

**DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES**

**SPATIAL AND SEASONAL VARIATION OF
AMBIENT AIR POLYCHLORINATED
BIPHENYL (PCB) AND POLYCYCLIC
AROMATIC HYDROCARBON (PAH)
CONCENTRATIONS IN ALİAĞA INDUSTRIAL
REGION**

**by
Elife KAYA**

**March, 2012
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REGION**

**A Thesis Submitted to the
Graduate School of Natural and Applied Science of Dokuz Eylül University
Master of Science
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**by
Elife KAYA**

**March, 2012
İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**SPATIAL AND SEASONAL VARIATION OF AMBIENT AIR POLYCHLORINATED BIPHENYL (PCB) AND POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONCENTRATIONS IN ALİAĞA INDUSTRIAL REGION**” completed by **ELİFE KAYA** under supervision of **PROF. DR. MUSTAFA ODABAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.


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ABSTRACT

Ambient air samples were collected during four seasons (winter, spring, summer, and fall) at forty different sites in Aliaga industrial region in Izmir, Turkey. Spatial and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined by passive sampling in 2009 and 2010. Study area included suburban and urban sites, a power plant, petroleum refinery, petrochemical industry, several steel plants with electric arc furnaces, scrap metal and slag storage areas, stack filter dust piles, paved and unpaved roads, coal screening plants, ship dismantling plants and several gas stations and tank fields. Phenanthrene was the most abundant PAH at all sites, and all samples were dominated by low to medium molecular weight PAHs (fluorene, fluoranthene and pyrene). The spatial distribution of ambient PAH concentrations indicated that the major PAH sources in the region were steel plants, petroleum refinery, and ship dismantling plants. At urban sites, PAH concentrations were higher in winter indicating that wintertime concentrations were affected by residential heating emissions. On the contrary, highest atmospheric PCBs concentrations were observed in summer, probably due to increased volatilization from polluted surfaces at higher temperatures. Low to medium molecular weight PCBs (tri-, tetra-, penta-CBs) were the most abundant compounds in air for both seasons. Results also indicated that steel plants and ship dismantling plants were the major PCB sources in the region. A similar spatial variation was observed for soil concentrations of PAHs and PCBs. Air and soil PAH and PCB concentrations were correlated significantly indicating the interaction of these compartments.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), ambient air concentrations, spatial and seasonal variation, passive sampling.

ALIAĞA ENDÜSTRİ BÖLGESİNDE POLİKLORLU BİFENİLLER (PCB) VE POLİSİKLİK AROMATİK HİDROKARBONLARIN (PAH) DIŞ HAVA KONSANTRASYONLARININ YEREL VE MEVSİMSEL DEĞİŞİMİ

ÖZ

Aliağa endüstri bölgesinde 40 farklı noktadan dört mevsimde (kış, ilkbahar, yaz ve sonbahar) dış hava örnekleri toplanmıştır. Polisiklik aromatik hidrokarbonlar (PAH'lar) ve klorlu bifenillerin (PCB'ler) konsantrasyonlarının yerel ve mevsimsel değişimleri pasif örnekleme ile 2009-2010 yıllarında belirlenmiştir. Çalışma alanı içerisinde kentsel ve yarı-kentsel alanlar, enerji santralleri, petrol rafinerisi, petrokimya endüstrisi, elektrikli ark ocakları ile çalışan çelik tesisleri, hurda metal ve cüruf depolama alanları, baca filtresi toz yığınları, asfalt ve kaplamasız yollar, kömür eleme tesisleri, gemi söküm tesisleri, akaryakıt dolum tesileri ve tank alanları bulunmaktadır. Tüm ölçüm noktalarında ve örneklerde konsantrasyonu en yüksek olan bileşiğin phenanthrene olduğu ve düşük-orta molekül ağırlıklı PAH bileşiklerinin (fluorene, fluoranthene ve pyrene) baskın olduğu gözlenmiştir. Dış hava konsantrasyonlarının yerel değişimi, önemli PAH kaynakları olarak demir-çelik tesisleri, petrol rafinerisi, gemi söküm ve petrokimya tesislerini işaret etmektedir. Dış havada ölçülen PAH seviyelerinin, evsel ısınmaya bağlı olarak kış mevsiminde arttığı görülmektedir. Buna karşın yaz mevsiminde artan PCB seviyelerinin, önceden kirlenilmiş olan yüzeylerden bu bileşiklerin sıcaklıkla orantılı olarak buharlaşması olduğu düşünülmektedir. Çelikhanelerin ve gemi söküm bölgesinin önemli PCB kaynakları olduğu gözlemlenmiştir. Tüm mevsimlerde dış hava örneklerinde düşük-orta molekül ağırlıklı PCB'ler (tri-, tetra-, penta-CBs) baskındır. Toprakta ölçülen PAH ve PCB konsantrasyonları da atmosferdeki konsantrasyonlara benzer bir yerel dağılım göstermektedir. Hava ve topraktaki PAH ve PCB konsantrasyonları arasındaki önemli ilişki bu iki ortamın etkileşim içinde olduğunu göstermektedir.

Anahtar Sözcükler: Polisiklik aromatik hidrokarbonlar (PAH'lar), Poliklorlu Bifeniller (PCB'ler), dış hava konsantrasyonları, yerel ve mevsimsel değişimler, pasif örnekleme.

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Persistent Organic Pollutants (POPs) such as PAHs, PCBs and organochlorine pesticides are toxic, carcinogenic, mutagenic, persistent compounds and can bioaccumulate in the food chain. These compounds may cause serious health problems such as dermal toxicity, teratogenicity, carcinogenicity, birth defects and problems in the immune, endocrine, nervous and reproductive systems of animals and humans (Vallack et al., 1998; Park, Wade, & Sweet, 2002; Bartkow, Booij, Kennedy, Muller, & Hawker, 2005; Roots & Sweetman, 2007; Aydin & Ozcan, 2009).

The United Nations Economics for Europe (UN-ECE) and Convention on Long-Range Transboundary Air Pollution (CLRTAP) defined criteria of persistent organic pollutant as follows:

- 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 Persistent Organic Pollutants was adopted with the objective of protecting human health and the environment from damages of persistent organic pollutants and was attended on May 17, 2004. The United Nations Environment Program (UNEP) is also proposed to reduce or eliminate the use, discharges and emissions of POPs (Harner et al., 2005).

POPs can transported over great distances from source regions with atmospheric activities. These pollutants have been found in far away locations even that they have never been used or produced, regions such Arctic and Antarctic (Pozo et al., 2004;

Aydin & Ozcan, 2009). Although the production and use of these compounds have been banned or restricted in most industrialized countries, they continue to remain in the environment (Pozo et al., 2004).

A set of 12 chemicals were identified as POPs including nine pesticides, polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins/furans (PCDD/Fs) (Harner et al., 2006a). In addition to the 12 POPs, polycyclic aromatic hydrocarbons (PAHs) were also included by the United Nations-European Committee (Nadal, Schuhmacher & Domingo, 2004). Polycyclic aromatic hydrocarbons are a complex class of organic compounds consisting of only hydrogen and carbon and they contain two to eight fused aromatic rings. There are hundreds of varieties of these aromatic rings (containing only carbon and hydrogen) (European Commission DG Environment, 2001; Odabasi, Cetin, & Sofuoglu, 2006a). The PAH family have 660 substances indexed by the National Institute of Standards and Technology. Approximately 30 to 50 of them commonly occur in the environment (Slaski, Archambault, & Li, 2000). Only 16 PAH compounds are included in the pollutant list of Environmental Protection Agency (EPA) as priority pollutants (Dabestani & Ivanov, 1999).

PAHs are ubiquitous environmental pollutants including some of the most carcinogenic materials and generated during the incomplete combustion of organic materials. PAHs in the atmosphere are usually originated from anthropogenic activities. Some PAHs are byproducts of natural activities such as forest fire and volcanic activities (Odabasi et al., 2006a; Kim, Park & Kang, 2002). Major anthropogenic sources for PAHs in the atmosphere include emissions from motor vehicles, waste incineration plants, domestic heating, oil refining, coal gasification, liquefying plants, carbon black, asphalt production, coke and aluminum production, activities in petroleum refineries and other industrial processes (Odabasi et al., 2006a; Cincinelli et al., 2007).

Polychlorinated biphenyls (PCBs) may also enter to the atmosphere from transformers and capacitors, incinerators, paints, plastics, landfills, sludge drying

beds. PCBs are a class of chlorinated aromatic compounds that were used extensively in industrial applications because of their stability and inertness, excellent dielectric properties, and their excellent solvent characteristics (EPA, 1983). The major source of PCBs to the atmosphere is volatilization from sites where they have been disposed or stored and incineration of PCB-containing materials (Simcik, Zhang, & Eisenreich, 1998). 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 Programme, [AMAP], 1998).

The concentrations of organic pollutants in air are traditionally measured by active sampling using high volume samplers. Active samplers used in sampling of semi-volatile organic compounds (SVOCs) e.g., PCBs and PBDEs are the most accurate method to monitor ambient air concentrations because of using a pump to draw known volumes of air through filters and sorbents. However, the cost and logistical limitations of high-volume sampler do not allow deployment of samples at a large number of sites simultaneously. More recently, several different passive air samplers (PAS) have used to measure the atmospheric concentrations of POPs in many studies (Jones et al., 2009; Santiago & Cayetano, 2007; Jaward, Farrar, Harner, Sweetman, & Jones, 2004a, b).

The basic principle of passive samplers is diffusion of organic chemicals through the laminar air to the sampling medium without electricity or any other power sources to operate. PAS are very easy to handle, cheap to produce and deploy, and can be easy by an untrained operator and do not require electricity (Jones et al., 2009; Harrad & Hazrati, 2007). Passive air sampler include semi-permeable membrane devices (SPMDs), polyurethane foam (PUF), XAD resin based samplers, tristearin-coated glass samplers (POGs) and polyethylene based samplers (Bartkow, Booij, Kennedy, Muller, & Hawker, 2005).

Polyurethane foam passive air samplers are one of the most widely used equipments for monitoring for SVOCs in air (Kennedy et al., 2010). PUF disk passive samplers are operated without aid of a pump, and are very hydrophobic and

have high retention capacity for target organic compound in the gas-phase (Bohlin, 2010). These are the reasons why PUF was used for measurement of ambient PAH and PCB concentrations in this study.

The main objectives of this study were to determine the seasonal and spatial variations of ambient air concentrations of PAHs and PCBs in an industrial region in Turkey and investigate their sources

This study 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 suggestions 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 PAH and PCB concentrations in the ambient air were also discussed in this chapter.

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are environmental pollutants and include some of the most carcinogenic and mutagenic materials (World Health Organization International Agency for Research on Cancer [IARC], 1984). PAHs are a complex class of organic compounds and contain two or more aromatic rings. There are hundreds varieties of these aromatic rings (containing only carbon and hydrogen). The PAH family includes 660 substances indexed by the National Institute of Standards and Technology (NIST) but only 16 PAHs are classified as priority pollutants by U.S. EPA. PAHs are produced primarily during the incomplete combustion of organic materials (e.g. coal, petrol, and wood) (Odabasi et al., 2006b).

PAHs can be generally divided into two groups according to their physical, chemical and biological characteristics such as: the semi-volatile PAHs (low molecular weight with 2- to 3-rings) and non-volatile PAHs (high molecular weight with 4- to 7-rings) (Nagpal, 1993). The lower molecular weight PAHs may exist in the atmosphere both as gaseous and attached to airborne particles by nucleation and condensation are less toxic to humans and they are not carcinogenic. Atmospheric residence time and transport distance depend on the meteorological conditions and the size of the particles which PAHs are sorbed into (Agency for Toxic Substances and Disease Registry [ATSDR], 1995). Heavier PAHs do not dissolve in the water, but stick to solid particles that settle to the sediments in the bottoms of lakes, rivers or streams. Several members of high molecular weight PAHs are known to be carcinogenic and very toxic (Pelkonen & Nebert, 1982).

2.1.1 Molecular Structure and Chemical Properties of PAHs

The chemical structures and important properties of the 16 PAHs that are defined as priority pollutants by the American Environmental Protection Agency (EPA) are illustrated in Table 2.1. PAHs are solids on atmospheric conditions and general characteristics that common to the class are high fusing and boiling points, low vapor pressure, and very low water solubility (Odabasi, 1998; World Health Organization [WHO], 1998). The aqueous solubility of PAHs decreases with increasing molecular weight. Their lipophilicity is high, as measured by octanol-water partition coefficients (K_{ow}). As a course of their hydrophobic nature, the dissolved PAH concentrations in water are very low (Henner, Schiavon, Morel & Lichtfouse, 1997). These organic pollutants are chemical substances that are resistant to environmental degradation, may remain in the environment for long periods thus they can be found all over the world, and cause adverse environmental effects. PAHs in environment may cause a risk not only to humans but also to all living organisms (Maliszewska-Kordybach, 1999).

The physical-chemical properties of organic pollutants determine their distribution and behavior in the environment (e.g. air, water, soil/sediment, and biota). Their physical-chemical properties can be illustrated as follows; water solubility, vapor pressure, Henry's law constant, octanol-water partition coefficient (K_{ow}), and organic carbon partition coefficient (K_{oc}) (ATSDR, 1995). PAHs have similar chemical structures but their physical-chemical properties vary. For example, a PAH consisting of two aromatic rings, have a vapor pressure of 0.085 mm Hg, another PAH compound, a five member aromatic ring structure, has a vapor pressure of 4.6×10^{-6} mm Hg (Bidleman, 1984; Wu, 2006). In other words, PAH persistence to degradation, reduction, and vaporization increases with increasing molecular weight, even as the solubility in water of these compounds decreases (Nagpal, 1993). These differences determine the fate and distribution of PAHs in the environment. An important physical-chemical property is their octanol-air partition coefficient (K_{oa}) in terms of their persistence and capacity for long-range transport (Mackay & Wania,

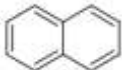
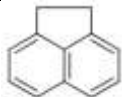
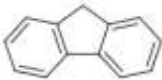
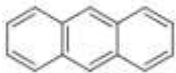
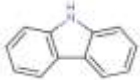
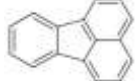
1995). K_{OA} is commonly used to describe the partitioning of a solute between the air and the organic substance. K_{OA} is defined as;

$$K_{OA} = C_{oct} / C_{air} \quad (2.1)$$

where C_{oct} and C_{air} are the concentrations (e.g., g m^{-3}) of the solute in octanol and air, respectively (Mackay & Wania, 1995). As shown in equation 2.1, K_{OA} is a dimensionless number and defines the partitioning of a compound between octanol and air. The values of K_{OA} for PAHs containing more aromatic rings are dominant to be found in organic phase in environment such as soil, vegetation, and the organic portion of aerosol particles (Wu, 2006).

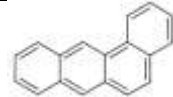
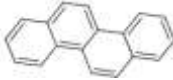
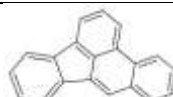
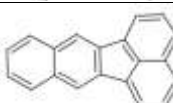
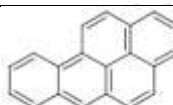
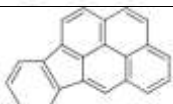
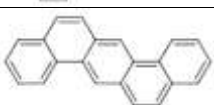
Another physical-chemical property is defined by Henry's law constant. It reveals the ratio of a chemical's concentration in air and water at equilibrium. This partition coefficient is used as a measure of a compound's volatilization. Henry's law constants for PAHs having low molecular weights are bigger than the high molecular weight PAHs. They are in range of 10^{-3} - 10^{-5} $\text{atm m}^3 \text{mol}^{-1}$ and 10^{-5} - 10^{-8} $\text{atm m}^3 \text{mol}^{-1}$, respectively. Octanol-water partition coefficient (K_{OW}) explains the potential for an organic chemical to move from water into lipid. Organic carbon partition coefficient (K_{OC}) is the ratio of the mass of a chemical that is adsorbed in the soil or sediment. The values of $\log K_{OW}$ and $\log K_{OC}$ increase with increasing number of PAH rings (ATSDR, 1995).

Table 2.1 The chemical structures and important properties of selected PAHs (Page 1 of 2)

PAHs	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	Structure
Naphthalene	C ₁₀ H ₈	128	80	218	31	8.50x10 ⁻²	4.40 x10 ⁻⁴	-	3.36	
Acenaphthylene	C ₁₂ H ₈	152	93	280	16.1	6.68 x10 ⁻³	1.14 x10 ⁻⁴	6.34	3.94	
Acenaphthene	C ₁₂ H ₁₀	154	93	279	3.9	2.15 x10 ⁻³	1.84 x10 ⁻⁴	6.52	3.92	
Fluorene	C ₁₃ H ₁₀	166	115	295	1.69	6.00 x10 ⁻⁴	9.62 x10 ⁻⁵	6.9	4.18	
Phenanthrene	C ₁₄ H ₁₀	178	99	340	1.15	1.21 x10 ⁻⁴	3.35 x10 ^{-5b}	7.68 ^b	4.46	
Anthracene	C ₁₄ H ₁₀	178	215	340	0.0434	2.67 x10 ^{-6d}	5.56 x10 ⁻⁵	7.71	4.45	
Carbazole	C ₁₂ H ₉ N	167	246	355	1.8	7.50 x10 ^{-7e}	1.16 x10 ^{-7b}	8.03 ^b	3.72	
Fluoranthene	C ₁₆ H ₁₀	202	108	384	0.26	9.22 x10 ⁻⁶	8.86 x10 ⁻⁶	8.76	5.16	
Pyrene	C ₁₆ H ₁₀	202	151	404	0.135	4.50 x10 ⁻⁶	1.19 x10 ⁻⁵	8.81	4.88	

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.

Table 2.1 The chemical structures and important properties of selected PAHs (Page 2 of 2)

PAHs	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	Structure
Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂	228	84	438	0.0094	2.10 x10 ⁻⁷	1.20 x10 ⁻⁵	10.28	5.76	
Chrysene	C ₁₈ H ₁₂	228	258	448	0.002	6.23 x10 ⁻⁹	5.23 x10 ⁻⁶	10.30	5.81	
Benzo[<i>b</i>]fluoranthene	C ₂₀ H ₁₂	252	168	-	0.0015	5.00 x10 ⁻⁷	6.57 x10 ⁻⁷	11.34	5.78	
Benzo[<i>k</i>]fluoranthene	C ₂₀ H ₁₂	252	217	480	0.0008	9.70 x10 ^{-10d}	5.84 x10 ⁻⁷	11.37	6.11	
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252	177	495	0.00162	5.49 x10 ^{-9d}	4.57 x10 ⁻⁷	11.56	6.13	
Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276	164	536	0.00019	1.25 x10 ⁻¹⁰	3.48 x10 ⁻⁷	12.43	6.7	
Dibenz[<i>a,h</i>]anthracene	C ₂₂ H ₁₄	278	270	524	0.00249	1.00 x10 ⁻¹⁰	1.23 x10 ⁻⁷	12.59	6.75	
Benzo[<i>g,h,i</i>]perylene	C ₂₂ H ₁₂	276	278	>500	0.00026	1.00 x10 ⁻¹⁰	3.31 x10 ⁻⁷	12.55	6.63	

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.

2.1.2 Sources of PAH

PAHs can be found in various fractions in the environment such as air, surface water, sediment, soil, food and in lipid tissues of both aquatic and terrestrial organisms (Department of the Environment and Heritage, Environment Australia, 1999).

Polycyclic aromatic hydrocarbons (PAHs) are produced due to incomplete combustion of organic substances (Maliszewska-Kordybach, 1999). PAHs come from either natural or anthropogenic sources. Although emissions from anthropogenic activities predominate, some PAHs in the environment originate from natural sources (Bozlaker, 2008). Natural sources of PAHs are volcanic eruptions and forest fires, while the anthropogenic sources mainly arise from wood burning, automobile exhaust, industrial power generators, aluminum smelting, carbon black production, iron smelting, production of coal tar, coke, asphalt and petroleum, incomplete combustion of coal, oil, gas, garbage, tobacco and charbroiled meat (Debastani & Ivanov, 1999; Canadian Council of Ministers of the Environment [CCME], 2008). The concentrations of PAHs in the atmosphere can depend on a number of factors including the emission rate of the source, its geographical location and the local climatic conditions (Baek et al., 1991).

2.1.3 Health Effects of PAHs

PAHs cause systemic, immunological, neurological, reproductive, developmental, genotoxic, and carcinogenic effects in human beings (ATSDR, 1995). The most important effect of PAHs is cancer. The effects of PAHs on human body depend on several parameters such that atmospheric conditions, concentrations in ambient air, the extent of exposure time and size distribution of airborne particles. PAHs are transformed in the environment, changing their toxic potencies (Petry et al., 1996). Many PAH compounds accumulate in the environment these may cause disruption of endocrine activity (Aoki, Y., 2001).

2.1.4 Distribution and Transformations of PAHs in the Environment

PAHs are reacted in the environment and as a result, biologically more inert products than the parent compound may be formed by these chemical and photochemical transformations. The fate of PAHs and in the environment depends on their physicochemical properties and the media they are exposed to (Dabestani & Ivanov, 1999).

The movement of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air. It can be summarized as follows: PAHs released to the air are subject to short- and long-range transport and are removed by wet and dry deposition onto soil, water and vegetation. Generally PAHs do not easily dissolve in water, and they can be volatilized, photolyzed, oxidized, biodegraded, bind to suspended particles or sediments, or accumulated in aquatic organisms. PAHs can be present in gas and particle-phases. They can travel long distances before they turn back to earth in rainfall or particle settling. Some of PAHs can be evaporated into the atmosphere from surface waters. However, most of them are sorbed to solid particles and settled to the bottoms of rivers or lakes. In sediments, PAHs can biodegrade or accumulate in aquatic organisms. In soils, PAHs are most likely to stick tightly to particles. PAHs can volatilize, undergo abiotic degradation (photolysis and oxidation), biodegrade, or accumulate in plants. Some PAHs evaporate from surface soils into air. PAHs in soil can also contaminate ground water and be transported within an aquifer. PAHs can be destroyed by reacting with sunlight and other chemicals in the atmosphere. In general, it can be taken over a period of days to weeks. Breakdown caused most by the actions of microorganisms in soil and water usually takes weeks to months (U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substance and Disease Registry, 1995).

PAHs are released to air from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks. They can also enter surface water through discharges from industrial plants and waste water treatment plants, and they can be

released to soils at hazardous waste sites if they leak from storage containers (ATSDR, 1995). PAHs entering the atmosphere derived from the combustion and from volatilization are shown in Figure 1. Atmospheric PAHs are distributed between the gas and particulate phases depending on the molecular weight of the compounds, temperature, humidity and precipitation (Fernandez, Vilanova & Grimalt, 1999). In general, the lower molecular weight compounds with 2-3 rings are present in air predominantly in the gas phase. Four rings PAHs exist both in the gas and particle-phases, and low-volatile PAHs with five or more rings are adsorbed on the airborne particles (Maliszewska-Kordybach, 1999; U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substance and Disease Registry, 1995).

