DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF SPATIAL AND HISTORICAL VARIATION OF AIR POLLUTION IN INDUSTRIAL REGIONS USING PAHs AND PCBs IN TREE COMPONENTS, SOIL AND AIR

by
Ezgi ÖZGÜNERGE FALAY

November, 2016
İZMİR

INVESTIGATION OF SPATIAL AND HISTORICAL VARIATION OF AIR POLLUTION IN INDUSTRIAL REGIONS USING PAHs AND PCBs IN TREE COMPONENTS, SOIL AND AIR

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Environmental Engineering, Environmental Engineering Program

by
Ezgi ÖZGÜNERGE FALAY

November, 2016
İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"INVESTIGATION OF SPATIAL AND HISTORICAL VARIATION OF AIR POLLUTION IN INDUSTRIAL REGIONS USING PAHs AND PCBs IN TREE COMPONENTS, SOIL, AND AIR"** completed by **EZGİ ÖZGÜNERGE FALAY** under supervision of **PROF. DR. TOLGA ELBİR** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Tolga ELBİR

Supervisor

Prof. Dr. Mustafa ODABAŞI

Thesis Committee Member

Prof. Dr. Sait C. SOFUOĞLU

Thesis Committee Member

Prof. Dr. Doğanay TOLUNAY

Examining Committee Member

Doç. Dr. İlkü Alver Şahin

Examining Committee Member

Prof. Dr. Emine İlknur CÖCEN

Director

Graduate School of Natural and Applied Sciences

ACKNOWLEDGEMENTS

Firstly, I would like to thank my advisor Prof. Dr. Tolga ELBİR for his invaluable suggestions, guidance, sincere and support during research and preparing of the thesis. His encouragement and valuable advice often served to give me a sense of direction during my studies. I would like to thank my thesis committee member Prof. Dr. Mustafa ODABAŞI and Prof. Dr. Sait Cemil SOFUOĞLU for their strong support, valuable suggestions on my research and helpful comments throughout this study. Also, I would like to thank Prof. Dr. Doğanay TOLUNAY who has made a significant contribution to this study by giving advice, guidance, and support.

This study supported by The Scientific and Technical Research Council of Turkey (TUBITAK) (Project No: TUB/110Y096). I would like to thank to TUBITAK for this financial support. In particular, I also thank to Dr. Yetkin DUMANOĞLU, Dr. Melik KARA, MSc. Barış YAMAN, Hasan ALTIOK and Hamza KESKİN for their help during my field and laboratory studies.

I am also thankful to MSc. Didem MUŞLU BAYSAL, MSc. Yağmur Meltem AYDIN and MSc. Gizem TUNA TUYGUN for their moral motivation and friendship. I especially would like to thanks to Dr. Duyuşen GÜVEN for her very valuable help and morally supports in every time.

I especially thank to my parents, Atila ÖZGÜNERGE, Aysun ÖZGÜNERGE, Mert ÖZGÜNERGE and Pelin BİLGEN ÖZGÜNERGE for their love, morally support, patience, encouragement and help during this time.

Finally, I would like to greatly thank to my husband Gökay FALAY who encouraged and supported me to overcome the difficulties of preparing this thesis. I dedicate my thesis to my lovely daughter Defne FALAY, because completion of this work would not have been possible without her presence and love.

Ezgi ÖZGÜNERGE FALAY

INVESTIGATION OF SPATIAL AND HISTORICAL VARIATION OF AIR POLLUTION IN INDUSTRIAL REGIONS USING PAHs AND PCBs IN TREE COMPONENTS, SOIL AND AIR

ABSTRACT

Several persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were measured in needle, branch, bark, and stem samples in pine tree species collected from 27 different sites (industrial and background sites) in Aliaga and Iskenderun that are the major industrial areas in Turkey. Soil, litter, and ambient air samples were also collected to investigate the relationships between the air and soil, litter, and tree components. Concentrations decreased with distance from the major sources and the lowest ones were measured at background sites. The spatial distribution of POPs indicated that the major sources in the regions are the iron-steel plants, ship-breaking, petrochemical plants and the petroleum refinery. Correlations of ambient air levels to those measured in soil, litter, and tree components were significant showing that POPs are exchanged between atmosphere and these compartments. Historical variations of all POP concentrations indicated an increasing trend with time in parallel to industrialization. These results indicated that tree components (needle, bark, branch), litter and soil could be used to determine the spatial variations while tree rings could be used to investigate the historical trends of atmospheric POPs in a region. Ambient air POP concentrations were also estimated using a bark/air partitioning model. The modeled/observed ratios were close to 1.0 for several compounds and the results showed that the atmospheric POP concentrations could be estimated from the bark measurements. Generally, the highest POP quantities were accumulated in the stem followed by needles according to the inventory study results. Overall, the highest POP quantities were accumulated in soil followed by trees and litter in Iskenderun while the highest POP amounts were stored in soil for PCBs and in trees for PAHs in Aliaga. It is showing that vegetation is an important reservoir accumulating the POPs in addition to soil in a region.

Keywords: Air pollution, historical variation, persistent organic pollutants, spatial variation, tree component, tree ring

AĞAÇ BİLEŞENLERİNDE, TOPRAK VE HAVADA PAH'LAR VE PCB'LER YARDIMIYLA ENDÜSTRİYEL BÖLGELERDEKİ HAVA KİRLİLİĞİNİN MEKANSAL VE TARİHSEL DEĞİŞİMİNİN İNCELENMESİ

ÖZ

Türkiye'deki önemli sanayi bölgelerinden olan İskenderun ve Aliağa'da 27 farklı noktadan (sanayi ve kontrol noktaları) toplanan çam ağacı örneklerinin ibre, dal, kabuk ve yıllık halkalarında bulunan polisiklik aromatik hidrokarbonların (PAH'lar) ve poliklorlu bifenillerin (PCB'ler) konsantrasyonları ölçülmüştür. Aynı noktalardan toprak, ölü örtü ve dış hava örnekleri de alınarak toprak-ölü örtü-ağaç bileşeni-hava arasındaki ilişkiler incelenmiştir. Kirletici konsantrasyonları kaynaklardan uzaklaştıkça azalmış, en düşük değerler bu bölgelerden uzak kontrol noktalarında ölçülmüştür. Kalıcı organik kirleticilerin yerel dağılımı bölgelerdeki önemli kirletici kaynakların demir-çelik tesisleri, petrol rafinerisi, gemi-söküm faaliyetleri ve petrokimya tesisleri olduğunu göstermektedir. Dış hava ile toprak, ölü örtü ve ağaç bileşenleri arasında önemli korelasyonların bulunması bu ortamlar arasında etkileşim olduğunu belirtmektedir. Yıllık halkalardaki kalıcı organik kirleticilerin (KOK'lar) konsantrasyonları endüstrileşmeye paralel olarak iki örnekleme bölgesinde de zamanla artış göstermiştir. Bu bulgular, bir bölge atmosferinde bulunan KOK'ların tarihsel gelişimi incelenirken ağaç halkalarının, yerel dağılımı incelenirken ise ağaç bileşenleri (ibre, dal, kabuk), ölü örtü ve toprağın kullanılabileceğini göstermektedir. Dış havadaki KOK'ların konsantrasyonları bir ağaç kabuğu-hava faz dağılım modeli kullanılarak da hesaplanmıştır. Modellenen / ölçülen KOK konsantrasyon oranları bir çok bileşik için 1,0'e yakın bulunmuştur. Bu durum ağaç kabuğunda ölçülen KOK konsantrasyon miktarının havada ölçülen KOK konsantrasyon miktarını tahmin etmek için kullanılabileceğini göstermiştir. Yapılan envanterleme çalışması sonuçlarına göre ağaç bileşenleri içerisinde en fazla birikimin sırasıyla yıllık halka ve ibrelerde olduğu görülmüştür. Envanterleme sonuçları ağaç, toprak ve ölü örtü dâhil olmak üzere genel olarak incelendiğinde en yüksek birikim miktarları İskenderun'da sırasıyla toprak, ağaç ve ölü örtüye aittir. Aliağa'da ise, PAH'lar en fazla ağaçlarda, PCB'ler ise toprakta birikmiştir. Bu durum ise bir bölgede toprağın yanı sıra

bitkilerin de önemli miktarda KOK biriktirme özelliğine sahip olduğunu göstermektedir.

Anahtar kelimeler: Ağaç bileşeni, hava kirliliği, kalıcı organik kirleticiler, tarihsel gelişim, yerel dağılım, yıllık halka

CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

CHAPTER ONE
INTRODUCTION

1.1 Introduction

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological and photolytic processes. Because of this, they are toxic chemicals that adversely affect human health and the environment around the world. They can be transported by wind and water therefore most POPs are generated in one country and they affect people and environment far from where they are used and released. They persist for long periods in the environment and they can accumulate and pass from one species to the next through the food chain (United States Environmental Protection Agency [U.S. EPA], 2002a).

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are the different classes of POPs. In the environment, PAHs have both natural and anthropogenic sources. Natural sources include forest fires, volcano activities, and biosynthesis by bacteria and plants. These sources contribute to the background level of PAHs in the environment. However, anthropogenic sources such as incomplete combustion of fossil fuels, waste incineration, vehicle exhausts, and industrial processes are the predominant emission sources of PAHs (U.S. EPA, 2003). Polychlorinated biphenyls (PCBs) have no natural sources and they have been commercially prepared by chlorination of biphenyl (Park, 2000). Due to their thermal stability, excellent dielectric properties, and resistance to oxidation, acids and bases, they were mostly used in the manufacture of dielectric fluids in transformers and capacitors, transmission fluids, paints, lubricants, plastics, adhesives, coating compounds, cars and electrical household appliances (Park, 2000; U.S. EPA, 2003). PCBs have been released into the environment by open burning, waste incineration, vaporization from contaminated surfaces and products containing PCBs, and improper disposal or leakage of oil from transformers and capacitors (Breivik et al., 2002a; U.S. EPA, 2003). Because of their toxicity and resistance to environmental degradation, the production and use of PCBs are banned in many countries.

However, due to their persistence, PCB levels in the environment are declining slowly, and this makes them ubiquitous.

POPs are partitioned between the gas and particle phases or primarily found in one of these two phases. They partitioning between the gas and particle phase based on their concentrations, the ambient air temperature, supercooled liquid vapor pressures (P_L), octanol-air partition coefficients (K_{OA}) and the concentration of particulate matter present in the air (Harner & Bidleman, 1996, 1998; Harner & Shoeib, 2002; Odabasi et al., 2006a; Cetin & Odabasi, 2008). Fate, transport, atmospheric residence time, and removal processes (dry deposition or wet deposition) of POPs are mainly affected by their gas and particle phase partitioning (Tasdemir et al., 2004a, 2004b). POPs are exchanged between atmosphere and natural surfaces (water, soil, and vegetation) via adsorption or volatilization (Cetin & Odabasi, 2007; Bozlaker et al., 2008a, 2008b).

POPs are widespread organic contaminants having adverse effects on environment. Therefore, atmospheric POP concentrations have to be monitored closely. Monitoring the POPs to determine their spatial variations has technical, physical, and economical limitations at several sites when active air samplers are used. Sampling and analyzing tree needles/leaves and barks have been used to determine the spatial distribution of POPs. This is a convenient and low-cost alternative method (Zhu & Hites, 2006; Wyrzykowska et al., 2006, 2007; Zhao et al., 2008; Loganathan et al., 2008; Salamova & Hites, 2010; Ratola et al., 2011a, 2011b; Gueguen et al., 2011; Hermanson & Johnson, 2007, 2015; Peverly et al., 2015; Odabasi et al., 2015).

Vegetation is an important environmental medium accumulating POPs since it contains hydrophobic lipids and waxes. It covers the majority of the terrestrial surface of earth (~80%) (Simonich & Hites, 1994). High surface roughness of forest canopies leads to fast uptake and this has been shown to be an effective filtering mechanism for atmospheric POPs (Su et al., 2007; Choi et al., 2008). Vegetation can be used to indicate atmospheric contamination levels of organic pollutants. Various

plants (moss and lichen), and tree components (leaves and bark) have been employed as bioindicators to monitor pollution levels of airborne POPs. In many recent studies, vegetation has been used as a passive sampler of POPs (Schulz et al., 1999; Alfani et al., 2001; Gerdol et al., 2002; Piccardo et al., 2005) to determine regional and global contamination patterns. The uptake mechanism of organic pollutants by vegetation is affected from the chemical and physical properties of pollutant (such as their molecular weights, aqueous solubilities, and vapour pressures), environmental conditions (the ambient air temperature), plant species and structure of plant (stoma number and surface area of leaf) (Simonich & Hites, 1995; Holoubek et al., 2000).

Recent studies on ambient air and soil sampling have indicated that Iskenderun and Aliaga industrial regions are polluted substantially by several POPs (Odabasi et al., 2010). Especially, iron and steel industries are "hot spots" in these regions because they emit significant amounts of PAHs and PCBs as POPs (Cetin & Odabasi, 2007; Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009, 2010).

Historical variations of atmospheric POPs are mainly determined by the analysis of dated sediment cores while sampling tree components like needles/leaves and bark are convenient to determine the spatial distribution of POPs. There are specific studies (Yin et al., 2011a, 2011b; Kuang et al., 2011, 2014, 2015; Rauert & Harner, 2016) that measured the organic pollutants in tree rings of trees to determine the historical trends of air pollution. However, there is no previous study investigating organic pollutants in tree rings in Turkey. Therefore, the novelty of this study is investigate the historical trends of air pollution by determining concentration of POPs using tree rings for the first time in Turkey. The aim of this study is investigate the spatial distribution of air pollution in the severely polluted industrial regions (Aliaga and Iskenderun) in Turkey by determining concentrations of organic pollutants sorbed in tree components (bark, needle, branch, stem), litter and soil.

The specific objectives of this study are;

1. Investigation of the relationships between soil-tree-ambient air compartments by measuring pollutant concentrations simultaneously in soil, tree components and ambient air

2. Evaluation of the total mass of POPs stored in different compartments by inventorying the amounts accumulated in tree components, litter, and soil

3. Optimization of a mathematical mass transfer model to estimate the ambient air POP concentrations by using measured POP concentrations in tree barks

For these purposes, concentrations of PAHs and PCBs were measured in needle, branch, bark, and tree ring samples from two pine tree species (*Pinus brutia* and *Pinus pinea*) commonly grown in Aliaga and Iskenderun industrial regions. Samples collected from 27 different sites (industrial and background sites) in each industrial region representing the spatial distribution of pollutants. Soil, litter and ambient air samples were also collected to investigate the correlations between the soil, tree and ambient air.

This study consists of five chapters. An overview and objectives of the study are presented in Chapter 1. Chapter 2 reviews the general information about persistent organic pollutants and previous studies related to this work. Experimental work, analyses, model and inventory studies are explained in Chapter 3. Results and discussions are presented in Chapter 4. Chapter 5 provides the conclusion and suggestions drawn from this study.

CHAPTER TWO
LITERATURE REVIEW

This chapter gives information about the uptake mechanism of organic pollutants by vegetation, effects of air pollutants on plants, general properties of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), transportation and environmental effects of persistent organic pollutants (POPs). At the end of the section, the previous work results about analyzed POPs are presented and discussed.

2.1 Vegetation and Organic Pollutants

Biomonitoring has been used for many years to assess the amounts of organic contaminants in the environment. Generally, vegetation has been used for biomonitoring to identify the global contamination level of organic pollutants (Calamari et al., 1991; Morosini et al., 1993; Strachan et al., 1994; Simonich & Hites, 1995). More than 80% of the Earth's land surface is covered with vegetation, and vegetation generally has 6-14 times more surface area than the land on which it is growing (Simonich & Hites, 1994). In addition, most plant surfaces exposed to the air are covered with a wax or lipid layer to prevent excessive evapotranspiration. This combination of high surface area and the presence of waxes and lipids suggest that vegetation probably plays a significant role in the annual POP cycling (Simonich & Hites, 1995). There are advantages to using plants instead of ordinary air sampling. Vegetation integrates contamination over time and it is much easier and cheaper to collect than air samples. POPs have been measured in plant components especially in needles and bark in several studies (Wang et al., 2004; Zhao et al., 2006; Netto et al., 2007; Wyrzykowska et al., 2007; Loganathan et al., 2008; Ratola et al., 2009, 2011a, 2011b; Yin et al., 2011a, 2011b; Kuang et al., 2011, 2014; Odabasi et al., 2015).

Forests play an important role in trapping atmospheric POPs and transferring them to terrestrial ecosystems with falling leaves (Simonich & Hites, 1995; Horstmann & McLachlan, 1998; Collins et al., 2006; Nizzetto et al., 2006). Several

studies have shown that forests are effective air filters for organic pollutants (Simonich & Hites, 1994; Barber et al., 2004; Su et al., 2007; Nizzetto et al., 2006; Choi et al., 2008). Although vegetation contains only a small percentage of the total global POP burden, it has a large surface area in intimate contact with the air, and undergoes marked short-term temperature fluctuations. The vegetation's POP burden is envisaged as constituting a large percentage of the readily exchangeable fraction of the global burden of POPs. The rapid cycling of POPs between vegetation and air may have the direct effect of buffering local air concentrations. Another important effect that vegetation has on atmospheric POP concentrations is the "*Forest Filter Effect*" (Nizzetto et al., 2006). Due to the high deposition velocities and canopy densities in forests, vegetation scavenges large quantities of POPs from the air and it reduces atmospheric POP concentrations. In addition, the POPs are subsequently deposited to the soil and soil POP concentrations increase below the canopy (Simonich & Hites, 1994; Meijer et al., 2003).

Different plant species have been used for biomonitoring of POPs within cities, countries, and continents. Evergreen plants such as conifers are well suited for biomonitoring of POPs both on local, regional and global level. They can be sampled all around the year and several year classes of needles can be found on the individual trees. Biomonitoring of organic contaminants with conifers has been used to observe spatial and temporal patterns of atmospheric organic pollutants (Tremolada et al., 1996; Weiss, 1998; Ockenden et al., 1998; Howsam et al., 2000; Piccardo et al., 2005; Wang et al., 2009; Oishi, 2013). In particular, pine trees (Piccardo et al., 2005; Wang et al., 2009; Lehndorff & Schwark, 2004; Ratola et al., 2010a, 2010b, 2011a, 2011b), lichens (Augusto et al., 2009, 2010; Blasco et al., 2006, 2008), and mosses (Holoubek et al., 2000; Gerdol et al., 2002; Liu et al., 2005; Krommer et al., 2007) are good bioindicators of atmospheric organic contaminants.

Pine trees can be used for biomonitoring mainly through the retention properties exhibited by the waxy layer of their needles (Simonich & Hites, 1995; Ratola et al., 2009). The worldwide presence of different pine species allows broad estimation of the levels of several POPs and establishes bioaccumulation or transport patterns

between different locations. Several studies have reported that the biomonitoring properties of needles collected from different pine species such as *Pinus sylvestris* (Tremolada et al., 1996; Holoubek et al., 2000), *Pinus strobus* (Wagrowski & Hites, 1997; Lang et al., 2000), *Pinus nigra* (Lehndorff & Schwark, 2004), *Pinus pinaster* (Piccardo et al., 2005), and *Pinus pinea* (Ratola et al., 2006) towards persistent organic pollutants.

2.1.1 Organic Pollutant Accumulation in Vegetation

Plants take organic pollutants from soil with roots and from air with aboveground components (leaves, needles, seeds, shoots, and bark) (Wimmer, 1997). These pollutants can be accumulated in various plant tissues, returned to the soil or the atmosphere and transported to different tissues of the plant (Weiss et al., 2003). Persistent organic pollutants are taken from atmosphere by aboveground plant components mostly through the stomata or cuticle in the leaves (Trapp, 2000). Structure of a leaf is given in Figure 2.1.

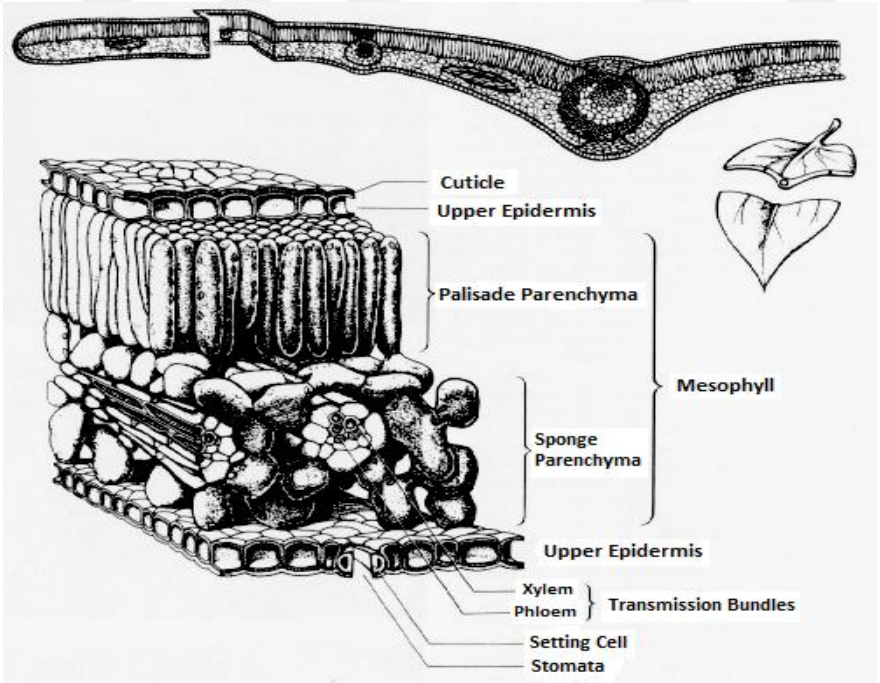


Figure 2.1 Structure of a leaf (Wimmer, 1997)

Leaf has a complex structure and it consist of four different tissues called the mesophyll, epidermis, phloem and xylem. The epidermis constitutes the outer wall of the leaf. In addition, waxy cuticle layer of leaf are released by cells of the epidermis that reduces the water loss of leaf. The thickness of the cuticle layer varies according to the plant species and climatic conditions. Mesophyll is the soft inner tissue in the middle of the leaf. Mesophyll cells are parenchyma cells filled with chloroplasts. These cells include spaces. Spaces in cells open to the atmosphere with stoma and thereby provide an effective photosynthesis by facilitating the exchange of gasses. The vessels of the leaf contain phloem and xylem. Xylem is above the vessels and phloem is below the vessels. Phloem transports substances from leaves to other plant organs when xylem transports water and water-soluble substances from roots to leaves (Graham et al., 2004).

Transpiration is controlled by stoma in plants. Stoma locates on the epidermis and provides the gas exchange between the atmosphere and the plant. Stoma can be above, below or both sides of the leaf according to the plant species. Stoma opens during the day and closes at night in many plants (Graham et al., 2004). Carbon dioxide (CO_2), oxygen (O_2) and air pollutants are taken from the atmosphere by plants directly. This process mostly takes place by diffusion through the stoma. In addition, pollutants can get into the leaf by diffusion and adsorption through the cuticle (Wimmer, 1997).

The cuticle is a heterogeneous layer and consists of both the polymer matrix and soluble cuticular lipids. Cutin is a three-dimensional polymerized tissue (fatty acids occured by the ester, peroxide and ether) and may constitute 20% to 84% of the cuticle layer (Wimmer, 1997). Wax layer (epicuticular wax) is embedded in the cutin layer. Epicuticular waxes can be moved away from the leaves by mechanical effects or degreasing agent. Various studies have revealed that precipitation of acid rains and harmful substances on the leaf surface disrupt the structure of epicuticular waxes and thus affect the permeability of the cuticle layer (Wimmer, 1997).

Persistent organic pollutants are adsorbed on the leaf surface and then entered into the cuticle layer by diffusion. Then, pollutants that reach the walls of the epidermal cells pass membrane of the cells and reach into the cells (Wimmer, 1997). Gaseous pollutants can also be entered into plants via lenticels. Gas (water vapor, O_2, CO_2, etc.) exchange of tissues in the plants are provided by lenticels. Lenticels come out slightly on the stem or branches and they can be seen with the eye. They can be line, oval or round-shaped structures (Graham et al., 2004).

Pollutants in the annual rings examine the historical changes of air pollution in a region. Dendrochemistry means that are analyze the pollutants in tree rings to study the historical changes in atmospheric chemistry. The basic assumption of dendrochemistry is the contaminants recorded in tree rings are not mobile and they could be used to reflect the historical change of the environment (Yin et al., 2011a, 2011b). Dendrochemistry has been used commonly for inorganic pollutants and trace elements. There have been relatively few reports on dendrochemistry tracing the historical changes in organic pollutants (Wang, 2004; Wilczynski, 2006; Yin et al., 2011a, 2011b; Kuang et al., 2011, 2014, 2015; Rauert & Harner, 2016).

2.1.2 Mechanism of POPs Uptake by Vegetation

The pollutant may enter the plant by partitioning from contaminated soil to the roots and be translocated in the plant by the xylem. The xylem transports water from the roots to the leaves by transpiration. Organic pollutants may also enter vegetation from the atmosphere by gas-phase and particle-phase deposition onto the waxy cuticle of the leaves or by uptake through the stoma and be translocated by the phloem. The phloem transports photosynthatates to the roots and to other plant tissues (Simonich & Hites, 1995; Chaney, 2000; Collins et al., 2006). These pathways are affected by three factors (Simonich & Hites, 1995; Holoubek et al., 2000; Howsam et al., 2000; Barber et al., 2004). These factors are chemical and physical properties of pollutant (lipophilicity, water solubility, Henry's law constant, molecular weight, vapor pressure), environmental conditions (ambient air temperature, organic content of soil), and properties of the leaf (surface area, lipid

content, stoma number, leaf morphology, and hairy/hairless condition of leaf). Physiological features of the leaves play an important role in determining the scavenging efficiency and retention of airborne particles on the leaf surface (Trapp & McFarlane, 1995; Howsam et al., 2000). Leaf surfaces vary greatly between plant species, both in morphology and chemistry of the waxy cuticle, the number and distribution of stoma, and in the presence or absence of hairs (Howsam et al., 2000).

Uptake from soil through a plant's roots is the predominant pathway of accumulation for organic compounds that have high water solubility, low Henry's law constants, and low K_{OW} values. Herbicides with a K_{OW} less than about 10^4 do not partition to organic rich soils largely (Trapp et al., 1994; Schroll et al., 1994; Simonich & Hites, 1995). These compounds move from the outer root to the inner root, are drawn into the plant by the xylem with short response times, and are distributed within the plant depending on their lipophilicity (Paterson et al., 1994). As hydrophilic compounds are translocated within the plant, they can be significantly metabolized (Trapp et al., 1994; Simonich & Hites, 1995). Most lipophilic (K_{OW} greater than approximately 10^4) organic pollutants such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), organochlorine pesticides (OCP), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) partition to the epidermis of the root and soil particles. They are not drawn into the inner root or xylem (Wild & Jones, 1991; Wang & Jones, 1994; Paterson et al., 1994; Schroll et al., 1994; Simonich & Hites, 1995). Uptake of lipophilic organic pollutants through roots is not a significant pathway of accumulation. In general, lipophilic pollutants are not translocated within the plant, and metabolism is not significant (Trapp et al., 1994; Wang & Jones, 1994).

The main accumulation pathway for lipophilic organic pollutants is uptake from air through the leaf surface (Simonich & Hites, 1995). Mechanism of organic pollutants uptake by vegetation are shown in Figure 2.2. As shown in Figure 2.2, the degree to which these pollutants accumulate in the leaf is dependent on vapor/particle partitioning in the atmosphere, the octanol-air partition coefficient (K_{OA}) and the plant species (Paterson et al., 1991; Tolls & McLachlan, 1994). The

lipid concentration and surface area of the leaf also influence the degree of accumulation (Simonich & Hites, 1994). The partitioning of lipophilic organic pollutants from the outer leaf to the inner leaf is slow and these compounds transported by the phloem. In general, gas-phase pollutants with a large K_{OA} are preferentially accumulated (Tolls & McLachlan, 1994; Simonich & Hites, 1994).

After POPs are sorbed by leaves/needles, they are translocated to other plant tissues by phloem sap. Unlike xylem (composed primarily of dead cells), phloem is composed of living cells. Pollutants have a chance to be adsorbed on xylem cellular membranes rich in lipid and lipophilic shoot solids (Collins et al., 2006). The xylem transports water and inorganic ions from the roots throughout the plant, it also replaces water lost during transpiration and photosynthesis. The movement in phloem is multidirectional whereas it is unidirectional (upward) in xylem. During the growth of a tree, the phloem is shed with the dead bark while the old xylem is retained, and may be used to conduct water for a few years. Xylem eventually provides just a structural support as the tree grows (Chaney, 2000). Therefore, water flow decreases toward the heartwood in the radial direction and the lipophilic organic pollutants (with high octanol−water partition coefficients, log $K_{OW} > 4$) tend to stay in the xylem cells (Chaney, 2000; Collins et al., 2006; Yin et al., 2011b; Odabasi et al., 2015). The rates of degradation and metabolism are considered negligible and experimental evidence suggests that most lipophilic organic pollutants are very persistent in plants (Thompson et al., 1998; McLachlan, 1999). A recent study indicated that lipophilic POPs in annual rings are not redistributed in the stem, thus consequently becoming historical tracers (Yin et al., 2011a, 2011b). All the POPs included in the present study are lipophilic with log K_{OW} values ranging between 3.94 - 6.90 and 5.83 - 8.20 for PAHs (Odabasi et al., 2006) and PCBs (Han et al., 2006), respectively.

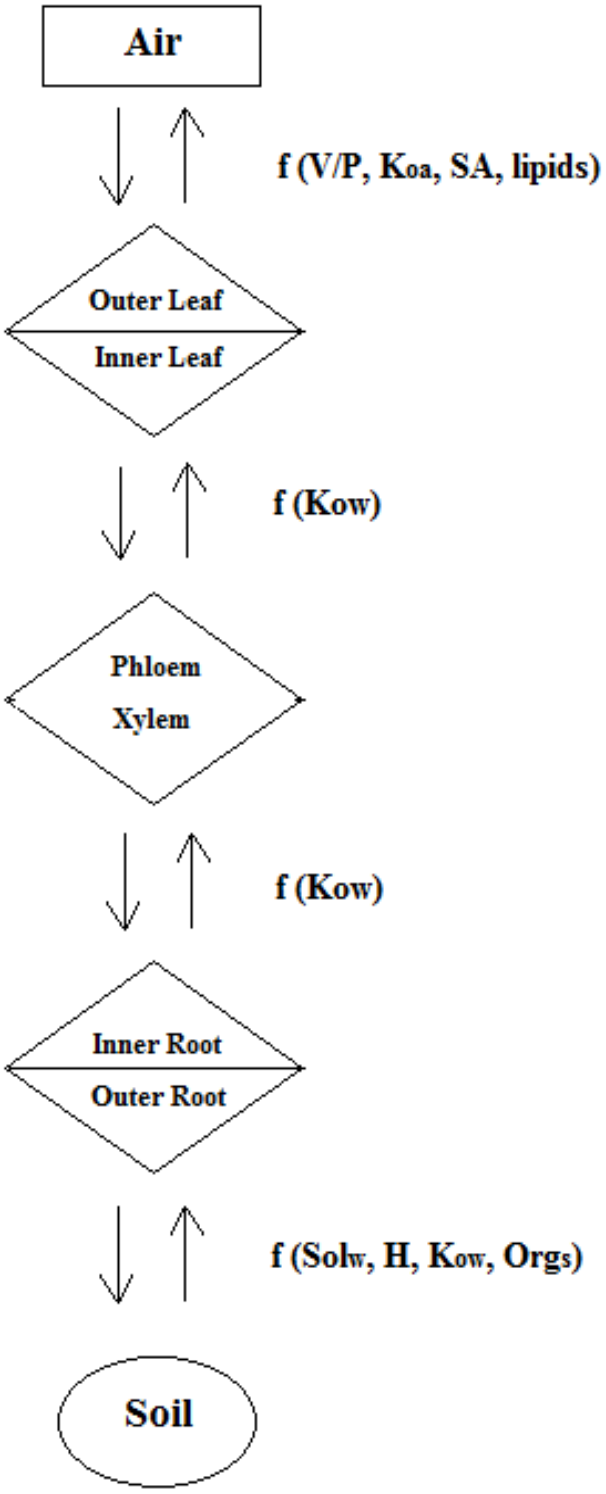


Figure 2.2 Simplified mechanism of pollutant uptake by vegetation. The mechanism is a function of the following: V/P (vapor-particle partitioning), Koa (octanol-air partition coefficient), SA (plant surface area), lipids (plant lipid concentration), Kow (octanol-water partition coefficient), Sol_w (water solubility), H (Henry's law constant), Org_s (organic content of the soil), and plant species (Simonich & Hites, 1995).

