Benz[*a*]anthracene was linked with diesel vehicle emissions (Harrison, Smith, & Luhana, 1996; Sofowote, McCarry, & Marvin, 2008; Tian, Li, Shi, Feng, & Wang, 2013). Thus, factor 3 extracted in this study was explained as vehicular exhaust emissions (gasoline and diesel exhaust).
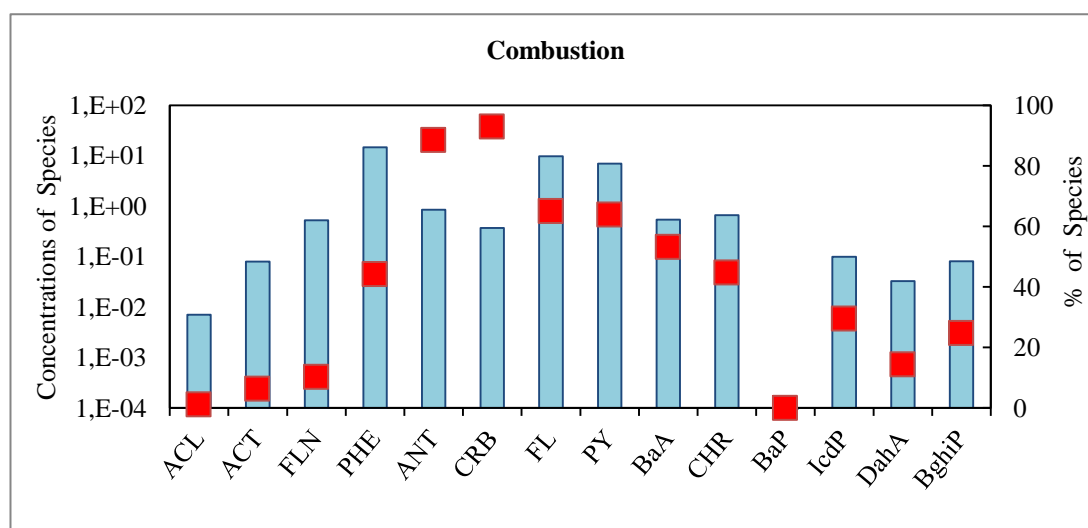
Figure 4.15 PMF profile of factor 1 for PAHs.
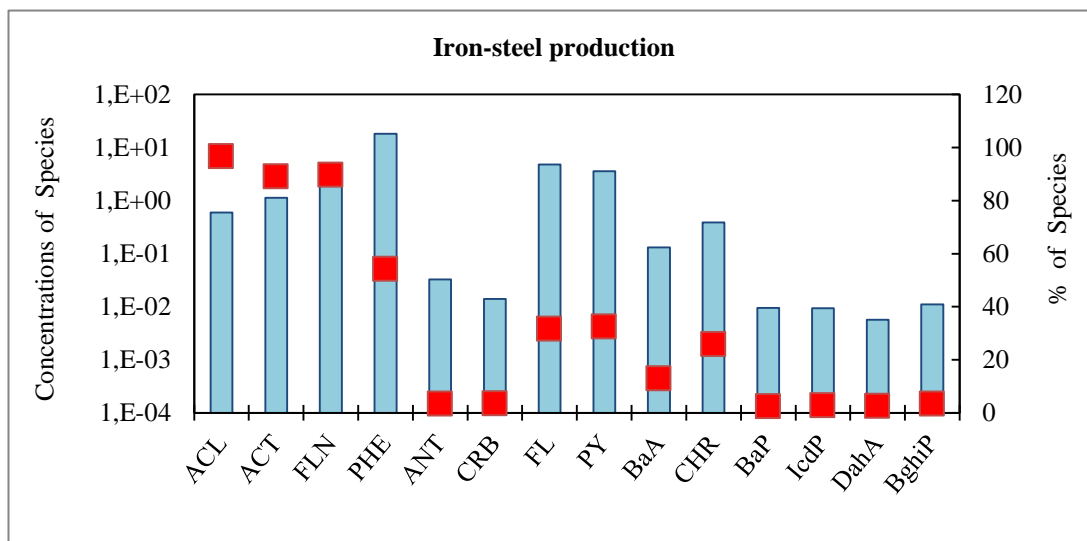
Figure 4.16 PMF profile of factor 2 for PAHs.
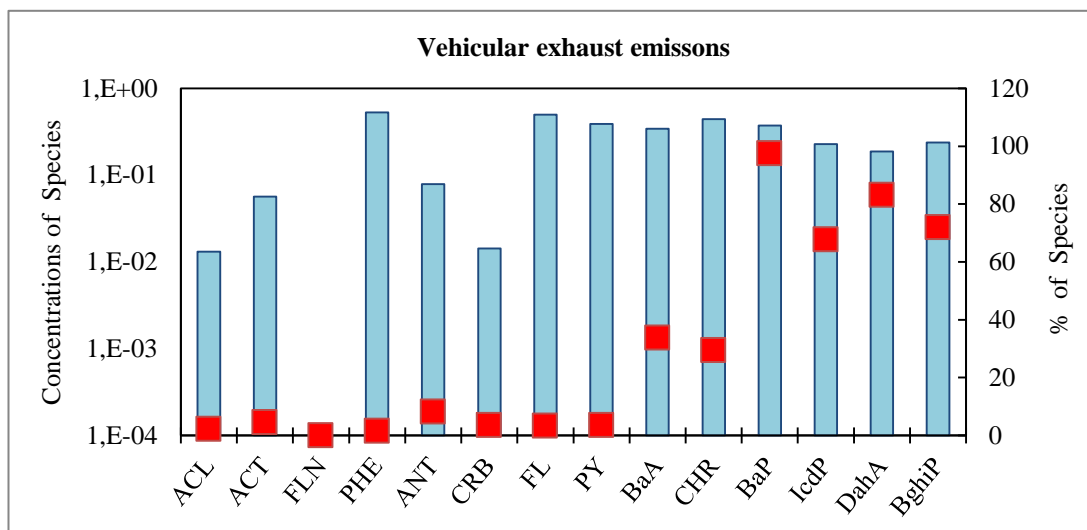
Figure 4.17 PMF profile of factor 3 for PAHs.