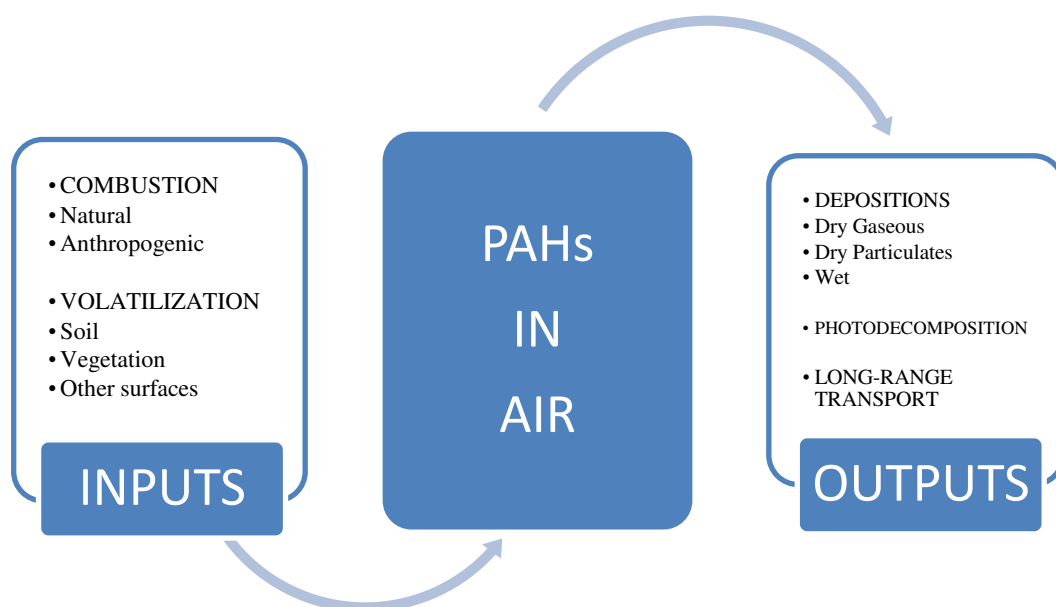


Figure 2.1. Schematic diagram of PAH fate in atmosphere (Maliszewska-Kordybach, 1999).

They can be transported through the atmosphere over long distances entering into the aquatic environment by wet and dry deposition and/or gas-water interchange. Once in the aquatic systems, most of the PAHs are associated to the particulate phase due to their hydrophobic properties giving rise to accumulation in the sediments. Sediments are therefore good environmental compartments for the record of long-range distribution of these compounds (Fernandez et al., 1999).

2.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of chlorinated aromatic compounds which were used extensively in industrial application because of their stability and inertness, excellent dielectric properties, and their excellent solvent characteristics (EPA, 1983).

PCBs contain 209 individual compounds known as congeners with varying harmful effects. PCBs are aromatic chemicals not occurring naturally in the environment. They are either oily liquids or solids that are colorless to light yellow and have no known smell or taste. They were used as coolants, insulating materials, lubricants in electric equipment, capacitors and other electrical equipment because they do not burn easily and are good insulators (ATSDR, 2000).

PCBs are used in the past as coolants and lubricants in electrical equipment. Their low dielectric constant and high boiling point make them ideal for use as dielectric fluids in electrical capacitors and transformers (UNEP, 2002). The historical global production of PCBs is estimated at 1.3 million tons based on manufactures' report (Breivik, Sweetman, Pacnya, & Jones, 2002). Whereas many of the characteristics make PCBs ideal for industrial applications, their persistent nature means they linger in the environment long after their use has been phased out. 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 Programme, [AMAP], 1998).

2.2.1 Molecular Structure and Chemical Properties of PCBs

PCBs are a group of aromatic, man-made compounds; consist of two benzene rings combined by a carbon-carbon bond, with chlorine atoms substituted on any or all of the remaining 10 carbon atoms (UNEP, 1999).

The chemical formula for PCBs is $C_{12}H_{(10-n)}Cl_n$, where n is the number of chlorine atoms within the range of 1-10 (UNEP, 1999). PCBs are a family of persistent

chemical compounds in which 2-10 chlorine atoms are attached to the biphenyl molecule (ATSDR, 2000). PCBs with a different number of chlorine atoms are called “congeners”, and with the same chlorine content but at different positions, “isomers” (Euro Chlor, 2002). They contain 209 individual isomers or (“congeners”). PCBs can also be categorized by degree of chlorination. The term “homologue” is used to refer to all PCBs with the same number of chlorine. Homologues with different substitution patterns are referred to as isomers (EMEP/CORINAIR Guidebook, 2005).

Figure 2.2 shows the basic structure of a biphenyl molecule. It can be seen from the structure that a large number of chlorinated compounds are possible. Congener of PCB is a single, unique, well-defined chemical compound. The name of the congener specifies the total number of chlorine substituent and the position of the each chlorine atoms (ATSDR, 2000). Figure 2.3 lists a few congeners and their names (EPA, 1983).

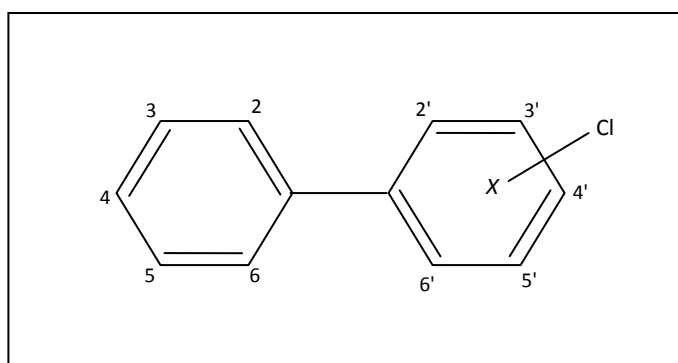


Figure 2.2 Basic molecular structure of a biphenyl molecule (UNEP, 1999).

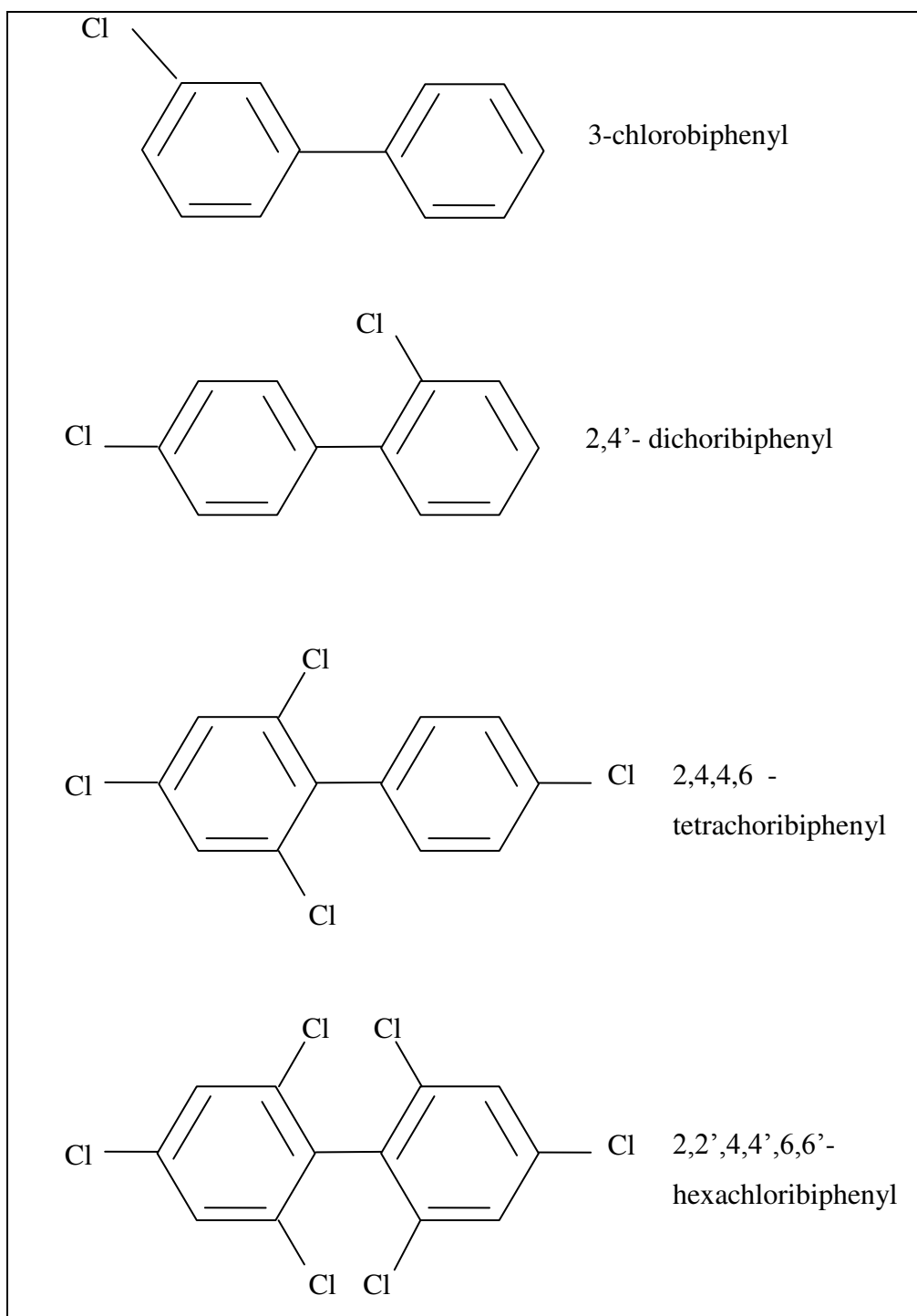


Figure 2.3 Molecular Structure and Names of Selected Polychlorinated Biphenyls (EPA 1983).

PCBs have high boiling points, low conductance, they are inert to oxidation, acids, bases, and other chemical agents, have good solubility in fats, oils and organic solvents, and are practically nonflammable (EMEP/CORINAIR Guidebook, 2005).

Pure individual PCB congeners are colorless to light yellow and have no smell or taste (ATSDR, 2000). The industrially produced PCB mixtures are also colorless or yellowish viscous liquids with boiling point from 325 to 390 °C (EMEP/CORINAIR Guidebook, 2005).

The amount of chlorine atoms on the biphenyl ring causes of the changes in physical-chemical properties between different congeners (Wu, 2006). While amount of the chlorine increases, PCBs also changes as well as other properties including their stability in the environment. Their viscosity, density and lipid solubility increase with increasing the chlorine substitution, whereas their water solubility and vapor pressure decrease. For example, as chlorination increases, PCB's volatility and also their solubility in water decrease (EMEP/CORINAIR Guidebook, 2005). PCB congeners with one chlorine atom can move all around the world without being deposited; however congeners consisting of 8-9 chlorines can be deposited closer to the sources because of the lower vapor pressures. The concentration of volatile PCB compounds or congeners with the inclusion of one chlorine atom is lower in tropical areas and higher in the temperature or Polar Regions (Wu, 2006).

2.2.2 Sources of PCBs

There are no natural sources of PCBs. Due to their ability to accumulate in the environment and to cause harmful effect, production and use of these compounds was banned in many countries, and they continue to be a common environmental contaminant because of their toxicity and persistence (Bozlaker, 2008). Today, the crucial source ambient PCB exposure appears to be environmental cycling of PCBs previously released into the environment. PCBs can be released into the environment from poorly maintained toxic waste sites; by illegal or improper dumping of PCB wastes, such as transformer fluids; through leaks or fugitive emissions from electrical transformers containing PCBs; and by disposal of PCB-containing consumer products in municipal landfills (ATSDR, 2000).

Some non-industrial and industrial usage and activities are continuing to release PCBs into the environment. These applications are the sources of PCB compounds. PCBs were used for lots of purposes of industrial applications prior to 1970. PCBs were used for close application in the production of electrical equipment, including hydraulic and heat transfer fluids, vacuum pumps, transformers and capacitors (Robertson, L.W., & Hanssen, L.G., 2001); The open usage of PCBs in variety of products as ink solvents carbonless-copy paper, as sealants in building materials, as plasticizers in polyvinyl chloride (PVC) plastics, in casting waxes, in paints, as pesticides and herbicides. The open application was banned in the 1970s without some products such as building sealants that are still contaminate the environment with using for some purpose. The third category is industrial and non-industrial combustion processes. These activities are municipal waste combustion; hazardous waste and medical waste incineration and cause account for a significant portion of PCBs emitted to the air (Urbaniak, M., 2007).

PCBs have been commonly used as dielectric fluids in transformers and capacitors, in heat transfer and hydraulic systems and other applications where chemical stability has been needed for safety, operation, or lastingness. PCBs are having been detected in practically all environmental media such as indoor and outdoor air, surface and ground water, soil and food in almost all over the world. Because of this property, PCBs are among the most widely distributed environmental pollutants and having lots of sources (UNEP, 1999). The main sources of PCB emissions into the environment can be divided into 5 groups (EMEP/CORINAIR Guidebook, 2005):

- production of PCBs and products (equipment) containing PCBs
- use of products containing PCBs
- utilization of PCBs and materials containing PCBs
- emission from reservoirs polluted by PCBs
- thermal processes such as closed system and heat transfer fluids (transformers, capacitors, fluorescent light ballasts, etc.)

Recycling products of oil, carbonless copy paper, PVC plastic and scrap metal that are PCB containing materials are also the other PCB sources to the environment. PCBs are emitted from transformer shell salvaging; heat transfer and hydraulic equipment; and shredding and smelting of waste materials in scrap metal recycling operation and iron-steel industries (UNEP, 1999; U.S. EPA & DEQ, 2005; Bozlaker, 2008). PCB emissions can be originated from several thermal process in the production of organic pigments, pesticides, chemicals such as PVC manufacturing and petroleum refining industries, cement, copper, iron-steel, and aluminum refining industries (UNEP, 1999; Bozlaker, 2008).

2.2.3 Health Effects of PCBs

PCBs were used from 1930s to 1970s in a range of industrial products. Any research about concentration of PCBs has no existed until 1966 (McConnell, Bidleman, Cothom & Walla, 1998). PCB congeners have half-lives ranging from three weeks to two years in air and more than six years in aerobic soils and sediments except for mono- and di- chlorobiphenyls (UNEP, 2002). Due to their stability and lipophilicity, if animals or humans exposed to PCBs, probably it can be stored in fatty tissues and bioaccumulate in food chains (ATSDR, 2000).

PCBs are mostly more toxic with increasing chlorine content (Tanabe, 1988). PCBs are defined as carcinogens by the U.S. Environmental Protection Agency (EPA). Toxic effects of PCBs cause a series of health problems in humans such as chloracne, pigmentation of skin and nails, excessive eye discharge, swelling of eyelids, distinctive hair follicles, and gastrointestinal disturbances. Toxicological action is dangerous not only for human body but also other living things, animals and plants as decreasing the ability of animals to reproduce. PCBs can also cause toxic symptoms, carcinoma, liver ailments, adenofibrosis, weight and hair loss, mouth and eyelid edema, acneform lesions, decreased hemoglobin, and gastric ulcers (Windholz, 1983).

As mentioned above, PCBs can bioaccumulate and cause potential health problems, because of their persistent nature. PCBs have proven to be causing terrible health effects. Studies have been shown that PCBs cause cancer in animals and a number of serious non-cancer health effects, including effects on the immune system, reproductive system, nervous system, endocrine system and other health effects. There are many researches in animals and human population to assess the potential carcinogenicity of PCBs. These pollutants may have serious potential effects on the immune systems of exposed individuals also decrease thyroid hormone levels and these decreases have resulted in developmental deficits in the animals, including deficits in hearing (U.S. EPA, 1998; ATSDR, 2000).

It is very important to note that the individual chemical makeup of each PCB mixtures changes following their release into the environment. The kinds of PCBs that tend to be stored in fish and other animals and bind to sediments happen to be the most carcinogenic congeners. As a result, when people exposed to PCBs such eating PCB-contaminated fish or other animal products and contact PCB-contaminated food over many years, PCBs can build up in their body fat (ATSDR, 2000).

2.2.4 Distribution and Transformations of PCBs in the Environment

PCBs are fairly stable and persistent pollutants in the environment, they can transported from one environmental media to another such as soil to water, water to air, air to water, sediment to water. The transport and partitioning behavior of PCB congeners depends on the number of chlorination as well as on the isomeric substitution (ATSDR, 2000).

PCBs can be transported to long distances and move from source regions to more remote locations. Because of this feature, PCBs have been detected in the biota from different regions of the globe, including places far from where they were used or produced (UNEP, 1999; ATSDR, 2000). PCBs are globally circulated and are present in all environments. Atmospheric transport is the most important mechanism

for global dispersion of PCBs (ATSDR, 2000). The factors that cause the global dispersion of PCBs in the environment are probably atmospheric deposition (Urbaniak, M., 2007).

PCBs are found both in the vapor phase and are sorbed to particles in the atmosphere (ATSDR, 2000). The higher chlorinated congeners are observed generally in aerosols and rainfall. Mono- and di-chlorobiphenyls are usually found in the gas phase and have low water solubility, therefore, are not washed out with rainwater from the atmosphere. On the other hand, the higher chlorinated isomers are adsorbed to particulates, and can be moved in the atmosphere on aerosols in rain drops (Urbaniak, M., 2007). PCBs in the vapor phase are more transportable than particle bound PCBs (Wania & Mackay, 1996).

PCBs are removed from the atmosphere with three major ways; by wet deposition, such as rain and snow, by dry deposition of fine and coarse particles, and also by vapor adsorption at the air-water, air-soil, and air-plant interfaces (Dickhut & Gustafson, 1995).

PCBs are predominantly entered the surface water from atmosphere deposition and the recycling of sediment-sorbed PCBs into the water column (ATSDR, 2000). PCBs in surface water are basically found in three phases; dissolved, particulate, and colloid associated (Baker & Eisenreich, 1990).

PCBs in water can move by diffusion and currents. On the basis of PCBs' water solubility and n-octanol-water partition coefficients, the heavier and less soluble chlorinated congeners are more likely to be associated with particles and are sorbed more strongly than the lower chlorinated isomers (ATSDR, 2000; Urbaniak, M., 2007). PCBs can be transferred from the water column by sorption to suspended solids and sediments, and can be stored in sediments. In other words, the concentrations of PCBs in water are reduced by sedimentation (ATSDR, 2000; Urbaniak, M., 2007).

PCBs in water have a affinity for accumulating in food chain through phytoplankton, zooplankton, and other biota. Aquatic invertebrate probably play an important role in the cycling of PCBs within and between ecosystems (Evans, Bathelt, & Rice, 1982). The movement of PCBs in soil through to ground water is not expected because of strong binding to soil (EPA, 1988). Another important loss mechanism is volatilization from soil that is more important for the lower chlorinated congeners than for the higher chlorinated ones (Hansen, 1999).

The chemical composition of each PCB congener determines its environmental behavior and fate. Although the lower chlorinated PCB congeners can move world-wide without being deposited, the higher chlorinated isomers tend to be deposited closer to the sources because of lower vapor pressures (Wu, 2006). The fate and transformation of PCBs in the environment is a function of a number of chemical, physical, and biological process properties such as water solubility, octanol-water partition coefficient, vapor pressure, Henry's law constant, volatility from water, adsorption to soils and sediments, atmospheric oxidation, photolysis, and biodegradation (EPA, 1983). One of the most important and critical events affecting the persistence and fate of PCBs is transformation. The effectiveness of degradation rates varies, depending on several conditions such that comprise degree of the biphenyl chlorination, position of the chlorine atoms, species of microorganisms, the structure of a given PCB compound and so on.

2.3 Sampling and Analyzing of PAHs & PCBs

2.3.1 Active Sampling

PAHs and PCBs in ambient air are commonly measured by high volume air samplers as the standard method on air monitoring. In the most common active sampling method a pump is used to draw ambient air into the sample collection. These samplers usually consists of two compartments; a glass or quartz fibre filter where the particle phase is sampled and a solid absorbent to collect the particle-associated and the gas phase pollutants such polyurethane foam (PUF) or XAD-resin

(Gioia, Sweetman & Jones, 2007). The air is drawn by a pump, through the sampling medium at a constant flow rate for a known period. The flow rates (R_p) of pumps can be kept under control by a flow meter. The pump works with electricity or battery. The concentration of the air (C_{air}) can be calculated by the following equation (Bohlin, 2010):

$$C_{air} (ng / m^3) = \frac{M_t - M_o}{R_p t} = \frac{M_t - M_o}{V} \quad (2.1)$$

where M_t is the amount of the pollutant in the filter + adsorbent or separated after the sampling period (t), M_o is the amount before sampling (i.e. blank values), and V is the volume of air drawn through the sampler (Bohlin, 2010).

2.3.2 Passive Sampling

Passive sampling can be defined as the collection of airborne gases and vapors at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane without the active movement of air through an air sampler (DiNardi, 1997). Since the active sampling operation is expensive; require electricity and a trained operator, air monitoring with ‘active’ or high volume air samplers are used at a very limited number of sites (Jones et al., 2006). One of the negative features of active sampling is that the requirement the use of electrical power to work as a consequence it would not provide the collection of samples in a number of sites for simultaneous investigation of organic pollution in air (Santiago & Cayetano; 2007). An alternative and more feasible sampler i.e., passive sampler is available for sampling of various chemical species and sites from air without pump and electricity.

Passive air sampling is based on a free flow of pollutant from the air to the collection medium. The concentration gradient is between the environment and the collecting medium. In contrast to active sampling, air is not drawn by a pump, through the sampling medium. Until equilibrium is reached or sampling is stopped,

analyte continues to accumulate towards the collecting medium (Wu, 2006). The capacity of accumulation for the analyte is relative with the passive sampling medium to air partition coefficient, which is a kind of a ratio between the analyte concentration in the medium and the air concentration when two phases are in equilibrium (Shoeb and Harner, 2002). The geometry of the passive air sampler, the physical-chemical properties of the pollutants, the diffusion coefficient of the pollutant, the concentration in the air, the exposure time, and the environmental conditions around the passive sampler help to determine the amount of pollutant adsorbed per unit time (Bohlin, 2010).

2.3.3 Advantages & Disadvantages of Passive and Active Samplers

Air concentrations in active sampling can be calculated more easily than passive sampling. Because, flow rate and exposure time (i.e. the volume) are set by the researchers. However, the applications of active samplers in monitoring studies also encounter limitations because of the need of electricity supply (Bohlin, 2010). This causes POP concentrations on a global scale cannot be obtained in most parts of the world. Passive air sampling can help to fill this data gap, due to its features of being inexpensive and simple to deploy and also not to require electricity (Harner, 2006). Advantages and disadvantages of passive and active sampling techniques are summarized in Table 2.1.