Although plants are able to take up POPs into the root system followed by their translocation via xylem, root uptake for most POPs from soil is limited due to their low partitioning to soil and water. Most lipophilic organic pollutants partition to the epidermis of the root or to soil particles, thus they are not drawn into the inner root or xylem (Simonich & Hites, 1995; Wang et al., 2004; Collins et al., 2006; Odabasi et al., 2015). However, the high lipid content of the xylem of coniferous trees enables stem to store and accumulate atmospheric POPs over time.

POPs are present in the air both gas phase and particle phase. The partitioning of POPs between these two phases depends on the ambient air temperature, the nature of the particulate material present in the air and the physical–chemical properties of the particular compound of interest (Barber et al., 2004). Temperature has a significant effect on partitioning of two phases in the air. It is often assumed that the surfaces of airborne particles behave similarly to octanol with respect to organic chemicals, so the octanol–air partition coefficient (K_{OA}) can be used to describe the partitioning of POPs between the particle and gas phases in the air (Barber et al., 2004). The octanol-air partition coefficient (K_{OA}) has become a key parameter in the understanding of pollutant sorption to leaf surfaces. K_{OA} can be calculated from the compounds air-water partition coefficient (K_{AW}-Henry's law constant) and octanol-water partition coefficient (K_{OW}), or measured directly (Harner & Mackay, 1995). Given that K_{OA} is a measure of a compound's preference for octanol (or the plant wax) over the air, K_{OA} should be strongly related, under equilibrium conditions, to the ratio of the concentration of lipophilic pollutant measured in the plant to the concentration measured in the air (Simonich & Hites, 1995). POPs partition to vegetation at low ambient air temperatures (autumn and winter) and some POPs volatilize back to the atmosphere at high ambient air temperatures (summer) (Simonich & Hites, 1994; Nakajima et al., 1995).

Different POPs exhibit different behaviour in the atmosphere (i.e. partitioning between the gas phase and particle phase). Because of the different structures and habitats of plants, the impact of each deposition processes may vary between different classes of compounds and different species of plants (Harner et al., 2006a).

Deposition of organic compounds to plants occurs by equilibrium partitioning for log K_{OA}<8.5, kinetically-limited gaseous deposition for log K_{OA} between 8.5 and 11, and particle-bound deposition for log K_{OA}>11 (Barber et al., 2004). This means that generally levels of gas phase PCBs and PCNs dominate over particulate bound ones, whereas the higher molecular weight PAHs, PCDD/Fs, and PBDEs can be found predominantly in the particulate phase (Harner & Shoeib, 2002). Plant species can capture particles with varying degrees of efficiency, dependent on leaf orientation, surface area and hairiness (Smith & Jones, 2000). Some plant species have been found to be much more efficient than others at collecting and/or retaining particulate matter, and the POPs contained upon them.

POPs are transferred from the atmosphere to the terrestrial surface by dry and wet deposition. It has been proposed that dry gaseous deposition is the major uptake pathway of POPs for plants (Welsch-Pausch et al., 1995). Dry deposition can occur as either the partitioning of gas phase chemicals from the air to the terrestrial surface. Dry gaseous deposition is probably dependent on octanol–air partition coefficient (K_{OA}). Dry particulate deposition is dependent on the settling rate of the particulate load of the air. It is determined by the particulate size distribution and wind speed. Wet deposition is washout of both gas phase and particulate bound chemicals during precipitation but it may also occur during dew formation, mists and fog. Wet deposition is dependent on the air–water partition coefficient (K_{AW}) and the particle scavenging efficiency of precipitation, respectively. Different types of precipitation (heavy rain, fine rain, snow, etc.) could have quite different effects on the level of wet deposition, and on the final destination (vegetation, soil, water run-off) of deposited POPs.

2.1.3 Effects of Air Pollutants on Plants

Air pollution may have adverse effects on all organisms. However, plants (especially trees) are more affected by air pollution in the environment because they cannot move (Weiss et al., 2003). Color loss of leaves, shape defects, early loss of leaves are seen in trees depending on the tree component properties and air pollutants

density in the atmosphere. Gaseous air pollutants have harmful effects on plants. These can be summarized as follows (Dassler, 1986):

- Damages on tissues, cells of leaves and chlorophyll
- Decline in photosynthesis
- Chlorosis and necrosis on leaves
- Reduction of leaf size and diameter increment
- Loss of older leaves
- Dilution of top
- Damage on pollens, flowering and insemination
- Damage on holding fruit
- Occurring acid burns in fruit and leaves by acid rain

In addition, particulate air pollutants have harmful effects on plants. These can be summarized as follows (Dassler, 1986):

- Creates a layer on the leaf surface and prevent photosynthesis
- Block stomata
- Prevent insemination and respiration
- Accumulate hairy leaves more than hairless leaves
- Creates brown spots on the fruits
- Distributes light and reduce the sunlight reaching the plants
- Dark color dust causes more heat absorption and increase temperature of leaf

There are also harmful effects of air pollutants on soil. For example, acid rain can cause acidification in the soil and damage to the soil microorganisms. If the soil pH falls below 4.5, aluminum oxides in the soil begin to disintegrate. Increased aluminum affects the decomposition of humus and plant nutrient circulation in soil. In addition, acid rains cause soil washing and change the chemical structure of the soil. Therefore, it causes deterioration of the soil structure and permeability reduction (Tolunay, 1992).

2.2 Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are a common group name of pollutants that are semi-volatile, bioaccumulative, persistent, and toxic (Vallack et al., 1998; Jones & de Voogt, 2000). POPs are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, and to have potentially significant impacts on human health and the environment (Ritter et al., 2007).

POPs are toxic chemicals that adversely affect human health and the environment around the world. Because they have a semi-volatile structure, they can spread over remote distances from their sources and easily transport in air, water and soil (Harner et al., 2006a). These chemicals are not easily destroyed therefore they persist for long periods in the environment (U.S. EPA, 2005). POPs can be spread to long distances in the atmosphere by air currents and they can accumulate in human and animal tissue by entering the food chains. Therefore, POPs constitute environmental and health problems at the global level.

POPs are ubiquitous and they have been measured on every continent and sites representing every major climatic zone and geographic sector throughout the world (U.S. EPA, 2003). Semi-volatility of these chemicals allows them to travel long distances through the atmosphere before being deposited. Thus, POPs can be found all over the world, including in areas where they have never been used and remote regions such as the middle of oceans and Antarctica (Ritter et al., 2007). Priority pollutants of POPs are organic pesticides (such as DDT), industrial chemicals (such as polychlorinated biphenyls, PCBs) and unintentional by-products of industrial processes (such as dioxins and furans). POPs are particularly used in the industrial production process that uses polyvinyl chloride (PVC), plastic and other chlorine. POPs are released as waste in these processes and spread into the environment because of combustion operations.

POPs are typically `water-hating' and `fat-loving' chemicals. In aquatic systems and soils, they partition strongly to solids, notably organic matter, avoiding the aqueous phase (Jones & de Voogt, 1999). POPs are characterized by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues. Their lipid solubility results in the ability to pass through biological phospholipid membranes and bioaccumulate in the fatty tissues of living organisms (Ritter et al., 2007).

POPs are represented by two important subgroups including both the polycyclic aromatic hydrocarbons (PAHs) and some halogenated hydrocarbons. This latter group includes several organochlorines that have proven to be most resistant to degradation and have wide production, use and release characteristics. These chlorinated derivatives are generally the most persistent group of all the halogenated hydrocarbons. POPs are frequently halogenated, usually with chlorine groups. Chlorine attached to an aromatic ring (benzene) is more stable for hydrolysis than chlorine in aliphatic structures (U.S. EPA, 2003). In general, it is known that the more highly chlorinated biphenyls tend to accumulate largely than the less chlorinated biphenyls; similarly, metabolism and excretion is also more rapid for the less chlorinated biphenyls than for the highly chlorinated biphenyls (Backe et al., 2004).

Temperature has a strong influence on the volatilization rates of POPs by affecting their vapor pressures (Backe et al., 2004). Less volatile POPs tend to partition into natural surfaces such as soil, vegetation, and sediment, where they may associate with organic matter. Warmer temperatures favor their volatilization and residence in the atmosphere as gases, while colder temperatures favor their deposition to the Earth’s surface and their incorporation into airborne particles. Generally, the lower molecular weight (less than 236 g/mol) POPs are expected to exist mainly in gas phase and tend to have the highest potential for long-range transport. However, the higher molecular weight POPs expected to be found mainly attached to particles and tends to remain concentrated around their sources (U.S. EPA, 2005). POPs with molecular weight lower than 236 g/mol are less toxic and

less persistent than higher molecular weight in the environment (Ritter et al., 2007). POPs released into the atmosphere from pollution sources can be diluted with dispersion, transformed into other compounds, moved distance, or transferred to environments such as soil, water, and vegetation by several mechanisms. Environmental transport mechanisms between the atmosphere and other media are convection in the gas phase (gas absorption and evaporation), dry deposition and wet deposition (precipitation) (Cetin & Odabasi, 2007; Bozlaker et al., 2008a; 2008b).

POPs were widely used in industrial production processes after World War II when thousands of synthetic chemicals were introduced into commercial use. Many of these chemicals provided beneficial in pest and disease control, crop production and industry. However there have had unforeseen effects of these chemicals on human health and the environment (U.S. EPA, 2005). Exposure to POPs can lead to serious health effects including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease and damages to the central and peripheral nervous systems. Because of these effects, United Nations Environment Programme (UNEP) has prepared the Stockholm Convention.

UNEP has started the intergovernmental negotiations towards POPs in 1998 for the first time. It made intergovernmental seven committee meetings until 2001. In 1995, the Governing Council of the UNEP called for global action to be taken on POPs. Following this, the Intergovernmental Forum on Chemical Safety (IFCS) and the International Programme on Chemical Safety (IPCS) prepared an assessment about the 12 most harmful persistent chemicals. The negotiations for the Convention were completed on 23 May 2001 in Stockholm. The Convention entered into force on 17 May 2004 with ratification by an initial 128 parties and 151 signatories (United Nations Environment Programme [UNEP], 1999). As of March 2016, there are 180 parties to the Convention (179 states and the European Union).

The Stockholm Convention is a global treaty to protect human health and the environment from POPs. In implementing the Convention, governments of member country will take measures to eliminate or reduce the release of POPs into the environment. The Stockholm Convention focuses on eliminating or reducing releases of the most harmful 12 POPs, the so-called "Dirty Dozen" (Dirty Dozen; aldrin, endrin, dieldrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, dichlorodifenyl trichloroethan (DDT), polychlorinated biphenyls (PCB), dioxins, furans). The countries participating in this Convention should not produce, use and sell these substances. In addition, they should destroy current stocks and should not create new persistent organic pollutants (UNEP, 1999).

Stockholm Convention of POPs is signed on 23 May 2001 by the T.C. Ministry of Environment and Urbanization. After passed approval of the Grand National Assembly of Turkey, it has adopted on 14 October 2009 as Act No. 5871 (Official Newspaper 14.04.2009, No.27200) by the Council of Ministers. Then, it was published in the 30 July 2009 (Official Newspaper 30.07.2009, No.27304) and entered into force on 12 January 2010 (UNEP, 1999). There is an obligation of "*National Implementation Plan on Persistent Organic Pollutants*" (NIP) development and execution for Turkey under Article 7 of Stockholm Convention. The purpose of the NIP is to inform the member countries and public about the present and a future attempt of Turkey. Turkey has to fulfill the requirements of the Stockholm Convention. These attempts are laws, secondary legislation, voluntary programs, standards, policies and actions to reduce unintentionally produced POPs (dioxins and furans, hexachlorobenzene-HCB and polychlorinated biphenyls-PCBs) (UNEP, 1999). NIP has been prepared for the first 12 persistent organic pollutants and forwarded to the Convention Secretariat on 5 April 2011 by T.C. Ministry of Environment and Urbanization.

Initially, 12 POPs were listed in annexes to the Convention in 2004. These 12 POPs have been recognized as causing adverse effects on humans and the ecosystem. These pollutants can be placed into 3 categories as pesticides, industrial chemicals and by-products. In August 2010, nine new additional POPs were added to the

Stockholm Convention's annexes (Stockholm Convention, 2009). Finally, the number of new POPs has increased to 10 by the addition of endosulfan to the Convention in 2011. The Convention recognizes that there are other chemicals that could pose similar risks to human health and the environment, therefore other chemicals may be added to the annexes in the future.

The objective of the Convention is the prohibition of production and use, reduction of emissions and wastes for the 22 (12+9+1) chemicals until 2025 by using the best available disposal techniques. Another aim of the Convention is destruction of oils and waste equipment containing PCBs until 2028 by environmentally compatible format (UNEP, 1999). POP species and groups in the Convention are given in Table 2.1, usage area of POPs are given in Tables 2.2 - 2.3.

Table 2.1 POP species in Stockholm Convention (UNEP, 1999)

Type	**Initial 12 POPs (Dirty Dozen)**	**New 10 POPs**
Pesticides	Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene	Chlordecone, Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Lindane, Pentachlorobenzene, Endosulfan
Industrial Chemicals	Hexachlorobenzene (HCB), Polychlorinated biphenyls (PCBs)	Hexabromobiphenyl, Hexabromodiphenyl ether and Heptabromodiphenyl ether, Pentachlorobenzene, Perfluorooctane sulfonic acid, Its Salts and Perfluorooctane sulfonyl fluoride, Tetrabromodiphenyl ether and Pentabromodiphenyl ether
By-products	Hexachlorobenzene, Polychlorinated dibenzo-P-dioxins and Polychlorinated dibenzofurans (PCDD/PCDF), Polychlorinated biphenyls (PCBs)	Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane Pentachlorobenzene

Table 2.2 Twelve persistent organic pollutants called as "Dirty Dozen" and their usage areas (UNEP, 1999)

Persistent Organic Pollutants	**Usage Area**
Aldrin	A pesticide applied to soils to kill termites, grasshoppers, corn rootworm, other insect pests, birds, fish, and humans.
Chlordane	Used extensively to control termites and as a broad-spectrum insecticide on a range of agricultural crops. Chlordane remains in the soil for a long time and has a reported half-life of one year.
DDT	DDT was widely used during World War II to protect soldiers and civilians from malaria, typhus, and other diseases spread by insects. After the war, DDT continued to be used to control disease, and it was sprayed on a variety of agricultural crops, especially cotton. DDT continues to be applied against mosquitoes in several countries to control malaria. Its stability, its persistence (as much as 50% can remain in the soil 10-15 years after application), and its widespread use have meant that DDT residues can be found everywhere; residual DDT has even been detected in the Arctic.
Dieldrin	Used principally to control termites and textile pests, dieldrin has also been used to control insect-borne diseases and insects living in agricultural soils. Its half-life in soil is approximately five years.
Endrin	This insecticide is sprayed on the leaves of crops such as cotton and grains. It is also used to control rodents such as mice and voles. It has a long half-life, however, persisting in the soil for up to 12 years.
Heptachlor	Primarily used to kill soil insects and termites, heptachlor has also been used more widely to kill cotton insects, grasshoppers, other crop pests, and malaria-carrying mosquitoes. Heptachlor is classified as a possible human carcinogen. Food is the major source of exposure for humans, and residues have been detected in the blood of cattle from the US and from Australia.

Table 2.2 Twelve persistent organic pollutants called as "Dirty Dozen" and their usage areas *(continue)* (UNEP, 1999)

Persistent Organic Pollutants	**Usage Area**
Polychlorinated dibenzo-p-dioxins (PCDD)	These chemicals are produced unintentionally due to incomplete combustion, as well during the manufacture of pesticides and other chlorinated substances. They are emitted mostly from the burning of hospital waste, municipal waste, hazardous waste, and from automobile emissions, peat, coal, and wood. There are 75 different dioxins, of which seven are considered to be of concern.
Polychlorinated dibenzofurans (PCDF)	These compounds are produced unintentionally from many of the same processes that produce dioxins, and during the production of PCBs. They have been detected in emissions from waste incinerators and automobiles. Furans are structurally similar to dioxins and share many of their toxic effects. There are 135 different types, and their toxicity varies. Furans persist in the environment for long times and are classified as possible human carcinogens.
Hexachlorobenzene (HCB)	It was widely used to control wheat bunt. It is also a byproduct of the manufacture of certain industrial chemicals and exists as an impurity in several pesticide formulations.
Mirex	This insecticide is used mainly to combat fire ants, and it has been used against other types of ants and termites. It has also been used as a fire retardant in plastics, rubber, and electrical goods.
Polychlorinated biphenyls (PCBs)	These compounds are used in industry as heat exchange fluids, in electric transformers and capacitors, and as additives in paint, carbonless copy paper, and plastics. Of the 209 different types of PCBs, 13 exhibit a dioxin-like toxicity. Their persistence in the environment corresponds to the degree of chlorination, and half-lives can vary from 10 days to one-and-a-half years.
Toxaphene	This insecticide is used on cotton, cereal grains, fruits, nuts, and vegetables. It has also been used to control ticks and mites in livestock. Up to 50% of a toxaphene release can persist in the soil for up to 12 years.

Table 2.3 New 10 persistent organic pollutants and their usage areas (UNEP, 1999)

Persistent Organic Pollutants	Usage Area
Endosulfan	Endosulfan is an insecticide that has been used since the 1950s to control crop pests, tsetse flies and ectoparasites of cattle and as a wood preservative. As a broad-spectrum insecticide, endosulfan is currently used to control a wide range of pests on a variety of crops including coffee, cotton, rice, sorghum and soy.
Alpha hexachlorocyclohexane	Although the intentional use of alpha-HCH as an insecticide was phased out years ago, this chemical is still produced as unintentional by-product of lindane.
Beta hexachlorocyclohexane	Although the intentional use of beta-HCH as an insecticide was phased out years ago, this chemical is still produced as unintentional by-product of lindane.
Chlordecone	Chlordecone is a synthetic chlorinated organic compound, which was mainly used as an agricultural pesticide. It was first produced in 1951 and introduced commercially in 1958. Currently, no use or production of the chemical is reported.
Hexabromobiphenyl	Hexabromobiphenyl is an industrial chemical that has been used as a flame retardant, mainly in the 1970s. According to available information, hexabromobiphenyl is no longer produced or used in most countries.
Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial name; octabromodiphenyl ether)	Commercial mixture of octaBDE is highly persistent, has a high potential for bioaccumulation, as well as for long-range transport. The only degradation pathway is through debromination and producing other bromodiphenyl ethers.

Table 2.3 New 10 persistent organic pollutants and their usage areas *(continue)* (UNEP, 1999)

Persistent Organic Pollutants	**Usage Area**
Lindane	Lindane has been used as a broad-spectrum insecticide for seed and soil treatment, foliar applications, tree and wood treatment and against ectoparasites in both veterinary and human applications. The production of lindane has decreased rapidly in the last few years and only few countries are still known to produce lindane.
Pentachlorobenzene (PeCB)	PeCB was used in PCB products, in dyestuff carriers, as a fungicide, a flame retardant. PeCB is also produced unintentionally during combustion, thermal and industrial processes. It also present as impurities in products such as solvents or pesticides.
Perfluorooctane sulfonic acid (PFOS), its salts and Perfluorooctane sulfonyl fluoride (PFOS-F)	PFOS is both intentionally produced and an unintended degradation product of related anthropogenic chemicals. The current intentional use of PFOS is widespread and includes electric and electronic parts, fire fighting foam, photo imaging, hydraulic fluids and textiles. PFOS is still produced in several countries.
Tetrabromodiphenyl ether and Pentabromodiphenyl ether (commercial name; pentabromodiphenyl ether)	Commercial mixture of pentaBDE is highly persistent in the environment, bioaccumulative and has a high potential for long-range environmental transport. These chemicals have been detected in humans in all regions. There is evidence of its potential for toxic effects in wildlife, including mammals.

Dichloro diphenyl trichloroethane (DDT) is a colorless, crystalline, tasteless and almost odorless organochlorine known for its insecticidal properties and environmental impacts (U.S. EPA, 1996). It was first synthesized in 1874, and then it was used in the second half of World War II to control malaria and typhus among civilians and troops. After the war, DDT was also used as an agricultural insecticide and its production and use duly increased. Usage of pesticide began with the use of DDT in Turkey. Because of Turkey is an agricultural country, plant protection is a

necessity. Use of chemical substance (particularly DTT) is the most effective method in fighting malaria carrier and plant protection. Since the 1940s, a large number of synthetic organochlorine pesticides have produced and these chemicals are used in plant protection. The most toxic of them (Aldrin, DDT and heptachlor) were used until the 1980s (UNEP, 1999). The prohibition of pesticide is begun in the 1970s in Turkey. The usage, manufacturing, imports and exports of these materials are prohibited by law. Dieldrin is prohibited in 1971, aldrin, chlordane, heptachlor and endrin are prohibited in 1979, toxaphene is prohibited in 1989. In addition, the registrations of plant protection products containing these active ingredients have been canceled. A usage license has never been given for mirex and the products obtained by mirex in Turkey. After the prohibition, there is no record for the production of POP pesticides in Turkey. Plant protection products are prepared by using imported active substances after registration. These active substances have never been manufactured in Turkey. The record of Ministry of Customs and Trade indicate that POPs substances have not imported or exported after they prohibited (UNEP, 1999).

2.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are formed from two or more benzene rings and do not contain different elements other than carbon and hydrogen in the molecule structures (Crimmins & Baker, 2006). Benzene rings of PAH compounds can be combined into a linear shape (anthracene) or angular shape (acenaphtylene) (Dabestani & Ivanov, 1999). The most environmentally important PAH compounds are between two benzene rings to (naphthalene, chemical formula; $C_{10}H_8$) seven benzene rings (coronene, chemical formula; $C_{24}H_{12}$).

PAHs are emitted into the atmosphere from both natural and anthropogenic sources (Simonich & Hites, 1995). Natural (volcanic eruptions, natural forest fires and biosynthesis) and anthropogenic sources (include vehicle emissions, domestic heating, industrial processes, electric power production, and waste incineration)

account for their diffusion in the environment, because of atmospheric transport, deposition and dispersion in the environment (Ratola, et al., 2006; Blasco, et al., 2006). In urban areas, motor vehicle exhaust is one of the dominant sources of these pollutants (Piccardo et al., 2005; Oishi, 2013). Although the predominant PAH emissions come from anthropogenic activities, natural resources are the source of some PAHs in nature. PAHs can be formed in three ways from natural sources including high temperature pyrolysis of organic materials, direct biosynthesis of microorganisms and plants, and diyagenez of organic material at a low and medium temperature to create fossil fuels (Nagpal, 1993). Agricultural burning, forest and steppe fires have the greatest proportion of PAH emissions. Other natural PAH sources are volcanic activities and biosynthesis of plant, algae, plankton and microorganisms. However, these emissions are less compared with fires (Nagpal, 1993; Odabasi, 1998).

In general, 2 to 3 rings group of PAHs (such as naphthalenes, fluorenes, phenanthrenes, and anthracenes), which have relatively low molecular weight, exist primarily in the gas phase of the atmosphere. PAHs with 5 to 6 rings (from chrysenes to coronenes), which have relatively high molecular weight, are more likely to be present in the particle-bound phase (Oishi, 2013). Furthermore, in 4 rings PAHs at intermediate vapor pressures, a temperature-dependent gas/particle phase partitioning occurs. These phases are closely related to the uptake or absorption of PAHs into plants and soils (Liu et al., 2005; Wang et al., 2009; Oishi, 2013).

PAHs occur in both gaseous forms and as adsorbents on particles in the atmosphere with their partitioning between these phases depending on the volatility of the PAHs species. Non-volatile PAHs (highly condensed molecules with four or more rings) tend to be largely particle-bound, whereas volatile PAHs (smaller molecules) mainly remain in the gas phase. PAHs tend to persist for relatively long periods in the environment due to their comparatively stable molecular structure and slow rates of photochemical deposition and biodegradation (Blasco, et al., 2006).

PAHs are ubiquitous environmental pollutants and several PAHs are known to be hazardous to human health due to their mutagenic and carcinogenic properties (Piccardo et al., 2005; Oishi, 2013). There are many PAH compounds in the environment, but only 16 of them are included in the "*Priority Pollutants*" list of the United States Environmental Protection Agency (U.S. EPA, 2005).

PAHs compounds are found in gas phase and particle phase in the atmosphere. Retention time and transport distances in the atmosphere depend on the meteorological conditions, reactivity and the particle size of the PAHs (Agency for Toxic Substances and Disease Registry [ATSDR], 1995). PAHs undergo photochemical oxidation in the presence of sunlight during transport in the atmosphere. This reaction occurs faster in gas phase than a particular phase. The most important mechanisms are the reaction with hydroxyl radicals. In addition, PAHs are oxidized by air pollutants such as ozone, nitrogen oxide and sulfur dioxide and these compounds can return to the diones, nitro and dinitro derivatives and sulfonic acid, respectively (Dabestani & Ivanov, 1999; Halsall et al., 2001). Chemical structures of the studied PAH compounds (U.S. EPA 16 priority PAHs and carbazole) are shown in Figure 2.3.

Transportation of organic pollutants between environmental media and distribution of organic pollutants between different phases are determined by their physicochemical properties. These properties are water solubility, vapor pressure, Henry's law constant, octanol/water partition coefficient (K_{OW}), and octanol/air partition coefficient (K_{OA}) (ATSDR, 1995). Physicochemical properties of PAHs vary with molecular weights. When the molecular weight of PAHs increases, the water solubility of these compounds decreases (Nagpal, 1993). Pure PAHs are usually colorless, white or light yellow-green solids at room temperature and melting or boiling points of them are high. Rate of partition in air and water balance phase is expressed by the Henry's law constant. This constant is used as a measure of a compound to evaporate. K_{OW} is used to estimate the potential of organic pollutants transported from water to the lipid. Thus, the relationship between biological concentrations and aquatic organisms can be found. Log K_{OW} values increase with

the number of rings in PAHs. High K_{OW} values indicate a relatively high potential for biological concentrations in organisms and adsorption of suspended particles in water and air (ATSDR, 1995). Values of log K_{OW} ranging from 3.36 - 6.63 for 16 PAH compounds at ambient conditions (National Library of Medicine [NLM], 2008).

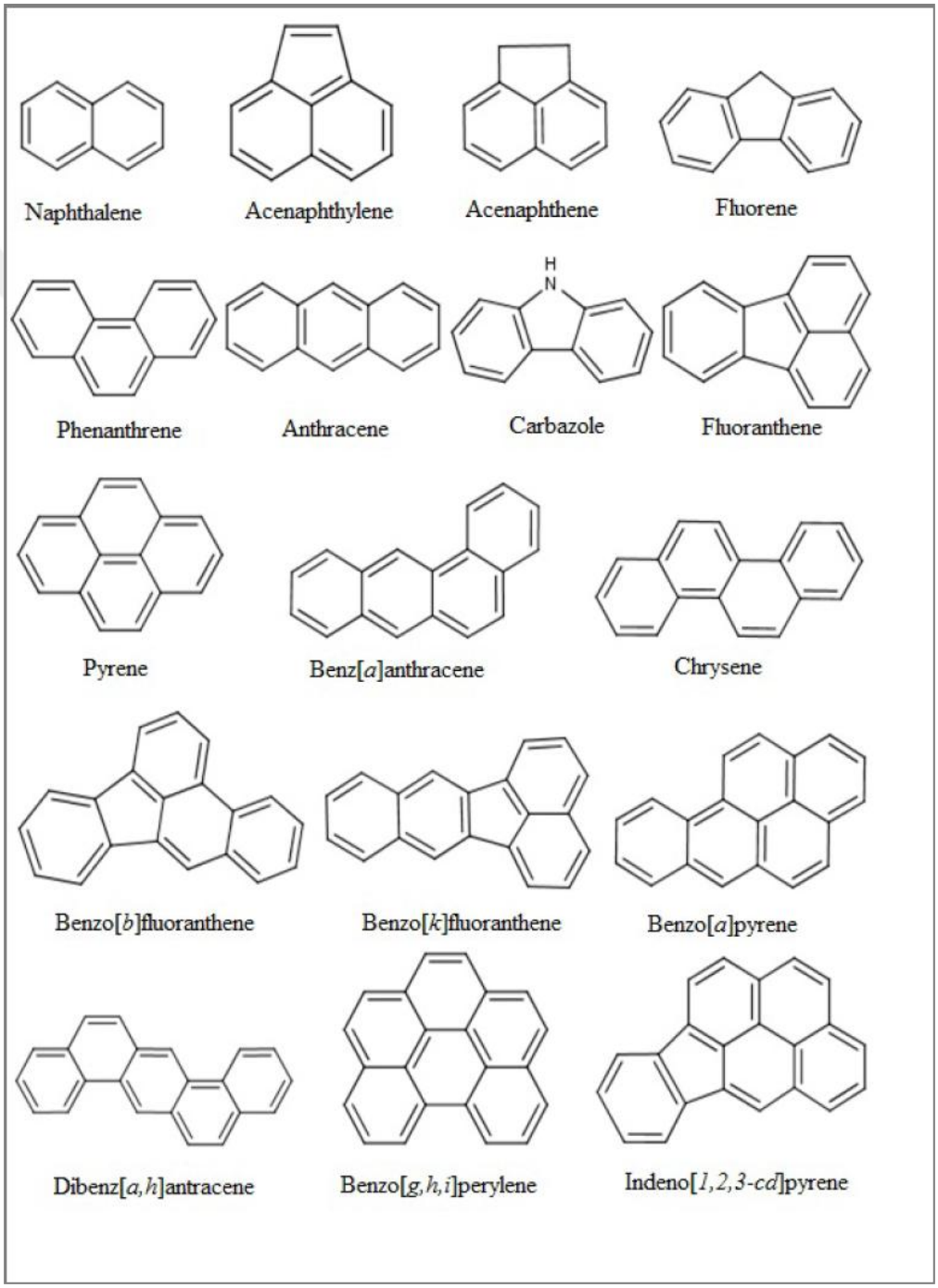


Figure 2.3 Chemical structures of the carbazole and priority 16 PAH compounds (UNEP, 1999)

Certain resources for commonly used PAH components are defined in the literature. Aydin (2013) stated that acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benz[a]anthracene and chrysene are the main component of iron and steel industry in her study. Aydin (2013) reported that carbazole, anthracene, fluoranthene, pyrene, phenanthrene and chrysene are the main component of combustion sources. Also benzo[*g,h,i*]perylene, dibenz[*a,h*]anthracene, indeno[*1,2,3-c,d*]pyrene, benzo[*a*]pyrene, benz[*a*]anthracene and chrysene are reported in traffic emissions in the same study.

2.2.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are aromatic and synthetic compound group that consisting of biphenyl molecule ($C_{12}H_{10}$) containing two benzene rings by the addition of chlorine (Cl) atoms (Nagpal, 1992). The general formula of PCBs is $C_{12}H_{10-n}Cl_n$. "n" value in the formula ranges from 1 to 10 (UNEP, 1999). The general structure of biphenyl molecule is shown in Figure 2.4.