4.2.2 Sources of PCBs

Application of PMF resolved 3 factors for PCBs. PCB emission sources were identified based on the markers for each source that are exclusively or largely appear in the factor. A total of three sources were identified by the PMF analysis. The emission sources of PCBs were determined as steel production (consisting of steel-making and ship dismantling), combustion (coal and wood), and technical PCB mixtures. The significant contribution (%59) to total PCBs was from steel-making plants emissions. It was followed by combustion and technical mixtures

that contributed to total PCBs by 28% and 18%, respectively. Figure 4.18 illustrates contributions of different PCB sources. The relationship between the measured and modeled concentrations was significant (R^2=0.99, p<0.01 and the slope of the regression line (1.02) was close to unity indicating a close agreement (Figure 4.19).
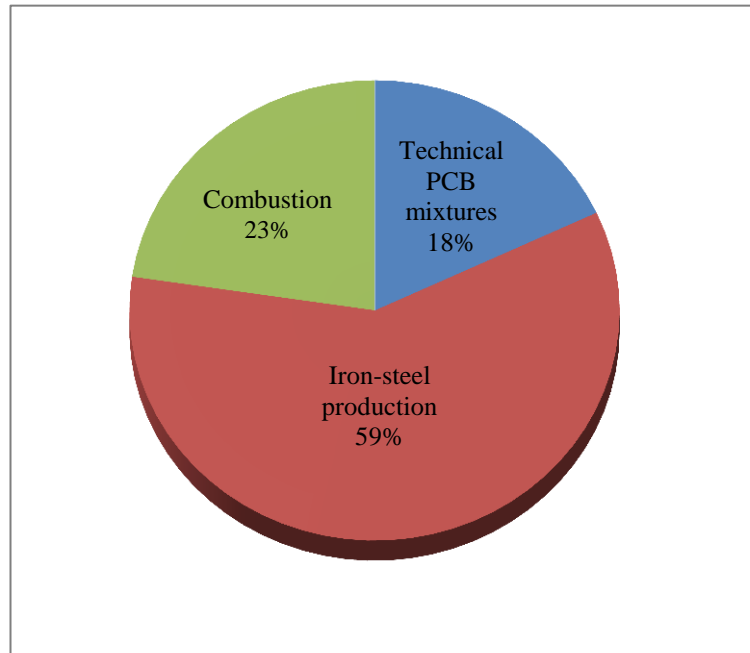
Figure 4.18 Source contributions to the total PCB concentrations.
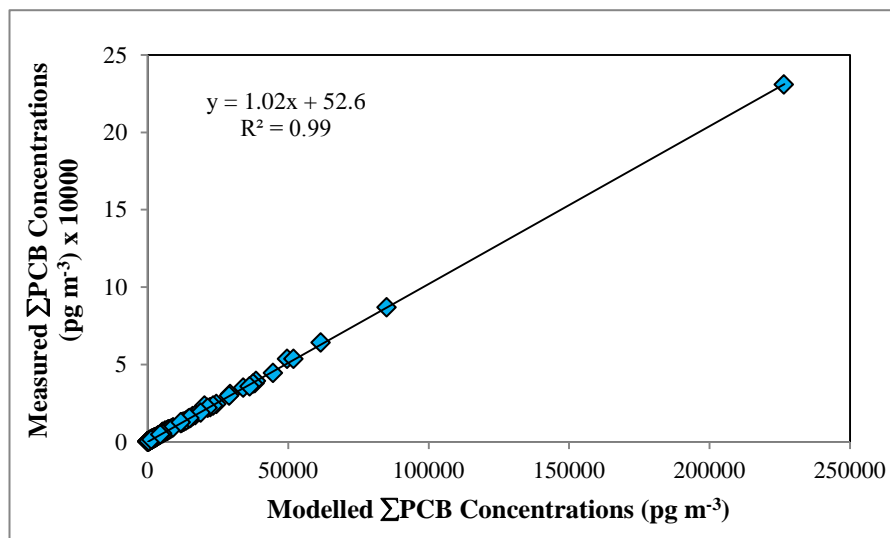
Figure 4.19 Relationship between the measured and modeled PCB concentrations.

The first factor has a contribution (%59) and 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 (Figure 4.20). Odabasi et al. (2009) have reported the emissions factors of steel-making plants (no pre-heating and with pre-heating) and determined that especially low molecular weight congeners (PCB-18, PCB-28, PCB-31, PCB-33) were dominated as source fingerprints of steel-making plants. Therefore this factor represents steel production 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, a very dense transportation activity of ferrous scrap trucks, a ship dismantling area, and busy ports with scrap iron dockyards).

The second factor explained 28% of the total variance and highly loaded on PCB-82, PCB-87, PCB-105, PCB-110, PCB-118, PCB-128, PCB-156 and also loaded with high molecular weight congeners (PCB-170, PCB-171, and PCB-206) (Figure 4.21). 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 combustion (coal and wood burning).