High volume samplers are costly, require maintenance and significant operator time, and can only be located where power is available. Therefore these samplers are deployed at a limited number of sites. Passive samplers are an alternative to the use of high volume samplers nowadays (Holsen, T.M., & Dhaniyala, S., 2008). There is a variety of passive air samplers for air monitoring of POPs. These are; semi-permeable membrane devices (SPMDs), polyurethane foam (PUF), polymer-coated glass (POGs); adsorbent based techniques, XAD-resin, Fan-Liroy sampler (Harner, 2006).

Table 2.1 Advantages and disadvantages of passive and active sampling techniques (Harner, 2006; Bohlin, 2010).

	Active Air Sampling	Passive Air Sampling
Advantages	• Accurate/Quantitative • Gas + Particle Phase • Short Sampling Time	• Economical • Simple to deploy • Do not require electricity • Unobtrusive • Easy to use • High spatial resolution
Disadvantages	• High financial costs • Logistical requirements • Require maintenance • Sensitive to extreme situation	• Semi-quantitative • Mainly gas phase • Low sampling rate • Affected by environmental factors • No means to measure the air flow • Long exposure times

2.3.4 Polyurethane foam (PUF)

Polyurethane (PUF) disk passive samplers are operated without aid of a pump, they are very hydrophobic and have a high retention capacity for target organic compounds in the gas-phase (Bohlin, 2010). Accumulation of a chemical during exposure is equivalent to the rate of uptake minus rate of loss. Uptake of PAHs and PCBs is air-side controlled and is initially linear and a function of the mass transfer coefficient (k_A) that is a function of temperature and strongly depends on wind speed, with higher values at higher air velocities, the planar area of the sampling media (A_{PUF}) and concentration of the compound in air (C_A). The complete uptake profile can be calculated using the following:

$$C_{PUF} = K'_{PUF-A} C_A (1 - \exp[-(A_{PUF})/(V_{PUF}) (k_A / K'_{PUF-A})]t) \quad (2.2)$$

$$K'_{PUF-A} = K_{PUF-A} \delta = V_{AIR}/V_{PUF} = C_{PUF}/C_{AIR} \quad (2.3)$$

where C_{PUF} is concentration (mass cm^{-3}) of analyte in the in the PUF disk. A_{PUF} and V_{PUF} are the planar surface area (cm^2) and volume (cm^3) of the PUF disk, δ is the density (mass cm^{-3}) of the disk, t is the exposure time in days and k_A is in cm d^{-1} (Pozo et al., 2004). K_{PUF-A} is the PUF-air partition coefficient (the maximum amount of chemical that may be taken up by the PUF disk) but differs from K'_{PUF-A} is dimensionless and t , is the time of integration. For PUF disk;

$$\text{Log } K_{PSM-A} = \log K_{PUF-A} = 0.6366 \times \log K_{OA} - 3.1774 \quad (2.4)$$

Above the mentioned formula, K_{PUF-A} is well correlated to K_{OA} that is known for many POPs as a function of temperature (Pozo et al., 2004). It is possible to interpret K'_{PUF-A} as the equivalent volume of air:

$$V_{AIR} = K'_{PUF-A} V_{PUF} (1 - \exp[-(A_{PUF})/(V_{PUF}) (k_A / K'_{PUF-A})]t) \quad (2.5)$$

It is also possible to measure sample volumes by adding depuration compounds (DCs) to the PUF disk before the deployment. DCs are semi-volatile and isotopically labeled chemicals that cannot be found in the environment. Importantly, they do not interfere with the analysis of target compounds. They can volatilize into the atmosphere if exposed to air. The rate of uptake of chemical is the same as the rate of loss. The amount of DCs lost depends on their physicochemical properties, exposure time, and wind speed (Jones et al., 2009). k_A can be calculated using the recovery of depuration compounds initially spiked into the PUF disk:

$$k_A (\text{m day}^{-1}) = \ln \left(\frac{C_t}{C_0} \right) \times D_{\text{film}} \times K'_{PUF-A} / t \quad (2.6)$$

where C_t and C_o (mass cm^{-3}) are the concentrations in the disk at the end and beginning of the sampling, respectively; D_{film} (m) is the effective film thickness. Sampling Rate is calculated by (Harner et al., 2002):

$$R \text{ (m}^3 \text{ day}^{-1}\text{)} = k_A \text{ (m day}^{-1}\text{)} \times A_{\text{PUF}} \text{ (m}^2\text{)} \quad (2.7)$$

Compound specific effective air volume V_{eff} ($\text{m}^3 \text{ sample}^{-1}$) is estimated as (Jones et al., 2009):

$$V_{\text{eff}} = K'_{\text{PUF-A}} \times V_{\text{PUF}} \times \{1 - \exp[-(t) \times (k_A)/(K'_{\text{PUF-A}})(\delta)]\} \quad (2.8)$$

Concentrations in the air $C_{\text{i,air}}$ can be calculated as:

$$C_{\text{i,air}} = C_{\text{i,PUF}}/V_{\text{eff}} \quad (2.9)$$

Where $C_{\text{i,PUF}}$ is the concentration of a target compound (i) in the passive samples [ng sample^{-1}]

2.4 Levels Measured in the Air

Ambient air concentrations of PAHs and PCBs are measured and reported for the different sites throughout the world. The concentrations of PAHs and PCBs are measured in industrial, urban, rural, or coastal areas using passive sampling methods. Their concentrations, sampling periods and properties of locations are presented in Table 2.2 and Table 2.3, respectively.

2.4.1 Atmospheric PAH Levels

Table 2.2 shows that PAHs levels in industrial and urban sites were higher than the other sites. In addition to this, concentration of PAH compounds in winter season is generally the highest in all sampling periods without extreme conditions. In Canada, PAHs were investigated in suburban, urban and rural sites and were

deployed for three different sampling periods from June 2000 to July 2001 (July-Oct 2000, Nov-March 2001 and April-June 2001). Seven sites were selected an urban-rural transect. According to their characteristics, these sites were classified as follows: Junction Triangle, Gage Building and South Riverdale were high-density residential/industrial urban. Downsvieview was considered medium-density residential/industrial urban. Two suburban sites, Richmond Hill and Aurora were low-density residential/industrial. The last site, Egbert was an agricultural/farming region. PAHs showed maximum concentrations at urban sites during the summer period (July-October) because of increasing in evaporative emissions from petroleum products such as asphalt. In this study, Σ_{17} -PAH concentrations ranged from 11.5 to 61.4 ng m⁻³ for the first period (July-Oct 2000), from 8.34 to 18.5 ng m⁻³ for the second period (Nov 2000 – March 2001), and from 3.53 to 18.8 ng m⁻³ for the third period (April – June 2001).

The investigation of the city of Fairbanks in Alaska were realized both indoor and outdoor environments during winter 2009. The average passive indoor air concentrations for Σ_{20} -PAH were monitored higher than passive outdoor air concentrations at 55 and 26 ng m⁻³ respectively. A similar study was realized in Sweden, Mexico and United Kingdom by Bohlin et al. in 2006. Air quality of indoors and outdoors were researched for three urban cities (Gothenburg in Sweden, Mexico City in Mexico and Lancaster in UK). The range of indoor and outdoor air concentration of Σ_{13} -PAH for Gothenburg, Mexico City and Lancaster is 14-180 ng m⁻³ and 7.7-68 ng m⁻³; 6.1-92 ng m⁻³ and 32-64 ng m⁻³; 8.5-60 ng m⁻³ and 6.8 ng m⁻³, respectively. The higher indoor PAH levels were measured in Gothenburg and outdoor levels tended to lower Gothenburg and Lancaster compared to Mexico City. The estimated levels of Σ_{13} -PAH range from 6.1 to 180 ng m⁻³ in all samples.

PAHs in ambient air in six residential areas; reflecting the influence of possible sources of emission of the pollutants at the sites in the Philippines during four sampling periods from May to December 2005 (May-July 2005, July-August 2005, August-October 2005 and October-December 2005). The sources of PAHs emissions generally come from traffic, major thoroughfares and power plants for this study.

Σ_{13} -PAH concentrations in different six areas, ranged from 41 to 100 ng m⁻³ for the first period (May-July 2005), from 41 to 67 ng m⁻³ for the second period (July 2005 – August 2005), from 50 to 108 ng m⁻³ for the third period (August – October 2005) and from 84 to 170 ng m⁻³ for the last period (October-December 2005).

Table 2.2 Air concentrations of total PAHs in ambient air (ng m⁻³).

Location	Area	Period	Comp. number	Σ PAH	References
Junction Triangle, Canada	Urban	July-Oct, 2000	17	61.4	Harner et al., 2005
Gage Building, Canada	Urban	July-Oct, 2000	17	55.6	Harner et al., 2005
South Riverdale, Canada	Urban	Nov-March, 2001	17	17.4	Harner et al., 2005
Downsview, Canada	Urban	April-June, 2001	17	7.45	Harner et al., 2005
Richmond Hill, Canada	Suburban	July-Oct, 2000	17	20.3	Harner et al., 2005
Aurora, Canada	Suburban	April-June, 2001	17	4.26	Harner et al., 2005
Egbert, Canada	Rural	July-Oct, 2000	17	11.5	Harner et al., 2005
Fairbanks, Alaska (Indoor)	Urban	Dec, 2008-April 2009	20	55	Gouin et al., 2010
Fairbanks, Alaska (Outdoor)	Urban	Dec, 2008-April 2009	20	26	Gouin et al., 2010
Göteborg, Sweden (Indoor)	Urban	March-April, 2006	13	14-180	Bohlin et al., 2008
Göteborg, Sweden (Outdoor)	Urban	March-April, 2006	13	7.7-68	Bohlin et al., 2008
Balagtas, Bulacan, Philippines	Rural	May-July, 2005	13	41	Santiago C., 2007
Taytay, Rizal, Philippines	Rural	July-Aug, 2005	13	57	Santiago C., 2007
Binan, Laguna, Philippines	Rural	Oct-Dec, 2005	13	135	Santiago C., 2007
Valenzuela, Metro Manila, Philippines	Urban	Oct-Dec, 2005	13	170	Santiago C., 2007
Quezon city, Metro Manila, Philippines	Urban	Aug-Oct, 2005	13	65	Santiago C., 2007
Paranaque, Metro Manila, Philippines	Urban	July-Aug, 2005	13	51	Santiago C., 2007

2.4.2 Atmospheric PCB Levels

There have several studies on atmospheric PCB levels measured all over the world. The results given in Table 2.3 show the atmospheric PCB levels that measured at different sites throughout the world. PCB concentrations in those studies

are given as total of PCBs but sometimes are given range of PCB. The both notation can be seen in Table 2.3.

The results reported by Harner et al. (2005) in Canada, PCB concentrations showed a strong decrease with distance from the urban area and industrial urban areas (characteristics of the study area are discussed in detail in previous section) in Toronto as emission sources of PCBs. There is a large gradient in concentrations ranging from $\sim 350 \text{ pg m}^{-3}$ at the downtown urban sites to $\sim 350 \text{ pg m}^{-3}$ at the rural end of the transect.

A large-scale passive air sampling research was implemented in Asia, specifically in China, Japan, South Korea and Singapore. PUF disk were placed among at 77 sites at the same time, between September 21 and November 16, 2004. The data indicate that Asian $\sum 29$ PCB concentrations were ranging from ~ 20 to 340 , from ~ 5 to 30 , from 7 to 250 , and from 12 to 80 pg m^{-3} for China, Singapore, Japan, and Korea, respectively. Levels of PCBs were significantly higher in China than the other countries, and PCB concentrations in South Korea were also determined generally low in sampling period.

The study in Czech Republic was realized around two important pollutants sources such DEZA Valasske Mezirici, a coal tar and mixed tar oils processing plant and Spolana Neratovice, a chemical factory. Levels of PCBs were measured for all sampling sites and sampling periods (January and July 2004). Six passive air samples were located on each site in DEZA Velasske Mezirici. The total of seven indicators for PCBs congeners varied between 5 and 91 ng . Five passive air samples were also located in Spolana Neratovice and maxima for PCBs were 66 ng outside and 90 ng at the gate in summer. The highest levels of PCBs were measured on the grounds of DEZA.

Table 2.3 Air concentrations of total PCBs in ambient air (pg m^{-3}).

Location	Area	Period	Comp. number	ΣPCB	References
Junction Triangle, Canada	Urban	July-Oct, 2000	13	343	Harner et al., 2004
Downsview, Canada	Urban	July-Oct, 2000	13	167	Harner et al., 2004
Aurora, Canada	Suburban	July-Oct, 2000	13	70	Harner et al., 2004
Egbert, Canada	Rural	July-Oct, 2000	13	116	Harner et al., 2004
China	Urban / Industrial	Sept.-Nov,2004	29	21-336	Jones et al., 2005
Singapore	Urban / Industrial	Sept.-Nov,2004	29	5-31	Jones et al., 2005
Japan	Urban / Industrial	Sept.-Nov,2004	29	7-247	Jones et al., 2005
South Korea	Urban / Industrial	Sept.-Nov,2004	29	12-84	Jones et al., 2005
VM-Krizma, Czech Republic	Residential District	Jan.-July, 2004	7	60-140	Klanova et al., 2006
Bynina, Czech Republic	Edge of Village	Jan.-July, 2004	7	78-200	Klanova et al., 2006
Mstenovice, Czech Republic	Small Village	Jan.-July, 2004	7	70-140	Klanova et al., 2006
Kohtla-Jarve, Estonia	Industrial	June-July, 2002	29	787.4	Roots et al., 2007
Lahemaa, Estonia	Back-ground	June-July, 2002	29	82.6	Roots et al., 2007
Cleveland, USA	Urban	August, 2008	151	300-4200	Hornbuckle et al., 2010
Chicago, USA	Urban	August, 2008	151	500-2600	Hornbuckle et al., 2010

The Environmental Chemistry and Ecotoxicology Group of Lancaster University accomplished a large European-scale (71 stations in 22 countries) air sampling campaign with *POPs Fate Modeling* project. Samplers were located rural and urban areas. In Estonian, sampling was realized in Lahemaa-background EMEP stations and Kohtla-Jarve industrial (oil shale chemistry) region stations. While Σ_{29} PCB concentrations in EMEP stations was 82.65 pg m^{-3} , Kohtla-Jarve site the sum of 29 PCBs was 787.41 pg m^{-3} – 99.17 ng/sample .

The results of study in Cleveland, Ohio and Chicago, Illinois show that the mean concentrations were higher in Cleveland ($1.73 \pm 1.16 \text{ ng m}^{-3}$) than in Chicago ($1.13 \pm 0.58 \text{ ng m}^{-3}$) during the August 2008 sampling period. The difference in ΣPCB concentrations is probably due to the different distribution of samplers within each

city: the Cleveland samplers covered more area and a larger variety of land uses. The area sampled in Cleveland is four times larger than the area of sampler placement in Chicago. Furthermore, the land uses in the area sampled in Cleveland include industrial, residential, and rural sites. Unlikely in Chicago, most of the sampling sites were urban residential.

According to the results of these and several other studies (Satern et al., 1997; Cousins & Jones, 1998; Currado & Harrad, 2000; Yeo et al., 2003; Montone et al., 2003; Cetin et al., 2007; Odabasi et al., 2008). PCB concentrations were measured higher during summer months in generally. Lower chlorinated PCB congeners were dominating in air. Atmospheric PCB concentrations tended to decrease with increasing number of chlorine atoms.

CHAPTER THREE

MATERIALS AND METHODS

Sampling sites and techniques and the data analysis methods used for the measurement of PAHs and PCBs in this study are explained in the following chapters.

3.1 Sampling Sites

Ambient air samples were collected during the four seasons at 40 different sampling sites in the Aliğa industrial region in Izmir, Turkey. The study area is about 1000 kilometers square. This area extends from Çandarlı which is the first point of this study, at north to Türkelli that is the last sampling point at south and also it lasts to provincial boundaries of Manisa at east. Some important regions such as downtown of Aliğa and Nemrut industrial zone were included in the study area. This industrial region has important pollutant sources including a large petroleum refinery, a petrochemicals complex, several iron smelters with scrap iron storage and classification sites, steel rolling mills, a chemical fertilizer plant, heavy road and rail traffic, and agricultural and residential areas. Locations of the forty sampling points are illustrated in Figure 3.1. There are several sampling sites in heavy metal industrial areas and some are placed nearby agricultural and residential areas.

The first sampling period was summer (July-2009 to August-2009) and the following sampling months were October to November, January to February and April to May, respectively. Sampling schedule is illustrated in Table 3.1.

Table 3.1 Summary of the sampling information

Sampling Period	Duration	Point Number	Sampling Time			Temperature (°C)	
			Minute	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	40	44572	120	31.0	19.9	1.1
Winter	04.01.2010-04.02.2010	40	44510	650	30.9	9.3	1.3
Spring	01.04.2010-01.05.2010	40	43159	117	30.0	15.9	0.9

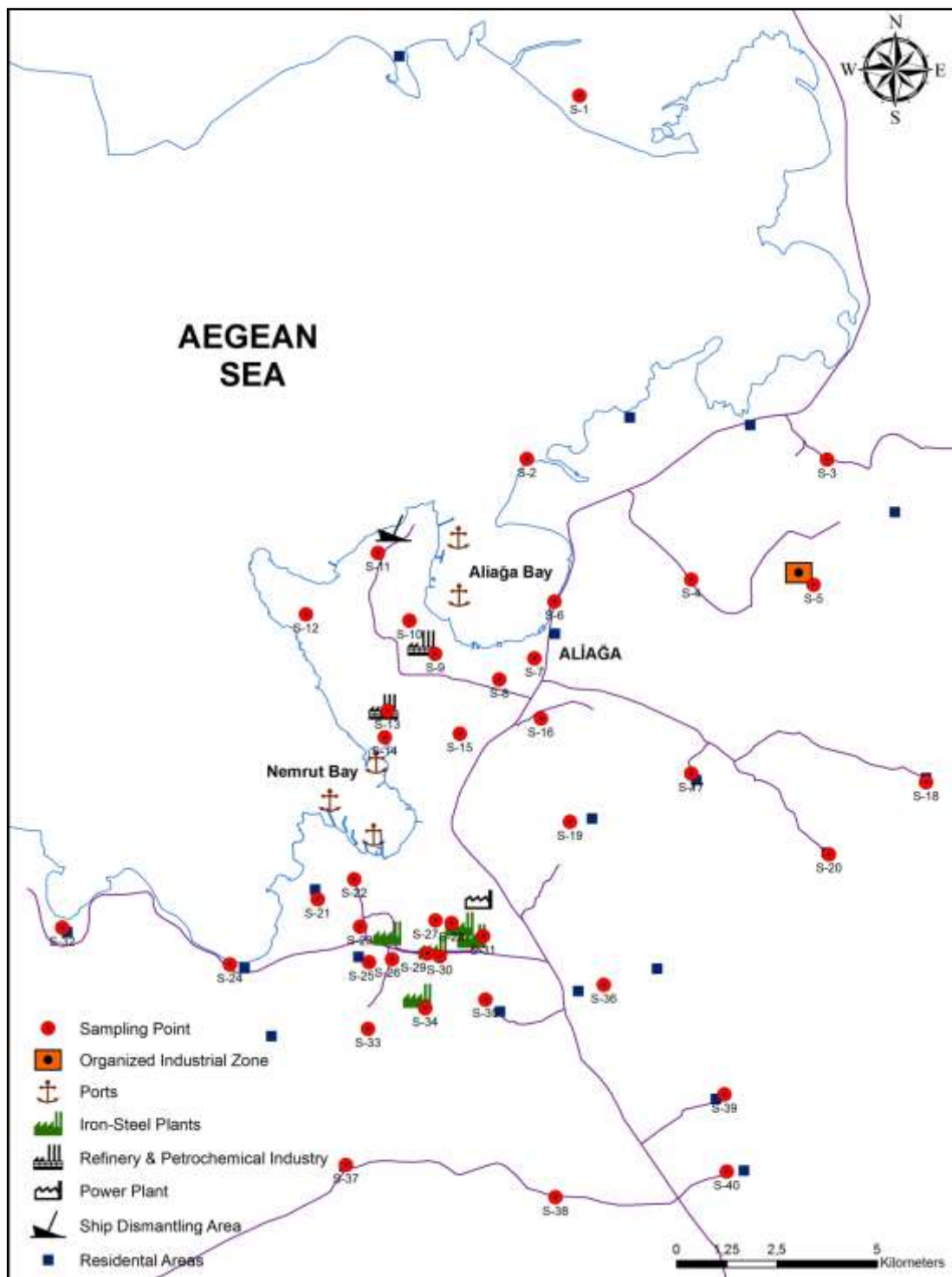


Figure 3.1 Locations of the sampling points ($n=40$) in the study area

Soil samples were also collected at 40 different points around the air sampling sites only during the first period (summer) to determine the spatial distribution of PAH and PCB contaminations in soils that can be related the local sources and to show relationship between the soil and air concentrations of these chemicals. Σ_{41} -PCB congeners were measured to determine ambient air and soil PCB concentrations. Σ_{14} -PAH were determined in ambient air and soil.

Meteorological data was provided from different meteorological stations (Foça, Aliaga, Menemen, Horozgediği and PETKIM stations) located in the study area. Monthly average air temperatures were 27 °C for summer, 20 °C for fall, 9 °C for winter and 16 °C for spring sampling periods. Wind roses of study periods (July 2009, October 2009, January 2010 and April 2010) were plotted in Figure 3.2. Meteorological data for wind roses were extracted from Horozgediği station in the study area. Generally northerly winds (WNW, NW) prevailed during the sampling programs. Southeast (SE) and South (S) winds observed especially in fall in this station. Meteorological parameters i.e. temperature, wind speed and direction measured during the sampling campaigns were not significantly different than the seasonal averages.

Table 3.2 shows the details of individual sampling points in the study area. Sites were classified as industrial and residential sites to investigate their differences.