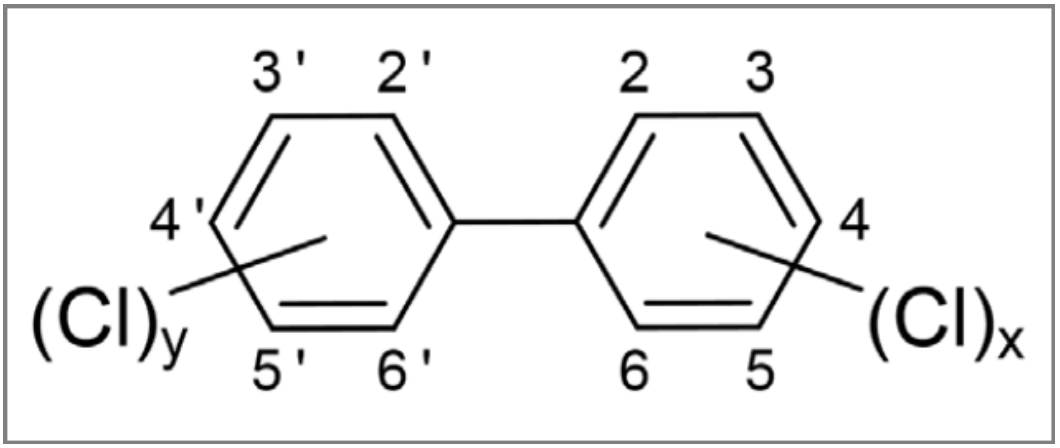


Figure 2.4 General structure of polychlorinated biphenyl molecule (UNEP, 1999)

PCBs have no natural sources and they have been commercially prepared by chlorination of biphenyl. Due to their thermal stability, resistant to electricity current, oxidation, acid and bases, PCBs were widely used in electrical equipment (mainly capacitors and transformers) and industrial applications until recently (UNEP, 1999). PCBs have been released into the environment by open burning, waste incineration, vaporization from contaminated surfaces and products containing PCBs, and improper disposal or leakage of oil from transformers and capacitors (Breivik et al., 2002a; U.S. EPA, 2005).

Because of their toxicity and resistance to degradation, the production and use of PCBs are banned in many countries. However, due to their persistence, PCB levels in the environment are declining slowly, and this makes them ubiquitous. Although PCB concentrations are known to be higher near urban industrialized areas, they were found even at remote locations such as the Arctic, the Antarctic, the Indian Ocean, and the Pacific Ocean (Tasdemir et al., 2004a).

PCBs exist in the atmosphere at gas and particle phase. Gas/particle partitioning and persistence of PCBs led them to accumulate in the environment and transport to remote and cleaner areas (Gouin et al., 2002; Manodori et al., 2006). Persistence of PCBs in the environment causes them to be transported to remote areas with long-range transport. PCBs are removed from the atmosphere by dry and wet deposition (Gambaro et al., 2005). Low molecular weight PCBs tend to be in the gas phase dominantly. Therefore, they transport far away from the sources more easily than particle phase PCBs. The high molecular weight PCBs tend to be in particle phase. They can be removed more easily from the atmosphere with precipitation (ATSDR, 2000).

Commercial PCBs occur due to a mixture of PCB compounds. However, after spreading to nature, the composition of PCB mixtures are changed through evaporation, decomposition, chemical and biological transport and bioaccumulation processes (U.S. EPA, 1996). Generally, biodegradation decreases with increase in chlorine amount. Evaporation probability of the PCB compounds having three or less

chlorine atoms are high and they are broken down biologically to a significant degree. The suspended particles having five chlorine atoms are resistant to biodegradation and they are kept in sediment and soil (Nagpal, 1992).

Physico-chemical properties of the PCB compounds often vary according to the position of chlorine atom and chlorination degree. Majority of the PCB compounds are solid at room temperature but commercial mixtures are mobile oils, viscous liquids or viscous resins (Nagpal, 1992). Pure PCB compounds are colorless and there is no taste and smell of them (ATSDR, 2000). Boiling point of them is quite high and they ignite for a very long time. The most important features that cause the widespread use of PCBs are thermal and chemical stability, excellent insulating properties and resistance to oxidation, acids, bases and other chemical agents (UNEP, 1999).

Generally, PCBs have low vapor pressure. Vapor pressure and Henry's law constant of them decrease with increasing chlorine amount (Nagpal, 1992). Therefore, PCB compounds that chlorine amount is excess are relatively non-volatile compounds. PCBs that vapor pressure greater than 10^{-4} mm Hg (mono- and di-CBs) present in the gas phase while vapor pressure smaller than 10^{-8} mm Hg present in the particle phase in the atmosphere. PCBs that vapor pressure is between 10^{-4} and 10^{-8} mm Hg (tri-hepta-CBs) disposed to each two phases (ATSDR, 2000). Because of PCBs are hydrophobic solvents, they can be dissolved in oils and organic solvents readily. However, they can be dissolved in water in very small amounts (UNEP, 1999). The water solubility of PCBs decreases with the degree of chlorine replacement. Solubility in a homologous group depends on the position of the chlorine atom in biphenyl structure (Nagpal, 1992).

PCBs are mostly associated with solid portion of the aquatic and terrestrial environment (particulate matter, sediments, soil). There is a high binding tendency to solids in highly chlorinated PCBs that have low water solubility and high K_{OW} values. Low molecular weight PCBs that have high water solubility, less K_{OW} values are less adsorbed by solids and substantially dissolved in the aquatic environment.

Thus, evaporation of highly chlorinated PCBs reduced significantly by binding of these compounds to solids in water and terrestrial environment (ATSDR, 2000).

PCBs were disposed for years without any prevention in the environment. As a result, large amounts of PCBs were released into the environment by the evaporation of the PCB containing products and contaminated surfaces. PCBs are released into nature by open burning, industrial and municipal waste combustion, illegal and improper storage of PCB waste in the garbage field and maintenance and repair of old electronic equipment containing PCBs (Vallack et al., 1998; UNEP, 1999; Breivik et al., 2007; U.S. EPA, 2005). Recycling of PCB containing materials is another PCB source. PCBs are spread into the environment by the recycling of transformers, crushing and melting of hydraulic equipment, cars and electrical household appliances (such as refrigerators, air conditioners, televisions and microwave ovens) in scrap metal recycling operations. In addition, PCBs are spread into the environment by iron and steel industry, electronic equipment containing PCBs and power cord isolated oil/grease (UNEP, 1999; U.S. EPA, 2005). PCB emissions can be caused by organic pigments, pesticides, chemicals, cement, copper, iron-steel and aluminum refining industries. PCBs are occurred with chlorine and hydrocarbon at high temperatures in the presence of catalyst (UNEP, 1999). PCBs can be burned at high temperature, but the combustion products may more dangerous than the first products. Combustion products contain hydrogen chloride and polychlorinated dibenzodioxins/dibenzofurans (PCDD/DFs). Pyrolysis of commercial PCB mixtures produces a large amount of PCDF.

There are limited numbers of studies that describing some PCB sources in the literature. Kim et al. (2002) have been reported PCB-38, PCB-40/57, PCB-77, PCB-85, PCB-107/108, PCB-126, PCB-129, PCB-128, PCB-157, PCB-169, PCB-171 PCB-172/192, PCB-170, PCB-189, PCB-203/196, PCB-194, PCB-206 as combustion source PCB compounds. In addition, these characteristic compounds have been identified in Kanechlors (commercial mixtures of PCBs) like Kanechlor 300 and 400, Kanechlor 500 and 600. PCB-77 and PCB-126 have been reported that results of the combustion process in another study (Ishikawa et al., 2007). Emissions

from household use of coal and wood contain a variety of PCB compounds. PCB-49 and PCB-41/64 are the most important PCBs consisting of both wood and coal burning. Jin et al. (2012) have been reported that PCB-11, PCB-12/13, PCB-15 and PCB-17 as PCB compounds emitted from waste burning in their study. Odabasi et al. (2009) have been determined emissions released from electric arc furnaces in the iron-steel industry and profiles of the PCB compounds in their study. Aydin (2013) has been reported PCB-17, PCB-18, PCB-28, PCB-31, PCB-33, PCB-44, PCB-49, PCB-52, PCB-70, PCB-74, PCB-82, PCB-87, PCB-95, PCB-99, PCB-101, PCB-105, PCB-110, PCB-118 and PCB-206 as the most obvious PCB compounds released from the iron-steel industry. Characteristic compounds in both Kanechlor and Aroclor mixtures are expressed in several studies (Takasuga et al., 2005, 2006; Du & Rodenburg, 2007; Ishikawa et al., 2007; Jin et al., 2012).

2.3 Transportation and Environmental Effects of POPs

Phase (gas or particle) partitioning of a compound in the atmosphere depends on the air temperature, the properties of the attached surface and the physicochemical properties of the compound (Howsam et al., 2000). Gas phase or particle phase air pollutants emitted from various sources are transported by air motion in the atmosphere. Transport distance varies according to pollutant properties, meteorological conditions and the shape of the earth. The transport of POPs from air to another environmental media is occurs via atmospheric deposition. Pollutants can be found in living organisms, soil and water. They can be accumulated by precipitation (rain, snow, fog, dew, frost) in this environment. Air pollutants can be deposited on the soil, water and vegetation directly by dry deposition. Especially living organisms are exposed to the harmful effects of air pollutants with dry deposition. Damages are occurred according to the duration of exposure, concentration of pollutants and living organisms' properties. Soil is often the ultimate environment for air pollutants (Wimmer, 1997; Trapp, 2000). POPs tend to accumulate in the soil over time, the deposition rates vary depending on the physical and chemical properties. Diffusion is an important process that affecting the

transportation rates of POPs between environmental media (Bozlaker et al., 2008a, 2008b).

POPs are highly toxic compounds that can be transported for long distances due to their semi-volatile features. POPs are often halogenated and chlorinated compounds according to chemical properties. Halogenated structures and lipophilic properties are caused accumulation in the fatty tissue. Organochlorines, DDT, hexachlorobenzene, PCBs, dioxins, furans, chlordane, mirex, toxaphene and heptachlor are the most soluble POP compounds in fatty tissue. They are showing the highest bioaccumulation in living organisms and therefore they are the most harmful pollutants. The molecular weight of these pollutants is also important on microbial, chemical and photochemical degradation in the environment. DDT and other chlorinated pesticides are very persistent in the environment due to their high molecular weight (Howsam et al., 2000).

POPs can be remained in the environment for a long time without degradation also they can be bioaccumulated in the fatty tissue of living organisms. Thus, people, animals and other organisms often exposed to POPs through the generations, because of this, both acute and chronic toxic effects occur in organisms (Pribylova et al., 2012). POPs are impersonated the chemical carrier that naturally occurring or producing in the body so they cause adverse effects on the reproductive systems by affect endocrine and immune system over time. In addition, exposure to high levels of these substances for long-term can cause infertility problem, more vunerable to disease, fall in intelligence level, disturbances in the endocrine system and some types of cancer in humans (UNEP, 1999).

The organic pollutants are usually xenobiotics (impurities) for plants because it is fabricated and consequently, there is no carrier of these compounds in plant membranes. Therefore, organic pollutants tend to enter a plant by simple diffusion depending on their chemical properties. One of the most important features in the uptake of organic pollutants is water solubility. Organic compounds that log K_{ow} value between 0.5 and 3 are sufficiently hydrophilic, they can pass directly through

the membrane of the lipid barrier and they can get into the cell due to their water solubility properties. Organic compounds that log K_{OW} value < 0.5 are very hydrophilic, they cannot pass the cell membrane and therefore they cannot be received by plant. Organic compounds that log K_{OW} value > 3 are very hydrophobic, they are attached with cell membrane and cell wall in the peripheral of the plant and they cannot enter the cell liquid (Macek et al., 2000).

2.4 Reported Levels of POPs in Literature

PAH and PCB concentrations in ambient air, litter, soil, and tree component samples have been previously measured at the urban, semi-urban, rural, industrial, agricultural, and forested sites throughout the world. Summary of reported PAH and PCB levels in literature are presented in Tables 2.4 – 2.9. Concentrations in different compartments (except ambient air) were provided on the dry weight basis. Some exceptions were indicated below the tables.

PAHs and PCBs are prevalent contaminants because of the heavy anthropogenic and industrial activities in Aliaga and Iskenderun. In this study, Σ_{16}PAH concentrations in ambient air samples were ranged from 21 to 314 ng/m^3 in Iskenderun and they ranged from 18 to 645 ng/m^3 in Aliaga, respectively. In addition, Σ_{41}PCB concentrations in ambient air samples ranged from 0.11 to 6.42 ng/m^3 in Aliaga and from 0.06 to 3.72 ng/m^3 in Iskenderun**.** Atmospheric POP concentrations measured in the present study were within the ranges reported in the literature and recently measured in two sampling regions (Cetin et al., 2007; Cetin & Odabasi, 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009, 2012; Kaya et al., 2012).

PAH and PCB concentrations measured in this study were within the range of previously reported values in other urban and industrial sites around the world (Tables 2.4 – 2.5). Ambient air total 16-PAH concentrations measured in this study are considerably higher than reported by Pozo et al. (2012) for industrial sites in Chile, by Zhang et al. (2016) for urban sites in China, and by Ruge et al. (2015) for

urban sites in USA. Ambient air total 41-PCB concentrations measured in this study are considerably higher than reported by Hogarh et al. (2012a) for urban sites in China, by Bohlin et al. (2008) for urban sites in Mexico, and by Li et al. (2012) for industrial sites in China.

The recorded concentrations of total PAHs in ambient air samples throughout the world were ranged from 838 to 2.3 ng/m^3 in literature (Kaya et al., 2012; Estellano et al., 2012) (Table 2.4). The ambient air total PAH concentration in Italy (Estellano et al., 2012) were found to be low compared with those reported for other countries in Table 2.4. In addition, higher ambient air PAH concentrations were observed in Turkey (Kaya et al., 2012; Cetin et al., 2017).

In addition, the measured concentrations of total PCBs in ambient air samples throughout the world were ranged from 231 to 0.045 ng/m^3 in literature (Kaya et al., 2012; Estellano et al., 2012) (Table 2.5). Similar to PAH results, the ambient air total PCB concentrations in Italy (Estellano et al., 2012) were found to be low compared with those reported for other countries in Table 2.5. Higher ambient air PCB concentrations were observed in Turkey (Kaya et al., 2012; Tasdemir et al., 2004a).

Table 2.4 Ambient air total PAH concentrations in the literature

Study Area	**Location**	**ΣPAH Concentration (ng/m^3)**	**Study**
Industrial/Urban	Istanbul - Turkey	Σ_{15}PAH= 11.7 – 302	Cetin et al. (2017)
Industrial/Rural	Iskenderun-Turkey	Σ_{16}PAH= 21 - 314	This study
Industrial/Rural	Aliaga - Turkey	Σ_{16}PAH= 18 - 645	This study
Suburban	Portugal	Σ_{17}PAH= 8.0 - 89.0	Albuquerque et al. (2016)
Urban	China	Σ_{15}PAH= 220	Zhang et al. (2016)
Industrial/Urban/Rural	Bangladesh	Σ_{8}PAH= 18.4	Nost et al. (2015)
Industrial	Italy	Σ_{16}PAH= 5.3 - 8.3	Loppi et al. (2015)
Urban	USA	Σ_{21}PAH= 140	Ruge et al. (2015)
Industrial	South Korea	Σ_{13}PAH= 43	Choi et al. (2012)
Industrial/Urban/Rural	Chile	Σ_{15}PAH= 30-230	Pozo et al. (2012)
Urban	Italy	Σ_{9}PAH= 0.89-3.5	Estellano et al. (2012)
Agricultural Area	Italy	Σ_{9}PAH= 2.11-4.7	Estellano et al. (2012)
Rural	Italy	Σ_{9}PAH= 0.30-2.30	Estellano et al. (2012)
Industrial	Aliaga - Turkey	Σ_{16}PAH= 1.62-838	Kaya et al. (2012)
Urban/Semi-urban	Mexico	Σ_{13}PAH= 6.1-180	Bohlin et al. (2008)
Industrial	Aliaga - Turkey	Σ_{15}PAH= 10.2-71.9	Bozlaker et al. (2008a)
Urban	19 European Countries[a]	Σ_{10}PAH= 0.97-63	Farrar et al. (2006)
Urban/Rural/Industrial	22 Countries[b]	Σ_{12}PAH= 0.50-61.2	Jaward et al. (2004b)
Rural	Netherlands and South Africa	Σ_{8}PAH= 0.19-3.73	Jaward et al. (2004a)
Urban	Chicago - USA	Σ_{13}PAH= 20-200	Harner & Bidleman (1998)
Urban	U.K.	Σ_{16}PAH= 59-166	Halsall et al. (1994)

[a]: Iceland, Ireland, U.K., Portugal, France, Spain, Netherland, Germany, Italy, Belgium, Hrvatska, Denmark, Greece, Sweden, Poland, Norway, Finland, Estonia, and the Russia

[b]: Czech Republic, Cyprus, Poland, Switzerland, Croatia, Estonia, Hungary, Kazakhstan, Iceland, Russia, Finland, Greece, Netherlands, Norway, Portugal, Sweden, Ireland, France, Germany, Italy, Spain, and the UK

Table 2.5 Ambient air total PCB concentrations in the literature

Study Area	**Location**	**ΣPCB Concentration (ng/m^3)**	**Study**
Industrial/Urban	Istanbul - Turkey	Σ_{41}PCB= 0.082 - 0.821	Cetin et al. (2017)
Industrial/Rural	Iskenderun - Turkey	Σ_{41}PCB= 0.06 - 3.72	This study
Industrial/Rural	Aliaga - Turkey	Σ_{41}PCB= 0.11 - 6.42	This study
Industrial/Rural/Forested	Istanbul - Turkey	Σ_{84}PCB= 0.13 - 0.584	Kuzu et al. (2016)
Industrial	Spain	Σ_{7}PCB= 0.0083 - 0.0511	Vilavert (2014)
Urban	China	Σ_{18}PCB= 0.0186 - 0.091	Xu et al. (2013)
Urban / Agricultural	USA	Σ_{92}PCB= 0.03 - 0.51	Sofuoglu (2013)
Industrial/Urban/Rural	Chile	Σ_{48}PCB= 0.04 - 0.35	Pozo et al. (2012)
Industrial	Aliaga-Turkey	Σ_{41}PCB= 0.134 - 231	Kaya et al. (2012)
Urban/Rural/Suburban	Japan	Σ_{202}PCB= 0.04 - 0.76	Hogarh et al. (2012a)
Urban/Rural/Suburban	China	Σ_{202}PCB= 0.3 - 2.5	Hogarh et al. (2012a)
Urban/Rural/Suburban	Korea	Σ_{202}PCB= 0.036 - 0.6	Hogarh et al. (2012a)
Urban/Rural/Suburban	Taiwan	Σ_{202}PCB= 0.317	Hogarh et al. (2012a)
Urban	Italy	Σ_{5}PCB= BDL[a] – 0.3	Estellano et al. (2012)
Rural	Italy	Σ_{5}PCB= BDL[a] – 0.045	Estellano et al. (2012)
Industrial	China	Σ_{12}PCB= 0.0323 – 0.167	Li et al. (2012)
Industrial	China	Σ_{19}PCB= 0.0146 - 0.0813	Li et al. (2011)
Agricultural Area	India	Σ_{48}PCB= 0.02 – 4.060	Pozo et al. (2011)
Rural	France	Σ_{18}PCB= 0.013 – 0.095	Castro-Jimenez et al. (2011)
Semi-rural	Italy	Σ_{7}PCB= 0.0314 – 0.0763	Castro-Jimenez et al. (2009)
Industrial	Aliaga-Turkey	Σ_{41}PCB= 0.618 - 1.164	Bozlaker et al. (2008b)
Urban/Semi-urban	Mexico	Σ_{7}PCB= 0.059 - 2.1	Bohlin et al. (2008)
Industrial/Urban	Aliaga-Turkey	Σ_{36}PCB= 0.847 - 1.371	Cetin et al. (2007)
Urban	19 European Countries[b]	Σ_{10}PCB= 0.014 – 1.7	Farrar et al. (2006)
Urban	Chicago - USA	Σ_{50}PCB= 0.42 – 8.31	Tasdemir et al. (2004a)
Urban	Chicago - USA	Σ_{36}PCB= 0.143 – 0.621	Harner & Bidleman (1998)

[a]BDL: Below the detection limit

[b]: Iceland, Ireland, U.K., Portugal, France, Spain, Netherland, Germany, Italy, Belgium, Hrvatska, Denmark, Greece, Sweden, Poland, Norway, Finland, Estonia, and the Russia

In this study, Σ_{16}PAH concentrations in soil samples were ranged from 89 to 43481 μg/kg in Iskenderun and they ranged from 32 to 2085 μg/kg in Aliaga, respectively. In addition, Σ_{41}PCB concentrations in soil samples ranged from 0.42 to 479 μg/kg in Aliaga and from 0.51 to 279 μg/kg in Iskenderun**.** Atmospheric POP concentrations measured in the present study were within the ranges reported in the literature (Cetin et al., 2016; Rhind et al., 2013; Mamontova et al., 2013; Kaya et al., 2012; Odabasi et al., 2010).

PAH and PCB concentrations measured in this study were within the range of previously reported values in other urban and industrial sites around the world (Tables 2.6 – 2.7). Total 16-PAH concentrations of soil samples measured in this study are considerably higher than reported by Tang et al. (2005) for urban sites in China, by Rhind et al. (2013) for rural sites in Scotland, and by Nam et al. (2008b) for agricultural sites in UK. Total 41-PCB concentrations of soil samples measured in this study are considerably higher than reported by Mamontova et al. (2013) for urban sites in Mongolia, by Armitage et al. (2006) for agricultural sites in Sweden, and by Wilcke et al. (2006) for urban sites in Russia.

The recorded concentrations of total PAHs in soil samples throughout the world were ranged from 27825 to 112 μg/kg in literature (Tang et al., 2005; Nadal et al., 2004) (Table 2.6). The total PAH concentration of soil in Spain (Nadal et al., 2004) were found to be low compared with those reported for other countries in Table 2.6. In addition, higher soil PAH concentrations were observed in China (Tang et al., 2005).

In addition, the measured concentrations of total PCBs in soil samples throughout the world were ranged from 3085 to 0.772 μg/kg in literature (Ruzickova et al., 2008; Kuzu et al., 2016) (Table 2.7). Total PCB concentrations of soil in Turkey (Kuzu et al., 2016) were found to be low compared with those reported for other countries in Table 2.7. Higher soil PCB concentrations were observed in 4 European Countries (Yugoslavia, Czech Republic, Serbia and Montenegro, Bosnia and Herzegovina) (Ruzickova et al., 2008).

Table 2.6 Soil total PAH concentrations in the literature

Study Area	**Location**	**ΣPAH Concentration (µg/kg)**	**Study**
Industrial/Rural	Aliaga-Turkey	Σ_{16}PAH= 32 - 2085	This study
Industrial/Rural	Iskenderun-Turkey	Σ_{16}PAH= 89 - 43481	This study
Industrial	Kocaeli-Turkey	Σ_{17}PAH= 61 - 6726	Cetin (2016)
Forested Area (After fire)	South Korea	Σ_{16}PAH= 6.27 - 274	Choi (2014)
Urban	China	Σ_{16}PAH= 7.9 - 2231	Zhang et al. (2013)
Rural	Scotland	Σ_{11}PAH= 33.9–12560	Rhind et al. (2013)
Industrial/Urban/Rural	Portugal	Σ_{16}PAH= 27.3-769.8	Augusto et al. (2010)
Industrial	Iskenderun-Turkey	Σ_{16}PAH= 4192	Odabasi et al. (2010)
Rural / Agricultural	China	Σ_{19}PAH= 17.5 - 1220	Wang et al. (2009)
Industrial	Iskenderun-Turkey	Σ_{16}PAH= 3725	Odabasi et al. (2008)
Agricultural/Rural	U.K.	Σ_{15}PAH= 42–11200	Nam et al. (2008b)
Agricultural/Rural	Norway	Σ_{15}PAH= 8.6–1100	Nam et al. (2008b)
Industrial	Spain	Σ_{16}PAH= 34.4 - 6056	Nadal et al. (2007)
Urban	Spain	Σ_{16}PAH= 41.8 - 1472	Nadal et al. (2007)
Rural	Spain	Σ_{16}PAH= 37.3 - 502	Nadal et al. (2007)
Rural/Agricultural	Hong Kong	Σ_{15}PAH= 7.0 - 410	Zhang et al. (2006)
Urban/Semi-urban	China	Σ_{16}PAH= 366-27825	Tang et al. (2005)
Industrial	Spain	Σ_{16}PAH= 166-1002	Nadal et al. (2004)
Urban	Spain	Σ_{16}PAH= 736	Nadal et al. (2004)
Rural	Spain	Σ_{16}PAH= 112	Nadal et al. (2004)
Industrial	France	Σ_{14}PAH= 450 - 5650	Motelay-Massei etal. (2004)
Industrial/Urban/Rural	Germany	Σ_{20}PAH= 0.16 - 186	Krauss & Wilcke (2003)

Table 2.7 Soil total PCB concentrations in the literature

Study Area	**Location**	**ΣPCB Concentration (µg/kg)**	**Study**
Industrial	Kocaeli-Turkey	Σ_{41}PCB= 1.4 - 1676	Cetin (2016)
Industrial/Rural/Forested	Istanbul - Turkey	Σ_{84}PCB= 0.0007 - 0.772	Kuzu et al. (2016)
Industrial/Rural	Iskenderun-Turkey	Σ_{41}PCB= 0.51 - 279	This study
Industrial/Rural	Aliaga-Turkey	Σ_{41}PCB= 0.42 - 479	This study
Rural	Scotland	Σ_{7}PCB= 0.04 - 11.2	Rhind et al. (2013)
Urban	Mongolia	Σ_{37}PCB= 0.53 - 114	Mamontova et al. (2013)
Industrial	Aliaga-Turkey	Σ_{41}PCB= 0.174 - 461	Kaya et al. (2012)
Industrial	Iskenderun-Turkey	Σ_{41}PCB=19.0 ± 18.0	Odabasi et al. (2010)
Industrial/Urban/Rural	4 European Countries[a]	Σ_{7}PCB= 0.7 - 3085	Ruzickova et al. (2008)
Rural	Antarctica	Σ_{7}PCB= 0.51 - 1.81	Klanova et al. (2008)
Industrial	Spain	Σ_{7}PCB= 0.256 - 17.90	Nadal et al. (2007)
Urban	Spain	Σ_{7}PCB=0.185 - 10.543	Nadal et al. (2007)
Rural	Spain	Σ_{7}PCB= 0.292 - 2.105	Nadal et al. (2007)
Rural/Agricultural	Sweden	Σ_{13}PCB= 1.6 - 55	Armitage et al. (2006)
Urban/Rural	Russia	Σ_{17}PCB= 3.1 - 42	Wilcke et al. (2006)
Industrial/Urban/Rural	France	Σ_{7}PCB= 0.09 - 150	Motelay-Massei et al. (2004)
Industrial/Urban/Rural	Germany	Σ_{12}PCB= 0.82 - 158	Krauss & Wilcke (2003)

[a]: Yugoslavia, Czech Republic, Serbia and Montenegro, Bosnia and Herzegovina

Piccardo et al. (2005) were observed at high PAHs levels (201.6 - 817.4 µg/kg) in needle samples collected from industrial areas while low PAHs levels (10.4-39.1 µg/kg) in needle samples collected from rural areas in their study. PAHs levels of pine needles were ranged between 213-1773 µg/kg in the study that made in different parts of Portugal and Spain (Ratola et al., 2009). Mean Σ_{16}-PAHs concentrations of *Pinus pinea* needles were measured in the range of 188 ± 117 µg/kg and 337 ± 153 µg/kg in rural and industrial areas in another similar study carried out in Portugal (Amigo et al., 2011). Similar spatial distribution was observed in this study and obtained results were comparable to literature (Zhou et al., 2014; Choi, 2014; Oishi, 2013; Kuang et al., 2011; Yin et al., 2011b).

In this study, Σ_{16}PAH concentrations in needle samples were ranged from 89 to 12161 μg/kg in Iskenderun and they ranged from 197 to 8813 μg/kg in Aliaga, respectively. In addition, Σ_{41}PCB concentrations in needle samples ranged from 1.19 to 105 μg/kg in Iskenderun and from 0.69 to 220 μg/kg in Aliaga**.** Atmospheric POP concentrations measured in the present study were within the ranges reported in the literature (Rauert & Harner, 2016; Zhou et al., 2015; Zhou et al., 2014; De Nicola et al., 2014; Choi, 2014; Zhao et al., 2008; Chen et al., 2006).

PAH and PCB concentrations measured in this study were within the range of previously reported values in other urban and industrial sites around the world (Tables 2.8 – 2.9). Total 16-PAH concentrations of needle samples measured in this study are considerably higher than reported by Ratola et al. (2009) for urban sites in Portugal and Spain, by Piccardo et al. (2005) for urban sites in Italy, and by Augusto et al. (2010) for industrial sites in Portugal. Total 41-PCB concentrations of needle samples measured in this study are considerably higher than reported by Chen et al. (2006) for urban sites in China, and by Chropenova et al. (2016) for rural sites in Slovania.

The recorded concentrations of total PAHs in needle samples throughout the world were ranged from 1773 to 71 μg/kg in literature (Ratola et al., 2009; Ratola et al., 2010a) (Table 2.8). The total PAH concentration of needle in Portugal (Ratola et al., 2010a) were found to be low compared with those reported for other countries in Table 2.8. In addition, higher needle PAH concentrations were observed in Portugal and Spain (Ratola et al., 2009).

In addition, the measured concentrations of total PCBs in needle samples throughout the world were ranged from 271 to 1.068 μg/kg in literature (Xu et al., 2004; Chropenova et al., 2016) (Table 2.9). Total PCB concentrations of needle samples in Slovania (Chropenova et al., 2016) were found to be low compared with those reported for other countries in Table 2.9. Higher needle PCB concentrations were observed in China (Xu et al., 2004). In this study, Σ_{16}PAH concentrations in bark samples were ranged from 13 to 1523 μg/kg in Iskenderun and they ranged

from 23 to 745 μg/kg in Aliaga, respectively. In addition, Σ_{41}PCB concentrations in soil samples ranged from 0.46 to 72 μg/kg in Aliaga and from 0.55 to 67 μg/kg in Iskenderun**.** Atmospheric POP concentrations measured in the present study were within the ranges reported in the literature (Choi, 2014; Zhou et al., 2014, 2015; Ratola et al., 2009; Wen et al., 2009; Zhao et al., 2008).

Total 16-PAH concentrations of bark samples measured in this study are considerably higher than reported by Ratola et al. (2009) for urban sites in Portugal and Spain. Total 41-PCB concentrations of bark samples measured in this study are considerably higher than reported by Zhao et al. (2008) for urban sites in China, and by Zhou et al. (2015) for industrial sites in China.

The recorded concentrations of total PAHs in bark samples throughout the world were ranged from 22700 to 196 μg/kg in literature (Choi, 2014; Ratola et al., 2009) (Table 2.8). Total PAH concentrations of bark in Spain (Ratola et al., 2009) were found to be low compared with those reported for other countries in Table 2.8. In addition, higher bark PAH concentrations were observed in Korea (Choi, 2014).

In addition, the measured concentrations of total PCBs in bark samples throughout the world were ranged from 140 to 5.19 μg/kg in literature (Gueguen et al., 2011; Zhou et al., 2015) (Table 2.9). Total PCB concentrations of bark in China (Zhou et al., 2015) were found to be low compared with those reported for other countries in Table 2.9. Higher bark PCB concentrations were observed in France and Germany (Gueguen et al., 2011).