The last factor (18% of the total variance) showed high correlations for high-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 similar correlation with Kanechlor 600 that is consisted of predominantly PCB-180, PCB-187, and PCB-170 (Takasuga et al., 2005). Therefore this factor was described as technical PCB mixtures (Figure 4.22).

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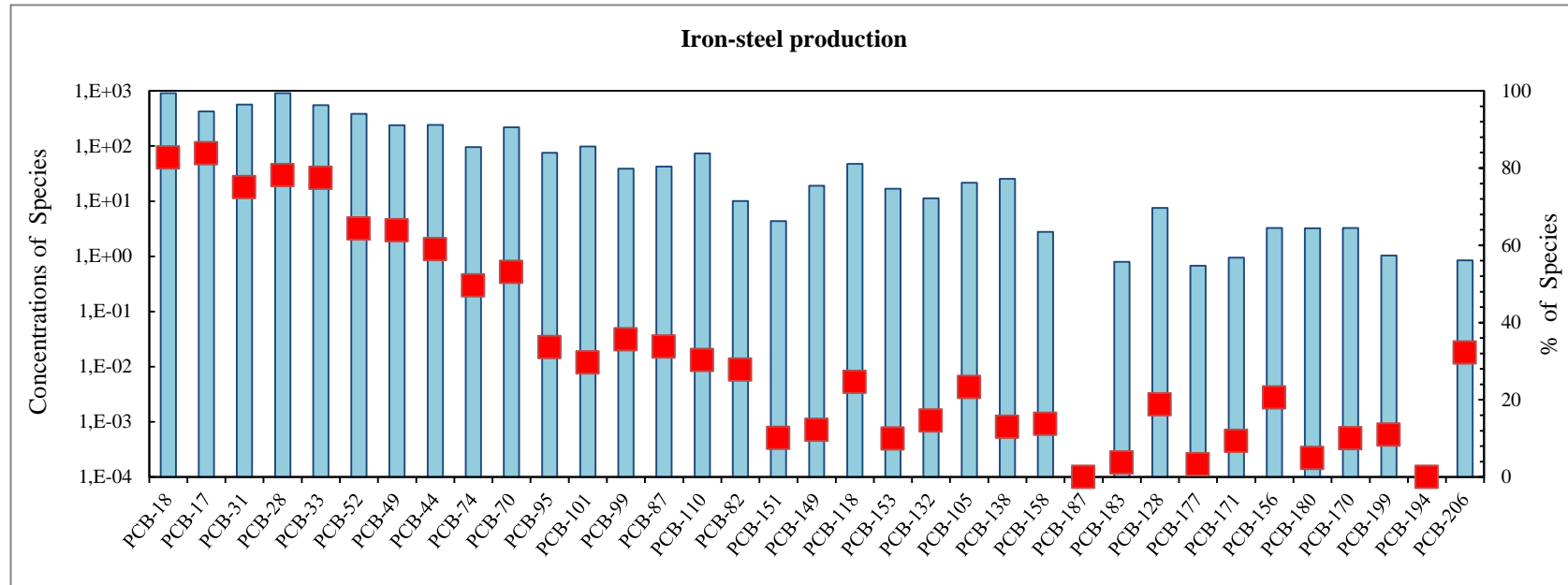
Figure 4.20 PMF profile of factor 1 for PCBs.
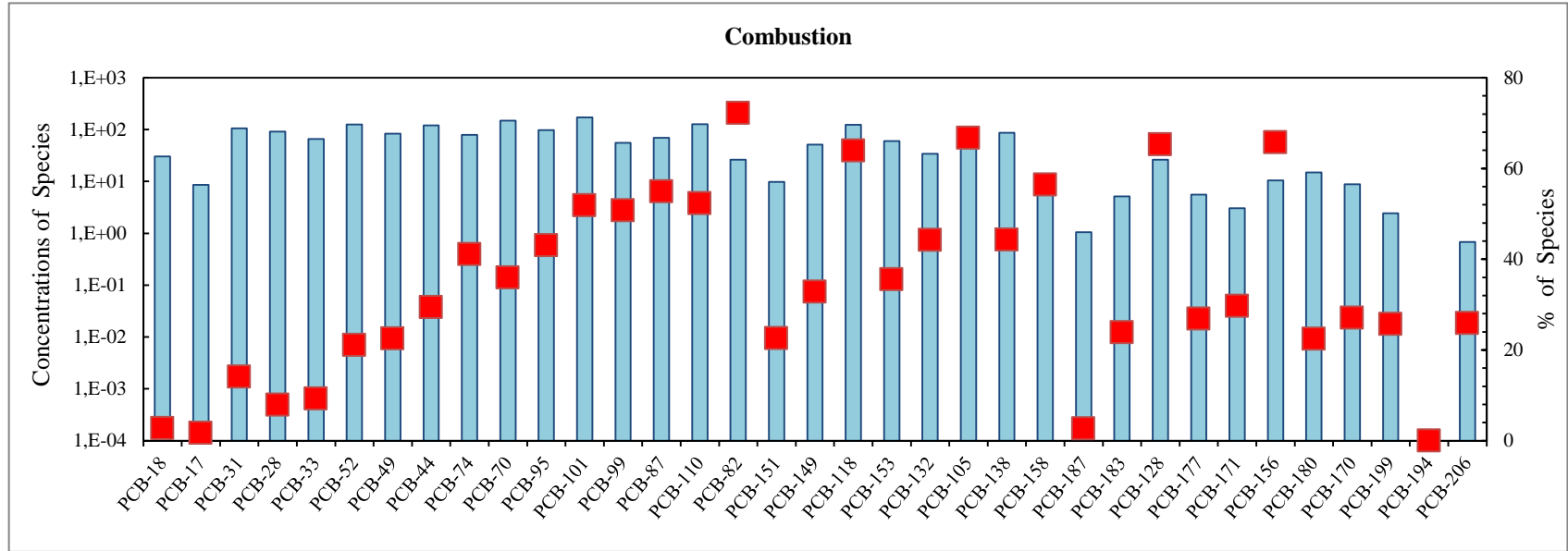
Figure 4.21 PMF profile of factor 2 for PCBs.
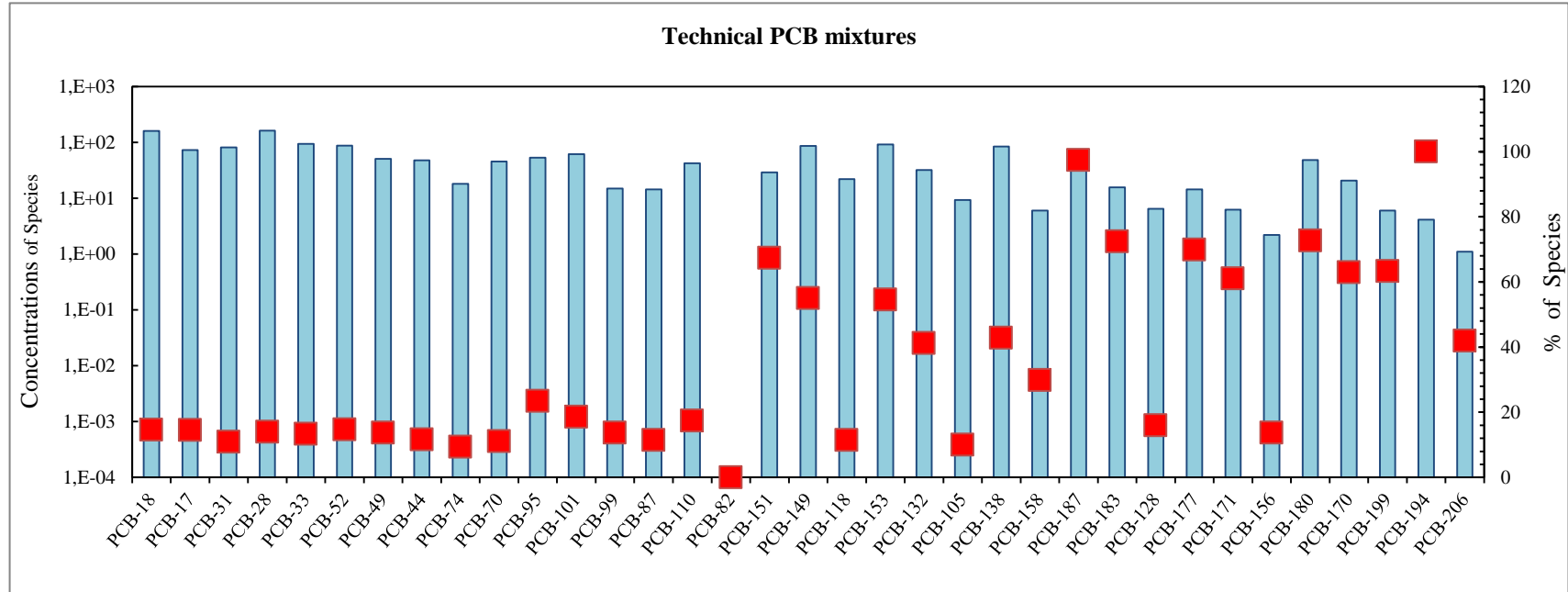
Figure 4.22 PMF profile of factor 3 for PCBs.