Table 3.2 Information details of individual sampling points

POINTS	X	Y	NAME	EXPLANATION
P1	498808	4308686	Çandarlı	Residential Point
P2	497501	4299642	Güzelhisar	Residential Point
P3	504976	4299630	Asphalt Plant	Industrial Point
P4	501597	4296643	ALOSBİ 1	Industrial Point
P5	504639	4296509	ALOSBI	Industrial Point
P6	498189	4296088	Aliğa 1	Residential Point
P7	498175	4296030	Aliğa Centre	Residential Point
P8	496817	4294154	Public Edu. Center	Residential Point
P9	495217	4294787	Petroleum Ref. 1	Industrial Point
P10	494577	4295615	Petroleum Ref. 2	Industrial Point
P11	493794	4297302	Ship Dis. Area	Industrial Point
P12	492000	4295774	Petrochemical Ind.3	Industrial Point
P13	494031	4293373	Petrochemical Ind.2	Industrial Point
P14	493970	4292715	Petrochemical Ind.1	Industrial Point
P15	495830	4292800	P. Public Housing	Residential Point
P16	497852	4293181	Public Hospital	Residential Point
P17	501591	4291814	Güzelhisar village	Residential Point
P18	507436	4291593	Uzunhisar village	Residential Point
P19	498571	4290612	Samurlu village	Residential Point
P20	505025	4299802	Çital village	Residential Point
P21	492300	4288680	Çakmaklı village	Residential Point
P22	493205	4289180	Harbors	Industrial Point
P23	493350	4288000	Iron Steel Plant	Industrial Point
P24	490115	4287055	Gencelli village	Residential Point
P25	493570	4287115	Horozgediği vil.	Residential Point
P26	494150	4287192	Cement Industry	Industrial Point
P27	495225	4288157	Coal screening plants	Industrial Point
P28	495630	4288090	Iron Steel Plant	Industrial Point
P29	495024	4287327	Iron Steel Plant	Industrial Point
P30	495330	4287264	Heliport	Industrial Point
P31	496410	4287760	Combined cycle plant	Industrial Point
P32	485935	4287975	Yeni Foça	Residential Point
P33	493550	4285450	Metal reclamation plant	Industrial Point
P34	494942	4285941	Steel Plant	Industrial Point
P35	496470	4286185	Bozköy village	Residential Point
P36	499418	4286552	Şehit Kemal vil.	Residential Point
P37	493002	4282062	Ilıpınar village	Residential Point
P38	498215	4281265	Eski Foça	Residential Point
P39	502356	4283756	Helvacı village	Residential Point
P40	501421	4281829	Türkelli village	Residential Point

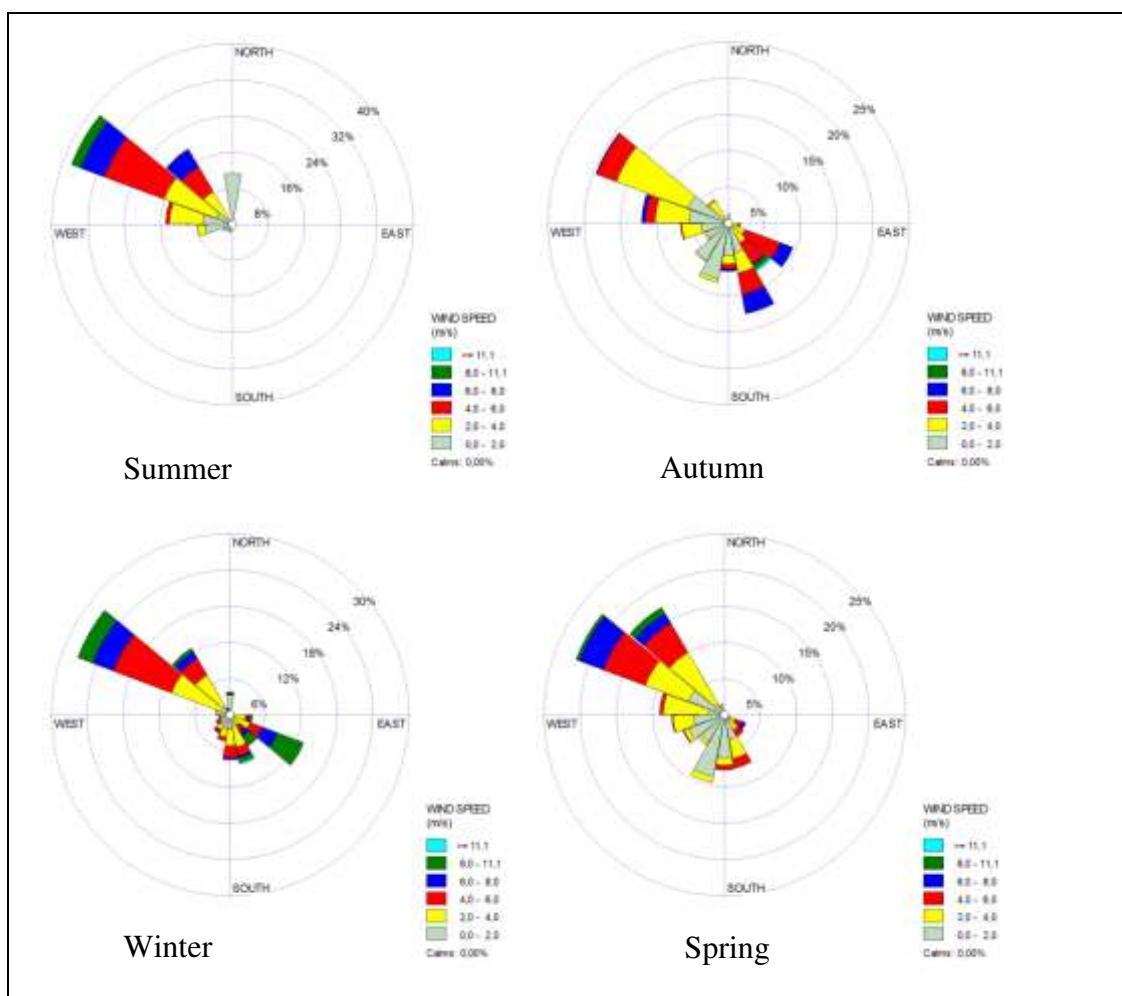


Figure 3.2 Wind-roses showing the frequency (%) of prevailing wind directions during the sampling periods.

3.2 Sampling Methods

3.2.1 Ambient Air Samples

Ambient air samples were collected using Polyurethane foam (PUF) disk passive air samplers (PAS). These samplers consist of a foam disk (14 cm diameter, 1.35 cm thick, surface area 365 cm², density 0.0213 g cm⁻³, mass, 4.40 g; volume, 207 cm³) were placed inside a stainless steel chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm. Figure 3.3 shows the design of a typical PUF sampler. This design protects the foam disk from direct precipitation and coarse particle deposition and eliminates ultraviolet radiation and minimizes the effects of wind speed on the uptake rate. In this study, sampling rates were determined using

depuration compounds. The amount of losing DCs depends on their physicochemical properties, exposure time, and wind speed.

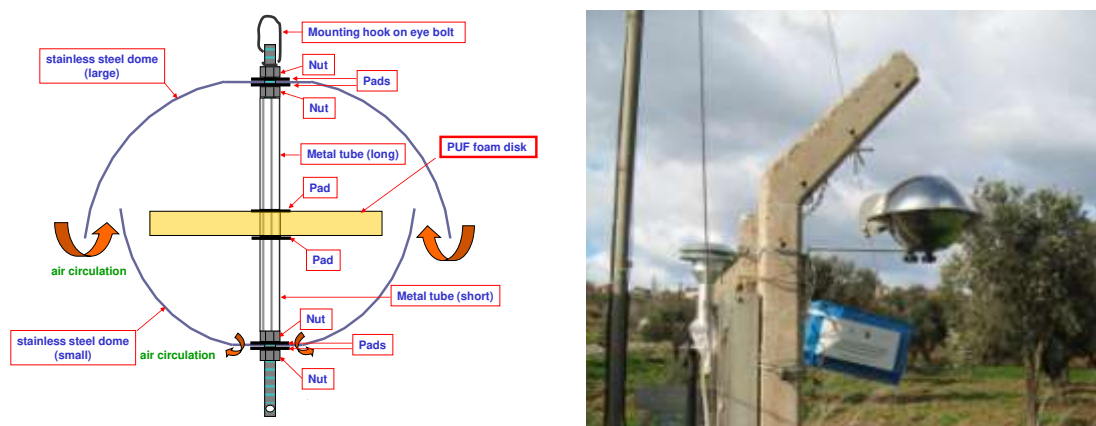


Figure 3.3 Schematic representation of the PUF disk and photo of PAS deployed.

3.2.2 Soil Samples

Approximately 0.5-1 kg of soil samples were taken from the top 5 cm of the soil manually. In the meantime, large stones and pieces of vegetation were removed. After packing in aluminum foil, soil samples were placed into airtight plastic bags and they were stored in the freezer.

3.3 Preparation for Sampling

3.3.1 Ambient Air Samples

PUF filters 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 exposure (about 10 days), 25 μL of a Depuration compound standard spiked to approximately 15 ml of hexane 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 until deployment in freezer. Then, passive samplers were transported to the field. PUF disk passive samplers were placed approximately 2 meters from the ground, and sampling lasted for one month.

3.3.2 Soil Samples

After the soil samples were carried to the laboratory, they were sieved through a 1.0 mm sieve to remove large particles and organic debris. Soils moisture was determined by weighing subsamples of soils before and after drying at 103 °C in an oven for 24 h. Further details for the estimation of soil concentration, sample preparation steps and instrumental analysis are described elsewhere (Cetin et al., 2007; Cetin and Odabasi, 2007; Bozlaker, A., 2008; Odabasi et al., 2009 and DEU, 2010).

3.4 Preparation for Analysis

3.4.1 Sample Extraction and Concentration

All ambient air samples were Soxhlet extracted with a volumetric mixture of ACE:HEX (50:50 by volume) for 12 h. For soils, before the extraction all samples and blanks were spiked with surrogate standards, and soaked in 40 ml of 1:1 acetone:hexane mixture overnight. Then, they were ultrasonically extracted for 30 min. After these stages the same processes were applied to air and soil samples.

Prior to extraction, all samples were spiked with 0.5 ml internal standard mixtures of PAHs and PCBs to monitor the analytical recovery efficiency. 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 N₂.

3.4.2 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 to remove moisture. 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 analysis.

3.5 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 μ m).

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

3.6 Quality Control and Assurance

3.6.1 Procedural Recoveries

Prior to extraction and clean-up, all sample and blank matrices were spiked with internal standard mixtures of PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂) and PCBs (PCB-14, 65, and 166) to determine the analytical recoveries. Each sample was checked for the internal standard recovery efficiencies if they were in the range of 50-120%. The recoveries of the internal standards were used to correct the amounts of the specific PAHs and PCBs found in the samples, correspondingly.

Average recoveries of PAH and PCB internal standards in all blank and sample matrices are given in Table 3.3. Naphthalene was identified but not quantified for all samples because of the high blank amounts.

Table 3.3 Average recovery efficiencies (%) of PAH and PCB internal standards (avg $\pm$ SD) in all blank and sample matrices.

Internal Standards	PUFs	Soil
Naphthalene-d8	75 $\pm$ 22	56 $\pm$ 14
Acenaphthene-d10	84 $\pm$ 20	71 $\pm$ 18
Phenanthrene-d10	107 $\pm$ 23	97 $\pm$ 17
Chrysene-d12	98 $\pm$ 24	72 $\pm$ 21
Perylene-d12	92 $\pm$ 23	68 $\pm$ 20
PCB-14	86 $\pm$ 12	80 $\pm$ 13
PCB-65	93 $\pm$ 13	84 $\pm$ 19
PCB-166	89 $\pm$ 11	83 $\pm$ 13

3.6.2 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 3.4.

Table 3.4 Average PAH & PCB amounts (ng, avg $\pm$ SD) in blanks.

PAHs	PUF	Soil	PCBs	PUF	Soil
ACL	10 $\pm$ 5	3 $\pm$ 0.3	PCB-18	1.4 $\pm$ 1.1	1.8 $\pm$ 0.04
ACT	15 $\pm$ 5	10 $\pm$ 0.2	PCB-17	1.1 $\pm$ 0.5	1.1 $\pm$ 0.23
FLN	34 $\pm$ 9	16 $\pm$ 0.3	PCB-31	1.0 $\pm$ 0.4	0.6 $\pm$ 0.01
PHE	108 $\pm$ 21	50 $\pm$ 2.7	PCB-28	1.4 $\pm$ 1.3	1.1 $\pm$ 0.05
ANT	6 $\pm$ 2	1 $\pm$ 0.1	PCB-33	0.3 $\pm$ 0.4	<i>nd</i>
CRB	2 $\pm$ 1	<i>nd</i>	PCB-52	0.5 $\pm$ 0.6	<i>nd</i>
FL	15 $\pm$ 4	5 $\pm$ 0.5	PCB-49	0.2 $\pm$ 0.2	<i>nd</i>
PY	15 $\pm$ 4	5 $\pm$ 0.4	PCB-70	0.2 $\pm$ 0.3	<i>nd</i>
BaA	1 $\pm$ 1	<i>nd</i>	PCB-99	0.3 $\pm$ 0.3	<i>nd</i>
CHR	2 $\pm$ 1	1 $\pm$ 0.1	PCB-87	0.5 $\pm$ 0.5	<i>nd</i>
BbF	<i>nd</i>	<i>nd</i>	PCB-101	0.1 $\pm$ 0.2	<i>nd</i>
BaP	0.2 $\pm$ 0.5	<i>nd</i>	PCB-110	0.1 $\pm$ 0.2	<i>nd</i>
IcdP	<i>nd</i>	<i>nd</i>	PCB-118	0.1 $\pm$ 0.3	<i>nd</i>
DahA	0.3 $\pm$ 0.5	<i>nd</i>	PCB-149	<i>nd</i>	<i>nd</i>

nd: Not detected.

3.6.3 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 detection of the method (LOD) 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. LOD for individual PAH and PCB compounds are presented Table 3.5.

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

Table 3.5 LODs (ng) for individual PAH & PCB compounds.

PAHs	PUF	Soil	PCBs	PUF	Soil
ACL	25	3.9	PCB-18	4.7	0.12
ACT	30	10.6	PCB-17	2.6	0.69
FLN	61	16.9	PCB-31	2.2	0.93
PHE	171	58.1	PCB-28	5.3	0.75
ANT	12	1.3	PCB-33	1.5	<i>nc</i>
CRB	5	<i>nc</i>	PCB-52	2.3	<i>nc</i>
FL	3	6.5	PCB-49	0.8	<i>nc</i>
PY	27	6.2	PCB-70	1.1	<i>nc</i>
BaA	4	<i>nc</i>	PCB-99	1.2	<i>nc</i>
CHR	5	1.3	PCB-87	2.0	<i>nc</i>
BbF	<i>nc</i>	<i>nc</i>	PCB-101	0.7	<i>nc</i>
BaP	1.7	<i>nc</i>	PCB-110	0.7	<i>nc</i>
IcdP	<i>nc</i>	<i>nc</i>	PCB-118	1.0	<i>nc</i>
DahA	1.8	<i>nc</i>	PCB-149	<i>nd</i>	<i>nc</i>

nc: Not calculated.

3.6.4 Calibration Standards

The PAH calibration standard solution contained 16 PAHs, carbazole, and five deuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) that were used to determine the analytical recoveries. Six levels of calibration standards (0.04, 0.4, 1.0, 4.0, 6.0, 10.0 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 $r^2 \geq 0.999$

3.7 Sampling Rates from Depuration Compounds

Sampling rates (R , m³ d⁻¹) were estimated using the loss of depuration compounds and listed in Table 3.6. Sampling rates for all sampling periods ranged from 4.21 to 4.93 m³ d⁻¹.

K'_{PUF-A} used (Eq. 2.6) for the calculation of the uptake rate (k_A) of PAHs and PCBs was $\log K_{OA}$ value for DCs corrected for the average temperature at the sampling sites for each sampling period using the equation:

$$\text{Log } K_{OA} = A + B/T \quad (3.1)$$

where coefficients A and B derived from regression of K_{OA} against temperature by Harner and Bidleman (1998). The R-values was estimated from the calculated k_A and the known value of the surface area of the PUF disk using equation 2.7.

Table 3.6 Sampling rates (m^3/day) obtained from depuration compounds for each sampling period.

Chemical	R ($\text{m}^3 \text{d}^{-1}$)			
	Sampling Period			
	Summer	Fall	Winter	Spring
^{13}C PCB-3	2.62	3.48	4.23	3.76
^{13}C PCB-9	5.02	5.72	6.45	6.05
^{13}C PCB-15	4.98	4.16	4.10	3.24
Average	4.21	4.45	4.93	4.35
Standard Dev.	1.37	1.15	1.32	1.50

The average sampling rate was used in calculating the volume of air sampled by the passive samplers. Air concentrations for the target chemicals were obtained from the amount accumulated in the PUF disk and the effective air volume. Equation 2.8 was used to calculate effective air volumes (V_{eff} , m^3). V_{air} values are given in Table 3.7 and Table 3.8 for PAHs and PCBs, respectively. Lower molecular weight chemicals had lower values for V_{air} as they approach equilibrium in the PUF disk during the sampling period because of their lower octanol-air partitioning (K_{OA}) and lower PUF-air partition coefficients $K_{\text{PUF-A}}$ (Harner et al., 2005).

Table 3.7 Effective air volumes (m^3) for individual PAH compounds for different sampling periods.

PAH	V_{air} (m^3)			
	Summer	Fall	Winter	Spring
Acenaphthylene	29.0	38.3	57.3	44.0
Acenaphthene	36.7	48.1	70.4	54.3
Fluorene	57.2	71.6	97.5	77.1
Phenanthrene	98.4	110.8	133.4	110.5
Anyhracene	99.9	112.1	134.5	111.5
Carbazole	110.3	121.7	142.7	119.3
Fluoranthene	114.8	132.0	148.8	126.4
Pyrene	126.0	132.5	149.1	126.7
Benz[a]anthracene	133.3	137.3	152.0	130.1
Chrysene	133.3	137.4	152.0	130.1
<i>Benzo[b]fluoranthene</i>	134.1	137.8	152.3	130.4
<i>Benzo[k]fluoranthene</i>	134.1	137.8	152.3	130.4
Benzo[a]pyrene	134.1	137.9	152.3	130.4
Indeno[1,2,3-cd]pyrene	134.3	137.9	152.3	130.5
Dibenz[a,h]anthracene	134.3	137.9	152.3	130.5
Benzo[g,h,i]perylene	134.3	137.9	152.3	130.5

Table 3.8 Effective air volumes (m^3) for PCB congeners for different sampling periods.

PCB Congeners	$V_{air} (\text{m}^3)$			
	Summer	Fall	Winter	Spring
PCB-18	95.0	108.6	132.5	109.1
PCB-17	95.9	109.4	133.0	109.6
PCB-31	110.6	121.1	141.6	118.6
PCB-28	111.0	121.4	141.8	118.7
PCB-33	113.4	123.3	143.1	120.1
PCB-52	118.8	127.3	145.8	123.0
PCB-49	119.6	127.8	146.2	123.4
PCB-44	122.1	129.7	147.4	124.8
PCB-74	126.4	132.7	149.3	126.9
PCB-70	126.8	133.0	149.4	127.1
PCB-95	127.1	133.2	149.6	127.3
PCB-101	128.8	134.4	150.3	128.1
PCB-99	129.2	134.6	150.5	128.3
PCB-87	130.3	135.4	150.9	128.8
PCB-110	130.8	135.7	151.1	129.0
PCB-82	131.2	136.0	151.3	129.2
PCB-151	131.3	136.0	151.3	129.2
PCB-149	131.7	136.3	151.4	129.4
PCB-118	132.4	136.8	151.7	129.7
PCB-153	132.3	136.7	151.7	129.7
PCB-132	132.4	136.8	151.7	129.7
PCB-105	132.9	137.1	151.9	130.0
PCB-138	132.9	137.1	151.9	129.9
PCB-158	132.9	137.1	151.9	129.9
PCB-187	133.1	137.2	152.0	130.0
PCB-183	133.2	137.3	152.0	130.1
PCB-128	133.3	137.3	152.0	130.1
PCB-177	133.5	137.4	152.1	130.2
PCB-171	133.5	137.5	152.1	130.2
PCB-156	133.7	137.6	152.2	130.3
PCB-180	133.6	137.6	152.1	130.2
PCB-191	133.7	137.6	152.2	130.3
PCB-169	133.7	137.6	152.2	130.3
PCB-170	133.8	137.7	152.2	130.3
PCB-199	133.9	137.7	152.2	130.3
PCB-208	134.0	137.8	152.3	130.4
PCB-195	134.0	137.8	152.3	130.4
PCB-194	134.1	137.8	152.3	130.4
PCB-205	134.1	137.8	152.3	130.4
PCB-206	134.1	137.9	152.3	130.4
PCB-209	134.2	137.9	152.3	130.5

CHAPTER FOUR

RESULTS AND DISCUSSIONS

This chapter presents the results of ambient air concentrations, spatial distributions and seasonal variations of PAHs and PCBs. Results of these measurements were compared to the values reported in the literature.

4.1 Polycyclic Aromatic Hydrocarbons (PAHs)

4.1.1 Ambient Air Concentrations of PAHs – Spatial and Temporal Trends

Atmospheric PAH concentrations for each site are represented in Table 4.1. The concentrations of $\Sigma_{16}\text{PAHs}$ ranged from 1.6 to 838 ng m^{-3} . This range included residential and industrial site concentrations of PAHs. The concentrations ranged from 2 to 358 ng m^{-3} and 1.6 to 838 ng m^{-3} for residential and industrial sites, respectively. PAH concentrations showed a strong increase in the industrial areas. For all periods, site average PAH concentrations showed a strong residential-industrial gradient, with total concentrations up to approximately 2 or 5 times higher in industrial sites than in the residential ones (Figure 4.1).

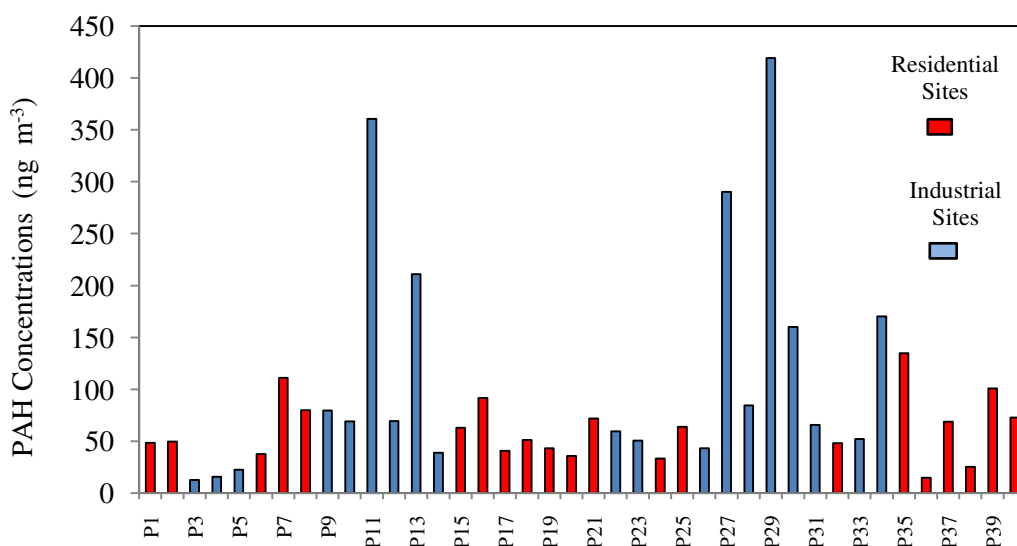


Figure 4.1 The average $\Sigma_{16}\text{PAH}$ concentrations (ng m^{-3}) for residential and industrial sites.