Table 2.8 Tree components total PAH concentrations in the literature

Study Area	**Location**	**Tree Species**	**Tree Component**	**ΣPAH (µg/kg)**	**Study**
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Branch	Σ_{16}PAH= 6.3 - 451	This study
Industrial/Rural	Aliaga- Turkey	Pine (*Pinus pinea and Pinus brutia*)	Branch	Σ_{16}PAH= 12 - 955	This study
Industrial/Rural	Iskenderun - Turkey	Pine (*Pinus pinea and Pinus brutia*)	Stem	Σ_{16}PAH= 178 - 4154	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Stem	Σ_{16}PAH= 340 - 18814	This study
Industrial/Rural	Iskenderun - Turkey	Pine (*Pinus pinea and Pinus brutia*)	Litter	Σ_{16}PAH= 113 -7848	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Litter	Σ_{16}PAH= 83 - 2774	This study
Industrial/Rural	Iskenderun - Turkey	Pine (*Pinus pinea and Pinus brutia*)	Bark	Σ_{16}PAH= 13 - 1523	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Bark	Σ_{16}PAH= 23 - 745	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	2-year needle	Σ_{16}PAH= 120 - 12161	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	2-year needle	Σ_{16}PAH= 261 - 8813	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	1-year needle	Σ_{16}PAH= 89 - 6524	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	1-year needle	Σ_{16}PAH= 197 - 3390	This study
Rural	Spain	Pine *(Pinus pinaster)*	Stem	Σ_{16}PAH= 137 ± 16.2	De Nicola et al. (2016)
Rural	Spain	Oak *(Quercus robur)*	Stem	Σ_{16}PAH= 140 ± 25.0	De Nicola et al. (2016)
Industrial/Rural	Toronto - Canada	Red Pine (*Pinus resinosa*)	Stem	Σ_{16}PAH= 0.2 - 35	Rauert & Harner (2016)
Industrial/Urban/ Rural	Italy	Holm oaks (*Quercus ilex*)	Litter	Σ_{16}PAH= 143 - 887	De Nicola et al. (2014)
Urban/Suburban/ Rural	China	Camphor (*Cinnamomum camphora*)	Bark	Σ_{15}PAH= 6.18 - 1560	Zhou et al. (2014)
Forested Area (After fire)	South Korea	Pine (*Pinus sp.*)	Bark	Σ_{16}PAH= 60.6 - 22700	Choi (2014)
Forested Area (After fire)	South Korea	Pine (*Pinus sp.*)	Litter	Σ_{16}PAH= 11.5 - 2480	Choi (2014)
Urban	Japan	Pine (*Pinus thunbergi*)	Needle	Σ_{16}PAH= 122.6 ± 50.5	Oishi (2013)

Table 2.8 Tree components total PAH concentrations in the literature *(continue)*

Study Area	Location	Tree Species	Tree Component	ΣPAH (µg/kg)	Study
Industrial	China	Pine (*Pinus massoniana)*	Stem	Σ_{16}PAH= 60.72 - 465	Kuang et al. (2011)
Rural	China	Gingko (*Gingko biloba*)	Stem	Σ_{18}PAH=313	Yin et al. (2011b)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinaster*)	Needle	Σ_{16}PAH= 574 ± 248	Ratola et al. (2011b)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinea*)	Needle	Σ_{16}PAH= 251 ± 102	Ratola et al. (2011b)
Industrial/Rural	Portugal	Pine *(Pinus pinea)*	Needle	Σ_{16}PAH= 188 - 337	Amigo et al. (2011)
Industrial/Rural	Portugal	Pine *(Pinus pinaster)*	Needle	Σ_{16}PAH= 96 - 866	Amigo et al. (2011)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinaster*)	1-year needle	Σ_{16}PAH= 90 ± 50	Ratola et al. (2010a)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinaster*)	3-year needle	Σ_{16}PAH= 1212 ± 436	Ratola et.al. (2010a)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinea*)	1-year needle	Σ_{16}PAH= 71 ± 33	Ratola et al. (2010a)
Industrial/Urban/ Rural	Portugal	Pine (*Pinus pinea*)	2-year needle	Σ_{16}PAH= 514 ± 317	Ratola et al. (2010a)
Industrial	Portugal	Pine (*Pinus pinea*)	Needle	Σ_{16}PAH= 83 - 467	Augusto et al. (2010)
Urban/Rural	Portugal and Spain	Pine (*Pinus pinaster* and *Pinus pinea*)	Bark	Σ_{16}PAH= 22-196	Ratola et al. (2009)
Urban/Rural	Portugal and Spain	Pine (*Pinus pinaster* and *Pinus pinea*)	Needle	Σ_{16}PAH= 213 - 1773	Ratola et al. (2009)
Urban	China	Pine (*Pinus massoniana*)	Bark	Σ_{18}PAH= 5.1-1770	Zhao et al. (2008)
Urban	Greece	Pine (*Pinus pinea*)	Needle	Σ_{13}PAH= 35 - 224	Ratola et al. (2008)
Rural	Iberian Peninsula	Pine (*Pinus pinea)*	Needle	Σ_{16}PAH= 21.86 - 339	Ratola et al. (2006)
Urban/Rural	Italy	Pine (*Pinus nigra*)	Needle	Σ_{9}PAH=12.19 - 507	Piccardo et al. (2005)
Urban/Rural	Italy	Pine (*Pinus pinaster*)	Needle	Σ_{9}PAH= 10.41 - 817	Piccardo et al. (2005)
Urban/Rural	Germany	Pine *(Pinus nigra)*	Needle	Σ_{15}PAH= 51 - 410	Lehndorff & Schwark (2004)

Table 2.9 Tree components total PCB concentrations in the literature

Study Area	**Location**	**Tree Species**	**Tree Component**	**ΣPCB (µg/kg)**	**Study**
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Branch	Σ_{41}PCB= 0.52 – 8.80	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Branch	Σ_{41}PCB= 0.41 – 14.7	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Stem	Σ_{41}PCB= 1.18 - 23.3	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Stem	Σ_{41}PCB= 3.82 - 135	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Litter	Σ_{41}PCB= 1.22 - 165	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Litter	Σ_{41}PCB= 0.95 - 286	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Bark	Σ_{41}PCB= 0.55 - 67	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	Bark	Σ_{41}PCB= 0.46 - 72	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	2-year needle	Σ_{41}PCB= 1.38 - 105	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	2-year needle	Σ_{41}PCB= 0.69 - 220	This study
Industrial/Rural	Iskenderun-Turkey	Pine (*Pinus pinea and Pinus brutia*)	1-year needle	Σ_{41}PCB= 1.19 - 45.6	This study
Industrial/Rural	Aliaga-Turkey	Pine (*Pinus pinea and Pinus brutia*)	1-year needle	Σ_{41}PCB= 0.75 - 37.5	This study
Rural	Slovania	Pine (*Pinus mugo*)	1-year needle	Σ_{7}PCB= 0.14 - 1.068	Chropenova et al. (2016)
Industrial/Rural	China	Camphor	Bark	Σ_{32}PCB= 0.58 - 5.19	Zhou et al. (2015)
Industrial/Urban	France and Germany	Pine species	Bark	Σ_{7}PCB= 4 - 140	Gueguen et al. (2011)
Industrial	China	Pine (*Cedrus deodara*)	Bark	Σ_{7}PCB= 112	Wen et al. (2009)
Urban	China	Pine (*Pinus massoniana*)	Bark	Σ_{10}PCB= 0.21 - 21.6	Zhao et al. (2008)
Industrial/Rural	Poland	Pine *(Pinus sylvestris)*	1- year needle	Σ_{9}PCB= 2.7 - 50	Wyrzykowska et al. (2007)
Urban	China	Pine *(Cedrus deodara)*	Needle	Σ_{9}PCB= 4.4	Chen et al. (2006)
Industrial/Rural	China	Pine *(Pinus tabulaeformis)*	Needle	Σ_{15}PCB= 21.0 - 271	Xu et al. (2004)

CHAPTER THREE
MATERIALS AND METHODS

Sampling sites, sampling program, sampling techniques, experimental methods used for the measurement of POPs, determination of concentrations, quality control and assurance, modeling of ambient air POP concentrations, and calculation of POP inventory are explained in this section.

3.1 Sampling Sites

The field studies were carried out in the forest areas and urban parks of Izmir-Aliaga and Hatay-Iskenderun in Turkey. These sampling areas are prominent sites in Turkey because of several industries. A large petroleum refinery, a petrochemical complex, a large integrated steel plant, several ferrous scrap processing iron−steel plants with electric arc furnaces (EAFs), scrap storage and classification sites, steel rolling mills, a natural gas−fired power plant, fertilizer plants, a cement plant, intense transportation of ferrous scrap trucks, intense vehicular traffic, ship breaking yards, and busy ports for product and raw material transportation are the several sources of air pollutants in the sampling regions. Many residential areas are also located in these regions (Figures 3.1 - 3.2). Number of major facilities in the industrial regions by the year 2010 and their starting periods are given in Tables 3.1 - 3.2.

The sampling sites were selected according to the locations of industrial facilities and meteorological conditions in these regions. Twenty-seven different sampling sites were selected to represent locations affected by the industrial emissions (n= 21 for Aliaga, n= 20 for Iskenderun) and the background (n= 6 for Aliaga, n= 7 for Iskenderun) locations for each region. Twenty sampling sites in Iskenderun and twenty-one sampling sites in Aliaga were selected from areas exposed to pollutant sources directly. The site selection was done depending on initial field trips and the results of recent studies conducted in these regions (Cetin & Odabasi, 2007; Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2008, 2009). Sampling sites

in the Hatay-Iskenderun and Izmir-Aliaga are shown in Figures 3.1 - 3.2, respectively.

Table 3.1 Number of facilities in Iskenderun industrial region and their starting periods

Pollution Source	**Facility Number**	**Operation Starting Period**
Fertilizer Plant	1	1950-1955
Cement Plant	1	1975-1980
Iron-Steel Plant	1	1945-1950
	2	1975-1980
	1	1980-1985
	1	1985-1990
	2	1990-1995
	1	2000-2005
	3	2005-2010

Table 3.2 Number of facilities in Aliaga industrial region and their starting periods

Pollution Source	**Facility Number**	**Operation Starting Period**
Petroleum Refinery	1	1971-1976
Ship Dismantling	1	1971-1976
Fertilizer Plant	1	1976-1981
Petrochemical Plant	1	1981-1986
Natural Gas Power Plant	1	2001-2006
Iron-Steel Plant	2	1981-1986
	3	1986-1991
	6	1991-1996
	2	1996-2001
	1	2001-2006
	2	2006-2011

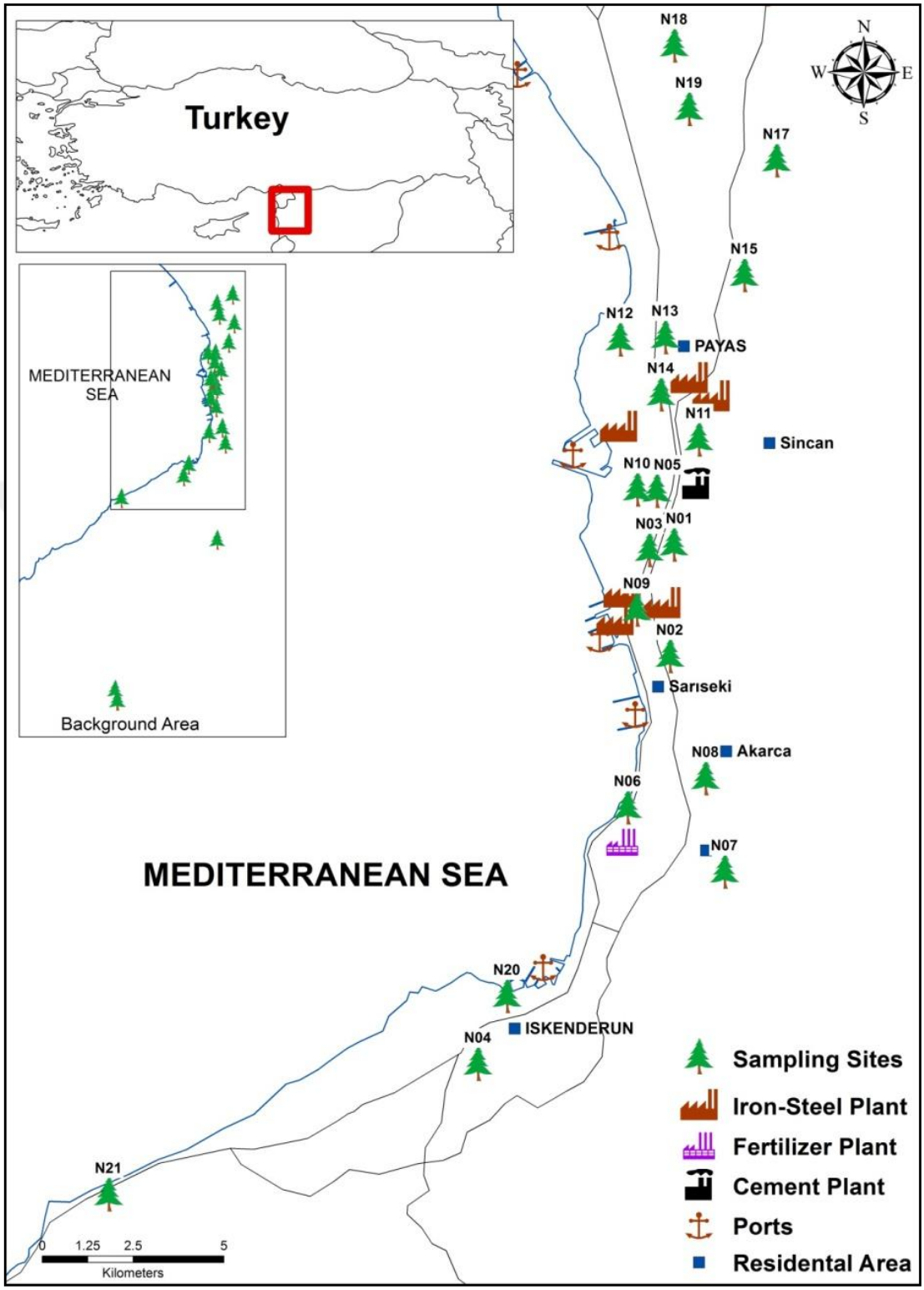


Figure 3.1 Map of the study area in Hatay-Iskenderun showing the major industries, residential areas, and sampling sites

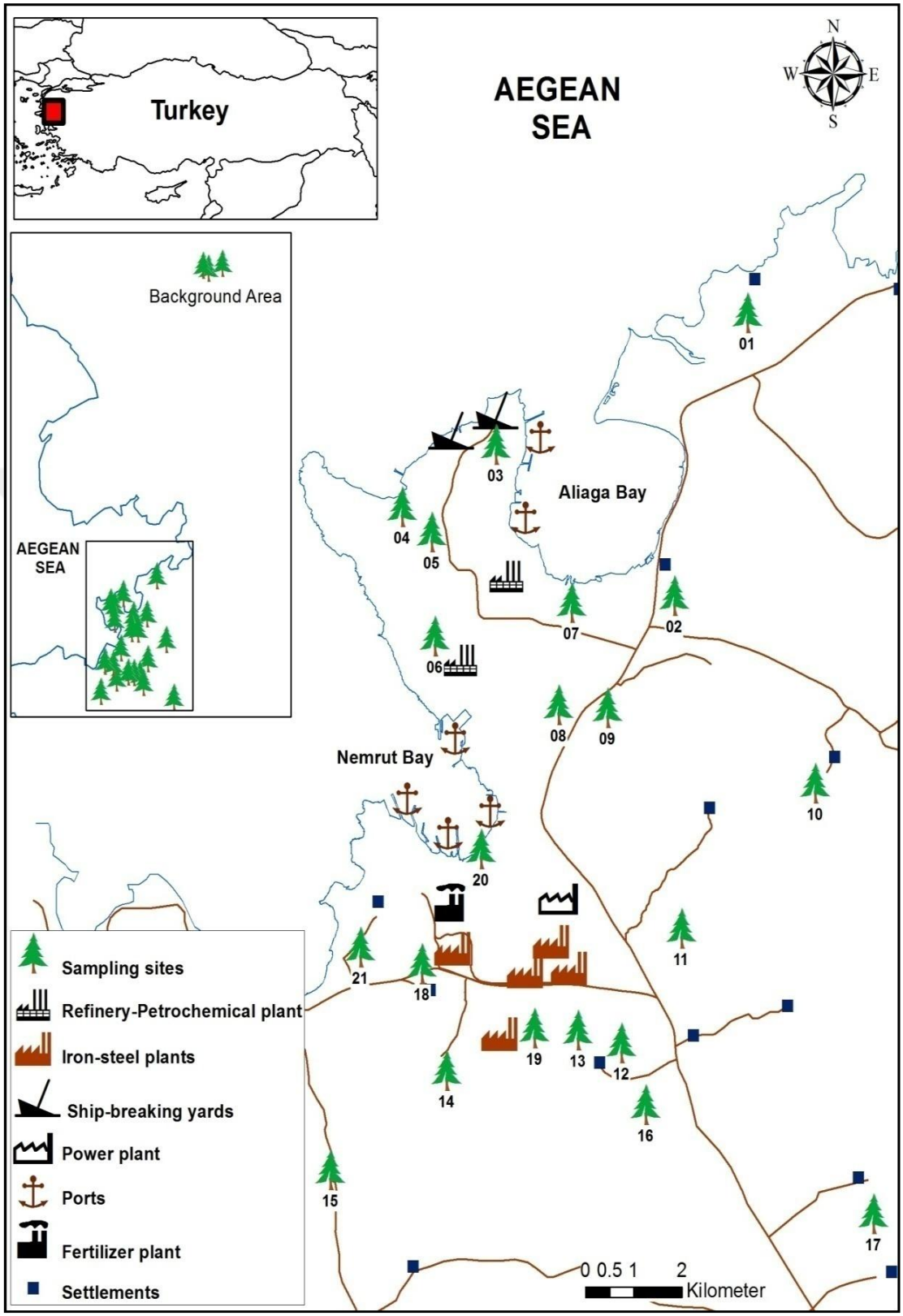


Figure 3.2 Map of the study area in Izmir-Aliaga showing the major industries, residential areas, and sampling sites

3.2 Sampling Program

Sampling studies were conducted in a dry period of autumn after growth of pine needles and stem wood were finished in the regions. Sampling studies were finished before the beginning of autumn rains so as not to wash pollutants deposited on trees by dry deposition. Pine needles (1-year and 2-year), bark, branch, stem, litter, and soil samples were collected from all sampling sites during the period of September 26 to October 04, 2011 in Izmir-Aliaga and November 7 and 14, 2010 in Hatay-Iskenderun. After preliminary field studies, it was confirmed that Red pine (*Pinus brutia*) and Stone pine (*Pinus pinea*) are the widespread species in the forest areas of these regions. Therefore, these pine species that *Pinus brutia* (Sites 6, 11, 12, 13, 14, 15, 16, 19, 20, 23, 25, 27 in Aliaga and Sites 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 14, 15, 16, 17, 18, 19, 20, 21, 22, 25 in Iskenderun) and *Pinus pinea* (Sites 1, 2, 3, 4, 7, 8, 9, 17, 18, 21, 22, 24, 26 in Aliaga and Sites 9, 13, 23, 24, 26, 27 in Iskenderun) were used for the sampling of tree components in the sampling regions. Either *Pinus brutia* or *Pinus pinea* were sampled in different sites of two sampling regions while both species were sampled at Sites 5 and 10 in Aliaga. Concentrations of PAHs and PCBs in 1-year needle, 2-year needle, bark, branch, and stem samples collected from collocated trees at Sites 5 and 10 were not substantially different with ratios (*Pinus pinea*/*Pinus brutia*) between 0.76 ± 0.47−1.14 ± 0.35 (average ± SD). Air samples were collected on polyurethane foam (PUF) disks using passive samplers (PAS) during a four months deployment period (October 2011 to January 2012) in Aliaga and over three months (November 2010 to February 2011) in Iskenderun. Tables 3.3 - 3.4 summarize the sampling programs for the two sampling regions.

Table 3.3 Sampling program for Hatay-Iskenderun

Sampling Site Number	Species of Sampled Tree	Needle[b]	Branch[c]	Bark[d]	Stem	Soil	Litter	Ambient air	Total
1	*Pinus brutia*	2	1	1	13	1	1	1	20
2	*Pinus brutia*	2	1	1	1	1	1	1	8
3	*Pinus brutia*	2	1	1	1	1	1	1	8
4	*Pinus brutia*	2	1	1	1	1	1	1	8
5	*Pinus brutia*	2	1	1	1	1	1	1	8
6	*Pinus brutia*	2	1	1	9	1	1	1	16
7	*Pinus brutia*	2	1	1	1	1	1	1	8
8	*Pinus brutia*	2	1	1	1	1	1	1	8
9	*Pinus pinea*	2	1	1	1	1	1	1	8
10	*Pinus brutia*	2	1	1	6	1	1	1	13
11	*Pinus brutia*	2	1	1	11	1	1	1	18
12	*Pinus brutia*	2	1	1	7	1	1	1	14
13	*Pinus pinea*	2	1	1	1	1	-[e]	1	7
14	*Pinus brutia*	2	1	1	6	1	1	1	13
15	*Pinus brutia*	2	1	1	1	1	1	1	8
16	*Pinus brutia*	2	1	1	1	1	1	1	8
17	*Pinus brutia*	2	1	1	1	1	1	1	8
18	*Pinus brutia*	2	1	1	6	1	1	1	13
19	*Pinus brutia*	2	1	1	7	1	1	1	14
20	*Pinus brutia*	2	1	1	1	1	1	1	8
21 Background[a]	*Pinus brutia*	2	1	1	1	1	1	1	8
22 Background[a]	*Pinus brutia*	2	1	1	1	1	1	1	8
23 Background[a]	*Pinus pinea*	2	1	1	1	–[f]	–[f]	–[f]	5
24 Background[a]	*Pinus pinea*	2	1	1	4	1	1	1	11
25 Background[a]	*Pinus brutia*	2	1	1	10	–[g]	–[g]	–[g]	14
26 Background[a]	*Pinus pinea*	2	1	1	11	1	1	1	18
27 Background[a]	*Pinus pinea*	2	1	1	6	–[h]	–[h]	–[h]	10
Total									**290**

[a] Not exposed directly to pollution
[b] One and two years aged needles
[c] Composite samples collected from stem sample trees
[d] Composite samples collected from stem sample trees
[e] Litter sample was not taken
[f] Same samples with Site 22
[g] Same samples with Site 24
[h] Same samples with Site 26

Table 3.4 Sampling program for Izmir-Aliaga

Sampling Site Number	Species of Sampled Tree	Needle[b]	Branch[c]	Bark[d]	Stem	Soil	Litter	Ambient Air	Total
1	*Pinus pinea*	2	1	1	6	1	1	1	13
2	*Pinus pinea*	2	1	1	9	1	1	1	16
3	*Pinus pinea*	2	1	1	6	1	1	1	13
4	*Pinus pinea*	2	1	1	4	1	1	1	11
5	*Pinus pinea & Pinus brutia*	2	1	1	9	2	2	1	25
6	*Pinus brutia*	2	1	1	3	1	1	1	10
7	*Pinus pinea*	2	1	1	12	1	1	1	19
8	*Pinus pinea*	2	1	1	9	1	1	1	16
9	*Pinus pinea*	2	1	1	4	1	1	1	11
10	*Pinus pinea & Pinus brutia*	2	1	1	7	2	2	1	23
11	*Pinus brutia*	2	1	1	4	1	1	1	11
12	*Pinus brutia*	2	1	1	5	1	1	1	12
13	*Pinus brutia*	2	1	1	12	1	1	1	19
14	*Pinus brutia*	2	1	1	3	1	1	1	10
15	*Pinus brutia*	2	1	1	6	1	1	1	13
16	*Pinus brutia*	2	1	1	8	1	1	1	15
17	*Pinus pinea*	2	1	1	3	1	1	1	10
18	*Pinus pinea*	2	1	1	3	1	1	1	10
19	*Pinus brutia*	2	1	1	8	1	1	1	15
20	*Pinus brutia*	2	1	1	4	1	1	1	11
21	*Pinus pinea*	2	1	1	4	1	1	1	11
22 Background[a]	*Pinus pinea*	2	1	1	12	1	1	1	19
23 Background[a]	*Pinus brutia*	2	1	1	16	1	1	1	23
24 Background[a]	*Pinus pinea*	2	1	1	11	1	1	1	18
25 Background[a]	*Pinus brutia*	2	1	1	12	1	1	1	19
26 Background[a]	*Pinus pinea*	2	1	1	12	1	1	1	19
27 Background[a]	*Pinus brutia*	2	1	1	13	- [e]	- [e]	- [e]	17
Total									**409**

[a] Not exposed directly to pollution
[b] One and two years aged needles
[c] Composite samples collected from stem sample trees
[d] Composite samples collected from stem sample trees
[e] Same samples with Site 26

3.3 Sampling Methods

3.3.1 Selection of Sampling Area

The size of the sampling area was selected as 10 m x 10 m = 100 m^2 if the trees in the forest are green and dense (Figure 3.3). Trees in the forest are aged and wide apart, the size of sampling area was selected as 20 m x 20 m = 400 m^2. Then, heights and diameters at breast height (1.3 m) of all the trees were measured (Figures 3.4 - 3.5). These diameter and height values were used for biomass calculation. Tree components (needle, bark, branch and stem) samples were collected from healthy (not broken top, not under stress) trees. Operations of industrial facilities were started at 35-40 years ago in the sampling regions. Because of this, it was planned that stem samples taken from at least 45-50 years old trees to determine the development of air pollution. Generally, the trees with bigger than age of 50 were not available in sampling sites of Iskenderun but the oldest trees (age of 27 – 50 for Iskenderun and age of 28 – 112 for Aliaga) were selected in the sampling sites.

Figure 3.3 Determination of sampling area

Figure 3.4 Measurement of tree diameter

Figure 3.5 Equipment used for measurement of tree height

3.3.2 Collection of Needle and Branch Samples

Branch and needle (1-year and 2-year) samples were collected from the same trees that were used for bark and stem sampling. With preliminary field studies, it was examined that there were maximum 2 years old needles at *Pinus brutia* in the most sampling sites. For this reason, 1 (belong to the studied year) and 2 (belong to the previous year) years old needles were collected from both *Pinus brutia* and *Pinus pinea* in two regions. Branch and needle samples were collected using a telescoping

pruning stick (4 m length) from the upper 1/3 of the crown (Figure 3.6). Then, the needle samples were separated into two parts as the current year's (6 months old) and past year's needles (1.5 years old) (Figure 3.7). These are referred as 1-year and 2-year needle samples in the present study. All branch and needle samples were placed into their pre-cleaned glass containers, they were transported to the laboratory, and they stored at 4°C until they were processed.

Figure 3.6 Collection of needle samples by using a telescoping pruning stick

Figure 3.7 Separation of needle samples as 1-year and 2-year

3.3.3 Collection of Bark Samples

Bark samples were collected at 1.5 m height from the ground, from the 4 sides of the stem, and from upper 0.5 cm using a bark knife (Figure 3.8). The bark samples were collected from at least 3-4 trees in each sampling site. Collected bark samples were placed into their pre-cleaned glass containers, they were transported to the laboratory, and they stored at 4°C until they were processed (Figure 3.9).

Figure 3.8 Collection of bark samples by using bark knife

Figure 3.9 Collected bark samples

3.3.4 Collection of Tree Ring Samples

Tree ring samples were collected at height of 1.5 m from the ground using an increment borer (Figures 3.10 - 3.11). Tree ring sampling depth covered the whole life span of the trees (between the center and bark). According to the analysis method of POPs with gas chromatography/mass spectrometry (GC/MS) technique, the 2-3 g mass of tree ring is needed for each sampling site. In order to reach this amount, the 4-5 different trees were sampled. Collected samples were transferred to the laboratory in their thoroughly pre-cleaned glass containers and they were kept at 4°C until they were prepared for analysis (Figure 3.12).

Ages of the sampled trees were determined by counting the annual rings under a magnifying glass and they ranged between 27 - 50 years in Iskenderun and 28 - 112 years in Aliaga. Sampling sites selected for determination of historical variation of pollutants, age and numbers of sampled trees are given in Table 3.5.

Figure 3.10 Collection of tree ring samples by using increment borer

Figure 3.11 Collected tree ring sample

(a) (b)

Figure 3.12 Storage (a) and transportation (b) of collected tree ring samples

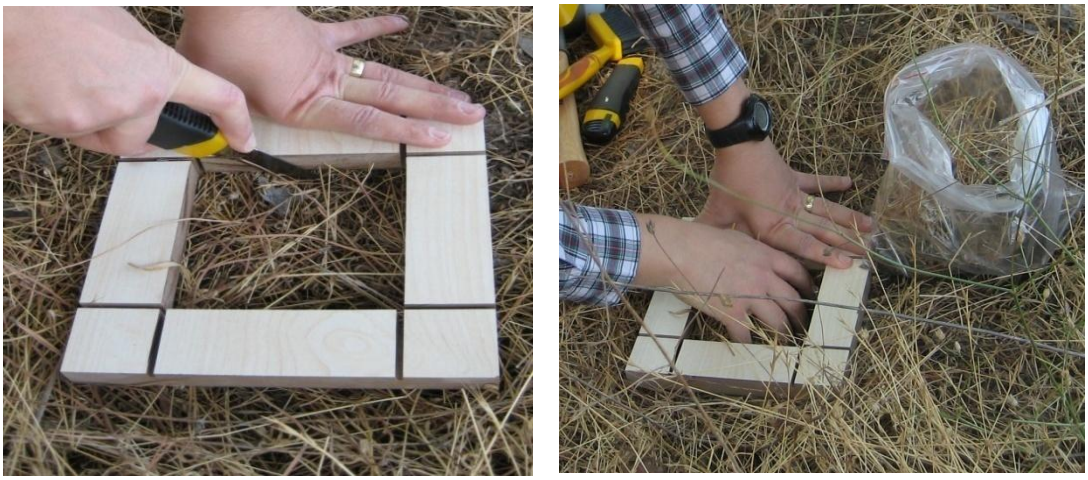
Table 3.5 Sampling sites selected for determination of historical variation of pollutants, ages and number of sampled trees

Iskenderun				Aliaga		
Sampling Sites	**Age Range of Trees**	**Number of Tree Rings [a]**		**Sampling Sites**	**Age Range of Trees**	**Number of Tree Rings [a]**
N-1	50-82	5		N-2	37-44	6
N-6	36-44	4		N-7	27-37	6
N-10	17-27	3		N-8	28-30	6
N-11	12-54	8		N-13	57-76	6
N-12	27-35	6		N-15	68-83	3
N-14	28-30	4		N-16	39-66	6
N-18	22-26	4		N-19	29-44	6
N-19	33-35	3		N-20	32-35	3
N-24	18-19	3		N-22	26-30	6
N-25	13-50	5		N-23	56-60	10
N-26	41-54	7		N-24	79-112	7
N-27	27-30	6		N-25	59-66	6
				N-26	60-76	6
				N-27	62-85	8

[a] Number of samples that were obtained by cutting samples into 5-year increments in laboratory

3.3.5 Collection of Litter Samples

Litter is an organic layer formed by the accumulation of dry shed branches, leaves, seeds and plant residues on the soil surface. Litter samples were mainly consisted of fallen pine needles. Four duplicates of litter were sampled by collecting the layer over the soil in a 10 x 10 cm area (Figure 3.13). Litter samples were placed into their pre-cleaned glass containers, they were transported to the laboratory, and they stored at 4 °C until they were processed.



(a) (b)

Figure 3.13 Equipment used for litter sampling (a) and collection of litter samples (b)

3.3.6 Collection of Soil Samples

The soil samples were collected manually at 0-5 cm depth from the surface (Figure 3.14). Equal portions of 10 replicates were collected over a ~ 100 m^2 area. Then the collected samples were combined and homogenized for each sampling site. Collected soil samples were placed into their pre-cleaned glass containers, they were transported to the laboratory, and they stored at 4 °C until they were processed.