4.2.3 Spatial Distribution of Marker Compounds

According to PMF analysis, source profiles and source contributions were determined in the region. Figures 4.23- 4.25 show the spatial distributions of some PAH and PCB marker compounds for the sources identified in the study area. These figures were drawn as examples for some distinct markers and some seasons that the highest concentrations were observed.

Wang et al. (2013) and Yunker et al. (2002) reported that anthracene is emitted from combustion processes (especially coal combustion) and petroleum products. Motelay-Massei et al. (2005) indicated that anthracene has petrogenic origin (unburned). Another study showed that it can be used as the marker of wood combustion (Zhang et al., 2012). These references indicate that anthracene is a marker for wood and coal combustion and also for petroleum products. Figure 4.23 shows the distribution of anthracene in the region during winter. The higher levels were observed around the residential sites and areas where the petroleum activities located. Ship dismantling areas with many different activities (ship breaking, unintentional fires, scrap storage) also had higher concentrations. Also, a similar observation was available around the iron-steel plants since they are associated with various combustion processes.

Odabasi et al. (2009) have reported that acenaphtylene is a distinctive marker of iron-steel production. On the other hand, Cao, Wang, & Chen (2011) and Tian et al. (2013) have reported that it is emitted from coal combustion processes. It can also be derived from gasoline emissions (Tian et al., 2013). The distribution of acenaphtylene concentrations in winter (Figure 4.24) indicates that the highest values were observed around the iron-steel plants. Other higher concentrations were located in residential/rural areas and highways because of combustion emissions and also gasoline vehicle emissions.

PCB-18, a low molecular congener, is a marker of iron-steel production (Odabasi et al., 2009). It can also be emitted from industrial mixed sources.

Figure 4.25 shows the distribution of PCB-18 during the summer. The highest concentrations were observed around the iron-steel plants.