Table 4.1 Atmospheric concentrations (ng m^{-3}) of $\Sigma_{16}\text{PAHs}$ measured at the air sampling sites.

Points	Min.	Max.	Geometric Mean	Median	Avg $\pm$ SD
P1	2.0	136.2	20.7	27.3	48 $\pm$ 60
P2	2.9	161.9	17.9	16.7	50 $\pm$ 75
P3	3.2	35.0	7.9	6.0	13 $\pm$ 15
P4	5.9	38.2	11.9	9.5	16 $\pm$ 15
P5	1.6	74.0	8.9	7.3	23 $\pm$ 34
P6	6.5	80.8	26.5	31.6	38 $\pm$ 32
P7	13.5	358.9	49.6	35.6	111 $\pm$ 166
P8	11.2	254.6	37.3	26.5	80 $\pm$ 117
P9	40.2	141.1	71.5	68.8	80 $\pm$ 44
P10	45.0	130.5	62.2	50.6	69 $\pm$ 41
P11	251.5	475.9	348.7	357.4	361 $\pm$ 106
P12	24.9	111.5	55.7	70.6	69 $\pm$ 48
P13	68.5	405.2	168.4	185.0	211 $\pm$ 153
P14	16.2	66.4	34.4	36.4	39 $\pm$ 21
P15	7.4	175.1	35.1	34.3	63 $\pm$ 76
P16	12.1	278.9	40.7	37.8	92 $\pm$ 127
P17	12.9	87.8	32.1	30.7	41 $\pm$ 33
P18	7.5	138.5	29.2	29.0	51 $\pm$ 60
P19	5.5	129.4	22.2	18.4	43 $\pm$ 58
P20	7.9	88.5	24.6	23.4	36 $\pm$ 36
P21	21.6	163.8	53.5	50.9	72 $\pm$ 64
P22	31.7	113.7	51.6	46.1	59 $\pm$ 38
P23	21.7	124.1	38.0	28.0	50 $\pm$ 49
P24	12.1	87.2	23.1	16.4	33 $\pm$ 36
P25	34.3	123.2	56.0	48.4	64 $\pm$ 40
P26	12.2	71.5	35.8	44.3	43 $\pm$ 25
P27	180.4	421.2	277.5	279.4	290 $\pm$ 99
P28	58.3	142.7	79.1	68.6	85 $\pm$ 39
P29	258.3	838.2	366.6	289.8	419 $\pm$ 280
P30	89.3	316.0	139.4	117.4	160 $\pm$ 106
P31	27.1	105.1	58.3	65.4	66 $\pm$ 34
P32	15.1	131.6	31.0	22.8	48 $\pm$ 56
P33	32.5	96.6	47.2	39.9	52 $\pm$ 30
P34	92.6	247.9	159.3	170.4	170 $\pm$ 68
P35	48.4	237.9	106.4	126.3	135 $\pm$ 96
P36	2.2	28.0	10.6	14.5	15 $\pm$ 11
P37	39.0	115.2	63.3	60.0	69 $\pm$ 33
P38	17.1	40.6	23.5	21.2	25 $\pm$ 11
P39	40.7	156.7	86.6	102.8	101 $\pm$ 58
P40	22.2	171.3	52.6	48.6	73 $\pm$ 69

Σ_{16} PAH concentrations in the air ranged from 1.6 to 838 ng m⁻³ for the summer 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 to 476 ng m⁻³ for the spring period. Figure 4.2 shows the atmospheric PAH concentrations for each sampling site and sampling period.

For all sites, the highest PAH concentrations except for five sampling points were found during the winter period. Higher PAH concentrations observed during winter were probably due to the increasing emissions from residential heating. Combustion-derived PAH emissions may be elevated during the colder months (Harner et al., 2009). Similar increases in winter for PAH concentrations were recently reported (Bae et al., 2002; Gevao, Hamilton-Taylor, & Jones, 1998; Kiss et al., 2001; Odabasi, Cetin, & Sofuoglu, 2006a; Park et al., 2002, 2001; Vardar et al., 2007). The lowest PAH concentrations were detected during the summer sampling period (July-August).

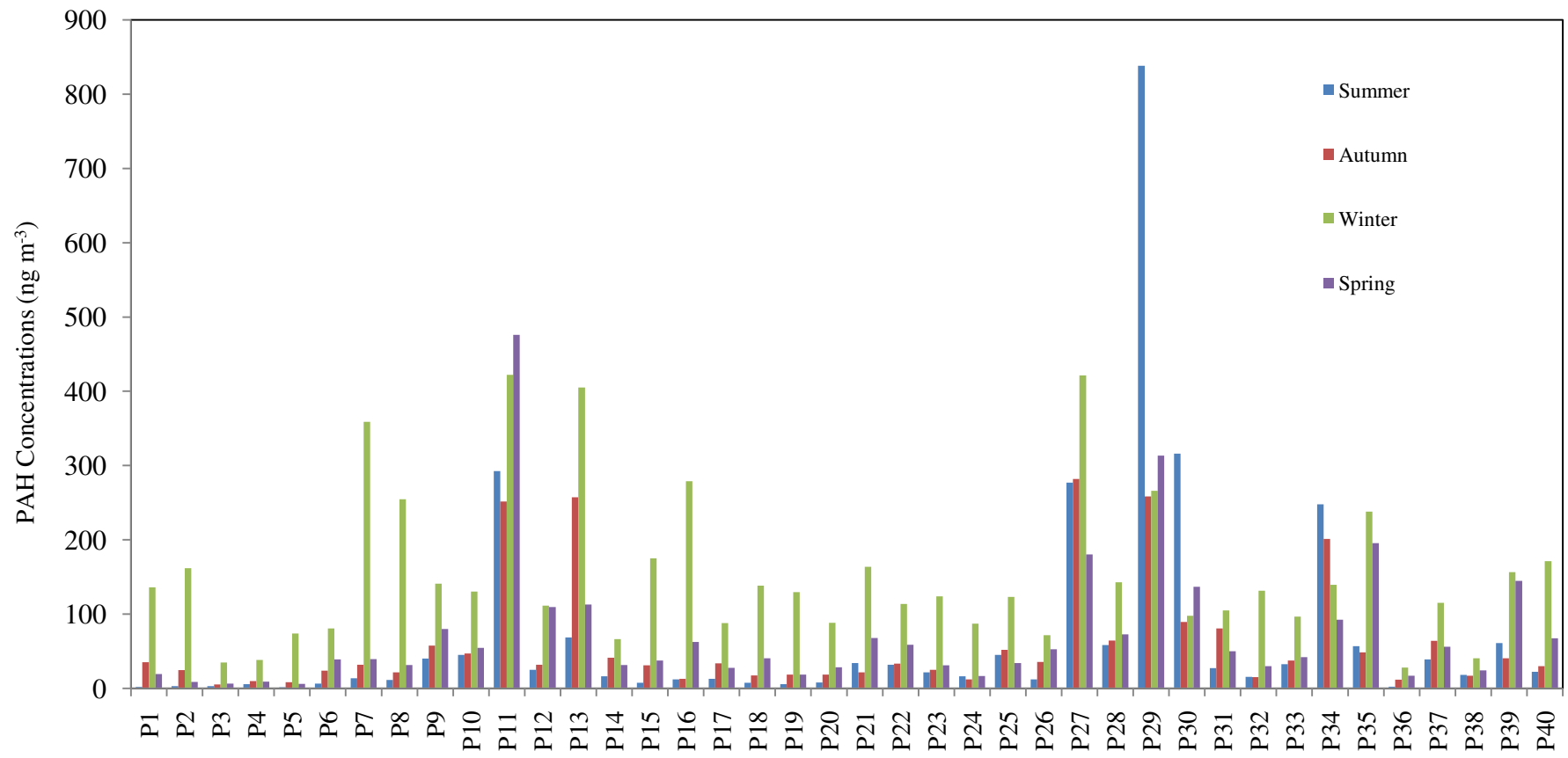


Figure 4.2 Σ_{16} PAH concentrations (ng m⁻³) for each sampling site and period.

Figure 4.3 shows the gas-phase concentrations individual PAH compounds in air. Σ_{16} PAHs were dominated by phenanthrene similar to those reported by Harner et al. (2009), Bozlaker (2008), Santiago & Cayetano, (2007), Gevao et al. (1998) and Odabasi et al. (1999). Atmospheric Σ_{16} PAH concentrations were dominated by more volatile compounds existing predominantly in the gas-phase. It was reported that contribution of PAH compounds to the total atmospheric concentrations decreased with increasing molecular weight (Bozlaker, A., 2008). Higher concentrations were observed for low molecular weight PAHs. Because of their higher volatility, low to medium molecular weight PAHs (3-5 rings) were more abundant in the gas-phase in the present study, similar to the previous studies (Fang et al., 2004; Gevao et al., 1998; Ohura et al., 2004; Tasdemir & Esen, 2007).

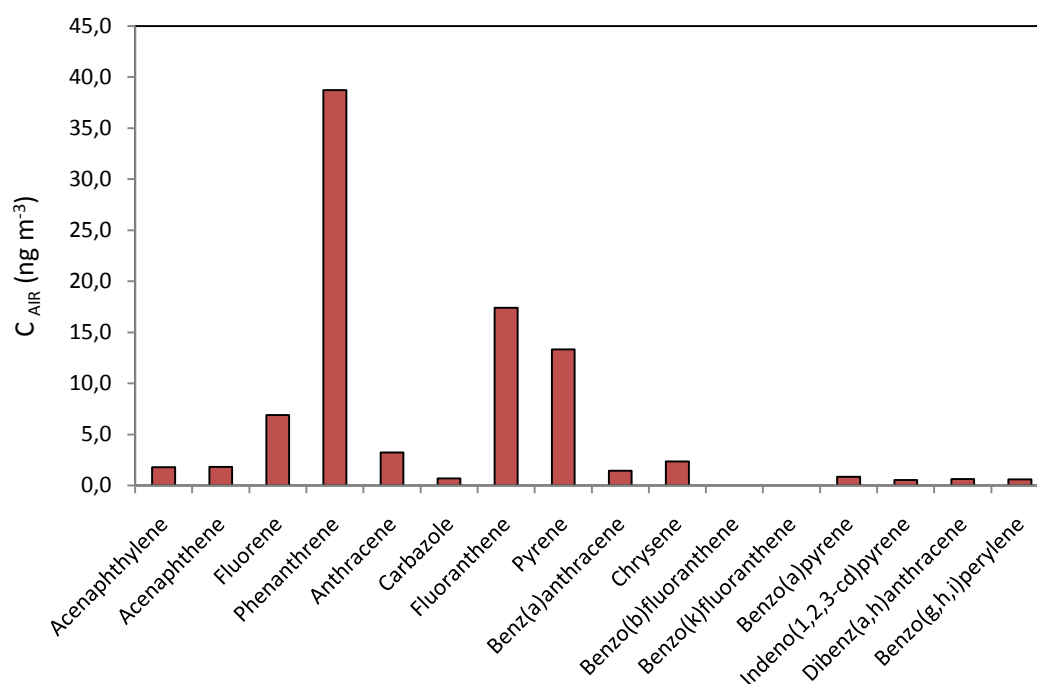


Figure 4.3 Average concentrations (ng m⁻³) (for all sites and seasons) of individual PAHs.

The spatial distribution of average PAH concentrations in the air ranged from 12 to 419 ng m⁻³. The site average of PAH air concentrations (89 ng m⁻³) in this study is higher than the general range (25-35 ng m⁻³) for passive derived air concentrations for 12 PAHs reported for London and Manchester (Jaward et al., 2004a,b; Santiago, E.C., & Cayetano, M.G., 2007). The highest concentration of 419 ng m⁻³ derived in

this study is lower than the highest concentration of 881 ng m^{-3} total PAHs reported among industrial zone in Taiwan by Fang et al. (2004). On the other hand, this value is higher than the reported by several studies (Santiago, E.C., & Cayetano, M.G., 2007; Harner et al., 2006a,b). Comparison of the passive sampling data from other studies is shown in Figure 4.4.

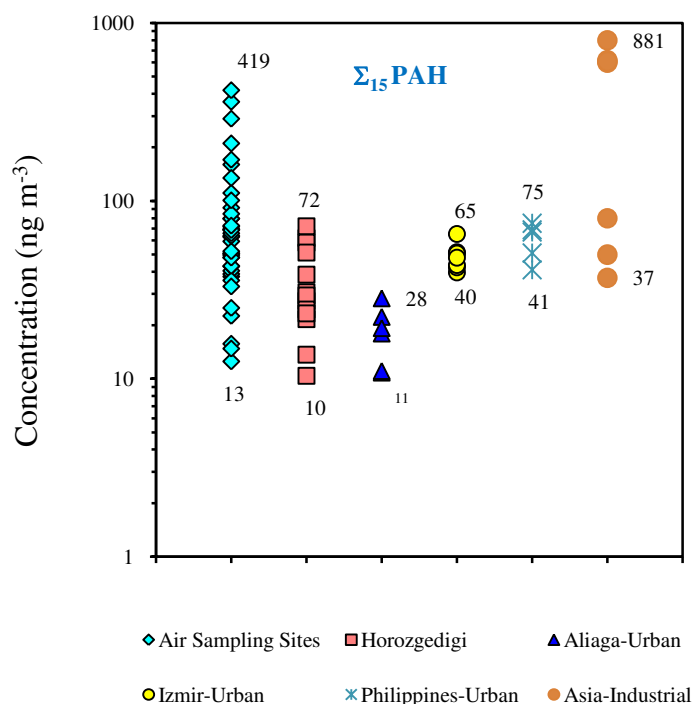


Figure 4.4 Comparison of PAH concentrations from other studies.

Figures 4.5-4.8 show that the spatial distribution of ambient air PAH concentrations (ng m^{-3}) for summer, fall, winter and spring periods, respectively while Figure 4.9 presents the site-averaged ambient PAH concentrations.

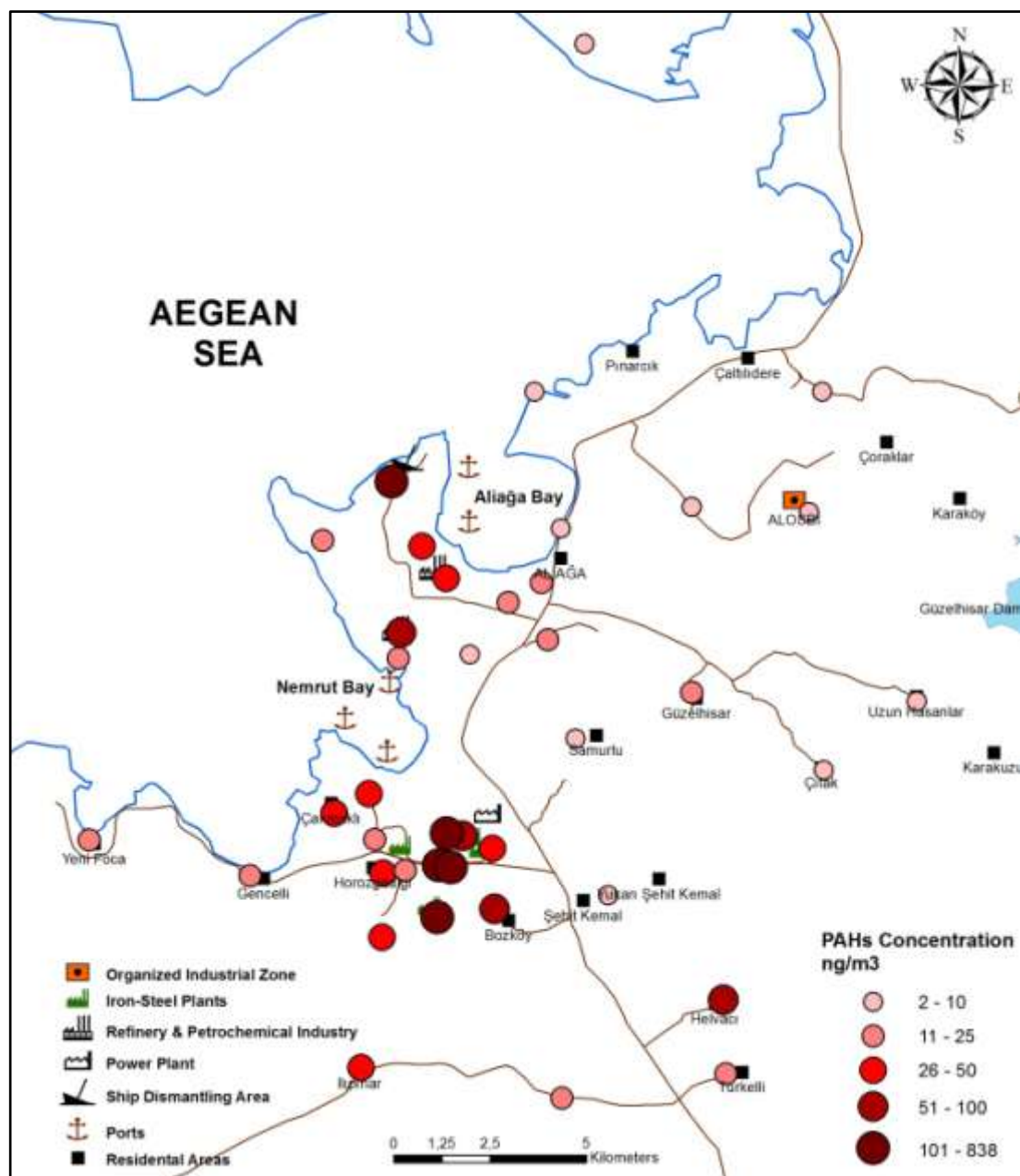


Figure 4.5 The spatial distribution of ambient air PAH concentrations (ng m^{-3}) for summer period.

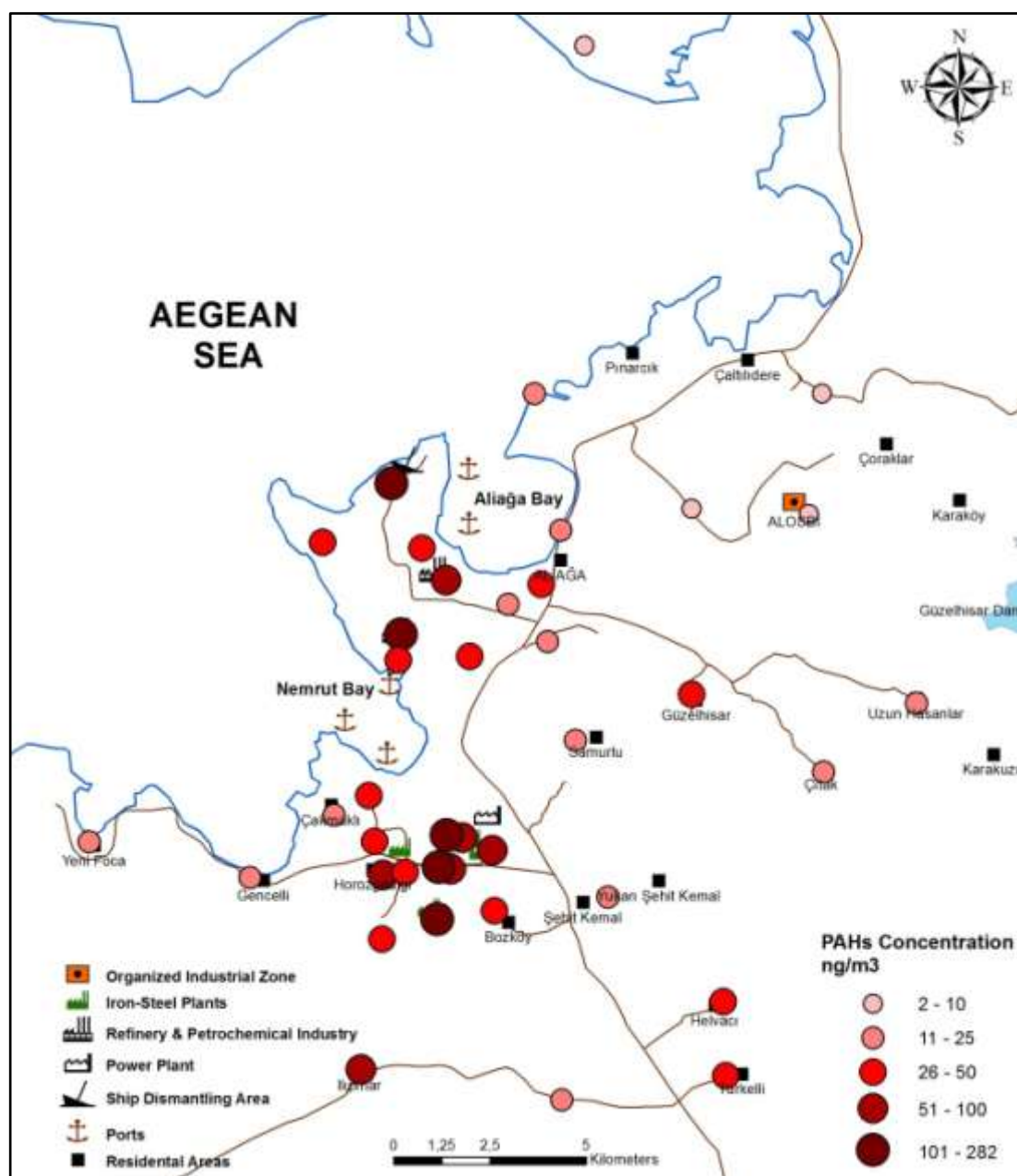


Figure 4.6 The spatial distribution of ambient air PAH concentrations (ng m^{-3}) for the fall period.