(a) (b)

Figure 3.14 Collection of soil samples (a), equipment used for sampling (b)

3.3.7 Collection of Ambient Air Samples

Ambient air samples were collected by using polyurethane foam (PUF) disk passive air samplers (Figure 3.15a). PUF disks (14 cm diameter, 1.35 cm thickness, 365 cm^2 surface area, 0.0213 g/cm^3 density, 4.40 g/mass, and 207 cm^3/volume) were placed inside a stainless steel chamber consisted of two stainless steel domes with external diameters of 30 cm and 20 cm (Figure 3.15b). The design of the sampler protects the PUF from precipitation, coarse particle deposition, UV radiation and minimizes the effects of wind speed on the uptake rate. Sampler-1 of ambient air samples was lost due to an unknown reason in Iskenderun. All ambient air samples were transferred to the laboratory in their thoroughly cleaned glass containers and they were kept at 4°C until they were prepared for analysis.

(a) (b)

Figure 3.15 Ambient air sampling (a), polyurethane foam (PUF) disk (b)

3.4 Laboratory Studies

3.4.1 Preparation of Samples for Analyses

3.4.1.1 Tree Components, Soil and Litter Samples

Collected soil samples were sieved through a 2.0 mm mesh plastic sieve to remove large particles, stones and organic debris. About 10 g of soil samples was used to determine their water and organic matter content while 5 g sample was used

for chemical analysis. Litter and tree component (needle, bark, branch and stem) samples were cut into small pieces (about 1 cm) before the extraction. Sample preparation stages shown are in Figure 3.16. For dating sites where trees older than 30 years (representing the industrialization period in the areas), tree ring samples were cut into 5-year increments and each increment was processed and analyzed separately. For the remaining sites, tree ring samples were processed as single samples. A magnifying glass was used in the slicing process due to ring width of old trees is very thin. A craft knife was used for the 5-yearly separation. Tree ring samples sliced 5-yearly segment were combined (Figure 3.17). Homogenized samples were put into their pre-cleaned glass containers and they stored at 4 °C until they were processed (Figure 3.18).

Prior to extraction of tree component, soil and litter samples, PAH (naphthalnene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) and PCB (PCB-14, PCB-65, PCB-166) surrogate standards dissolved in 0.5 mL hexane were spiked into samples to monitor the analytical recovery efficiency. Soil, litter, and plant samples (5−10 g) were soaked in 40 mL of 1:1 acetone:hexane overnight. Then, they were ultrasonically extracted for 30 min. The extract volumes were reduced to 2 mL and they were transferred into hexane using a rotary evaporator and a high purity N_2 stream. Then, litter, soil and tree component samples were cleaned up using gel permeation chromatography (GPC) with ethyl acetate:cyclohexane (1:1) as the mobile phase at 5 mL/min for 65 min (13 min-matrix elution, 42 min-sample collection, 10 min-GPC column postcleaning). Sample volumes were reduced to 2 mL. All samples were cleaned up and fractionated on an alumina-silicic acid column containing 3 g silicic acid (deactivated with 4.5% DI water) and 2 g alumina (deactivated with 6% DI water). The column was prewashed with 20 mL dichloromethane (DCM) and 20 mL petroleum ether (PE). Then, the sample was added to the column and PCBs were eluted with 35 mL PE (Fraction 1) while PAHs were eluted with 20 mL DCM (Fraction 2) (Figure 3.19). The final extracts were solvent exchanged into hexane and they were concentrated to 1 mL under a stream of N_2.

(a) (b)

Figure 3.16 Sample preparation stages; Soil samples were passed through a 2 mm mesh plastic sieve (a), Branch samples were divided into approximately 1 cm pieces by using scissors (b)

Figure 3.17 Tree ring samples sliced 5-yearly segment

Figure 3.18 Homogenizated samples

(a) (b)

Figure 3.19 Clean up columns (a) and fractionation process (b) of samples

3.4.1.2 Ambient Air Samples

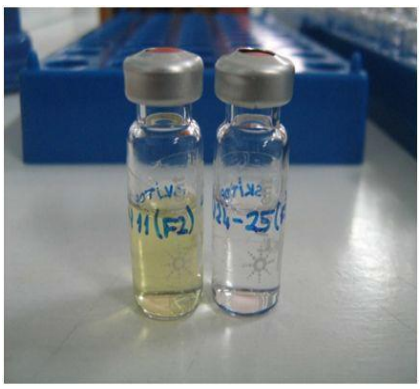
PUF filters were Soxhlet extracted for 24 hours with 1:1 acetone:hexane. After extraction, they were dried in an oven at 70°C overnight, and stored in a freezer in glass jars capped with Teflon-lined lids. Prior to air sampling, depuration compounds (DCs) (not in nature, a part of the organic compounds labeled with carbon-13, ^{13}C-PCB 3, ^{13}C-PCB 9, ^{13}C-PCB 15, PCB 30, PCB 107, PCB 198) were spiked (17.5−20 ng per sample in 20 mL hexane) evenly onto PUF disks in order to determine the sampling rate of POPs. Then, PUFs were placed into glass containers and hexane was evaporated using a gentle stream of N_2. PUFs were kept for 1 week in their closed containers in a freezer. Then, PUF disk passive samplers were transported to the field.

Prior to extraction, ambient air samples were spiked with PAH and PCB surrogate standards to monitor the analytical recovery efficiency. Ambient air samples were Soxhlet extracted for 12 hours with 1:1 acetone:hexane. Then, the extract volumes were reduced to 2 mL and they were transferred into hexane using a rotary evaporator and a high purity N_2 stream. All samples were cleaned up and fractionated on an alumina-silicic acid column containing 3 g silicic acid (deactivated with 4.5% DI water) and 2 g alumina (deactivated with 6% DI water). The column was prewashed with 20 mL dichloromethane (DCM) followed by 20 mL petroleum ether (PE). Then, the sample in 2 mL hexane was added to the column and PCBs

were eluted with 35 mL PE (Fraction 1) while PAHs were eluted with 20 mL DCM (Fraction 2). The final extracts were solvent exchanged into hexane and they were concentrated to 1 mL under a stream of N_2. Stages of preparing ambient air samples are shown in Figure 3.20.

(a) (b)

(c)



(d) (e)

Figure 3.20 Stages of preparing ambient air samples; Soxhlet extraction process (a), Volume reduction of samples by using rotary evaporator (b), Clean up columns and fractionation process of samples (c), Solvent exchange of samples by using a high purity N_2 stream (d), Ambient air samples prepared to analysis (e)

3.4.2 Analyses

3.4.2.1 Persistent Organic Pollutants

All samples were analyzed for 16 PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h) anthracene, benzo(g,h,i)perylene), and 41 PCBs (PCB-18, 17, 31, 28, 33, 52, 49, 44, 74, 70, 95, 101, 99, 87, 110, 82, 151, 149, 118, 153, 132, 105, 138, 158, 187, 183, 128, 177, 171, 156, 180, 191, 169, 170, 199, 208, 195, 194, 205, 206, 209) with using a gas chromatograph (GC, Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD) system. PAHs and PCBs were analyzed in electron impact ionization (EI) mode. The capillary column used for the analysis of PAHs and PCBs was HP5-MS (30 m, 0.25 mm, 0.25 μm). Helium and methane were used as the carrier gas and reagent gas (for chemical ionization), respectively. Fraction 1 was used for the analysis of PCBs. Then, equal volumes of Fraction 1 and Fraction 2 were combined and they were analyzed for PAHs because low molecular weights PAHs are eluted in part by Fraction 1. Compounds were identified based on their retention times, target and qualifier ions, and they were quantified using the calibration procedure of internal standards. Analysis parameters of PAHs and PCBs for GC/MS are given in Table 3.6.

Table 3.6 Analysis parameters of PAHs and PCBs for GC/MS

Compound	**Column Type**	**Operation Parameters**	**Analysis Mode**
PAH	HP5-MS (30 m, 0,25 mm, 0,25 µm)	Initial oven temperature was held at 50°C for 1 min, was raised to 200°C at 25°C/min and from 200 to 300°C at 8°C/min, 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, 45 cm/s linear velocity).	Electron impact ionization (EI), selected ion monitoring mode (SIM)
PCB	HP5-MS (30 m, 0,25 mm, 0,25 µm)	Initial oven temperature was held at 50°C for 1 min and was raised to 200 ºC at 25ºC/min, from 200 to 300 ºC at 8ºC/min, and was held for 3 min. The injector, ion source, and quadrupole temperatures were 250, 230, and 150°C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 ml/min, 45 cm/s linear velocity).	Electron impact ionization (EI), selected ion monitoring mode (SIM)

3.4.2.2 Other Analyses

3.4.2.2.1 Determination of Moisture Content. Moisture contents of the soil and litter/tree component samples were measured as gravimetrically by drying subsamples for 24 hours in an oven at 105°C and 60°C, respectively. Moisture contents of samples are given in Appendix-1 (Tables A1.1 – A1.2).

3.4.2.2.2 Determination of Lipid Content. Lipid contents of tree components and litter samples were determined. Lipid content was determined by gravimetrically using an aliquot of sample extract that was evaporated until dryness under N_2 stream. Lipid contents of samples are given in Appendix-2 (Tables A2.1 – A2.2).

3.4.2.2.3 Measurement of Bark Surface Area. Ambient air POP concentrations were estimated with the help of a mathematical mass transfer model by using bark POP concentrations. Water displacement method was utilized to measure the bark density. "Specific Surface Area (SSA)" is one of the parameter used in the mathematical model. Specific surface area of bark samples was measured by nitrogen sorption. Scanning electron microscope (Scanning Electron Microscope SEM, Jeol JSM-6060) in the Metallurgical and Materials Engineering Department of Dokuz Eylul University was used for determining specific surface area of bark samples. The average specific surface area of the bark samples was ranged between 5.47 ± 1.98 m^2/g (average ± SD), respectively.

3.5 Quality Control and Quality Assurance

3.5.1 Procedural Recoveries

Prior to extraction, all samples and blank matrices were spiked with PAH and PCB surrogate standards to determine the analytical recoveries. Each sample was checked for the recovery efficiencies of surrogate standards if they were in the range of 50-120%. The recovery of the surrogate standards was used to correct the amounts of the specific PAHs and PCBs found in the samples, correspondingly.

Following average surrogate standards recoveries (average ± SD) were observed for different sample matrices: 52-113% (acenaphthene-d_{10}), 56-121% (phenanthrene-d_{10}), 59-112% (chrysene-d_{12}), 55-105% (perylene-d_{12}), 58-99% (PCB-14), 64-108% (PCB-65), 59-94% (PCB-166). Average recovery efficiencies of PAHs and PCBs surrogate standards in all blank and sample matrices are given in Table 3.7. Naphthalene was identified but not quantified in all samples because of the high blank amounts.

Table 3.7 Average recovery efficiencies of PAH and PCB surrogate standards (%, average ± SD) in all blank and sample matrices

	Ambient air	Soil	Bark	Litter	Needle	Branch	Stem
	PAH						
Acenaphthene-d10	112.9 ± 15.1	90.9 ± 14.1	53.8 ± 7.4	51.9 ± 5.3	55.7 ± 7.2	56.9 ± 5.0	61.8 ± 21.7
Phenanthrene-d10	121.2 ± 23.8	102.0 ± 14.7	56.4 ± 8.0	61.1 ± 7.0	62.4 ± 11.5	64.3 ± 7.6	69.3 ± 23.9
Chrysene-d12	111.5 ± 24.1	95.5 ± 17.7	58.7 ± 12.8	60.2 ± 7.5	63.4 ± 13.1	62.2± 8.6	75.6 ± 29.7
Perylene-d12	104.7 ± 23.9	90.8 ± 18.6	61.7 ± 24.0	54.9 ± 5.6	59.8 ± 13.0	59.4 ± 5.6	61.9 ± 17.1
	PCB						
PCB-14	99.2 ± 6.3	85.3 ± 13.9	57.6 ± 16.3	65.0 ± 14.1	68.1 ± 13.1	68.5 ± 17.2	80.2 ± 23.5
PCB-65	107.8 ± 9.4	89.7 ± 15.3	63.6 ± 19.2	67.7 ± 18.6	78.7 ± 13.5	77.7 ± 21.5	79.1 ± 19.1
PCB-166	93.9 ± 9.4	82.8 ± 14.1	59.0 ± 16.0	63.8 ± 11.7	71.4 ± 15.6	78.4 ± 17.0	82.8 ± 19.1

3.5.2 Blanks

PUF disk blanks for ambient air samples and solvent blanks for soil, litter and tree component samples were analyzed. Blank samples were prepared to determine the amount of contamination during sample collection, handling, and preparation. Four blank samples were prepared for each sample group in the analyses. All blank samples were extracted and analyzed in the same manner as the samples. All analyses preparation stages and procedures were repeated for blank samples. POP blank concentrations of all samples are given in Tables 3.8 - 3.9.

Table 3.8 PAH blank concentrations of tree component**,** soil, litter and ambient air samples (ng/ml)

PAH	Ambient Air		Soil		Litter-Branch-Needle-Bark		Stem	
	Isken derun	Aliaga	Isken derun	Aliaga	Isken derun	Aliaga	Isken derun	Aliaga
Acenaphthylene	29.2	30.0	28.3	28.3	32.1	15.6	17.0	0.8
Acenaphthene	56.7	39.0	37.7	37.3	47.4	21.4	40.7	4.8
Fluorene	185.7	71.0	69.9	68.5	66.0	56.1	61.5	4.7
Phenanthrene	240.4	129.5	128.4	127.6	196.1	220.2	173.7	14.7
Anthracene	22.3	4.6	3.9	3.4	n.d.	5.2	n.d.	0.5
Carbazole	2.7	2.6	1.5	0.6	1.8	n.d.	1.4	n.d.
Fluoranthene	21.5	16.5	14.6	14.7	26.8	27.2	18.7	3.0
Pyrene	16.9	12.7	12.8	12.9	54.9	30.1	28.7	5.7
Benz(a) anthracene	4.1	1.7	2.2	1.2	n.d.	2.7	0.01	0.6
Chrysene	15.2	3.9	4.5	2.8	14.6	9.1	2.7	0.2
Benzo(b) fluoranthene	n.d.	n.d.	2.8	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(k) fluoranthene	n.d.	n.d.	1.8	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(a)pyrene	2.4	n.d.	1.7	1.2	1.5	1.0	0.7	0.9
Indeno(1,2,3-cd) pyrene	5.0	3.0	2.1	1.2	0.9	0.1	0.5	0.2
Dibenz(a,h) anthracene	5.3	2.3	1.1	0.6	n.d.	n.d.	n.d.	n.d.
Benzo(g,h,l) perylene	5.9	4.2	2.2	1.5	1.2	0.4	0.6	0.2

n.d.: Not detected

Table 3.9 PCB blank concentrations of tree component, soil, litter and ambient air samples (ng/ml)

PCB	Ambient Air		Soil		Litter-Branch-Needle-Bark	Stem	
	Iskenderun	Aliaga	Iskenderun	Aliaga		Iskenderun	Aliaga
PCB-18	1.18	0.91	0.47	0.46	n.d.	n.d.	n.d.
PCB-17	0.48	0.52	0.24	0.30	n.d.	n.d.	n.d.
PCB-31	0.49	0.45	0.31	0.24	n.d.	n.d.	n.d.
PCB-28	0.52	0.54	0.37	0.31	n.d.	n.d.	n.d.
PCB-33	0.35	0.30	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-49	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-44	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-74	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-101	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-99	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-87	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-110	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-151	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-149	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-118	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-153	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-132	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-105	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-138	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-158	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-187	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-183	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-128	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-177	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-171	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-180	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-199	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: Not detected

3.5.3 Detection Limits

Detection limits of all analyzed compounds were determined for sample preparation (LOD), instrumental (IDL) and analysis method (MDL). Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. For 1 µl injection, the quantifiable amounts were 0.15 and 0.10 pg for PAHs and PCBs, respectively. The instrumental detection limit was used for the compounds that were not detected in blanks. For the compounds detected in blanks, method detection limit (MDL) was defined as the mean blank mass plus three standard deviations (MDL=Mean blank value+3SD). Average analyte amounts in blanks were generally less than 5% of the amounts found in samples. Sample quantities exceeding the MDL were quantified and blank–corrected by subtracting the average blank amounts from sample amounts. MDL for individual PAH and PCB compounds in tree component, soil, litter and ambient air samples are given in Tables 3.10 - 3.11.

Table 3.10 Method detection limits for PAHs in tree component, soil, litter and ambient air samples (air concentrations in ng/m^3, all other concentrations in µg/kg)

PAH	Ambient Air		Soil		Litter-Branch-Needle-Bark		Stem	
	Iskenderun	Aliaga	Iskenderun	Aliaga	Iskenderun	Aliaga	Iskenderun	Aliaga
Acenaphthylene	0.778	0.928	7.07	7.26	11.22	4.85	5.90	2.99
Acenaphthene	1.090	0.890	8.78	8.88	16.17	5.71	23.50	9.97
Fluorene	2.520	0.921	16.17	15.77	22.57	11.33	38.07	16.56
Phenanthrene	1.781	0.925	29.49	29.70	53.11	48.62	82.43	45.48
Anthracene	0.197	0.034	1.03	0.92	0.02	1.04	0.05	1.82
Carbazole	0.020	0.024	0.94	0.19	0.52	0.02	0.47	0.04
Fluoranthene	0.152	0.081	3.41	3.65	6.41	6.08	6.93	9.77
Pyrene	0.128	0.067	3.02	3.22	13.74	7.61	10.23	11.98
Benz(a) anthracene	0.062	0.010	1.22	0.38	0.02	0.69	0.05	1.19
Chrysene	0.236	0.024	2.08	0.83	5.79	2.74	1.04	1.82
Benzo(b)fluoranthene	0.001	0.001	2.16	0.03	0.02	0.02	0.05	0.04
Benzo(k)fluoranthene	0.001	0.001	1.35	0.03	0.02	0.02	0.05	0.04
Benzo(a)pyrene	0.048	0.001	0.74	0.43	0.26	0.78	0.34	0.98
Indeno(1,2,3cd)pyrene	0.068	0.042	1.13	0.54	0.19	0.10	0.22	0.18
Dibenz(a,h)anthracene	0.092	0.032	0.59	0.34	0.02	0.02	0.05	0.04
Benzo(g,h,l)perylene	0.070	0.033	1.09	0.65	0.33	0.15	0.21	0.26

Table 3.11 Method detection limits for PCBs in tree component, soil, litter and ambient air samples (air concentrations in ng/m^3, all other concentrations in µg/kg)

PCB	Ambient Air		Soil		Litter-Branch-Needle-Bark		Stem	
	Isken-derun	Aliaga	Isken-derun	Aliaga	Isken-derun	Aliaga	Isken-derun	Aliaga
PCB-18	0.0086	0.0062	0.14	0.16	0.015	0.016	0.087	0.001
PCB-17	0.0052	0.0039	0.05	0.11	0.015	0.016	0.087	0.001
PCB-31	0.0029	0.0038	0.14	0.07	0.015	0.016	0.087	0.001
PCB-28	0.0039	0.0034	0.12	0.09	0.015	0.016	0.087	0.001
PCB-33	0.0026	0.0023	0.02	0.02	0.015	0.016	0.087	0.001
PCB-52	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-49	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-44	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-74	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-70	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-95	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-101	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-99	0.0005	0.0005	0.02	0.02	0.015	0.016	0.087	0.001
PCB-87	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-110	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-82	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-151	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-149	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-118	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-153	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-132	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-105	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-138	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-158	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-187	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-183	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-128	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-177	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-171	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-156	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-180	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-191	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-169	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-170	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-199	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-208	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-195	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-194	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-205	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-206	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001
PCB-209	0.0005	0.0004	0.02	0.02	0.015	0.016	0.087	0.001

3.5.4 Calibration Standards

The PAH calibration standard solution that contains 16 PAH congeners, carbazole, and five deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) 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 for PAHs, and deuterated PAHs at a fixed concentration of 8 μg/ml) were used to calibrate the GC/MS system. The PCB calibration standard solution contains 41 PCB congeners and internal standard mixtures (PCB-14, PCB-65, and PCB-166). Five point calibration curves were used to calibrate the analytical system. Number of calibration standards and concentration range of standards for analyzed POP groups are given in Table 3.12. In every case, the range of the linear calibration curve (r^2) was $\geq$ 0.999. System performance was verified by the analysis of the mid-point calibration standard for every 12 hours during the analysis period. Analysis was continued if the variation of calibration standard concentration less than 10%. In case the value is higher than 10%, calibration was renewed and analysis was continued.

Table 3.12 Number of calibration standards and concentration range of standards

POP groups	**Number of calibration standard**	**Range of concentration (ng/mL)**	**Range of linear calibration (r^2)**
PAH	6	40 - 10000	>0.999
PCB	5	1 - 100	>0.999

3.5.5 Determination of Concentrations

3.5.5.1 Ambient Air

Accumulation of an organic compound on a PUF disk during exposure time is equivalent to the rate of uptake minus rate of loss. Uptake of PAHs and PCBs 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, the planar area of the sampling media and concentration of the organic compound in the air (Kaya, 2012).

The effective air sampling volumes (V_{air}, m^3) for individual PAH and PCB compounds/congeners during the sampling period were determined using the methodology by Shoeib & Harner (2002). For the calculation of V_{air}, it was assumed that both gas phase and particle phase compounds have similar sampling rates. PUF disk effective air volume ($V_{air,}$, m^3) was calculated as:

$$V_{air} = (K'_{PSM-A})\, x\, (V_{PSM})\, x \left[1 - \exp\left(-\frac{k_A}{K'_{PSM-A}}\, x\, \frac{t}{D_{film}}\right)\right] \quad (3.1)$$

$$K'_{PSM-A} = K_{PSM-A}\, x\, \rho_{PSM} \quad (3.2)$$

$$\log K_{PSM-A} = log K_{PUF-A} = 0.6366 \log K_{OA} - 3.1774 \quad (3.3)$$

where V_{PSM} is the volume (cm^3) of the PUF disk, ρ_{PSM} is the density (g/cm^3) of the PUF disk, t is the sampler exposure time (day) with ambient air, k_A is the airside mass transfer coefficient (MTC) (cm/d). D_{film} (m) is the effective film thickness (Pozo et al., 2004), K_{OA} is the octanol–air partition coefficient, K_{PSM-A} is the passive sampling medium (PSM)–air partition coefficient but differs from the K'_{PSM-A} (dimensionless) (Shoeib & Harner, 2002).

Sample volumes were measured 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 target compounds in the analysis. They can volatilize into the atmosphere if exposed to air. The rate of chemical uptake is equivalent to rate of chemical loss. The amount of lost DCs depends on their physicochemical properties, exposure time, and wind speed (Kaya, 2012). Airside mass transfer coefficient ($k_{A,}$ m/day) was calculated by using the recovery efficiency of depuration compounds initially spiked into the PUF disk:

$$k_A = \ln\left(\frac{C_t}{C_o}\right) D_{film}\, K'_{PSM-A} \left(\frac{1}{t}\right) \quad (3.4)$$

where C_o and C_t (mass/cm^3) are the concentrations in the disk at the beginning and end of the sampling, respectively. A_{PSM} is the planar surface area (m^2) of the PUF disk. Sampling rate for air samples (R, m^3/day) was calculated as (Shoeib & Harner, 2002):

$$R = k_A\, A_{PSM} \quad (3.5)$$

Average sampling rates for air samples (R, m^3/day) were determined by using the Equation 3.4 and Equation 3.5. The average air sampling rate (R) values were ranged between 1.25 and 2.48 m^3/day (1.82 ± 0.37 m^3/day, average ± SD) for Aliaga and 1.42 to 3.07 m^3/day (2.14 ± 0.46 m^3/day, average ± SD) for Iskenderun, respectively. Then, the airside MTCs (k_A) were calculated specifically for each measurement sites by using these sampling rates (R). Calculated k_A and compound–specific K'_{PSM-A} values were used to determine the effective air sampling volumes (V_{air}) (Equation 3.1) for individual PAH and PCB compounds.

Concentrations in ambient air ($C_{i,air}$, ng/m^3) were calculated as:

$$C_{i,air} = \frac{m_i}{V_{air}} \quad (3.6)$$

where m_i is the mass of a target compound *(i)* in the passive samples (ng/sample).

3.5.5.2 Soil, Litter and Tree Components

Concentrations of analyzed pollutants in soil, litter, and tree component samples (C_i, mg/kg or µg/kg) were calculated as:

$$C_i = \frac{m_i}{M_{sample}} \tag{3.7}$$

where m_i (mg/sample or µg/sample) is the mass of a target compound *(i)* in the samples and M_{sample} (kg) is weight of sample on a dry basis.

3.6 Modeling of Ambient Air POP Concentrations

In the present study, the model by Zhao et al. (2008) was used to estimate the ambient air POP concentrations using those measured in bark samples. Model is based on the assumption that lipids in the bark absorb organic compounds and n-octanol is a compound that represents the lipid content of bark. The model is expressed as:

$$K_{BA} = \left\{2 \times 10^{-6}(LipCont)^{1.67}\ K_{OA}^{0.542}\ exp\left[\left(-0.964\ \Delta H_{vap} + 3.130\right)\left(\frac{1}{T} - \frac{1}{302.05}\right) \times \frac{10^3}{R}\right] + 210\ B\ (SSA)^{0.706}\ \left(\frac{P_{ptn}}{154}\right)^{-0.766}\ TSP\ K_{OA}\right\} / (1 + B\ (TSP)\ K_{OA}) \tag{3.8}$$

where K_{BA} is the bark-air partition coefficient, *LipCont* is the lipid content of bark samples (g/m^3), K_{OA} is the octanol-air partition coefficient, ΔH_{vap} is the enthalpy of vaporization of sub-cooled liquid (kj/mol), T is the temperature (K), R is the ideal gas constant (8.314 Pa m^3/mol), *SSA* is the specific surface area of the bark samples

(m^2/m^3), P_{ptn} is the precipitation amount (mm), and *TSP* is the concentration of total suspended particulates in the air ($\mu g/m^3$). *B* ($m^3/\mu g$) is a constant expressed as:

$$\frac{C_P}{C_G} = B(TSP)K_{OA} \tag{3.9}$$

where C_P and C_G are the particle phase and gas phase POP concentrations in air (pg/m^3), respectively. K_{BA} could also be determined experimentally using the measured POP concentrations of bark (C_B) and air (C_A) samples:

$$K_{BA} = \frac{C_B}{C_A} \tag{3.10}$$

Ambient air POP concentrations (C_A) were also calculated from the K_{BA} values (estimated from Equation 3.8) and measured bark concentrations using the Equation (3.10). ΔH_{vap} values for POPs were taken from the literature and K_{OA} values were adjusted for the average temperature during the sampling period (Falconer & Bidleman, 1994; Harner & Bidleman, 1996, 1998; Lei et al., 1999; Wong et al., 2001; Su et al., 2002; Harner & Shoeib, 2002; Braekevelt et al., 2003; Cetin & Odabasi, 2005; Odabasi et al., 2006a, 2006b). The average temperature and total precipitation amount during the sampling period were obtained from the General Directorate of Meteorology. Values of the some parameters used in the model are given below:

- *LipCont*= 6313±6192 g/m^3 (Iskenderun), 10699±13985 g/m^3 (Aliaga) (using the measured lipid content of 1.66±1.63% (Iskenderun), 2.81±3.68% (Aliaga) and bark density 0.38 g/cm^3)
- *T*=14°C (Iskenderun), 14.1°C (Aliaga)
- *SSA*=2.08x10^6 m^2/m^3 (using the surface area of 5.47 m^2/g and bark density 0.38 g/cm^3)
- P_{ptn}=190 mm (Iskenderun), 226 mm (Aliaga)
- *TSP*=100 $\mu g/m^3$ (assumed based on a recent study in the similar area, Odabasi et al., 2009).

Zhao et al. (2008) have suggested that values of $1.88x10^{-12}$ (PAHs) and $1.50x10^{-12}$ (PCBs) could be used for the constant B. When these values were used, model substantially overestimated the measured atmospheric POP concentrations. Constant *B* values could also be estimated based on experimental data using Equation (3.9). In the present study, *B* values for individual POPs were estimated using the experimental data from a recent study conducted in a similar industrial area in Turkey (Odabasi et al., 2009). Estimated *B* values ranged between $1.14x10^{-14}$ and $4.23x10^{-11}$ for PAHs, $1.04x10^{-14}$ and $2.13x10^{-12}$ for PCBs. It should be noted that the estimated *B* values for individual compounds range in one to three orders of magnitude within different groups of POPs. Therefore, individual *B* constants for each compound should be used instead of average values assigned to different POP groups.

3.7 Calculation of POP Inventory

3.7.1 Biomass Amounts

The number of trees, their heights and stem diameters at breast height were measured in the each surrounded sampling area. Measured heights and diameters were used to estimate the amount of biomass (kg) per unit area (ha). The method in "Intergovernmental Panel on Climate Change, (IPCC)" (2003) was used for biomass calculations. In this method, biomass amount has been calculated multiplying stem volume of trees by biomass conversion and expansion factors designated for tree components.

Biomass amounts of tree components for *Pinus brutia* forests were calculated as follows:

$$B_i = (V)\ (BCEF_i) \qquad (3.11)$$

where *B* is the biomass amount of tree components (tons/tree), *V* is the stem volume including bark (m^3/tree), *BCEF* is the biomass conversion and expansion factor, and *i* is the tree components (needle, branch, stem, and bark). *BCEF* factors for stem,

branch, and needle are 0.478, 0.108, and 0.045 tones/m^3, respectively (Tolunay, 2013). The bark amount of *Pinus brutia* was estimated using the ratio of bark volume prepared by Sun et al (1978). Bark biomass amount was determined multiplying bark volume ratio by bark volume weight (0.380 tones/m^3).

Volume of stem including bark was calculated as:

$$V = D^2 (0.0000366463 + 0.0000279378\ H) \quad (3.12)$$

where *D* is the stem diameter at breast height (cm) and *H* is the tree height (m) (Catal, 2009).

Biomass amounts of tree components for *Pinus pinea* forests were calculated using the Equations 3.13 - 3.16 (Correia et al., 2008; Cutini et al., 2013). These equations are given below:

$$\text{Ln (Needle) (kg/tree)} = -3.822 + 2.271\ \text{Ln (D)} \quad (3.13)$$

$$\text{Ln (Stem including bark) (kg/tree)} = -3.641 + 2.694\ \text{Ln (D)} \quad (3.14)$$

$$\text{Ln (Stem including bark + Branch) (kg/tree)} = -3.88 + 2.819\ \text{Ln (D)} \quad (3.15)$$

$$\text{Bark (kg/tree)} = 6.85 \times (3.14\ D/100)^{1.46}\ H^{0.54} \quad (3.16)$$

Needle and bark amounts were determined using Equations 3.13 - 3.16, respectively. Stem amount was determined by subtracting the bark amount calculated by Equation 3.16 from the amount (stem+bark) found using Equation 3.14. Branch amount was determined by subtracting the amount (stem+bark) calculated by Equation 3.14 from the amount (stem+bark+branch) found using Equation 3.15.

After biomass amount of tree components were determined, total aboveground biomass amount was calculated by Equation 3.17.

Total aboveground biomass (kg/tree) = Needle + Bark + Branch + Stem (3.17)

The equations used for calculation of needle amounts give the total amounts of 1-year and 2-year needles. It was assumed that needle amounts are equally distributed between 1-year and 2-year needles. The upper layer of 5 cm (sampling depth) was considered for the soil calculations. Litter was sampled by collecting the content over the soil in a 100 cm^2 area. The litter amount per sample (g) was determined by weighting the sample dried at 60°C for 24 hours. The litter amount per unit area was calculated by dividing the amount per sample (g) by sampling area (100 cm^2).

3.7.2 POP Amounts

POP amounts per unit area (mg/ha) were calculated by multiplying the measured concentrations in tree components (mg/kg), litter, and soil by the estimated amounts of these components per unit area (kg/ha).

3.8 Data Analysis

Microsoft Excel and SPSS software were used for statistical analysis and calculation of data. The maps showing the spatial distribution of the pollutants were prepared using geographical information system software (ArcGIS).

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the spatial variations and historical trends of individual PAH and PCB compounds in tree components, soil, litter and ambient air samples in Aliaga and Iskenderun. In addition, results of modeling ambient air POP concentrations and POP inventory are given in this chapter. Statistically analysis of data is also presented in this chapter. All results were compared with the values reported in the literature.