The prevailing wind direction in the region is northwesterly. Therefore, in addition to the sites near the sources, some sites located downwind to the sources (i.e., S11 and S40) have been affected and high concentrations were also measured at these sites.

The spatial distributions of marker compounds as discussed above supports the findings of the receptor modeling.
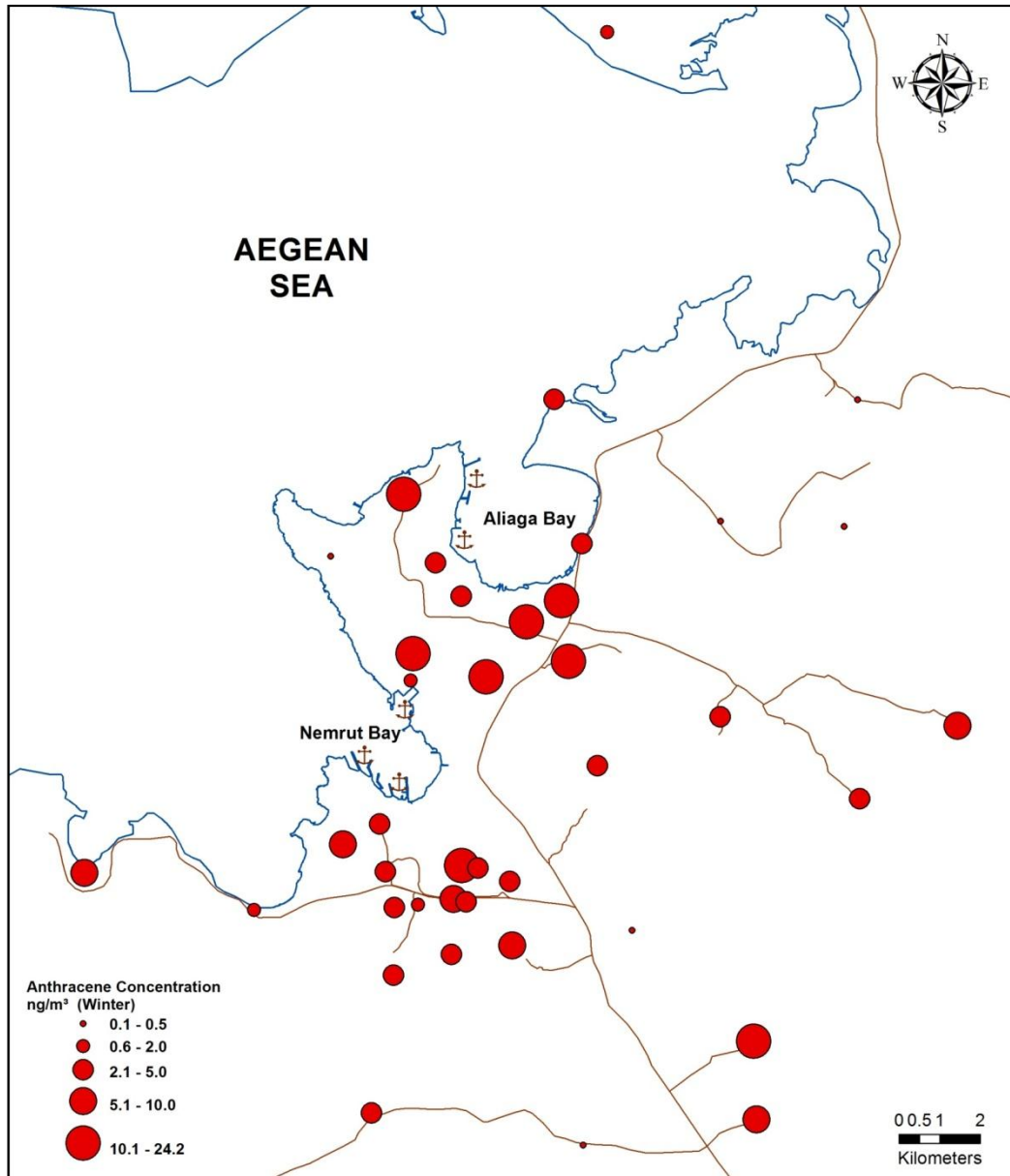
Figure 4.23 Spatial distribution of anthracene concentrations during winter.
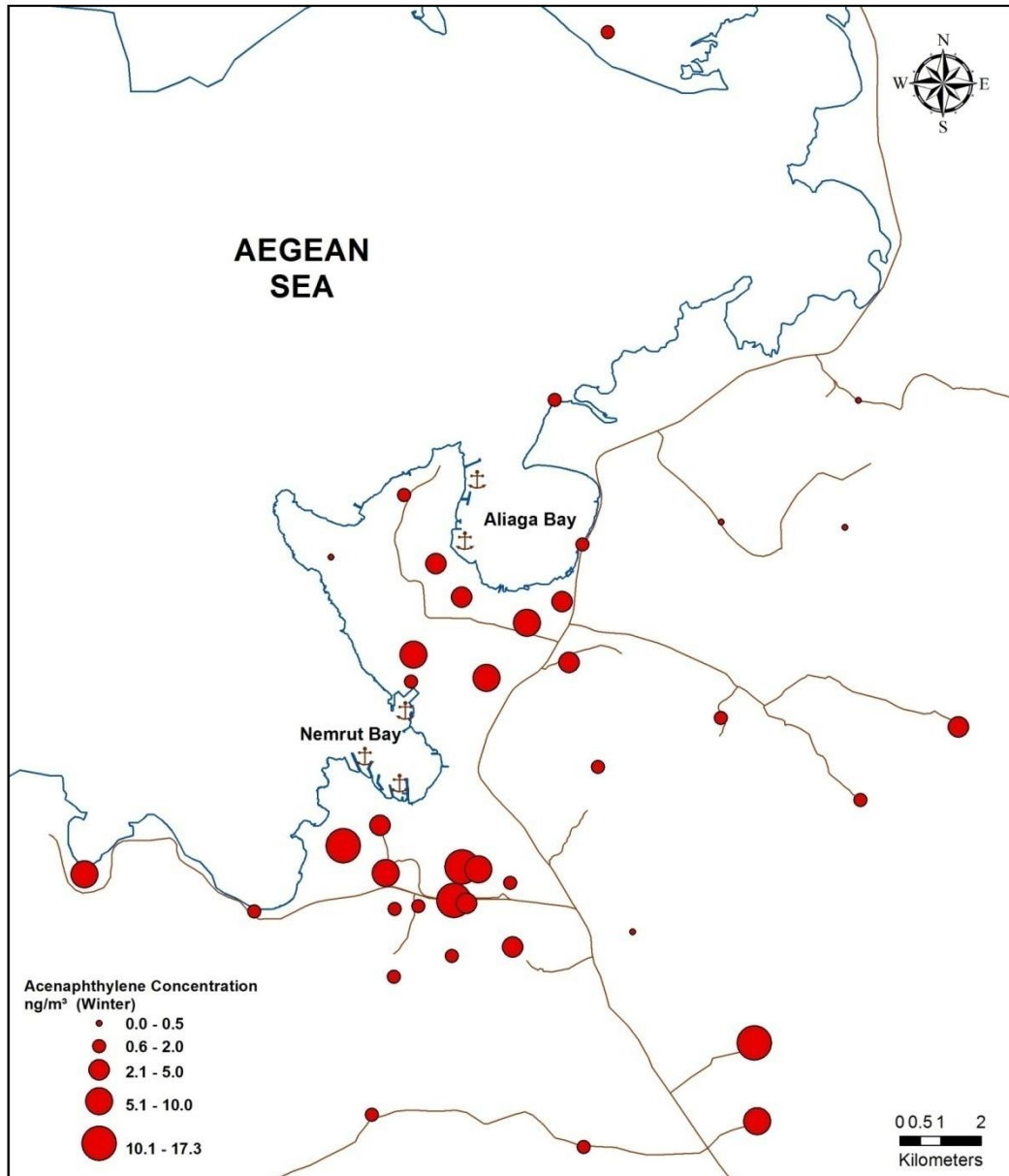
Figure 4.24 Spatial distribution of acenaphthleyene concentrations during winter.
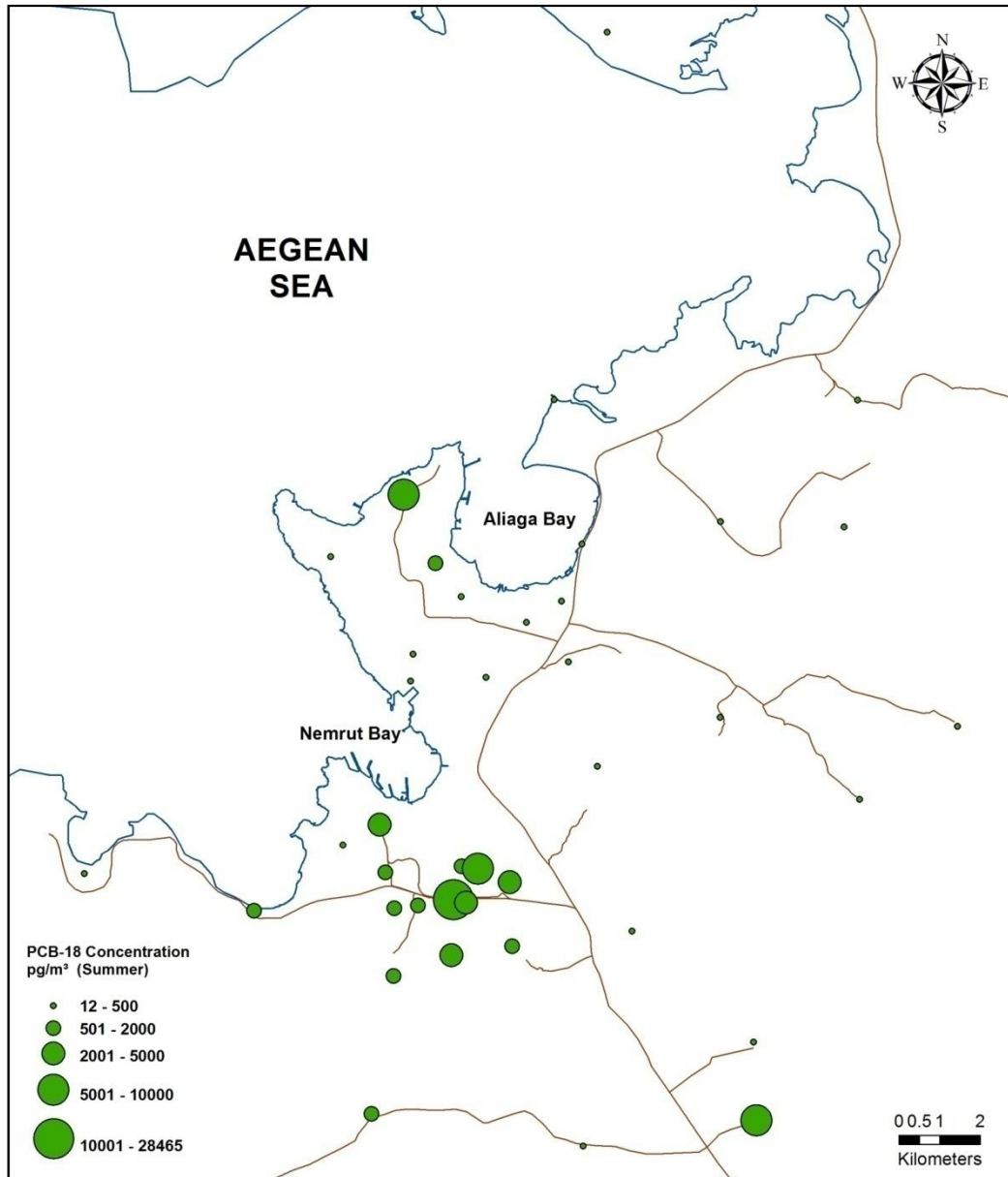
Figure 4.25 Spatial distribution of PCB-18 concentrations during summer.