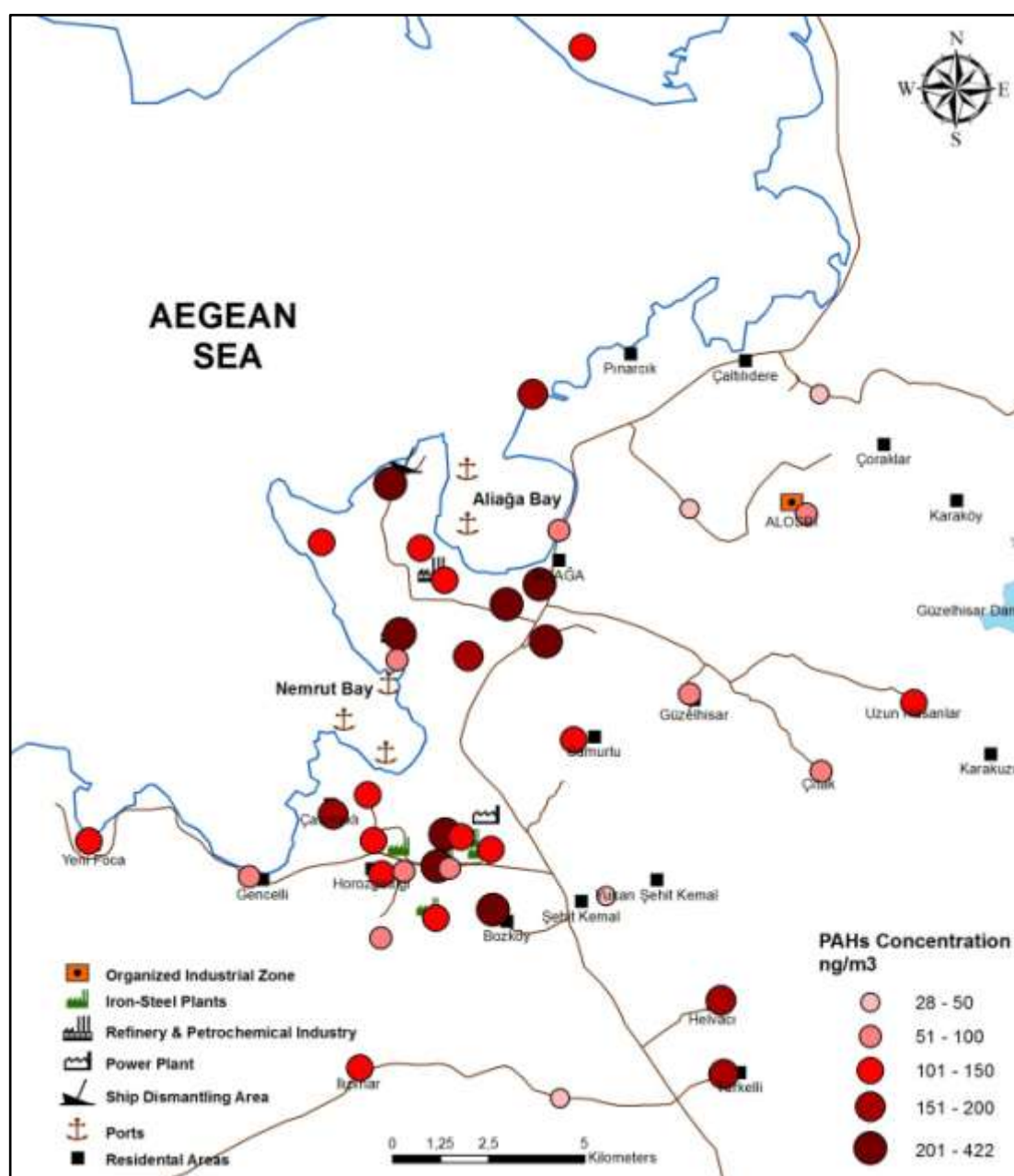


Figure 4.7 The spatial distribution of ambient air PAH concentrations (ng m^{-3}) for the winter period.

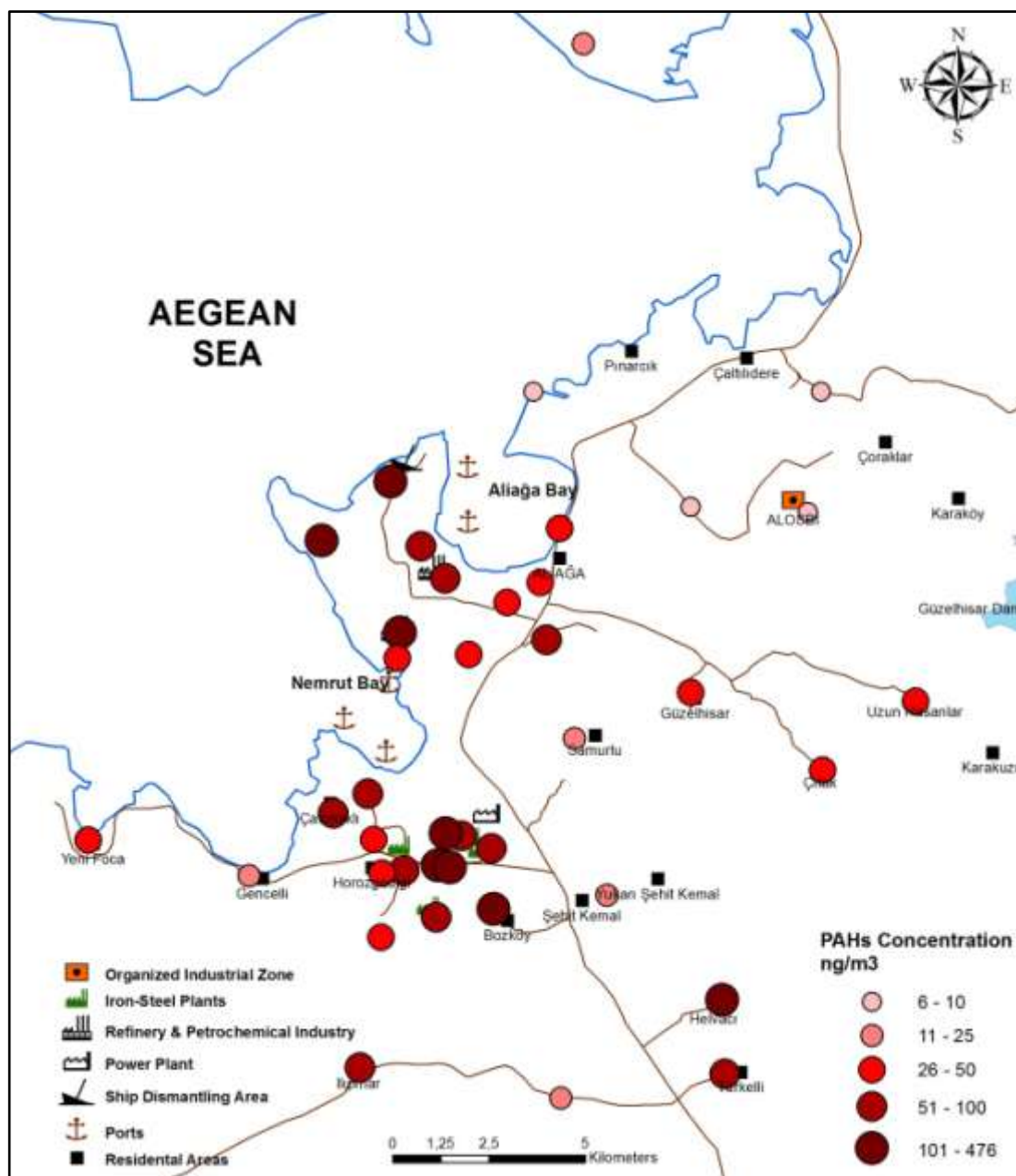


Figure 4.8 The spatial distribution of ambient air PAH concentrations (ng m^{-3}) for the spring period.

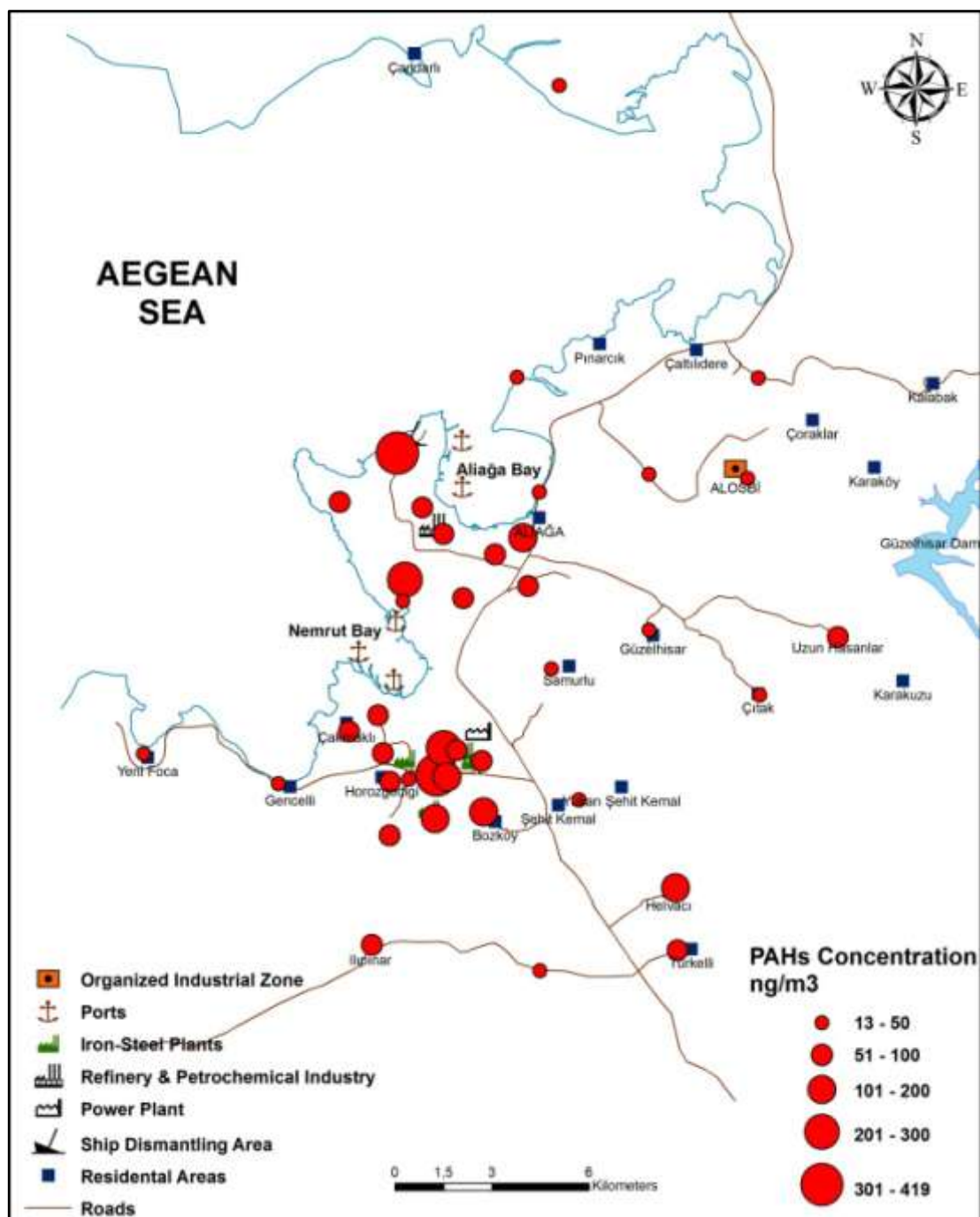


Figure 4.9 The spatial distribution of site-averaged ambient air PAH concentrations (ng m^{-3}).

The spatial distribution of ambient PAH concentrations indicated that the major PAH sources in the region were steel plants, petroleum refinery, and ship dismantling plants.

4.1.2 Soil Concentrations of PAHs

The average PAH concentrations measured in soil samples and the site having maximum and minimum concentrations of PAH are presented in Table 4.2. Σ_{16} PAHs in soil were dominated by medium to high molecular weight compounds. The composition of PAHs was characterized by the medium (202 g mol^{-1}) and high molecular ($228\text{-}275 \text{ g mol}^{-1}$) weight PAHs, among which fluoranthene, pyrene, and chrysene were most dominant components. These results can be explained by the fact that 4-6 ring-PAHs can be deposited more easily close to the point sources than the lower molecular PAHs which are mainly in gas-phase and transported at long-ranges (Nadal et al., 2004).

Table 4.2 PAHs concentrations ($\mu\text{g kg}^{-1}$ dry weights) for soil samples in study area.

PAHs	Min	Max	Geometric Mean	Median	Avg.	SD
Acenaphthylene	0.025	54	0.4	0.4	3.3	8.5
Acenaphthene	0.003	13	0.4	0.3	2.1	3.5
Fluorene	0.04	27	0.6	0.6	2.9	5.3
Phenanthrene	0.2	347	5.9	5.8	32.8	59.2
Anthracene	0.02	74	0.7	0.7	6.2	13.1
Carbazole	0.03	13	0.3	0.2	1.1	2.2
Fluoranthene	0.1	173	6.0	9.8	24.1	34.9
Pyrene	0.1	143	5.1	7.1	21.8	30.2
Benz(a)anthracene	0.04	107	3.6	3.8	16.4	22.8
Chrysene	0.1	105	4.3	4.2	18.0	25.1
Benzo(b)fluoranthene	0.2	165	8.3	7.4	30.2	41.2
Benzo(k)fluoranthene	0.1	63	3.6	3.8	11.9	15.4
Benzo(a)pyrene	0.04	64	3.4	3.4	13.2	17.7
Indeno(1,2,3-cd)pyrene	0.1	76	3.2	2.6	13.1	18.7
Dibenz(a,h)anthracene	0.1	51	2.4	2.3	8.7	12.6
Benzo(g,h,i)perylene	0.1	119	3.5	3.1	15.7	23.9

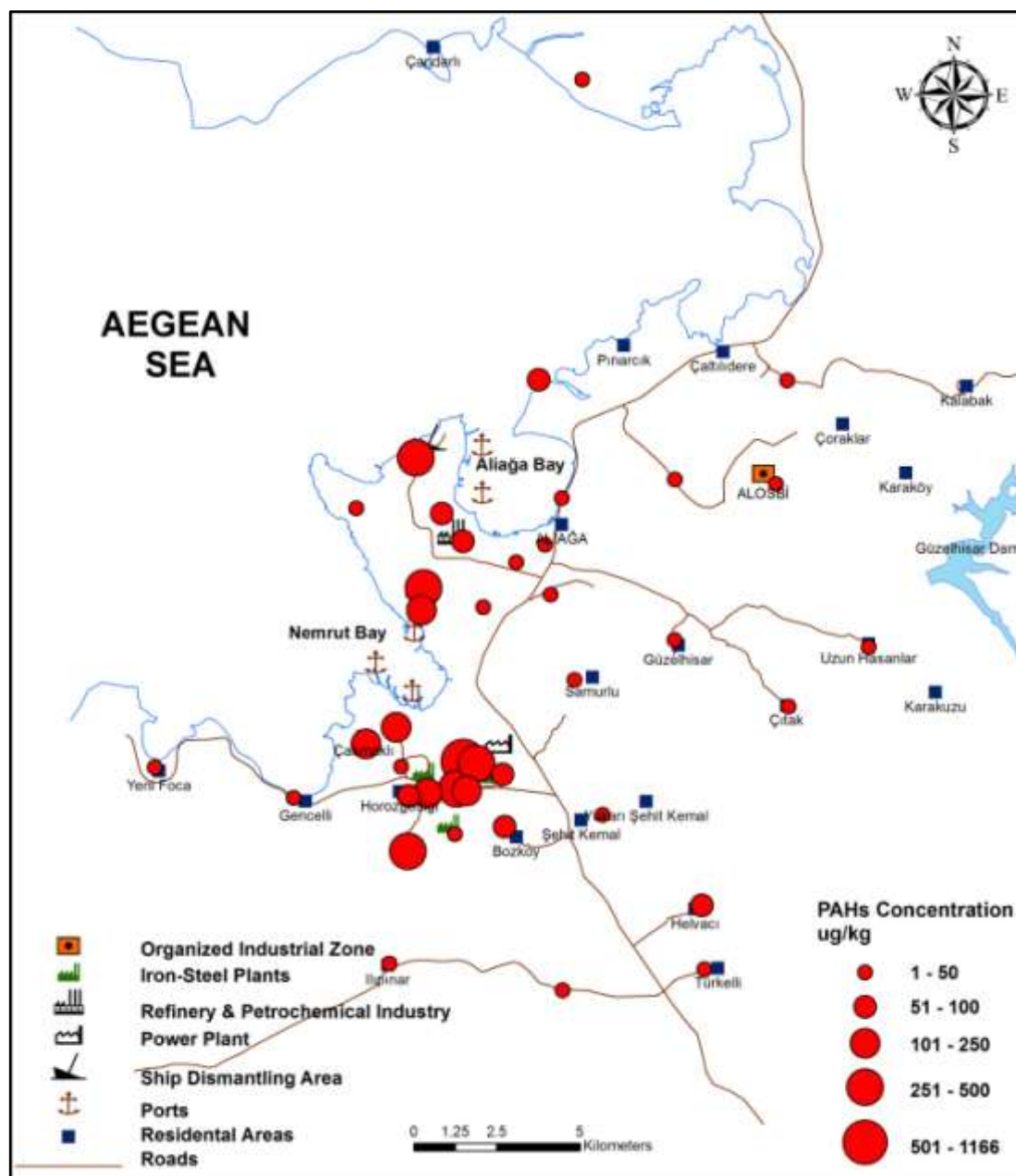


Figure 4.10 The spatial variation of soil PAH concentrations ($\mu\text{g kg}^{-1}$).

The opposite was observed for ambient air PAH concentrations and they were dominated by low molecular weight compounds. The reason of this difference in air and soil PAH profiles can also be explained with their different partitioning behaviors such low molecular weight PAHs have low soil-air partitioning coefficients. Volatilization of PAHs from soil as a result of increasing ambient air temperature and wind speed also causes loss of especially the low molecular weight PAHs (Bozlaker, 2008).

The total PAH concentrations in soil measured in this study range between 1 to 1166 $\mu\text{g kg}^{-1}$ (dry weight). The highest soil PAH concentrations were measured around the Aliaga town, steel plants, petroleum refinery, and the petrochemical plant confirming that these are the major PAH sources in the area (Figure 4.10). Spatial distribution and levels of PAHs in soil also showed a similar distribution with ambient air PAHs (see Figures 4.9 and 4.10).

Soil concentrations measured in this study were used to investigate the relationship between the soil and air concentrations. Air and soil PAH and PCB concentrations were correlated significantly ($r^2=0.39$, $p<0.01$) indicating the interaction of these compartments (Figure 4.11).

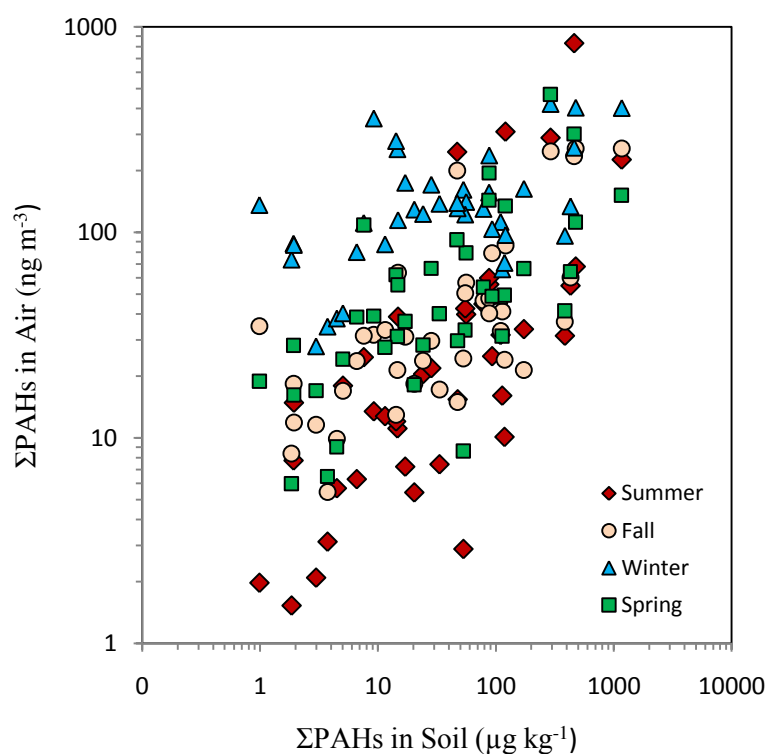


Figure 4.11 Relationship between the soil and air concentrations of ΣPAHs ($r^2=0.39$ $p<0.01$).

The statistically significant relationship between air and soil concentrations indicates that PAHs are exchanged between air and soil. However, the direction of

exchange should be further investigated on a compound basis by calculating the fugacity ratios for different seasons.

4.2 Polychlorinated Biphenyls (PCBs)

4.2.1 Ambient Air Concentrations of PCBs – Spatial and Temporal Trends

The use of PCBs is currently forbidden or restricted in many countries but emissions of PCBs to ambient air are continued to be released from point sources such as industrial or urban areas where they were heavily used now or in the past (Breivik, Sweetman, Pacnya, & Jones, 2002; Harner et al., 2005).

Table 4.2 shows the ambient air PCBs concentrations in the study area. $\Sigma_{41}\text{PCB}$ (sum of the 41 individual congeners) concentrations ranged from 0.2 to 231 ng m⁻³ for summer period (July-August, 2009), from 0.4 to 87 ng m⁻³ for fall period (October-December, 2009), from 0.2 to 22 ng m⁻³ for winter period (January-February, 2010) and from 0.5 to 45 ng m⁻³ for the spring period (April-May, 2010). Site- averaged PCB concentrations in the air ranged from 0.34 to 94.4 ng m⁻³. Seasonal variability is also shown in Figure 4.12.

Average seasonal PCB concentrations were approximately 4-5 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 that reporting similar observations (Cousins & Jones, 1998; Currado & Harrad, 2000; Hillery et al., 1997; Montone et al., 2003; Simcik et al., 1998; Stern et al. 1997; Yeo et al., 2003). In a seasonal basis, summer concentrations were higher than in winter concentrations in industrial sites, while the opposite was observed for some residential sites as observed by Odabasi et al. (2007).

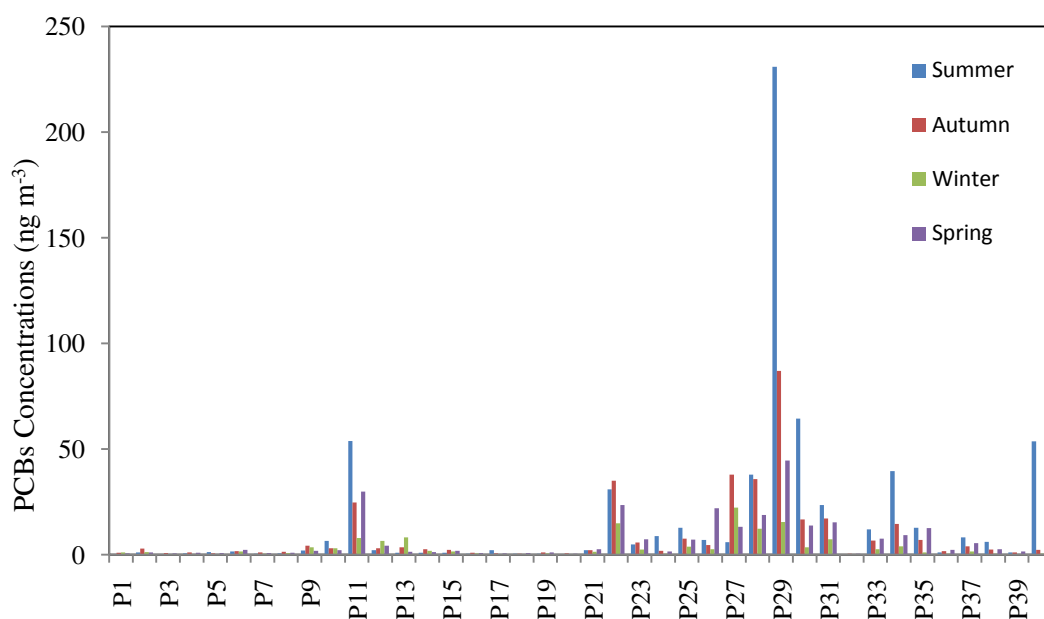


Figure 4.12 Atmospheric Σ_{41} PCB concentrations (ng m⁻³) for each sampling site and sampling period.