4.1 Measured POP Concentrations in Sampling Regions

The extractable lipid contents of 1-year needle, 2-year needle, bark, branch, stem, and litter were 3.76, 3.40, 2.81, 3.31, 13.13, 2.19% in Aliaga and 3.97, 3.05, 1.66, 2.82, 5.03, 2.24% in Iskenderun, respectively (Appendix-2, Tables A2.1- A2.2). Lipid contents of tree components were generally comparable to those reported recently (Odabasi et al., 2015) while bark lipid levels were closer to the lower bound literature values. POP concentrations in plant samples have been reported on dry weight basis or as normalized by the lipid content. However, there has been no consensus on this issue. It was suggested that the cutin and suberin (a component of cell walls) found in different parts of the plants (Taiz & Zeiger, 2010) might also act like lipids. Since cutin and suberin are polymers, they could not be extracted by the solvents during sample processing (Ockenden et al., 1998; Chen et al., 2012). As a result, the actual lipid contents of plant samples may be higher than measured by the method used in the present study. Furthermore, significant correlations between POP concentrations measured in different matrices and lipid contents were not observed (r^2 = 0.0001−0.27, generally < 0.1, p > 0.01). Therefore, the concentrations were reported on dry weight basis in the present study. Total PAH and PCB concentrations (Σ_{16}PAHs and Σ_{41}PCBs, sum of individual compounds/congeners) measured in tree components, soil, litter, and ambient air are summarized in Tables 4.1 - 4.2. Sampler-1 of ambient air samples was lost due to an unknown reason in Iskenderun and the ambient air results were evaluated over 26 sampling sites for this region. Σ_{16}PAH

concentrations in ambient air samples ranged from 21 to 314 ng/m^3 (average ± SD, 146 ± 107 ng/m^3) in Iskenderun and from 18 to 645 ng/m^3 (average ± SD, 109 ± 118 ng/m^3) in Aliaga, respectively. In addition, Σ_{41}PCB concentrations in ambient air samples ranged from 0.21 to 6.42 ng/m^3 (average ± SD, 2.2 ± 1.7 ng/m^3) in Aliaga and from 0.49 to 3.72 ng/m^3 (average ± SD, 1.6±0.9 ng/m^3) in Iskenderun. Atmospheric POP concentrations measured in the present study were within the ranges reported in the literature and recently measured in two sampling regions (Cetin et al., 2007; Cetin & Odabasi, 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009, 2012; Kaya et al., 2012). Concentration ratios (industrial/background) were higher than 1.0 in all cases. This ratio was varied from 1.3 (stem) to 23.0 (soil) for PAHs and 2.2 (stem) to 29.6 (soil) for PCBs in Iskenderun. In Aliaga, this ratio was varied from 1.5 (stem) to 9.3 (litter) for PAHs and 2.3 (stem) to 48.0 (soil) for PCBs (Tables 4.1 - 4.2).

Table 4.1 Summary of PAH concentrations in industrial and background sites (air concentrations in ng/m^3, all other concentrations in μg/kg dry weight)

Σ_{16}PAH	Industrial		Background		Industrial / Background
	Mean	SD	Mean	SD	
ALIAGA					
Air	118	124	31	18	3.8
Soil	407	467	51	15	8.0
Litter	1027	795	111	31	9.3
Bark	210	157	100	51	2.1
1-year needle	1016	684	358	101	2.8
2-year needle	2157	2098	509	188	4.2
Branch	204	193	56	40	3.6
Stem[a]	2565	3686	1767	673	1.5
ISKENDERUN					
Air	170	101	29	12	5.9
Soil	3660	9433	159	54	23.0
Litter	1881	1786	203	106	9.3
Bark	345	350	51	31	6.8
1-year needle	1158	1334	136	60	8.5
2-year needle	2567	2445	299	200	8.6
Branch	174	104	92	55	1.9
Stem[a]	573	908	458	359	1.3

[a]Stem concentrations reported in this table were calculated as (i) for the samples analyzed without cutting into 5-year increments by dividing the analyte amount (μg) by the sample dry weight (kg), (ii) for the samples analyzed in 5-year increments by dividing the sum of analyte amounts from all increments (μg) by the total dry weight of all increments (kg) of the sample.

Table 4.2 Summary of PCB concentrations in industrial and background sites (air concentrations in ng/m^3, all other concentrations in μg/kg dry weight)

Σ_{41}PCB	**Industrial**		**Background**		**Industrial/ Background**
	Mean	**SD**	**Mean**	**SD**	
ISKENDERUN					
Air	1.6	0.9	0.18	0.14	8.9
Soil	26.6	61.6	0.90	0.56	29.6
Bark	8.6	14.2	1.3	0.69	6.6
Litter	54.4	37.8	4.7	4.7	11.6
1-Year needle	16.8	10.5	2.5	1.6	6.7
2-Year needle	41.0	25.6	4.3	4.2	9.5
Branch	3.3	1.9	1.2	0.57	2.8
Stem[a]	6.4	4.8	2.9	2.22	2.2
ALIAGA					
Air	2.2	1.7	0.17	0.06	12.9
Soil	57.6	101.2	1.2	0.54	48.0
Bark	22.7	21.2	1.5	0.63	15.1
Litter	93.2	87.5	2.9	1.6	32.1
1-Year needle	9.4	9.5	2.1	2.3	4.5
2-Year needle	52.7	61.9	1.7	1.9	31.0
Branch	4.5	3.4	1.1	0.20	4.1
Stem[a]	15.6	26.8	6.7	2.1	2.3

[a]Stem concentrations reported in this table were calculated as (i) for the samples analyzed without cutting into 5-year increments by dividing the analyte amount (μg) by the sample dry weight (kg), (ii) for the samples analyzed in 5-year increments by dividing the sum of analyte amounts from all increments (μg) by the total dry weight of all increments (kg) of the sample

Σ_{16}PAH and Σ_{41}PCB concentrations of tree components, litter and soil in Iskenderun and Aliaga were shown in Figures 4.1 - 4.2. As seen Figures 4.1 - 4.2, highest POP concentrations were measured in 2-year needle (PAHs), stem (PAHs), litter (PCBs), and soil (PCBs) samples in Aliaga. In addition, highest POP levels were found in 2-year needle (PAHs and PCBs), soil (PAHs), and litter (PCBs) samples in Iskenderun. Branch samples had the lowest POP concentrations for both regions. On average, POP concentrations in 2-year needle were (2−5 times for Aliaga, 1.8−2.4 times for Iskenderun) higher than 1-year needle. This could be attributed to higher accumulation during longer exposure to polluted air (Ratola et al., 2010a, 2010b). Among the all POPs groups, the highest levels were measured for PAHs, followed by PCBs (Figures 4.1 - 4.2, Tables 4.1 - 4.2).

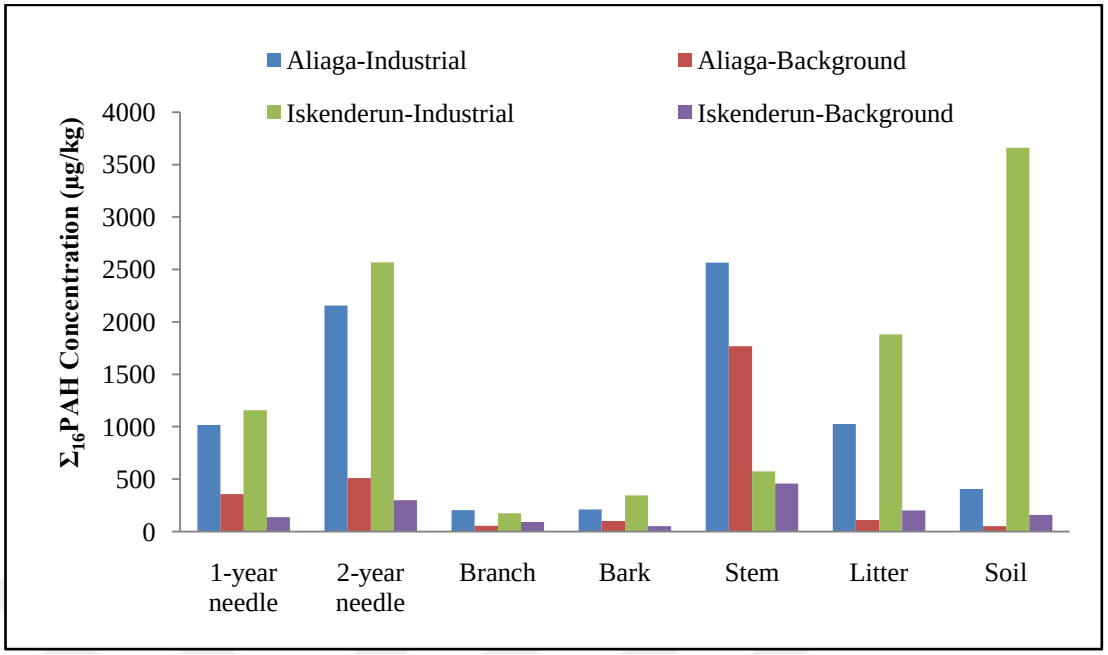


Figure 4.1 Σ_{16}PAH concentrations of tree components, litter and soil samples in both regions

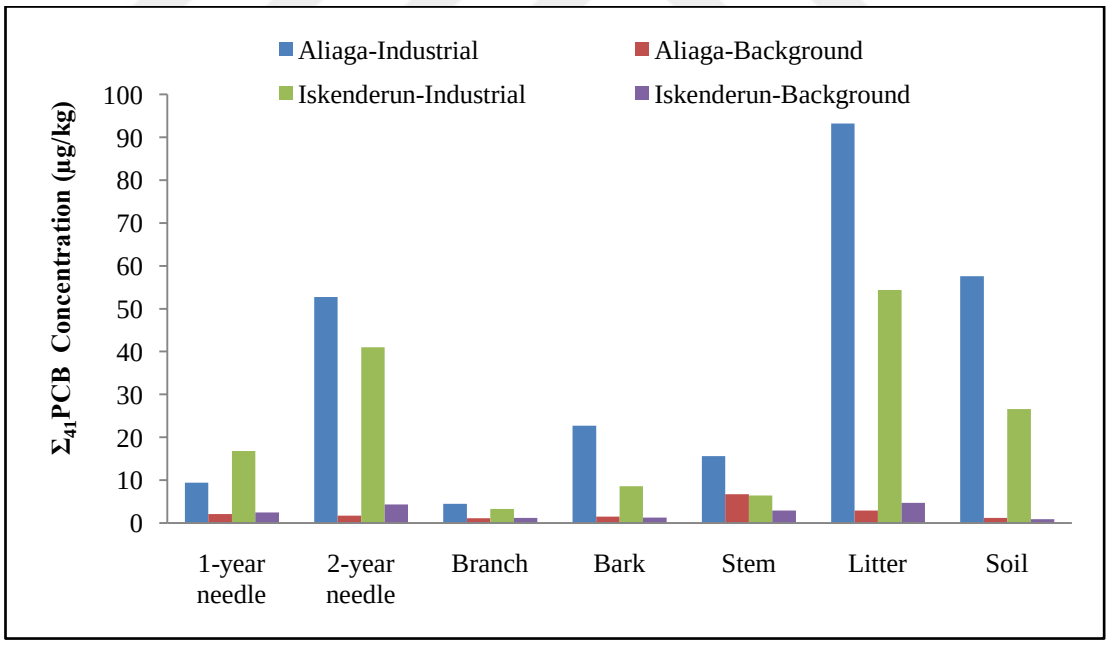


Figure 4.2 Σ_{41}PCB concentrations of tree components, litter and soil samples in both regions

4.2 Profiles of POPs in Sampling Regions

Ambient air PAH and PCB profiles were dominated by low to medium molecular weight (MW) compounds (phenanthrene, fluorene, fluoranthene, and pyrene for PAHs; PCB-18, 17, 31, 28, 33, 52, 44, 70, and 101 for PCBs) in both regions. Compound profiles were similar for ambient air, needles, branch, and stem samples both sampling regions. However, medium to high MW compounds dominated the POP profiles in soil while their contributions to total POPs were relatively higher for litter and bark compared to branch, stem, and needles in both regions.

Industrial sampling sites were relatively close to the local sources (a few hundred meters to a few kilometers). Therefore, the difference in POP profiles can be seen because of high MW compounds are mainly in particle phase and deposited more easily close to their sources compared to the lower MW ones which are mainly in the gas phase and could be transported to relatively longer distances (Bozlaker et al., 2008a, 2008b). This was supported by the observation that soil, litter and bark POP profiles were similar to air POP profiles at background sites.

The difference between ambient air, soil, litter, and bark POP profiles may also be due to different partitioning behaviors of the individual compounds (low MW compounds have relatively low K_{OA} values, their partition to organic matter is relatively low) (Cetin & Odabasi, 2007; Bozlaker et al., 2008a, 2008b). Measured POP profiles also suggest that particle phase deposition is an effective mechanism for accumulation in soil, litter, and bark while gas phase uptake and translocation is relatively more important for accumulation in needles, branch, and stem. Concentrations of individual 16 PAH and 41 PCB congeners in soil, litter, tree components and ambient air samples are given in Appendices 3 and 4.

Generally, Σ_{16}PAH concentrations measured in Iskenderun were higher (except stem samples) than measured in Aliaga (Appendix-3). Phenanthrene, fluorene, fluoranthene, and pyrene were the dominating PAH compounds in Iskenderun while phenanthrene, fluoranthene, pyrene, and chrysene were the dominating PAH

compounds in Aliaga. Similarly, 3-ring and 4-ring PAH compounds were found higher concentrations in branch and bark samples in both sampling regions (Figures 4.4 and 4.8). Netto et al. (2007) is reported that these compounds had a significant share in the total PAH concentrations and they were highlight compounds in tree components. Profiles of 16-PAH and 41-PCB congeners in sampling regions are shown in Figures 4.3 - 4.10.

Phenanthrene and chrysene concentrations were higher in needle samples (Figures 4.6 - 4.7) in Aliaga while the phenanthrene and fluoranthene concentrations were higher in Iskenderun. Soil samples PAH concentrations were measured higher values in Iskenderun as the other samples (Appendix-3, Table A3.7). Detected PAH compounds in soil samples were different the other samples. 5-ring benzo(b)fluorenthene, 4-ring benzo(a)anthracene, chrysene, pyrene and fluoranthene were have high contribution to total PAH concentrations in soil samples of both regions (Figure 4.9). Phenanthrene, chrysene, fluoranthene and unlike other samples benzo(b)fluoranthene were observed higher concentrations in soil samples of both regions. Concentration difference in soil samples between the two regions were found to be approximately 7 times for each PAH compounds (Appendix-3, Table A3.7).