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions and Recommendations

Spatial and seasonal variations 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 determined using positive matrix factorization (PMF). Contributions of the pollutant sources in this region were also specified. Three different factors were identified for both PAHs and PCBs. Sources of PAHs were determined as combustion (residential coal and wood combustion, industrial coal combustion), iron-steel production, and vehicular exhaust emissions with contributions of 48, 47, and 5%, respectively. PCB sources were determined as steel production (consisting of steel-making and ship dismantling) emissions, combustion (coal and wood burning), and evaporative emissions from technical PCB mixtures with contributions of 59, 23, and 18% to the measured total PCB concentrations. The spatial distributions of marker compounds were also investigated and those results supported the findings of the receptor modeling.

According to PMF results especially iron-steel plants are the most considerable sources in the region because of their 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.

In the present study PMF was applied using concentrations measured at different sites in the area. PMF could also be applied using several concentrations measured at a single site. Applicability of the other receptor models for POPs (i.e., Unmix) can be investigated to compare PMF3.0 model results.

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APPENDICES

<u>**Appendix A**</u>

PCA results for PAH and PCB compounds

Table A1. Rotated component matrix of PAHs

Rotated Component Matrix[a]			
	Factor 1	Factor 2	Factor 3
Carbazole	0.943		
Pyrene	0.888		
Chrysene	0.873		
Fluoranthene	0.752		0.527
Benzo[g,h,i]perylene		0.973	
Dibenz[a,h]anthracene		0.942	
Indeno[1,2,3-c,d]pyrene		0.936	
Benz[a]anthracene		0.805	
Benzo[a]pyrene		0.666	
Fluorene			0.878
Acenaphthene			0.776
Anthracene	0.545		0.742
Acenaphthylene			0.724
Phenanthrene	0.645		0.699
% of Variance	29.8	29.5	25.8
Cumulative %	29.8	59.4	85.2

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 6 iterations.

Table A2. Rotated component matrix of atmospheric PAHs

Rotated Component Matrix[a]		
	Factor 1	**Factor 2**
PCB-82	0.927	
PCB-99	0.919	
PCB-105	0.913	
PCB-70	0.909	
PCB-87	0.908	
PCB-74	0.908	
PCB-118	0.908	
PCB-110	0.905	
PCB-52	0.900	
PCB-49	0.897	
PCB-44	0.896	
PCB-31	0.889	
PCB-101	0.888	
PCB-33	0.885	
PCB-28	0.877	
PCB-95	0.875	
PCB-128	0.871	
PCB-156	0.852	0.504
PCB-18	0.850	
PCB-158	0.839	0.527
PCB-17	0.809	0.513
PCB-132	0.802	0.588
PCB-138	0.792	0.602
PCB-149	0.726	0.672
PCB-153	0.714	0.691
PCB-187		0.975
PCB-183	0.555	0.824
PCB-180	0.574	0.813
PCB-177	0.595	0.797
PCB-199	0.510	0.781
PCB-171	0.635	0.768
PCB-151	0.615	0.765
PCB-170	0.667	0.738
PCB-194	0.647	0.726
PCB-206	0.564	0.577
% of Variance	63.0	33.7
Cumulative %	63.0	96.7

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 3 iterations.

Appendix B

PMF diagnostics file for PAHs and PCBs for three factor model

Table B1. PMF diagnostics file for PAHs

**** Input Data Statistics **** Species	Category	S/N	Min	25th	Median	75th	Max
Acenaphthylene	Strong	984	0.002	0.210	0.609	1.8	17.3
Acenaphthene	Strong	1060	0.001	0.367	0.875	2.0	15.8
Fluorene	Strong	5387	0.001	1.50	3.3	9.7	44.3
Phenanthrene	Strong	44736	0.103	9.15	20.1	59.2	302
Anthracene	Strong	4818	0.001	0.159	0.643	2.9	38.7
Carbazole	Strong	1535	0.001	0.067	0.274	0.594	18.8
Fluoranthene	Strong	26533	0.086	3.79	8.0	21.9	144
Pyrene	Strong	23113	0.010	2.63	6.6	15.3	210
Benz[a]anthracene	Strong	2796	0.001	0.139	0.477	1.46	22.0
Chrysene	Strong	5752	0.001	0.389	0.843	1.88	63.3
Benzo[a]pyrene	Strong	1128	0.001	0.001	0.001	0.168	7.7
Indeno[1,2,3-c,d]pyrene	Strong	1228	0.001	0.049	0.117	0.281	10.8
Dibenz[a,h]anthracene	Strong	1871	0.001	0.026	0.067	0.173	21.1
Benzo[g,h,i]perylene	Strong	1795	0.001	0.054	0.112	0.270	19.0