During all seasons, PCB concentrations showed a strong increase in the industrial sites compared to the residential sites (Figure 4.12), confirming the continuing role of industrial areas in Aliğa as PCB emission sources (Bozlaker, 2008). High PCB concentrations were measured in this study at some sampling sites close to the iron-steel plants and ship dismantling plants, which all kind of scrap iron steel materials are stored, classified, cut into parts, and melted.

Figure 4.13 shows the distribution of ambient PCB concentrations as it is seen clearly, these industries may have a significant contribution to the PCB pollution in the study area. PCBs are 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 (Bozlaker, 2008; Integration Pollution Prevention and Control [IPPC], 2001). These industries may have contributed to the PCB pollution in the study area.

Table 4.2 Atmospheric Σ_{41} PCB concentrations (ng m^{-3}) measured at the air sampling sites.

Points	Min.	Max.	Geometric Mean	Median	Avg $\pm$ SD
P1	0.30	1.10	0.67	0.80	0.7 $\pm$ 0.4
P2	1.04	2.83	1.42	1.18	1.6 $\pm$ 0.9
P3	0.22	0.71	0.40	0.46	0.5 $\pm$ 0.3
P4	0.31	1.08	0.67	0.78	0.7 $\pm$ 0.3
P5	0.33	1.15	0.65	0.70	0.7 $\pm$ 0.3
P6	1.44	2.25	1.70	1.60	1.7 $\pm$ 0.4
P7	0.46	1.01	0.65	0.64	0.7 $\pm$ 0.3
P8	0.61	1.31	0.88	0.87	0.9 $\pm$ 0.3
P9	1.84	4.19	2.71	2.74	2.9 $\pm$ 1.1
P10	2.08	6.51	3.33	3.01	3.7 $\pm$ 2.0
P11	7.83	53.7	23.6	27.2	29 $\pm$ 19
P12	2.19	6.53	3.68	3.63	4.0 $\pm$ 1.9
P13	0.92	8.09	2.47	2.47	3.5 $\pm$ 3.3
P14	0.97	2.51	1.54	1.55	1.6 $\pm$ 0.7
P15	0.89	2.28	1.52	1.63	1.6 $\pm$ 0.6
P16	0.52	0.84	0.67	0.68	0.7 $\pm$ 0.1
P17	0.14	2.05	0.56	0.57	0.8 $\pm$ 0.8
P18	0.13	0.69	0.35	0.41	0.4 $\pm$ 0.2
P19	0.41	1.10	0.71	0.81	0.8 $\pm$ 0.4
P20	0.18	0.54	0.34	0.39	0.4 $\pm$ 0.2
P21	1.35	2.58	2.00	2.15	2.1 $\pm$ 0.5
P22	14.9	35.0	24.8	27.2	26 $\pm$ 8.9
P23	2.44	7.24	4.72	5.31	5.1 $\pm$ 2.0
P24	0.49	8.73	1.84	1.64	3.1 $\pm$ 3.8
P25	3.74	12.7	7.13	7.37	7.8 $\pm$ 3.7
P26	2.52	21.9	6.48	5.76	9.0 $\pm$ 8.8
P27	5.88	37.8	15.9	17.7	20 $\pm$ 14
P28	12.3	35.7	23.6	27.3	26 $\pm$ 13
P29	15.4	231	60.9	65.7	95 $\pm$ 96
P30	3.44	64.5	15.0	15.2	25 $\pm$ 27
P31	7.28	23.5	14.6	16.3	156 $\pm$ 7
P32	0.18	0.53	0.32	0.33	0.3 $\pm$ 0.2
P33	2.53	12.0	6.27	7.14	7.2 $\pm$ 3.9
P34	3.92	39.5	12.0	11.9	17 $\pm$ 16
P35	1.10	12.8	5.94	9.78	8.4 $\pm$ 5.5
P36	0.36	2.31	1.10	1.36	1.3 $\pm$ 0.8
P37	1.45	8.15	3.99	4.68	4.7 $\pm$ 2.8
P38	0.48	6.02	2.05	2.48	2.9 $\pm$ 2.3
P39	0.21	1.45	0.76	1.04	0.9 $\pm$ 0.5
P40	0.38	53.6	3.82	3.47	15 $\pm$ 26

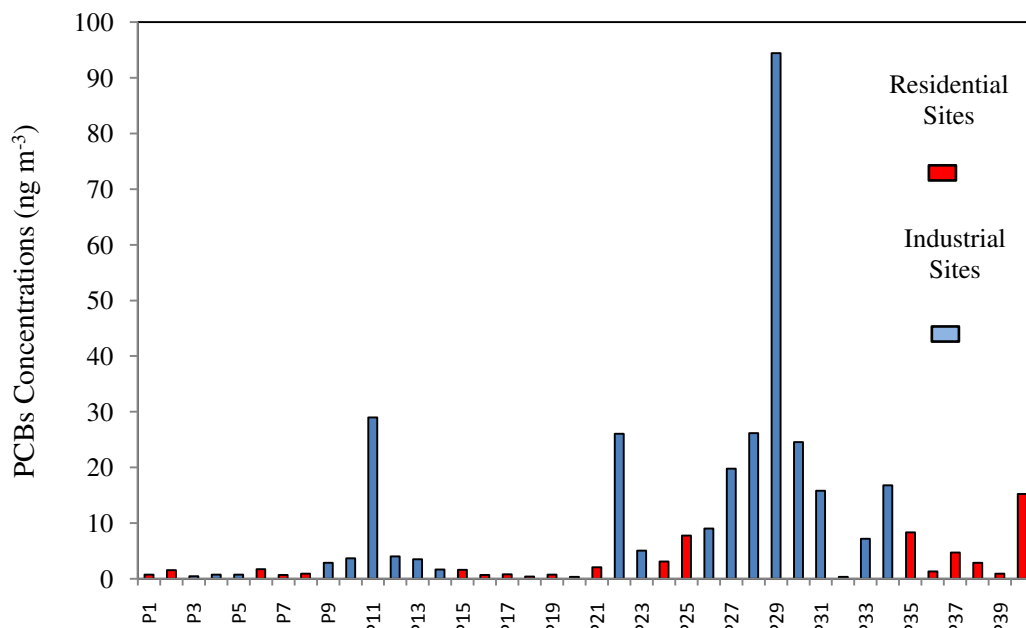


Figure 4.13 Average Σ_{41} PCB concentrations (ng m⁻³) for residential and industrial sites.

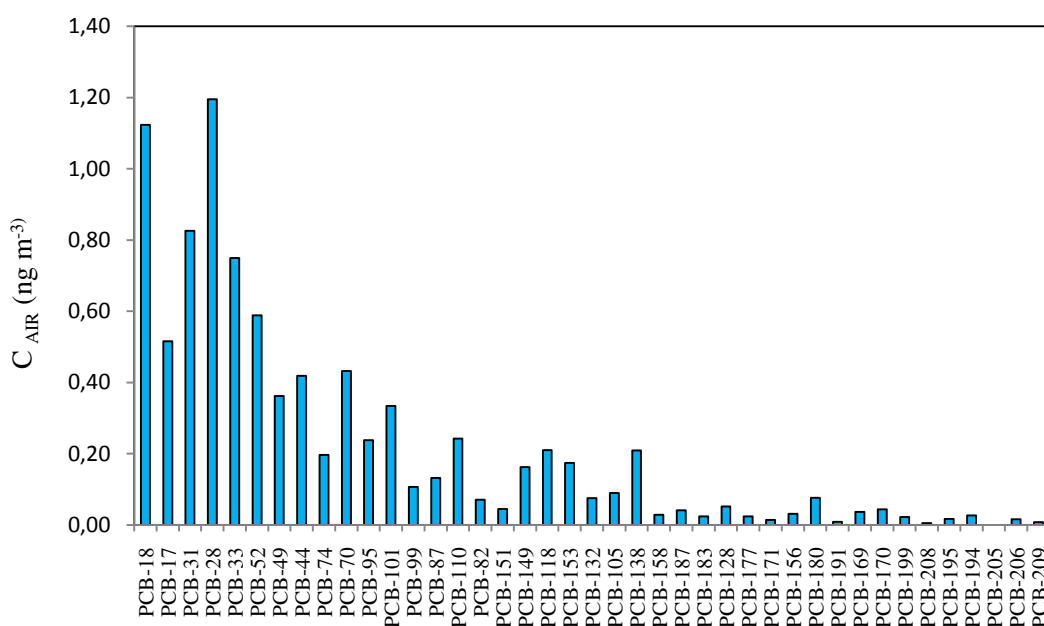


Figure 4.14 Average concentrations (ng m⁻³) of PCB congeners.

Total PCB concentrations in air were dominated by lower chlorinated congeners for all periods. Average gas-phase concentrations of PCB congeners and homolog groups are shown in Figures 4.14 and 4.15. Lower chlorinated congeners were

detected in higher values for all sampling periods (Figure 4.15). This might be due to their volatilization ability that is higher than the heavier PCBs at the same temperatures.

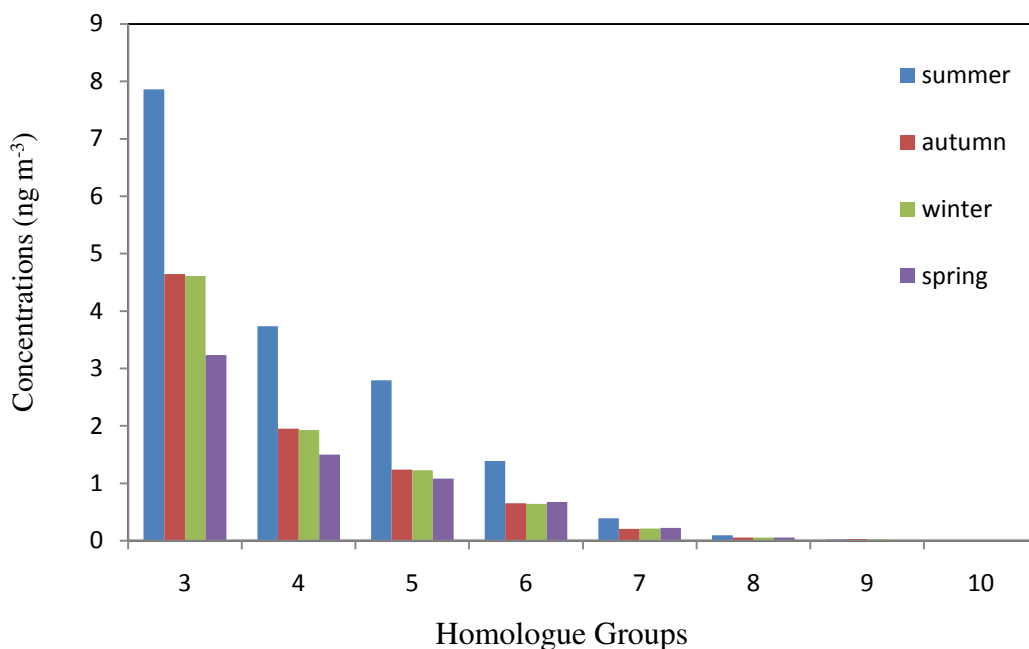


Figure 4.15 Average concentrations of PCB homologue groups (ng m⁻³) for sampling period.

Σ_{41} PCB concentrations from this study are relatively high in comparison with previously reported values for other industrial and urban or rural sites in Figure 4.16. Harner 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 level for the sum of 29 PCBs was approximately measured 787 pg m⁻³ by Roots et al. (2007) in an industrial site. For most samples, 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, 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 (2006) 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 et al., 2004).

It can be clearly seen from Figure 4.16 that the concentrations measured in Aliaga town were usually similar to other studies observed for urban air. However, PCB concentrations measured in Aliaga industrial site were significantly higher than those measured in other studies.

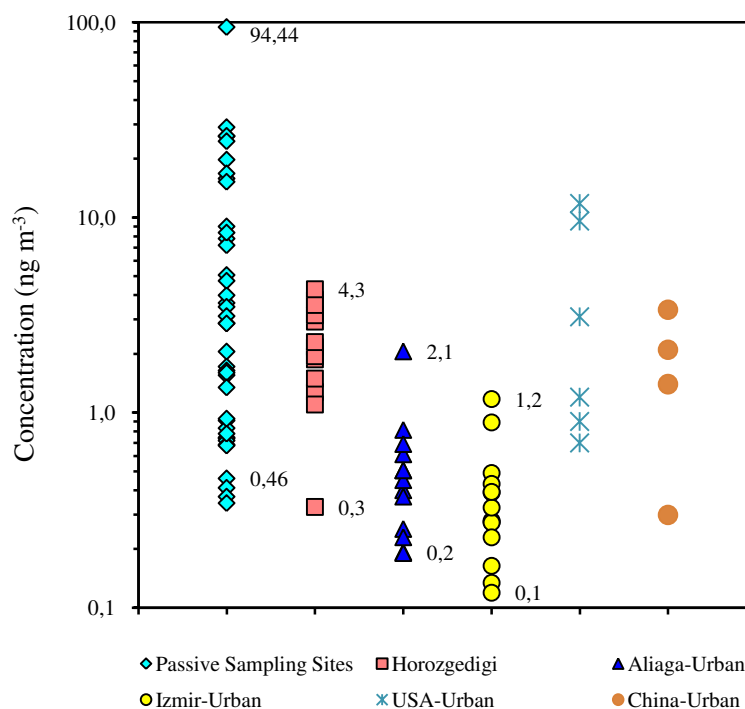


Figure 4.16 Comparison of total PCB concentrations with other studies.

Ambient air Σ_{41} PCB concentrations (ng m⁻³) measured during the different sampling periods in the study area shown in Figures 4.17 to 4.21.

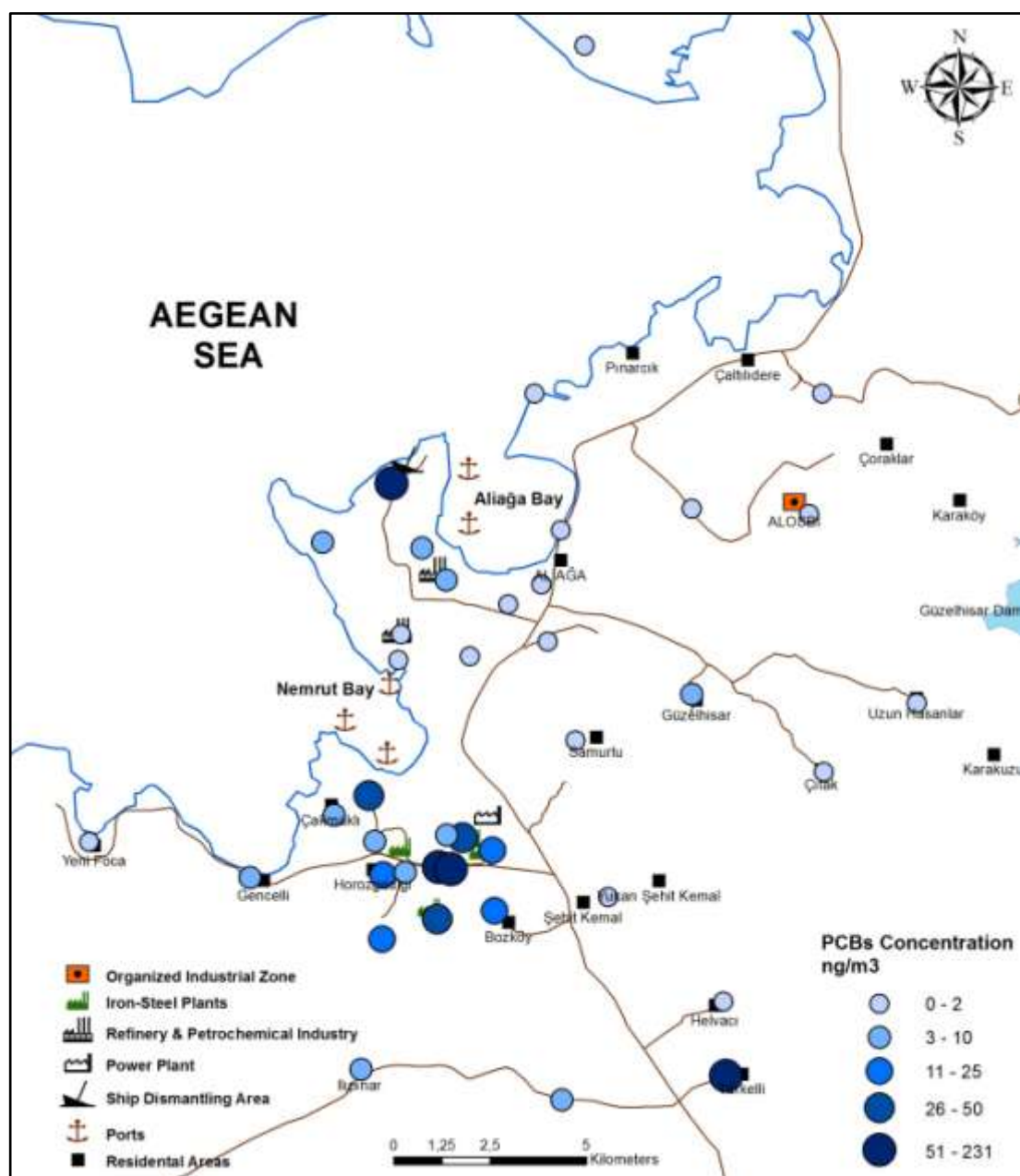


Figure 4.17 Spatial distributions of ambient air $\Sigma_{41}\text{PCB}$ concentrations (ng m⁻³) for summer period.

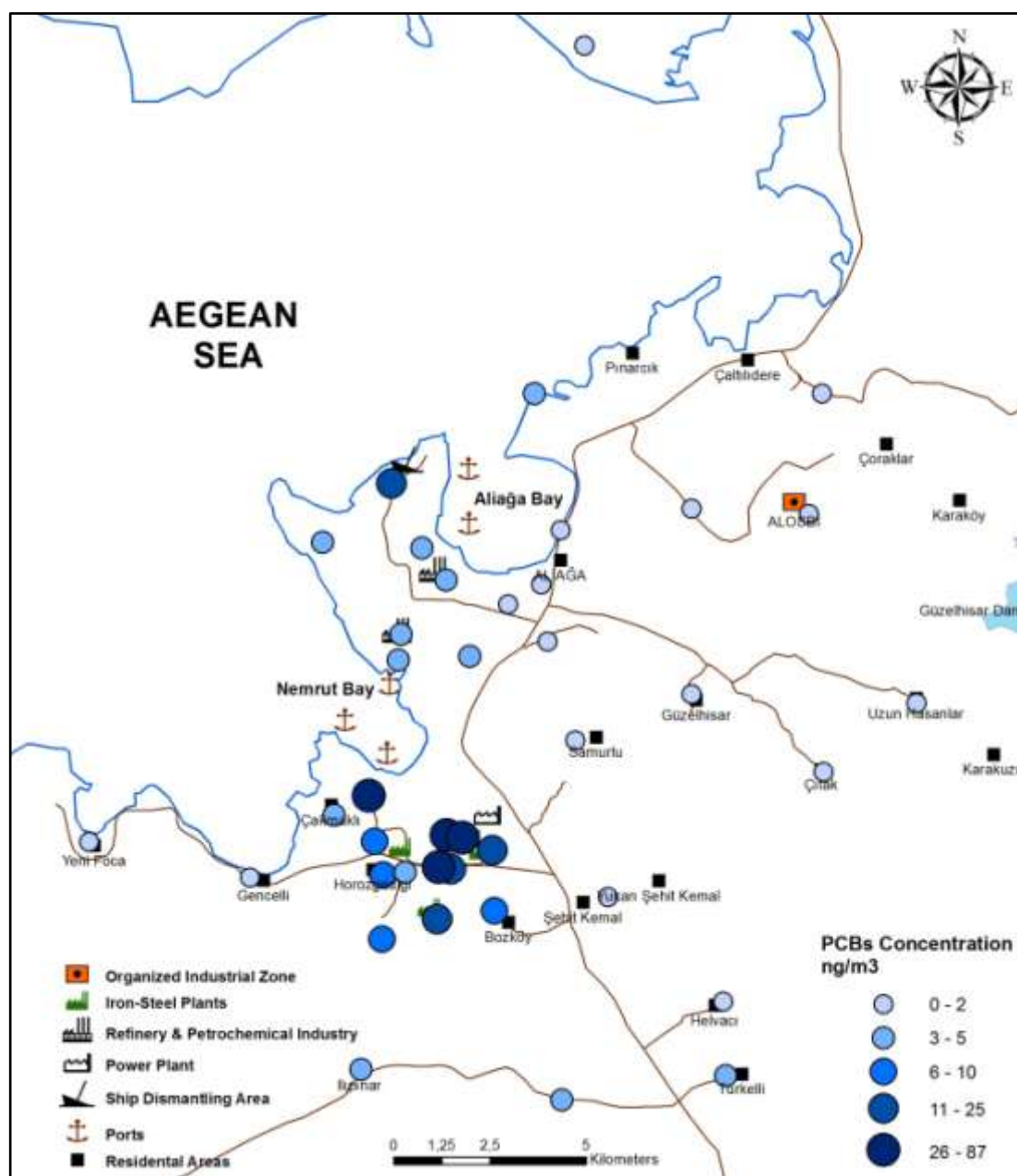


Figure 4.18 Spatial distributions of ambient air $\Sigma_{41}\text{PCB}$ concentrations (ng m^{-3}) for fall period.