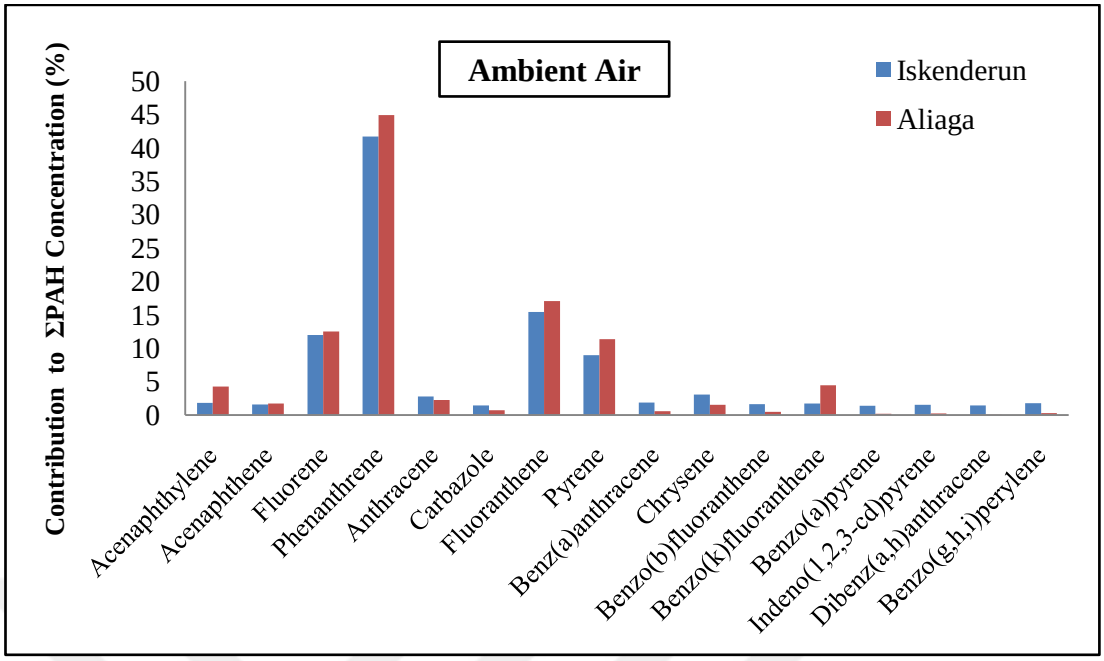


Figure 4.3 16-PAH congener profiles of ambient air samples in sampling regions

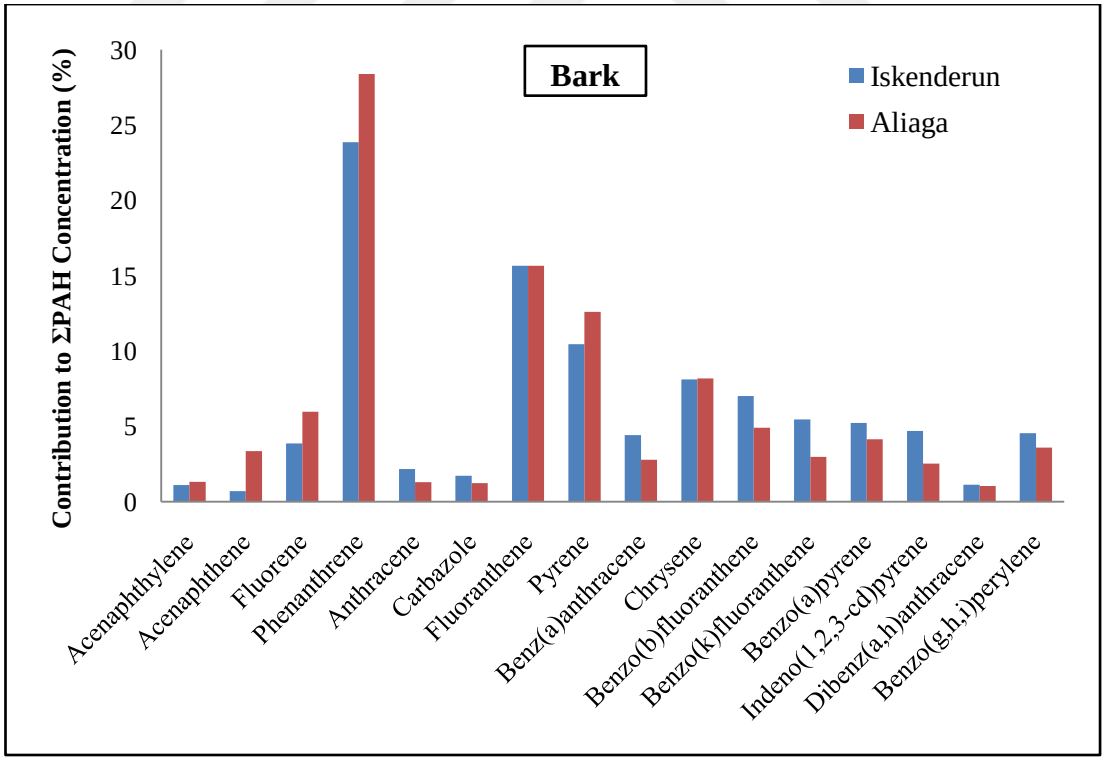


Figure 4.4 16-PAH congener profiles of bark samples in sampling regions

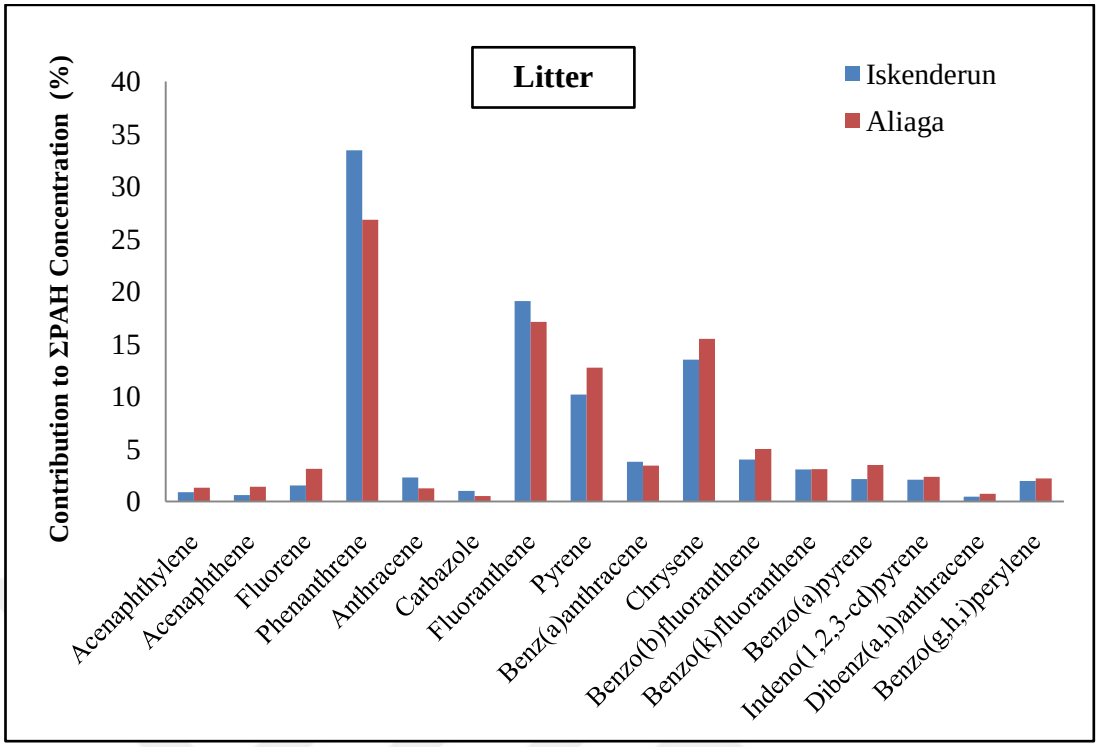


Figure 4.5 16-PAH congener profiles of litter samples in sampling regions

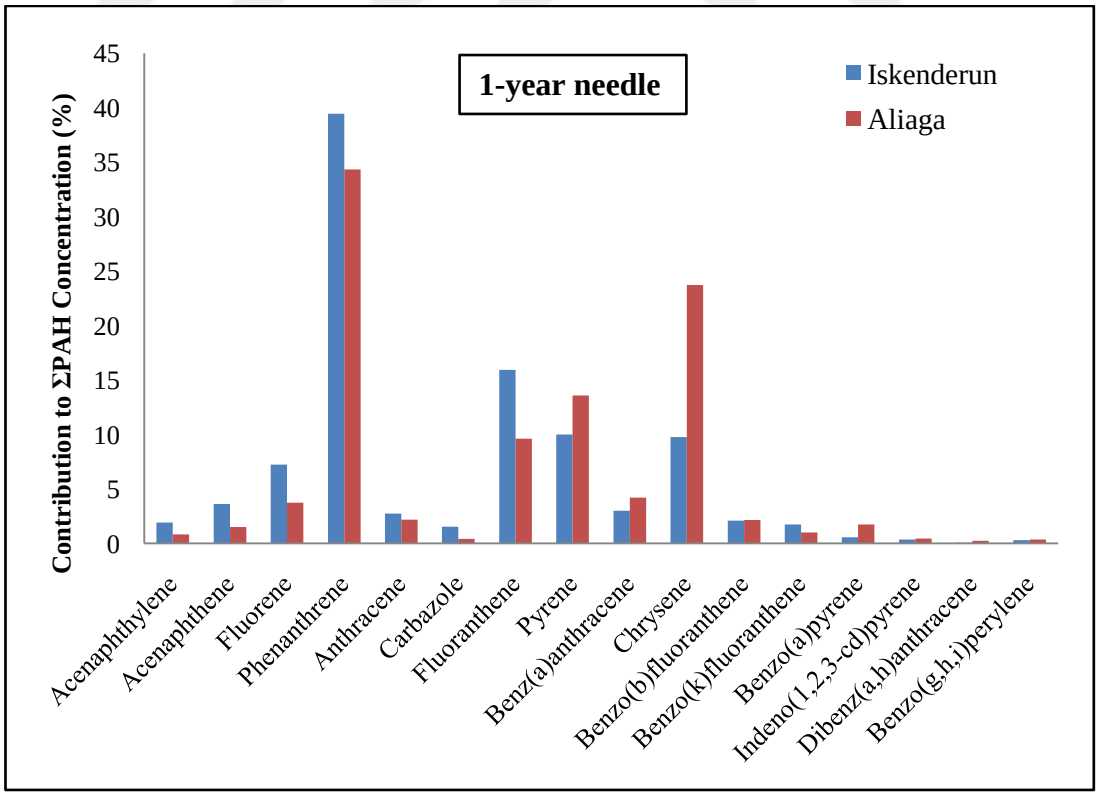


Figure 4.6 16-PAH congener profiles of 1-year needle samples in sampling regions

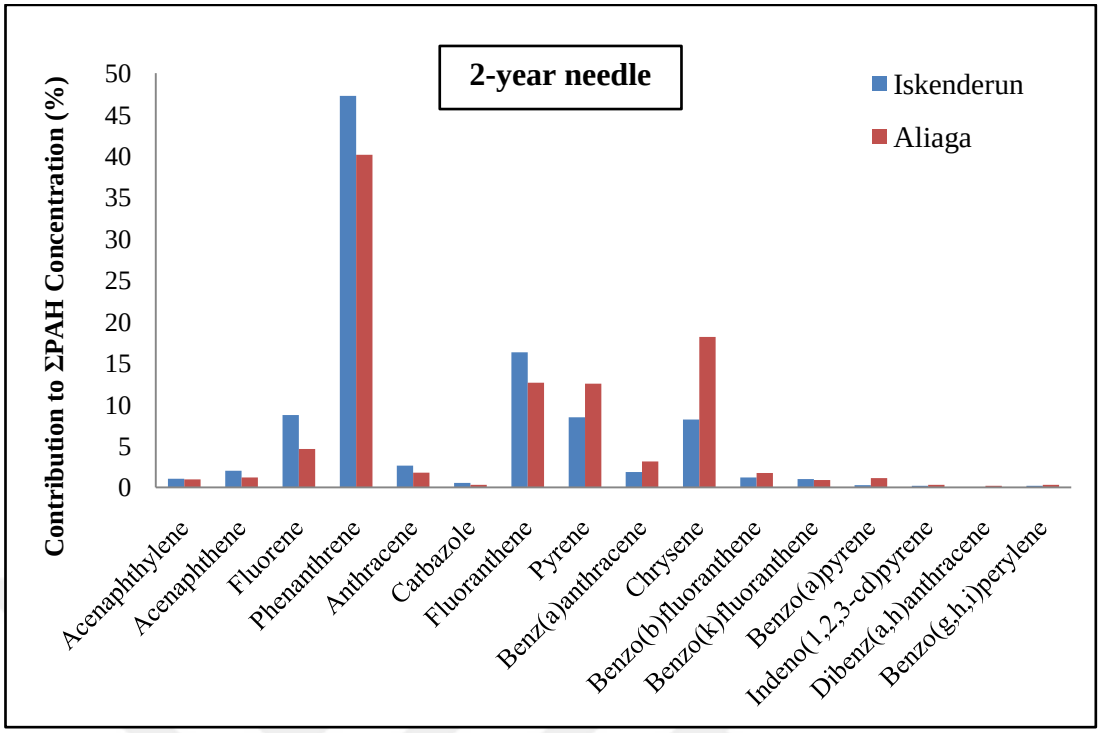


Figure 4.7 16-PAH congener profiles of 2-year needle samples in sampling regions

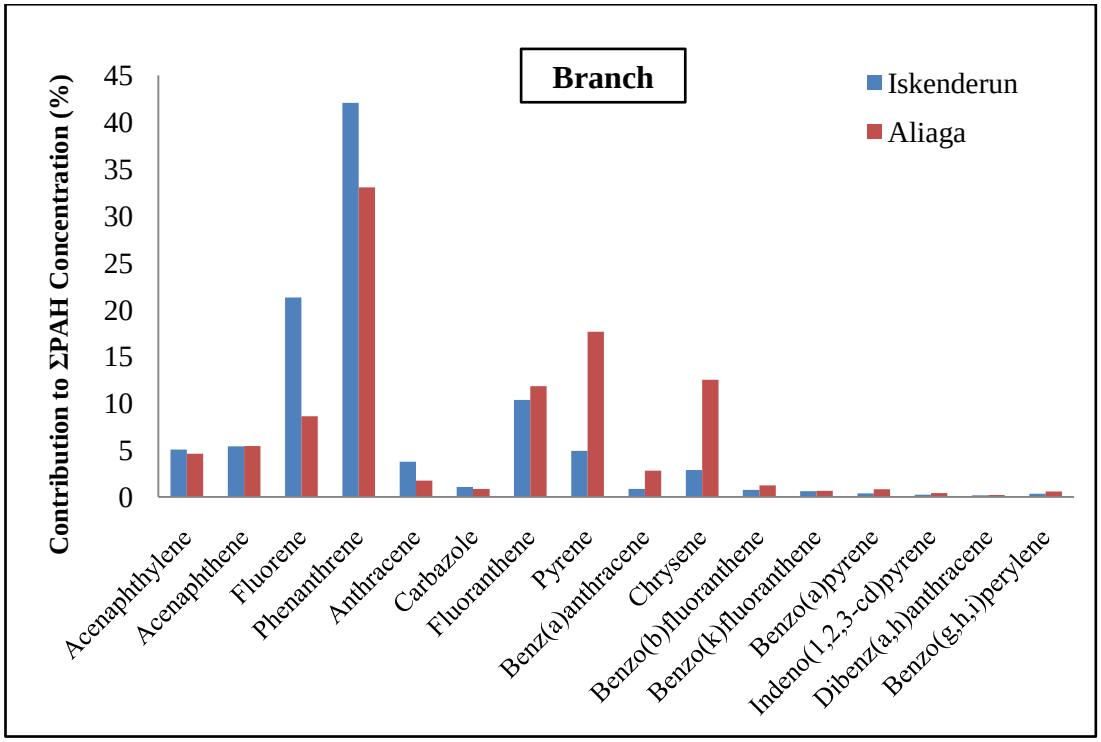


Figure 4.8 16-PAH congener profiles of branch samples in sampling regions

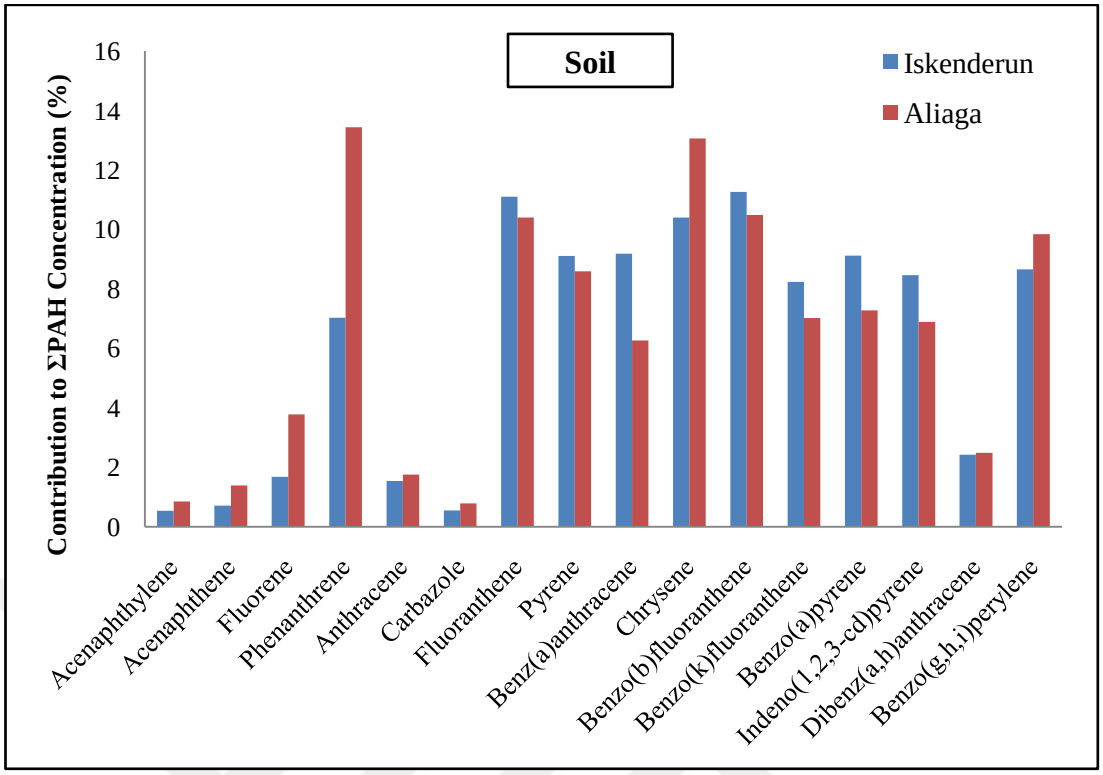


Figure 4.9 16-PAH congener profiles of soil samples in sampling regions

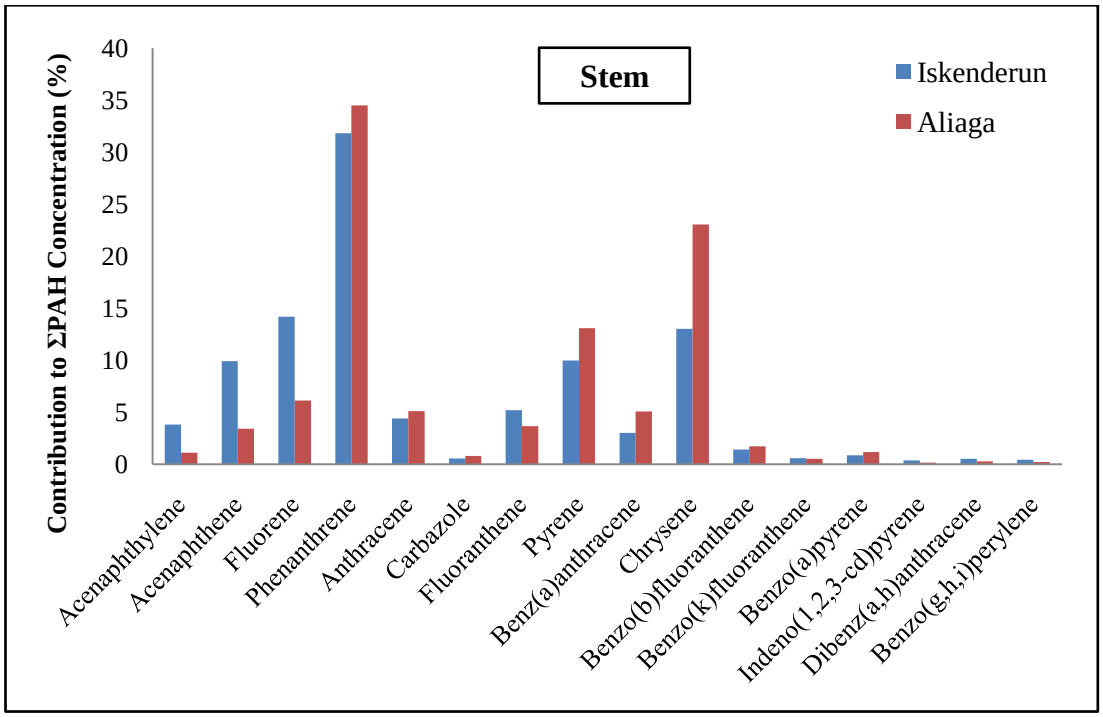


Figure 4.10 16-PAH congener profiles of stem samples in sampling regions

Σ_{41}PCB concentrations measured in Aliaga were higher than measured in Iskenderun (Appendix-4). Low molecular weight compounds (PCB-18, 28, 31, 33 and 52) were mainly available in ambient air, 1-year needle, 2-year needle, and stem samples (Figures 4.11 - 4.14 - 4.15 – 4.18). In addition to low molecular weight compounds, medium and high molecular weight compounds such as PCB-110, 118, 138, 149, 153, 180 are also available in litter, bark, and soil samples (Figures 4.12 - 4.13 - 4.17). PCB compounds (PCB-28, 101, 118, 153, 138 and 180) that measured in the bark samples of Aliaga region (Figure 4.12) were similar to study prepared by Wen et al. (2009). Ratio of low molecular weight compounds in total PCB of soil samples is very low by high molecular weight compounds in both sampling regions (Figure 4.17).

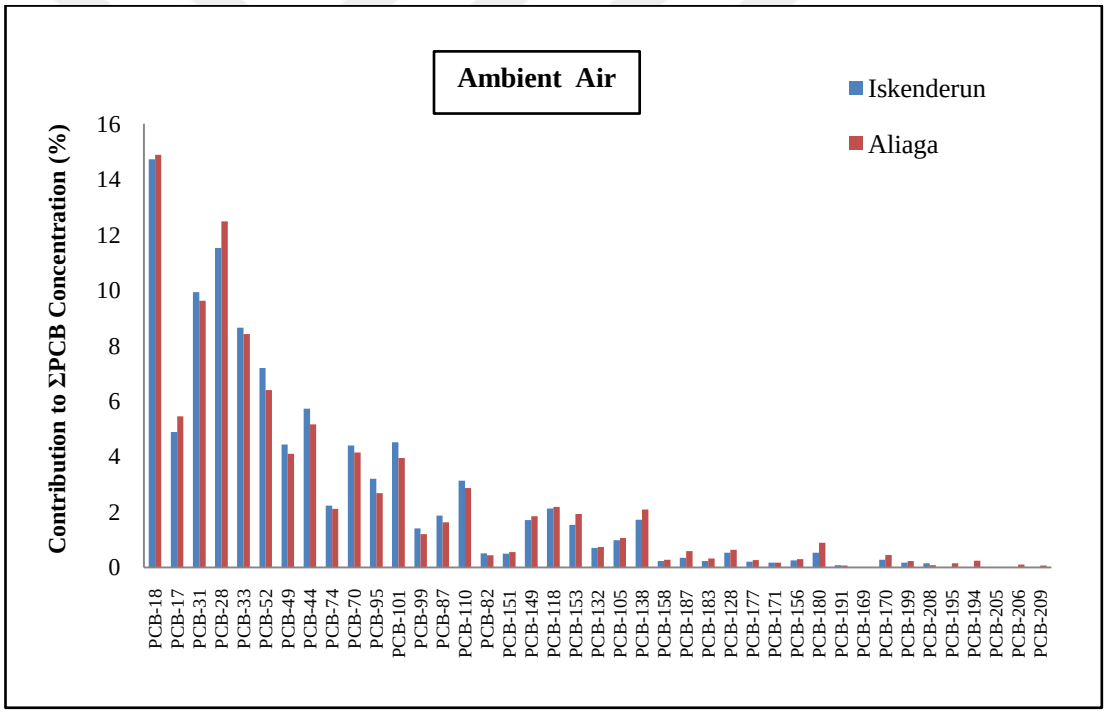


Figure 4.11 41-PCB congener profiles of ambient air samples in sampling regions

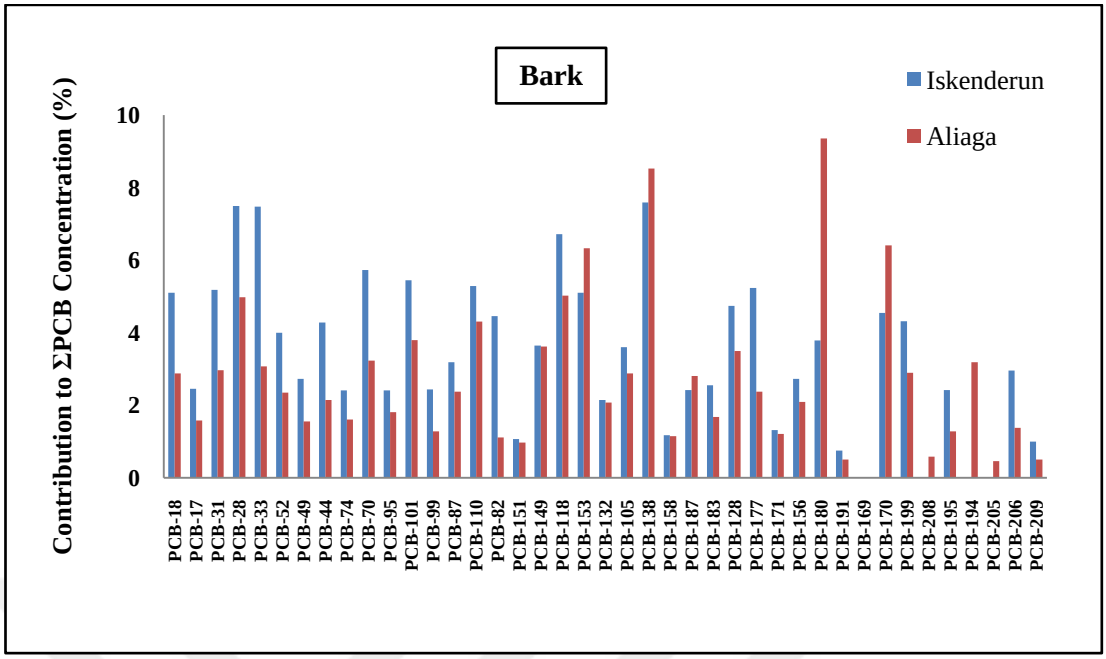


Figure 4.12 41-PCB congener profiles of bark samples in sampling regions

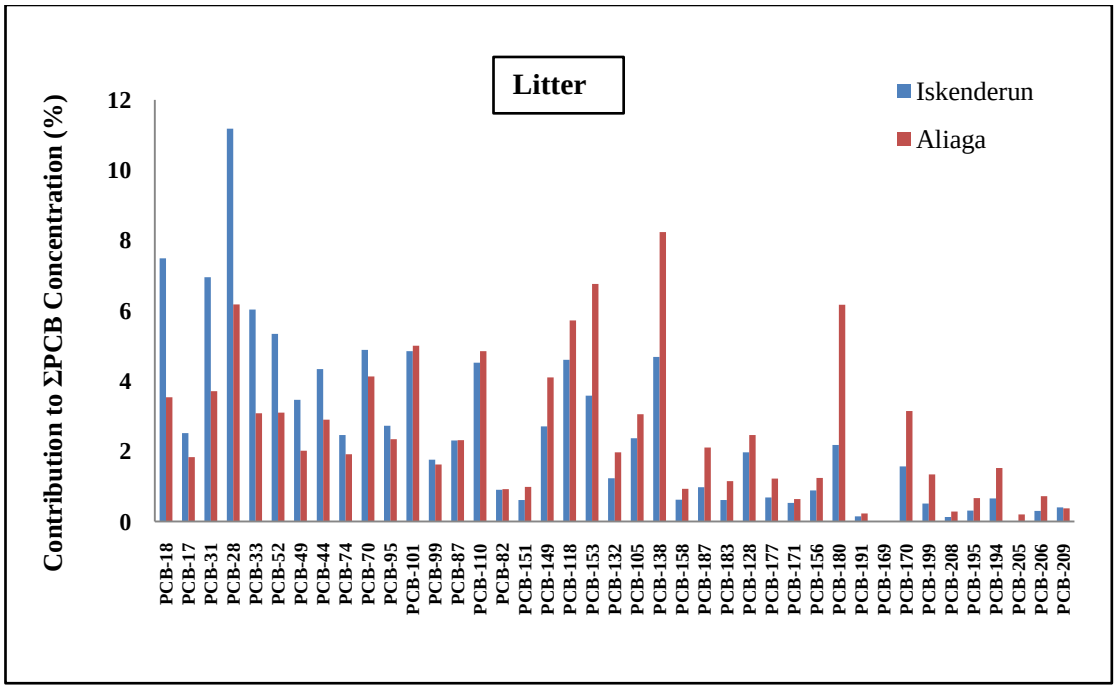


Figure 4.13 41-PCB congener profiles of litter samples in sampling regions

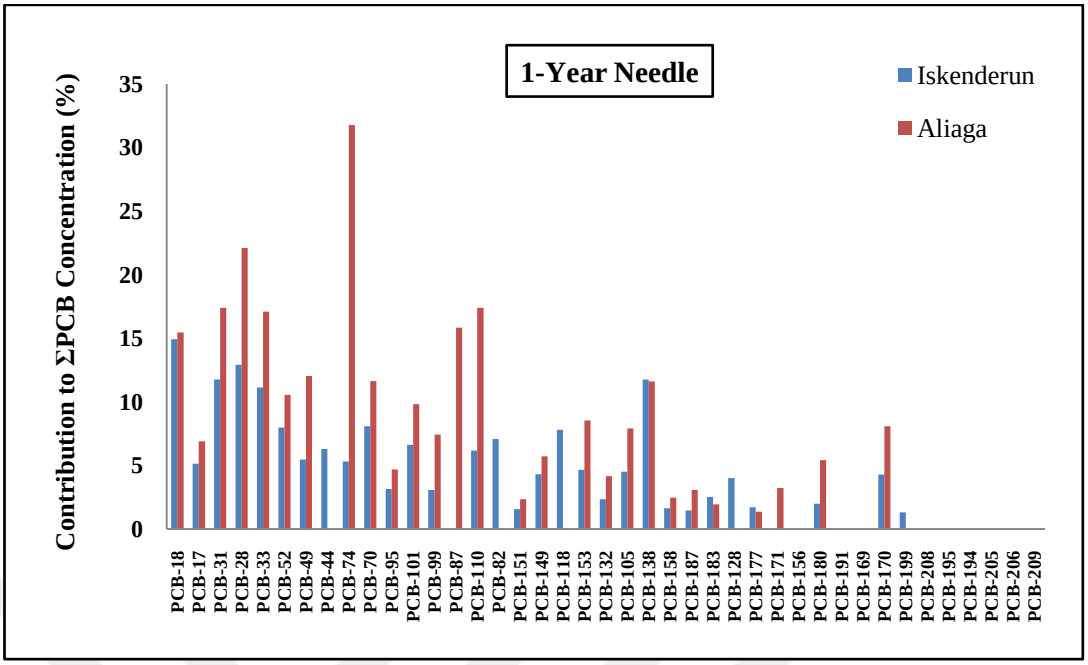


Figure 4.14 41-PCB congener profiles of 1-year needle samples in sampling regions

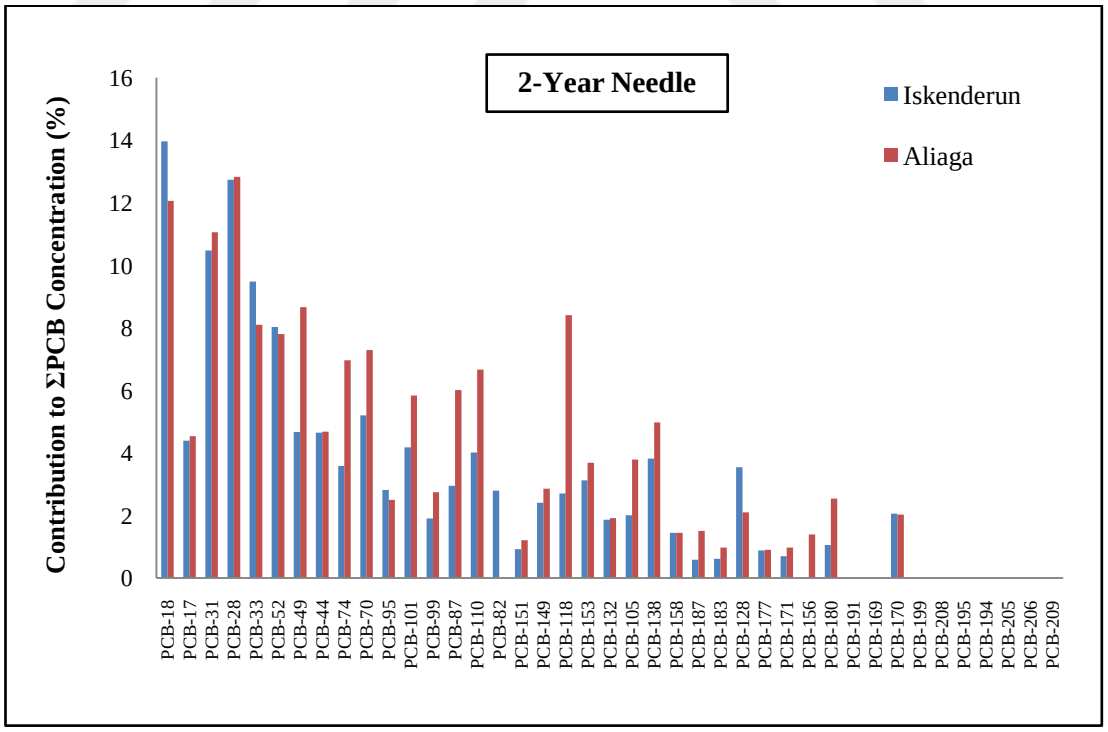


Figure 4.15 41-PCB congener profiles of 2-year needle samples in sampling regions

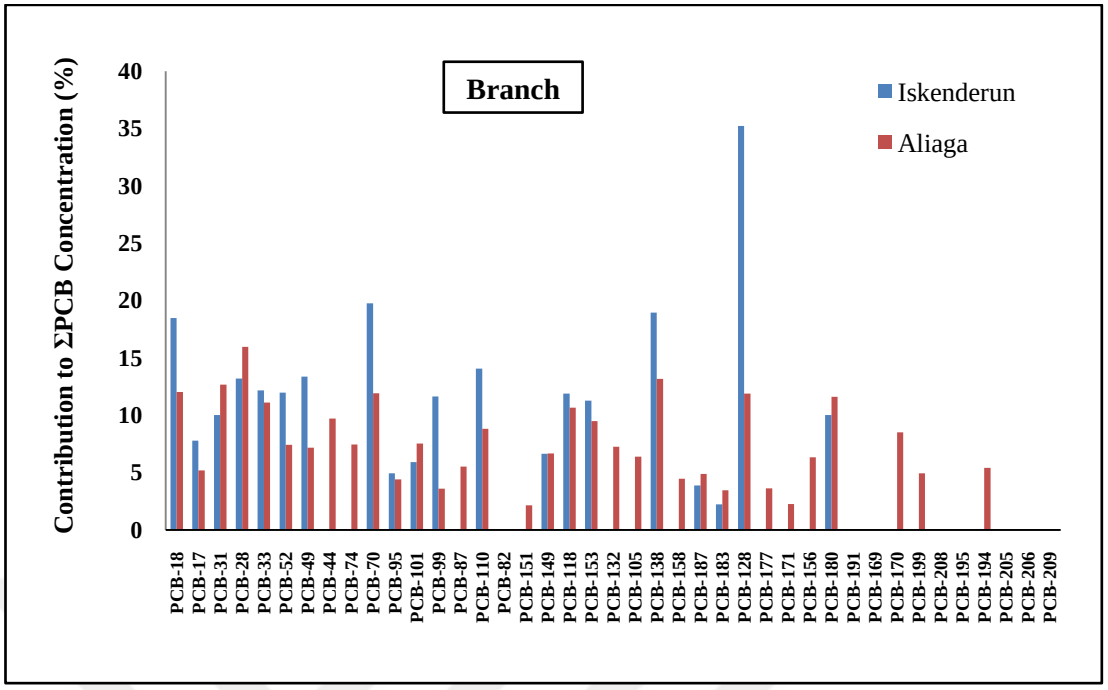


Figure 4.16 41-PCB congener profiles of branch samples in sampling regions

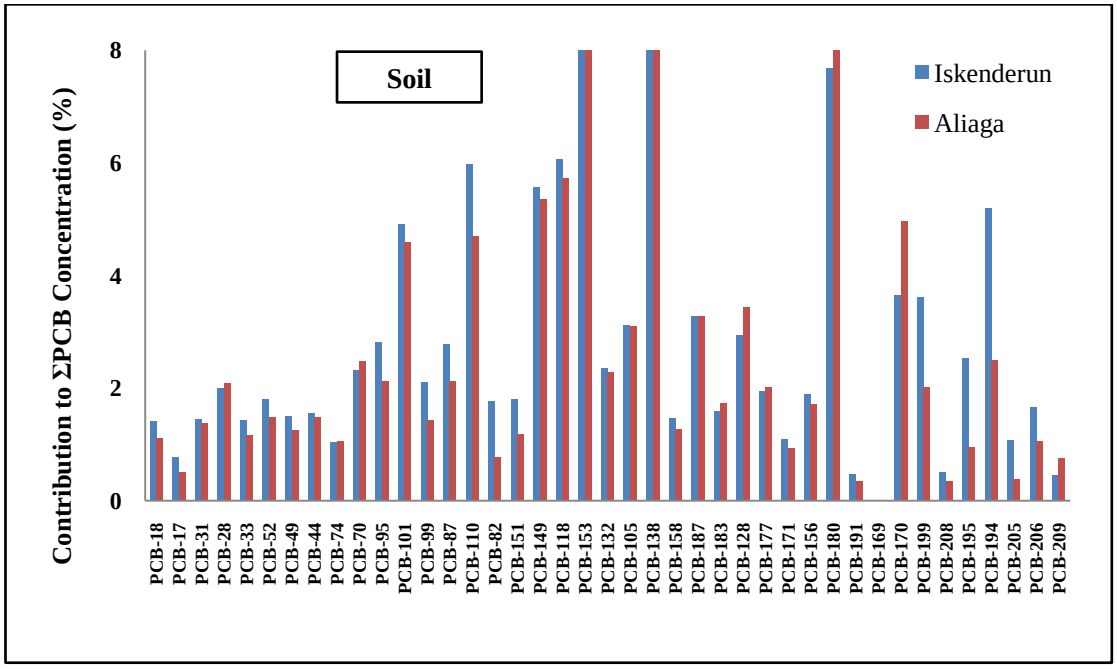


Figure 4.17 41-PCB congener profiles of soil samples in sampling regions

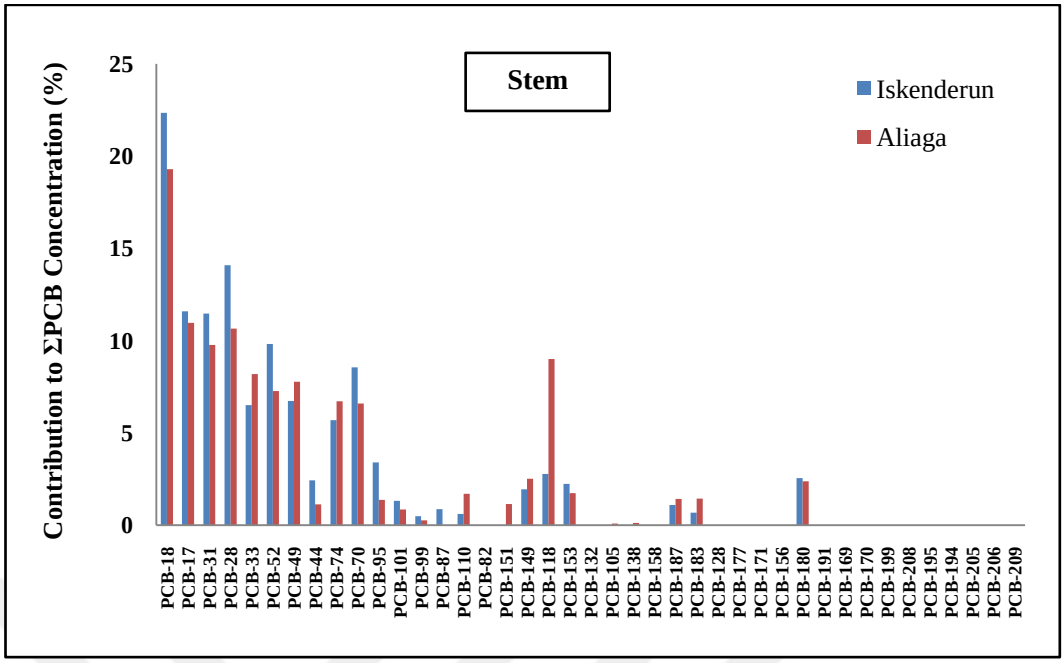


Figure 4.18 41-PCB congener profiles of stem samples in sampling regions

4.3 Spatial Variations of POPs in Sampling Regions

Spatial variations of ambient air, 2-year needle, and soil POP concentrations in Aliaga and Iskenderun are illustrated in Figures 4.19 - 4.30. Background sites were not shown on the maps because of the actual position of these sites was outside of the map area. According to all figures, the lowest POP levels in all sample types were measured in background sites, away from specific local sources while the highest concentrations were observed in industrial sites close to the local sources in two sampling regions. POPs in plant samples have also been investigated around the world. Similar to the present study, it was reported that the lowest POP levels in plant samples were found in rural areas while the highest concentrations were measured in urban and industrial areas (Wyrzykowska et al., 2007; Loganathan et al., 2008; Ratola et al, 2011a, 2011b; Yin et al., 2011a, 2011b; Kuang et al., 2011, 2014).

The prevailing wind direction in Aliaga is northwest (Odabasi et al., 2009). Therefore, highest POP concentrations were measured at sites located southeast of the major sources. The spatial distribution of ambient air PAH concentrations indicated that the major PAH sources in Aliaga were steel plants, petroleum refinery,

petrochemical complex, and ship dismantling activities (Figure 4.19). In addition, spatial variation of the ambient air PCB concentrations indicated that iron–steel plants and ship dismantling plants where all kinds of scrap iron and steel materials are stored, classified, cut into pieces, and melted were the major PCB emitters in the region (Figure 4.20). As verified this case, highest POP concentrations were measured at sites located around the iron-steel plants with electric arc furnaces (EAFs) and the integrated steel plant in Aliaga. The findings of the present study are in agreement with other recent studies in the area indicating that iron−steel plants, ship-breaking activities, petroleum refinery, and petrochemical plant are major POP emitters (Cetin & Odabasi, 2007; Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009, 2012; Kaya et al., 2012).

Petroleum refineries are significant PAH emitters in Aliaga. Refinery processes like distillation, catalytic cracking, storage and handling, and fuel combustion units are the major contributors to PAH emissions (Singh et al., 2010; Kaya et al., 2012). Recent studies conducted in Aliaga have also suggested that the petroleum refinery located in the area is an important source for PAHs (Bozlaker et al., 2008a; Kaya et al., 2012).

Another important source in Aliaga is iron–steel production. Iron–steel production is an important industrial process in Turkey. In Turkey, 31.52 million tons of steel was produced in 2015, making the country 9th biggest producer in the world. Iron and steel requirement of Turkey could be produced either from iron ore at integrated steel plants or from ferrous scrap by electric arc furnaces (EAFs). Plants processing scrap iron with EAFs accounted for 77% of this production. In Turkey, 25.2 million tons of ferrous scrap was consumed in 2015. Turkey takes first place with 22% (19.7 million tons) of the global scrap import in the world (World Steel Association, 2015).

EAFs emit persistent organic pollutants like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Integrated Pollution Prevention and Control [IPPC], 2001; Alcock et al., 2003; U.S. EPA, 2008; Odabasi et al., 2009). The major units of integrated steel plants (sinter plants, coke ovens, and blast

furnaces) are also significant emitters of PAHs and PCBs. Significant amounts of PAHs are emitted by coke ovens (IPPC, 2001; Odabasi et al., 2010). POPs covered in this study are emitted by different mechanisms. PAHs may be present in the scrap and are thermally desorbed during production processes or they may form as result of incomplete combustion of scrap organic matter, fuels, and additives like coal. PCBs are also present in the scrap and they are thermally desorbed during steel production. They may also form by de novo synthesis during thermal processes (IPPC, 2001; Kaya et al., 2012).

The spatial variation of POP concentrations has also implicated the ship dismantling activities as significant PAH and PCB emitters in the region. Aliaga ship dismantling site accounts for ~11% of the Turkey's scrap iron demand (Neser et al., 2008; Kaya et al., 2012). The presently used technology in the ship–breaking process is relatively simple and labor–intensive. The ship is stripped entirely and then cut into fragments using oxygen torches. Cranes are used for loading and unloading of heavy machinery and for dragging the ship further up the shore. The process itself as well as the fires that burn the non–recyclable waste materials produces toxic fumes (Basha et al., 2007; Kaya et al., 2012). PCBs were widely used on ships in 1960–1980s, so their break–up and metal recycling may be an important and uncontrollable source. Recently, ship–breaking activities have also been implicated as potential sources for the elevated air concentrations of PCBs occasionally measured in India using passive air samplers (Breivik et al., 2011).

Similar to ambient air concentrations, the highest soil and 2-year needle PAH concentrations were measured around the iron–steel plants, petroleum refinery, petrochemical plant and ship dismantling area confirming that these are the major PAH sources in the region (Figures 4.21 - 4.23). In addition, the highest soil and 2-year needle PCB concentrations were also measured around the iron–steel plants and ship dismantling area confirming that these are the major PCB sources in the area (Figures 4.22 - 4.24). High atmospheric PAH concentrations were also observed at some urban sites of two sampling regions relatively far from the air pollution sources. These sites are near the residential areas. This could be attributed to the

increased residential heating emissions during the sampling period (November - February). Fossil fuel is a source of PAH emissions and it is used for heating in these regions. It is believed that these emissions increased the PAH concentrations in these areas (Figures 4.19 - 4.25).