Table B1. Continued

**** Base Run Summary ****					
Number of base runs:	**20**				
Base random seed:	**Random**				
Number of factors:	**3**				
Extra modeling uncertainty (%):	**20**				
Base run summary table:					
	Run #	**Q(Robust)**	**Q(True)**	**Converged**	**# Steps**
	1	9927	10605	Yes	1046
	2	10040	10608	Yes	956
	3	9302	9918	Yes	450
	4	9775	10456	Yes	1002
	5	9927	10605	Yes	543
	6	10297	11070	Yes	942
	7	10201	11037	Yes	488
	8	9444	10132	Yes	630
	9	**9266**	**9982**	**Yes**	**538**
	10	9266	9982	Yes	597
	11	9266	9982	Yes	501
	12	9302	9918	Yes	648
	13	9267	9982	Yes	507
	14	9266	9982	Yes	508
	15	9266	9982	Yes	504
	16	9267	9982	Yes	489
	17	9757	10276	Yes	776
	18	9302	9918	Yes	583
	19	10040	10608	Yes	762
	20	9302	9918	Yes	661

Table B2. PMF diagnostics file for PAHs

**** Input Data Statistics **** Species	Category	S/N	Min	25th	Median	75th	Max
PCB-18	Strong	3350	11.9	76.6	231	966.4	28465
PCB-17	Strong	1479	0.981	33.4	104	418.8	11496
PCB-31	Strong	2843	5.65	49.7	152	706.6	23140
PCB-28	Strong	3929	0.406	82.2	250	1058.8	30655
PCB-33	Strong	2595	0.400	50.8	152	610.6	20675
PCB-52	Strong	2035	6.51	48.3	115	512.9	15662
PCB-49	Strong	1239	0.387	29.2	78.6	314.5	9419
PCB-44	Strong	1487	0.382	35.4	91.5	332.0	11263
PCB-74	Strong	714	0.374	19.2	42.5	161.4	5321
PCB-70	Strong	1651	7.64	32.7	90.7	345.7	12410
PCB-95	Strong	850	0.372	26.0	60.2	225.9	6423
PCB-101	Strong	1252	0.369	35.7	77.9	310.6	9490
PCB-99	Strong	426	2.05	11.3	26.4	94.3	3307
PCB-87	Strong	493	0.367	14.1	30.5	100.6	3731
PCB-110	Strong	981	5.82	23.5	56.5	208.9	7426
PCB-82	Strong	251	0.365	0.365	12.0	33.1	2003

Table B2. Continued

PCB-151	Strong	151	0.365	7.2	12.6	36.7	901
PCB-149	Strong	582	3.70	22.2	41.0	122	3854
PCB-118	Strong	783	0.363	21.5	50.1	150	5828
PCB-153	Strong	620	4.22	21.7	43.0	132	3979
PCB-132	Strong	255	0.363	11.6	22.6	62.9	1733
PCB-105	Strong	338	0.362	11.1	24.2	67.5	2516
PCB-138	Strong	765	0.363	24.6	50.0	155	5186
PCB-158	Strong	82.0	0.362	3.03	6.54	20.8	593
PCB-187	Strong	127	0.362	6.07	11.7	33.9	610
PCB-183	Strong	76.7	0.362	3.38	6.15	17.8	411
PCB-128	Strong	160	0.362	5.57	11.7	32.4	1158
PCB-177	Strong	73.3	0.362	3.43	6.15	16.5	412
PCB-171	Strong	35.8	0.362	1.36	3.28	8.70	203
PCB-156	Strong	72.1	0.361	0.361	5.65	17.0	506
PCB-180	Strong	264	0.361	9.01	18.1	51.6	1403
PCB-170	Strong	133	0.361	4.53	9.70	28.1	771
PCB-199	Strong	40.4	0.361	0.361	3.32	9.87	194
PCB-194	Strong	32.9	0.361	0.361	0.361	6.84	186
PCB-206	Strong	14.5	0.361	0.361	0.361	7.08	65.2

Table B2. Continued

**** Base Run Summary ****					
Number of base runs:	**20**				
Base random seed:	**Random**				
Number of factors:	**3**				
Extra modeling uncertainty (%):	**15**				
Base run summary table:					
	Run #	**Q(Robust)**	**Q(True)**	**Converged**	**#Steps**
	1	8115	9029	Yes	353
	2	8117	9028	Yes	678
	3	8115	9029	Yes	451
	4	8117	9027	Yes	571
	5	8120	9023	Yes	442
	6	8749	9300	Yes	255
	7	8123	9020	Yes	390
	8	8118	9027	Yes	331
	9	8117	9027	Yes	570
	10	8121	9022	Yes	447
	11	**8115**	**9029**	**Yes**	**433**
	12	8117	9028	Yes	728
	13	8117	9028	Yes	712
	14	8115	9029	Yes	412
	15	8118	9027	Yes	249
	16	8115	9028	Yes	501
	17	8118	9026	Yes	658
	18	8118	9027	Yes	479
	19	8127	9015	Yes	310
	20	8118	9026	Yes	422

Appendix C

Q values for 3-5 factor models outputs

Table C1. Q values for PAHs

# of factors	Q_{true}	Q_{robust}	$Q_{theoretical}$
3	9982	9266	1760
4	7308	6872	1600
5	5075	5261	1440

Table C2. Q values for PCBs

# of factors	Q_{true}	Q_{robust}	$Q_{theoretical}$
3	9029	8115	5120
4	6854	6363	4960
5	5487	5377	4800