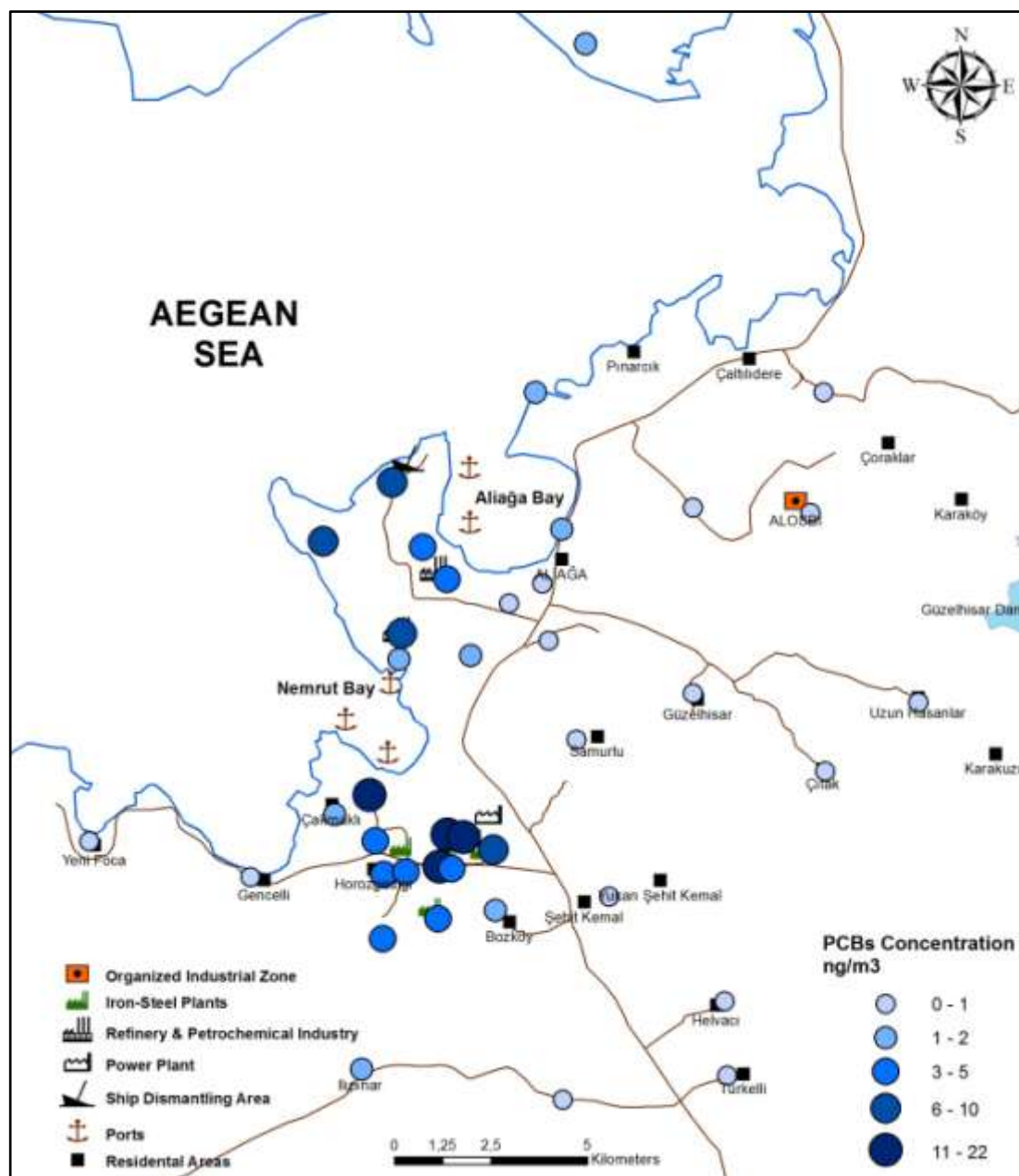


Figure 4.19 Spatial distributions of ambient air $\Sigma_{41}\text{PCB}$ concentrations (ng m^{-3}) for winter period.

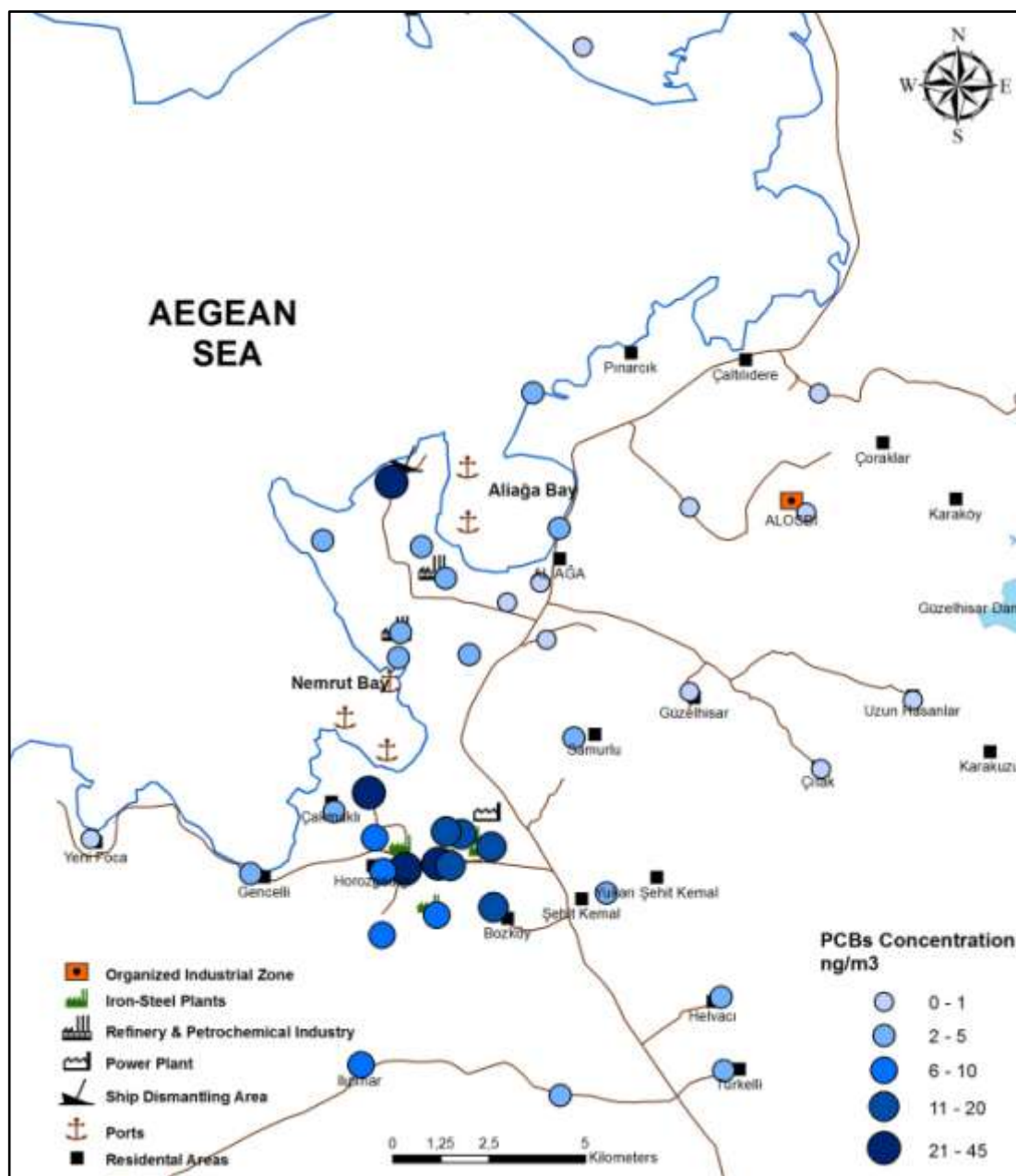


Figure 4.20 Spatial distributions of ambient air $\Sigma_{41}\text{PCB}$ concentrations (ng m⁻³) for spring period.

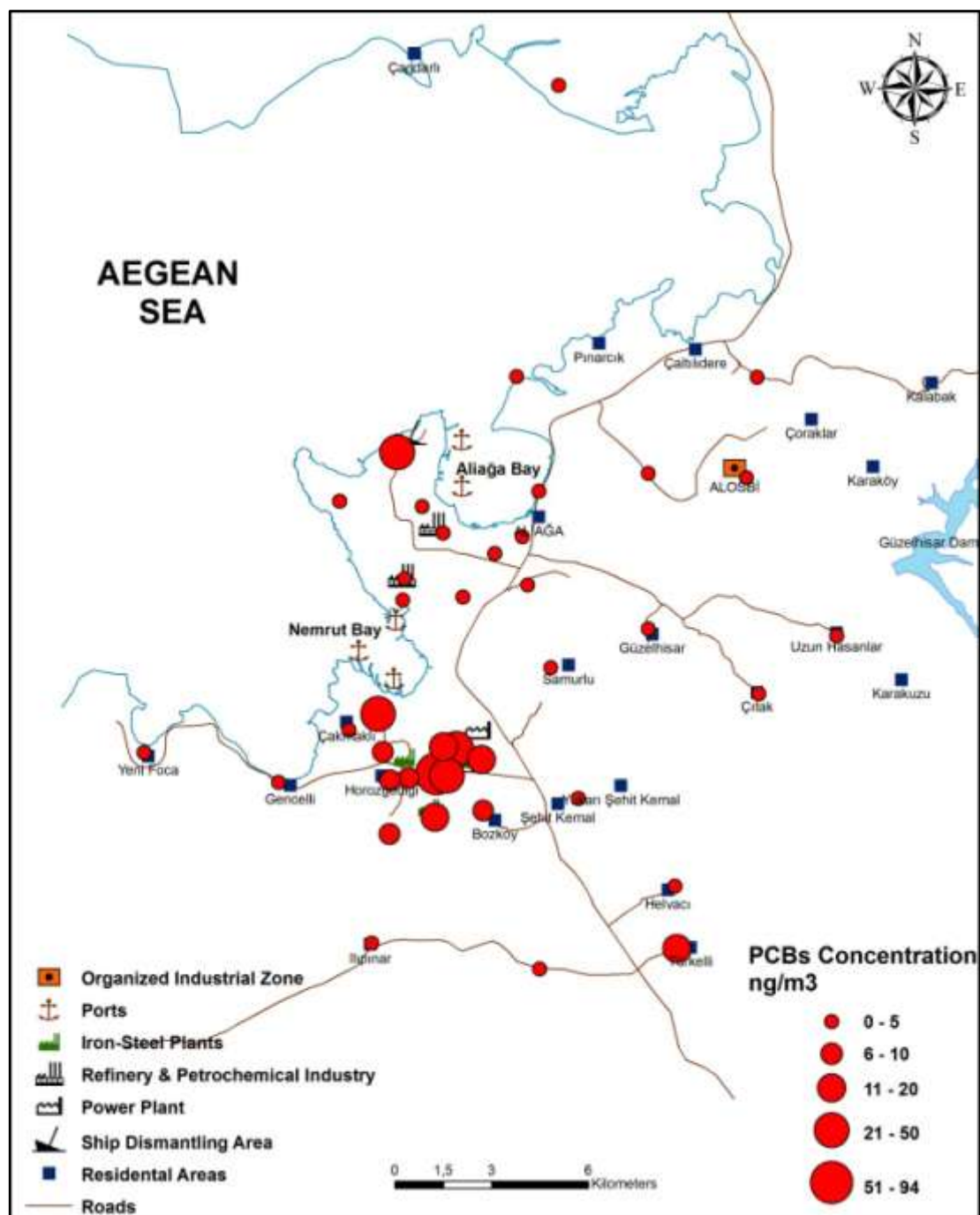


Figure 4.21 Spatial distributions of site-averaged ambient air $\Sigma_{41}\text{PCB}$ concentrations (ng m⁻³).

4.2.1 Soil Concentrations of PCBs

PCBs in soil originate primarily from particulate deposition, wet deposition, and releases from electrical transformers (WHO 1993). The sorption capacity of PCBs onto soil particles depends on the degree of chlorination of individual congeners, soil type, organic matter content, soil pH, and soil moisture content. Table 4.17 shows the PCB concentrations of homologue groups in soil measured at the sampling sites of this study. PCB profiles in rural soil were dominated by the lower chlorinated PCBs. Higher chlorinated congeners were detected especially in sampling points located in industrial sites. This can be explained with the higher chlorinated congeners adsorb more easily onto soil particles than lower chlorinated species and they can be deposited more quickly and low molecular weight compounds have relatively low soil-air partition coefficient.

Table 4.17 PCB concentrations ($\mu\text{g kg}^{-1}$ dry weight) for soil samples in the study area.

Homologue Groups	Min	Max	Geometric Mean	Median	Average	SD
Tri-CBs	0.001	55.65	0.17	0.09	2.01	6.00
Tetra-CBs	0.008	28.57	0.22	0.12	1.56	4.03
Penta-CBs	0.006	24.57	0.19	0.12	1.15	2.91
Hexa-CBs	0.008	22.50	0.22	0.18	1.05	2.53
Hepta-CBs	0.004	8.15	0.13	0.10	0.54	1.24
Octa-CBs	0.009	1.72	0.08	0.07	0.18	0.31
Nona-CBs	0.009	0.83	0.06	0.05	0.10	0.15
PCB-209	0.007	0.78	0.05	0.04	0.09	0.15

The soil Σ_{41} PCB concentrations measured at 40 different sampling points in the Aliğa region were highly variable, and ranged between 0.3 to 461 $\mu\text{g kg}^{-1}$ (dry weight). Similar to air concentrations, the highest soil PCBs concentrations were measured around the iron-steel plants and ship dismantling plants confirming that these are the major PCB sources in the area (see Figures 4.21 and 4.22).

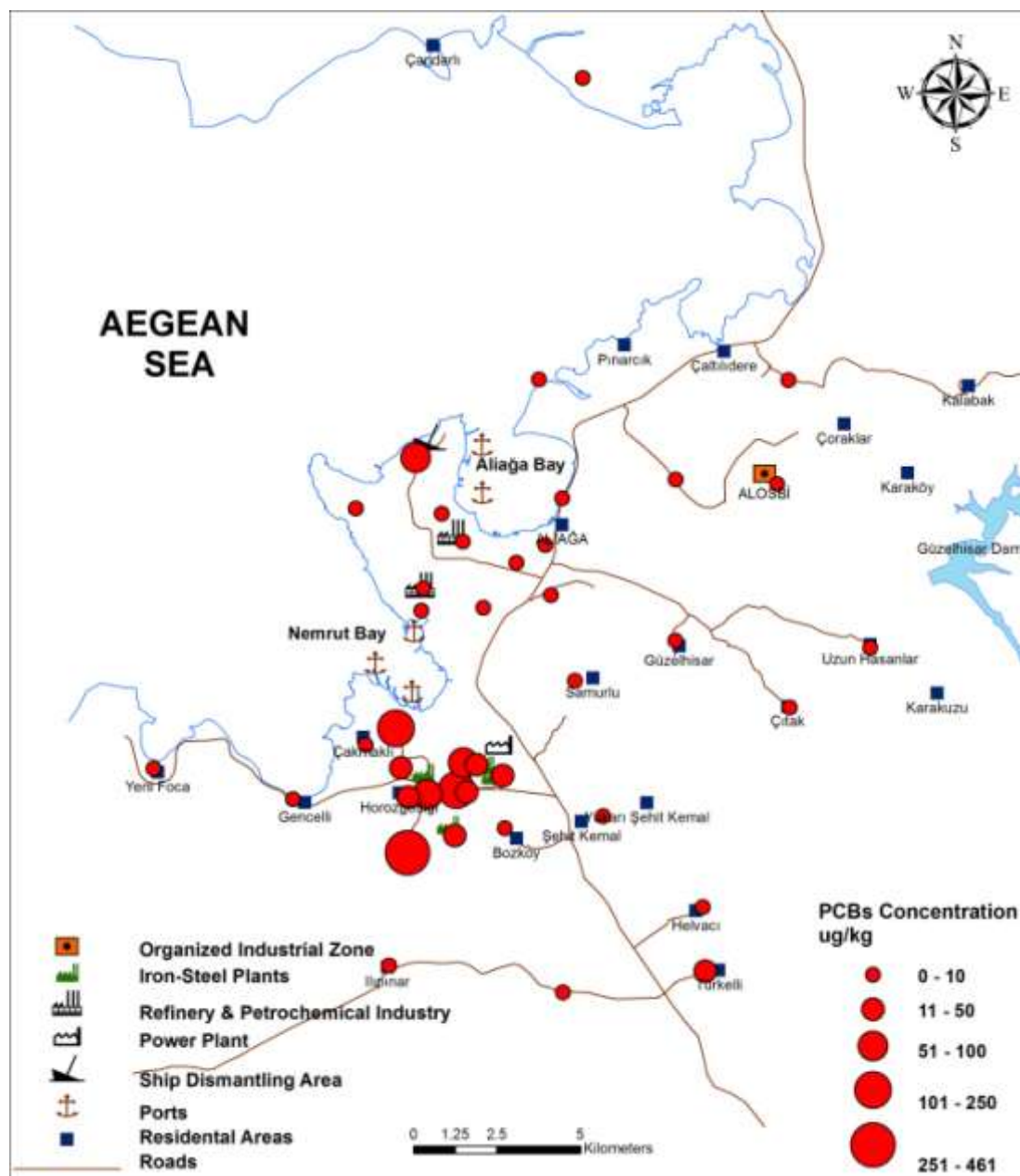


Figure 4.22 The spatial variation of soil PCBs concentrations $\mu\text{g kg}^{-1}$.

Figures 4.10 and 4.22 shows that $\Sigma_{16}\text{PAH}$ and $\Sigma_{41}\text{PCB}$ distribution in soils around the Aliaga study area were similar to each other, suggesting that soils levels may have been influenced by similar sources.

Regression analysis of the data for PCBs gave a strong positive correlation ($r^2=0.80$, $p<0.01$) between the soil and atmospheric concentrations (Figure 4.23). Similar to

PAHs, The statistically significant relationship between air and soil concentrations indicates that PCBs are also exchanged between these two media.

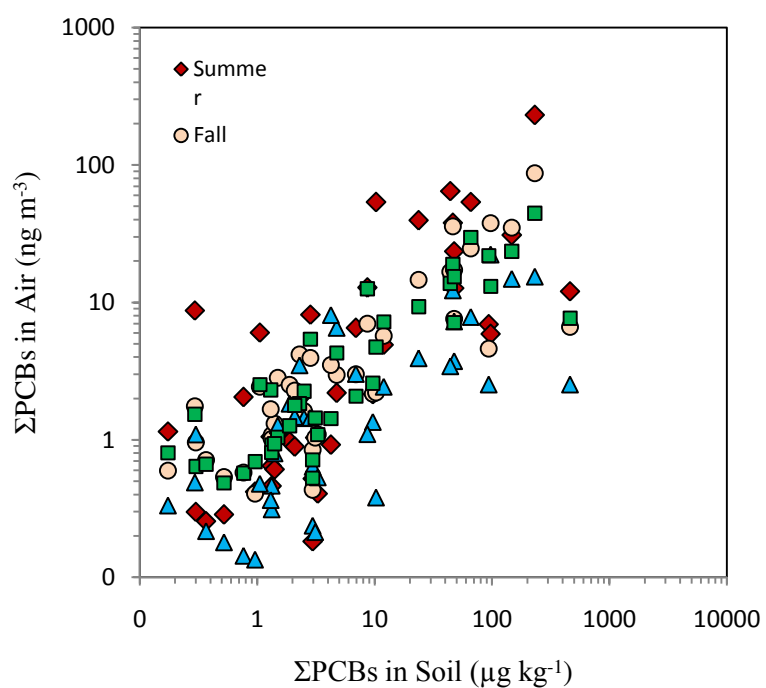


Figure 4.23 Relationship between the soil and air concentrations of ΣPCBs ($r^2=0.80$, $p<0.01$)

CHAPTER FIVE

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

Ambient air samples were collected during four seasons (winter, spring, summer, and fall) at forty different sites in Aliğa industrial region in Izmir, Turkey. Spatial and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined by passive sampling in 2009 and 2010. Study area included suburban and urban sites, a power plant, petroleum refinery, petrochemical industry, several steel plants with electric arc furnaces, scrap metal and slag storage areas, stack filter dust piles, paved and unpaved roads, coal screening plants, ship dismantling plants and several gas stations and tank fields. Phenanthrene was the most abundant PAH at all sites, and all samples were dominated by low to medium molecular weight PAHs (fluorene, fluoranthene and pyrene). The spatial distribution of ambient PAH concentrations indicated that the major PAH sources in the region were steel plants, petroleum refinery, and ship dismantling plants. At urban sites, PAH concentrations were higher in winter indicating that wintertime concentrations were affected by residential heating emissions. On the contrary, highest atmospheric PCBs concentrations were observed in summer, probably due to increased volatilization from polluted surfaces at higher temperatures. Low to medium molecular weight PCBs (tri-, tetra-, penta-CBs) were the most abundant compounds in air for both seasons. Results also indicated that steel plants and ship dismantling plants were the major PCB sources in the region. A similar spatial variation was observed for soil concentrations of PAHs and PCBs. Air and soil PAH and PCB concentrations were correlated significantly indicating the interaction of these compartments.

Conclusions drawn from this study can be highlighted as follows:

- Ambient air concentrations of PAHs were found to be higher in winter than the other periods, indicating that wintertime concentrations were affected by residential heating emissions.

- Results for PAHs showed that *steel plants, petroleum refinery, ship dismantling plants, and petrochemical plant* are the major sources in the region
- Recent studies have shown that even the banned PCBs still have ongoing sources. The results of the present study confirmed these findings.
- High PCB concentrations measured in this study were probably due to proximity of the sampling sites to the steel plants. Higher concentrations measured during summer may be due to volatilization from terrestrial surfaces as a result of warmer temperatures.
- PCBs may be present in the scrap, emitted when the material is heated up during steel production or they may form as a result of thermal process.
- The most important PCB sources in study area were observed as *steel plants and ship dismantling plants*.
- The statistically significant relationship between air and soil PAH and PCB concentrations indicated that these pollutants are exchanged between these two media. However, the direction of exchange should be further investigated on a compound basis by calculating the fugacity ratios for different seasons.

5.2 Suggestions

The results of the present study have indicated that petrochemical complex, petroleum refinery, iron-steel plants and ship dismantling areas in Aliaga industrial region are potential PAH and PCB sources. Therefore, emissions from these sources have to be reduced.

In addition to PAHs, PCBs, other persistent organic pollutant concentrations must also be measured in the area and their possible sources must be determined. Then, elimination or restriction the production, use and release of these chemicals should be kept under control to protect human health and the environment. Precautions must be taken by the authorities to reduce their possible risk to human health and to the

environment. According to results of this study, Aliaga industrial region is an effectively contributing area to atmospheric PAHs and PCBs. Considering the toxic effects of these chemicals it could be concluded that these compounds cause health risks for humans particularly living and working around the industrial area.

Considering the fate and behavior of PAHs and PCBs in environmental media like soil, sea water, sediment and also living organisms (i.e., vegetation), studies related to the Aliaga industrial region should be expanded in order to determine concentrations of these pollutants in other media.

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