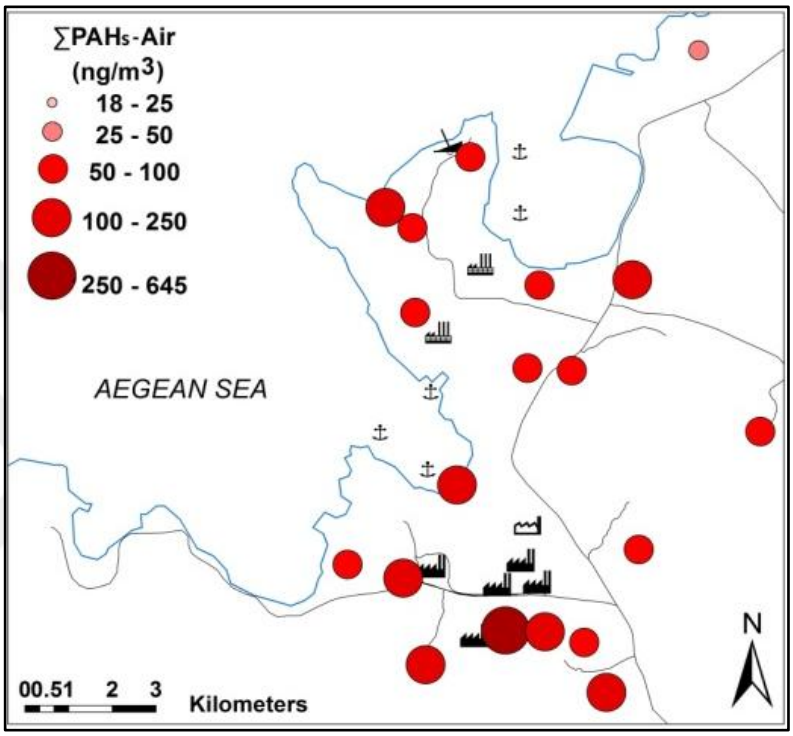


Figure 4.19 Spatial variations of ambient air Σ_{16}PAH concentrations in Aliaga

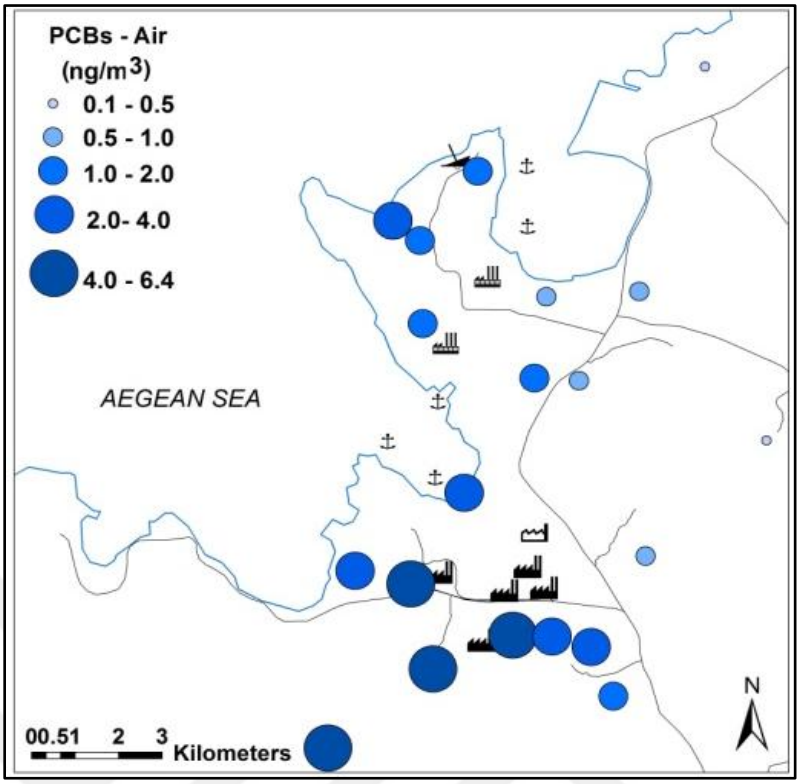


Figure 4.20 Spatial variations of ambient air Σ_{41}PCB concentrations in Aliaga

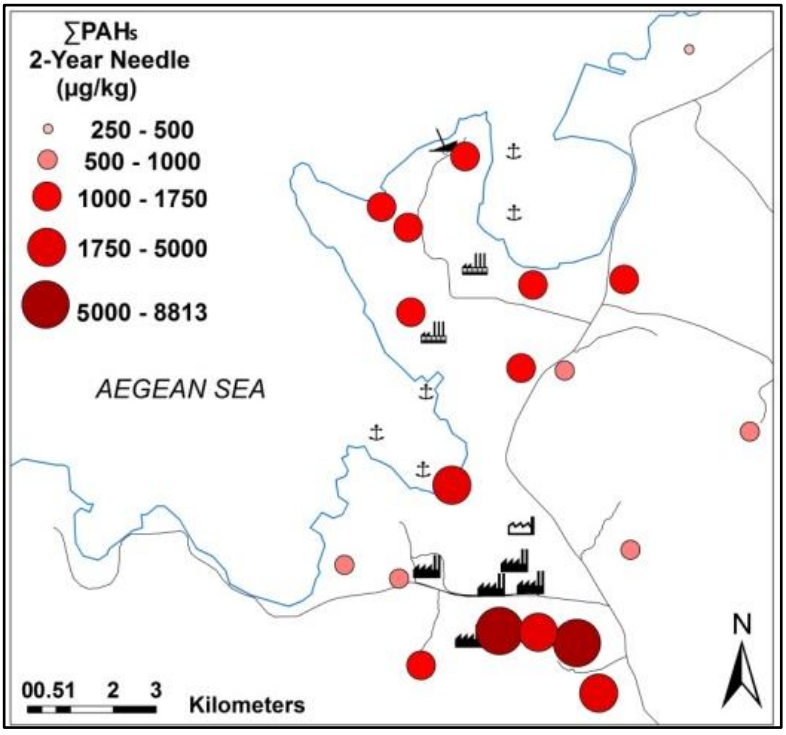


Figure 4.21 Spatial variations of 2-year needle Σ_{16}PAH concentrations in Aliaga

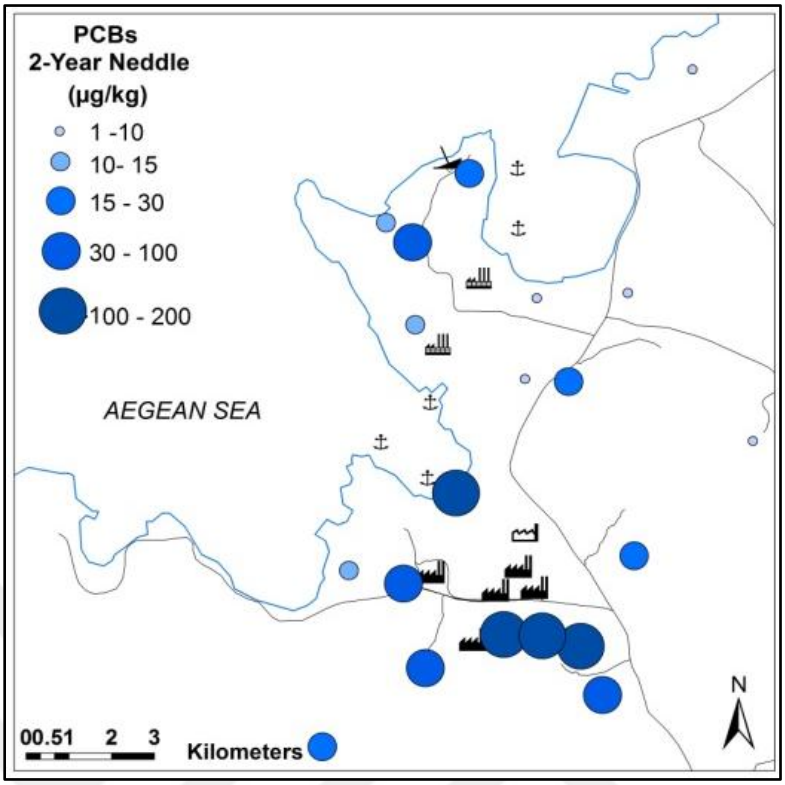


Figure 4.22 Spatial variations of 2-year needle Σ_{41}PCB concentrations in Aliaga

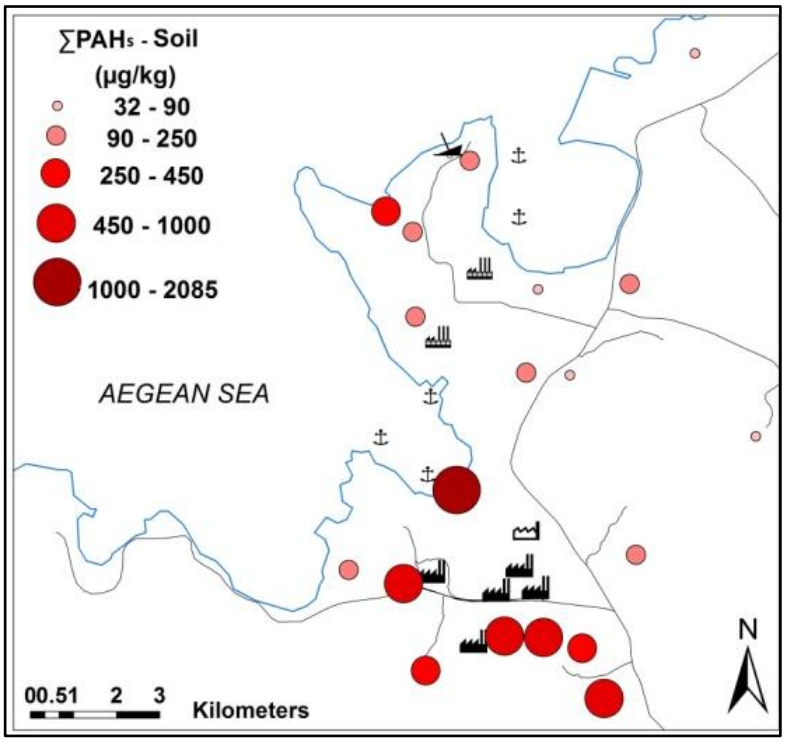


Figure 4.23 Spatial variations of soil Σ_{16}PAH concentrations in Aliaga

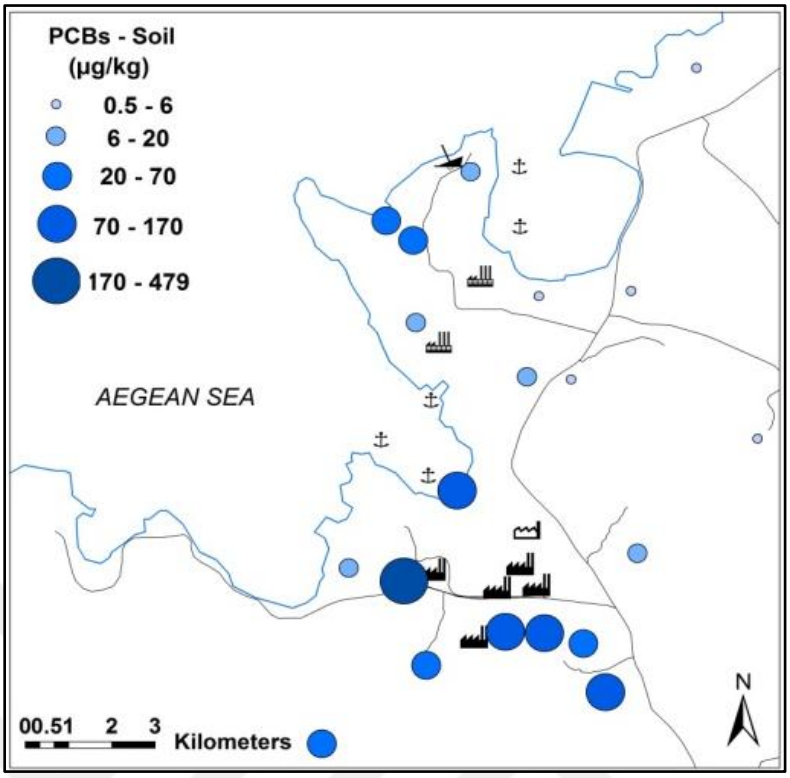


Figure 4.24 Spatial variations of soil Σ_{41}PCB concentrations in Aliaga

Iskenderun industrial region with several ferrous scrap processing steel plants, steel rolling mills, and an integrated steel plant is similar to the Aliaga industrial region that has been studied extensively (Cetin et al. 2007; Cetin & Odabasi 2007; 2008; Bozlaker et al. 2008a, 2008b; Bayram et al. 2008; Odabasi et al. 2009). The plants in Aliaga and Iskenderun regions have comparable iron-steel production capacities, 11.3 and 16.4 million tones/year, respectively (Turkish Association of Iron-Steel Producers, 2015). However, due to the locations of the plants and residential sites and prevailing wind directions, the population density that is exposed to iron–steel plant emissions may be significantly higher in Iskenderun region compared to Aliaga region (Odabasi et al., 2010).

It is reported that southerly winds prevail in Iskenderun (Odabasi et al., 2010). Thus, high POP levels were generally found at sites placed north of the main sources. The highest POP concentrations were measured at sites located north of the iron-steel plants with electric arc furnace (EAFs) and the integrated steel plant where their

emissions were transported by the prevailing winds (Figures 4.25 - 4.26 - 4.27 - 4.28 - 4.29 - 4.30). However, higher PAH concentrations in Iskenderun could be attributed to the PAH emissions of the integrated steel plant with coke ovens (Odabasi et al., 2010). Payas county and iron–steel plant housings are among the sites with high ambient air and soil POP concentrations. Payas is mainly affected by the emissions from the integrated steel plant while the steel plant housings are affected from the scrap processing steel plants with EAFs located south. Spatial variation of POP concentrations indicated that iron–steel plants in Iskenderun area are important sources emitting these pollutants, similar to the plants located in Aliaga region.

According to the figures, ambient air PAH concentrations measured in Iskenderun were higher than measured in Aliaga (Figures 4.19 - 4.25) because of features of scrap used in the iron-steel industry. Results indicated that the iron-steel plants were the major sources of POPs in the Iskenderun region. This is consistent with the recent study conducted in Iskenderun region reporting that iron-steel production from scrap is a significant source for POPs (Odabasi et al., 2010).

The sources of PAHs may also be identified by using diagnostic ratios in soil samples. It is reported that a phenathrene/anthracene ratio > 15 and a fluoranthene/pyrene ratio < 1 indicates crude oil while phenathrene/anthracene < 10 and fluoranthene/pyrene > 1 indicates combustion sources (Wang et al. 2004; Odabasi et al., 2010). In the present study, phenathrene/anthracene ratio was < 10 (average 4.65 and 9.08) and fluoranthene/pyrene > 1 (average 1.38 and 1.39) suggesting combustion was the dominating source of soil in Iskenderun and Aliaga, respectively.

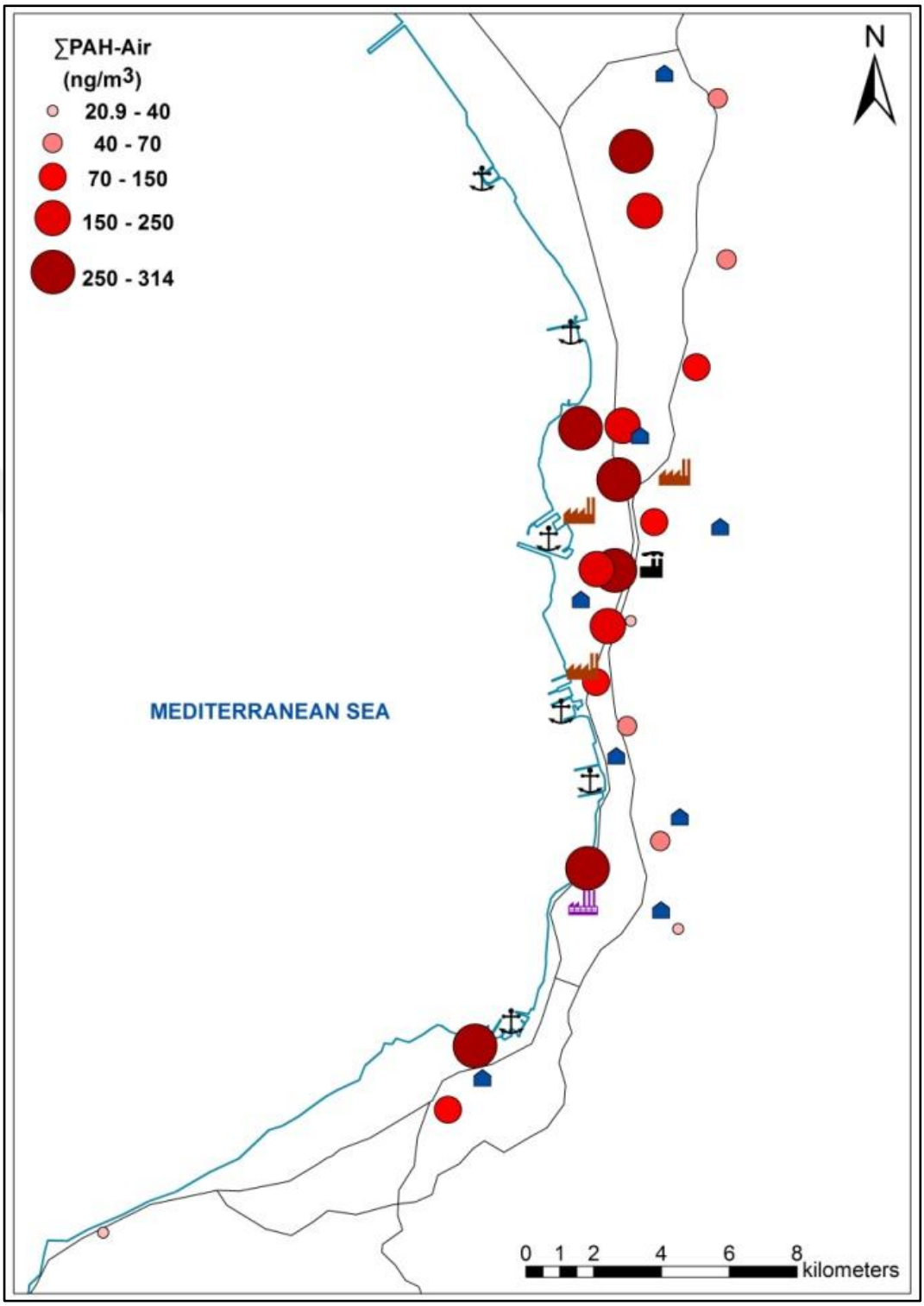


Figure 4.25 Spatial variations of ambient air Σ_{16}PAH concentrations in Iskenderun

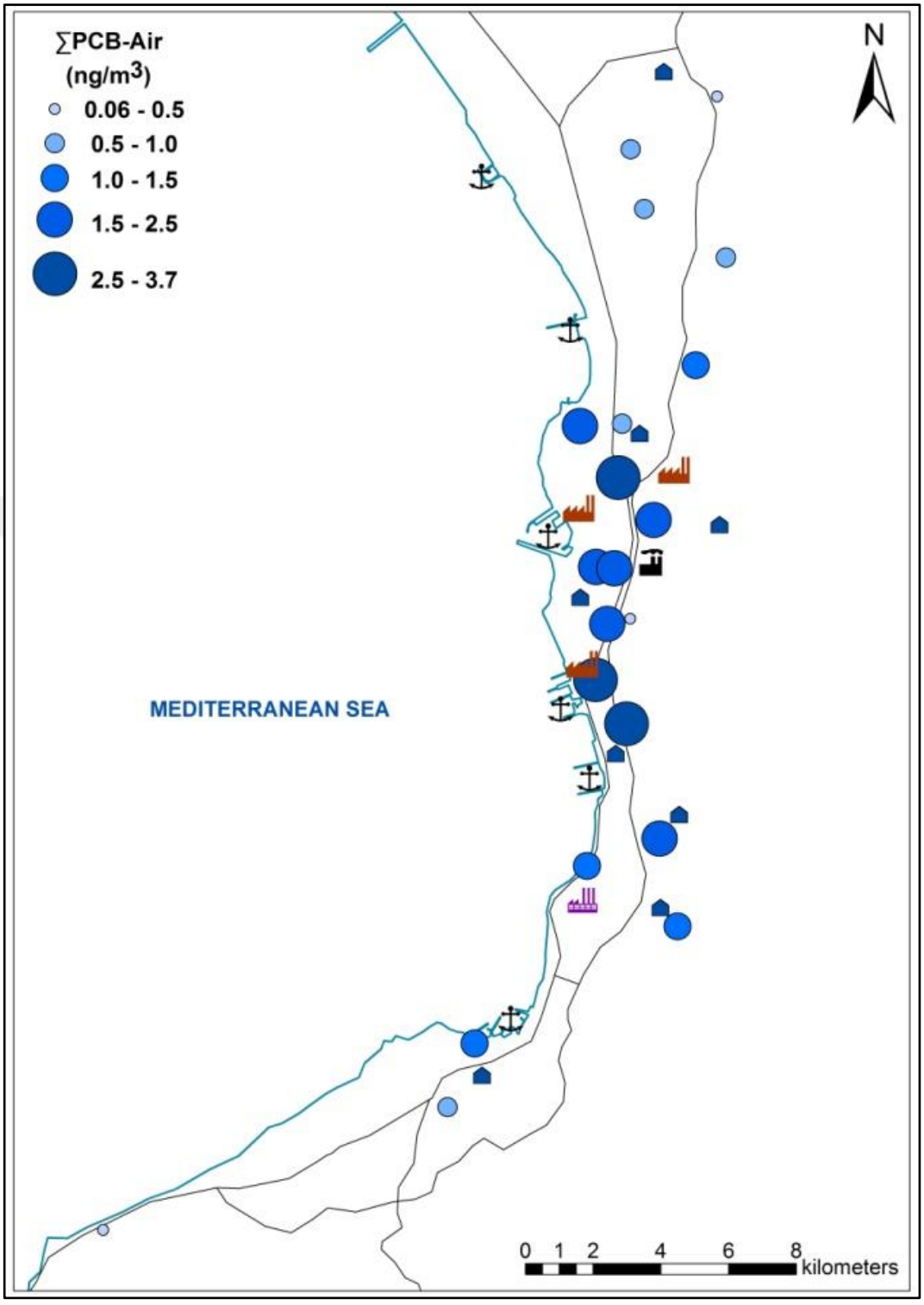


Figure 4.26 Spatial variations of ambient air Σ_{41}PCB concentrations in Iskenderun

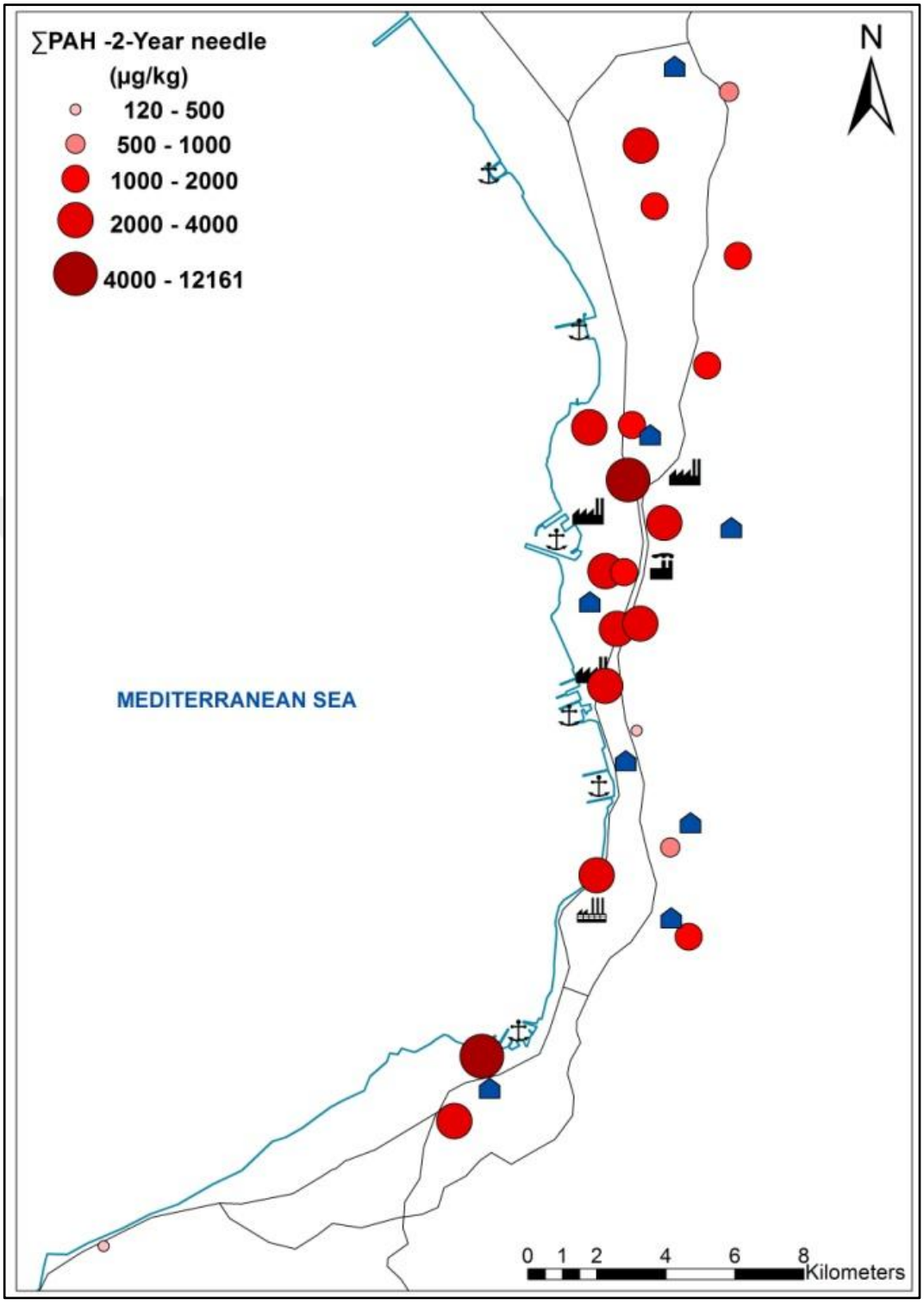


Figure 4.27 Spatial variations of 2-year needle Σ_{16}PAH concentrations in Iskenderun

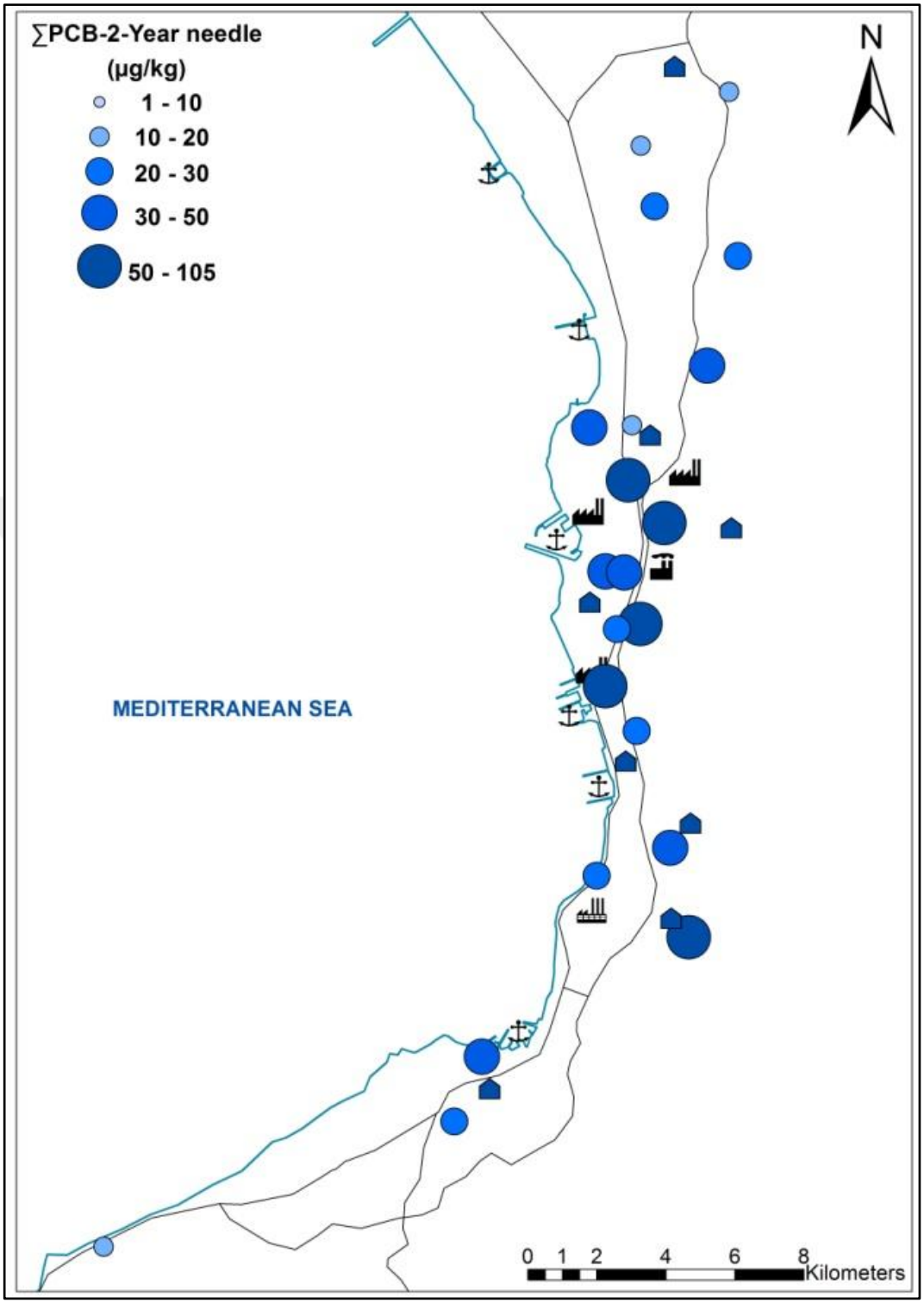


Figure 4.28 Spatial variations of 2-year needle Σ_{41}PCB concentrations in Iskenderun

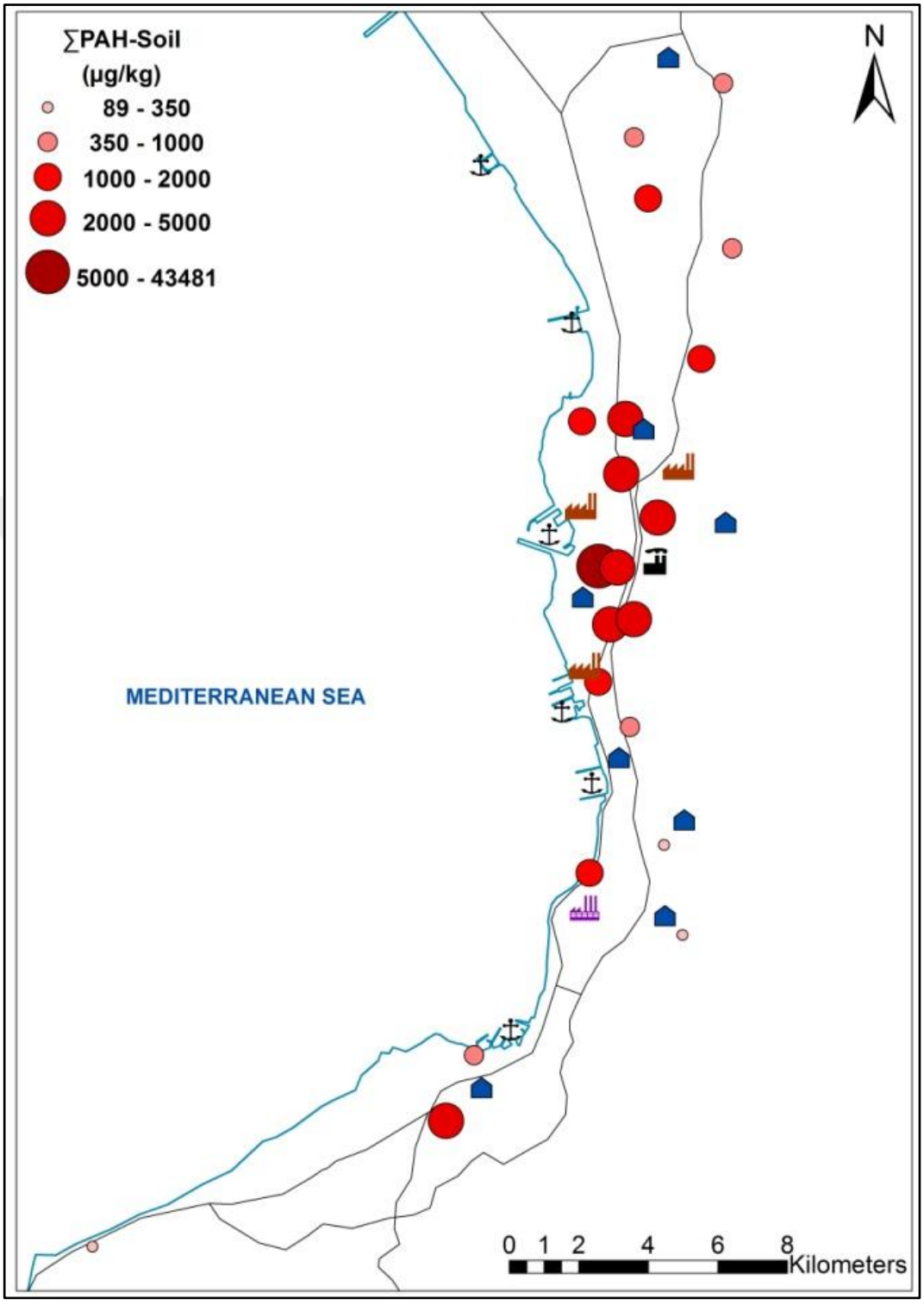


Figure 4.29 Spatial variations of soil Σ_{16}PAH concentrations in Iskenderun

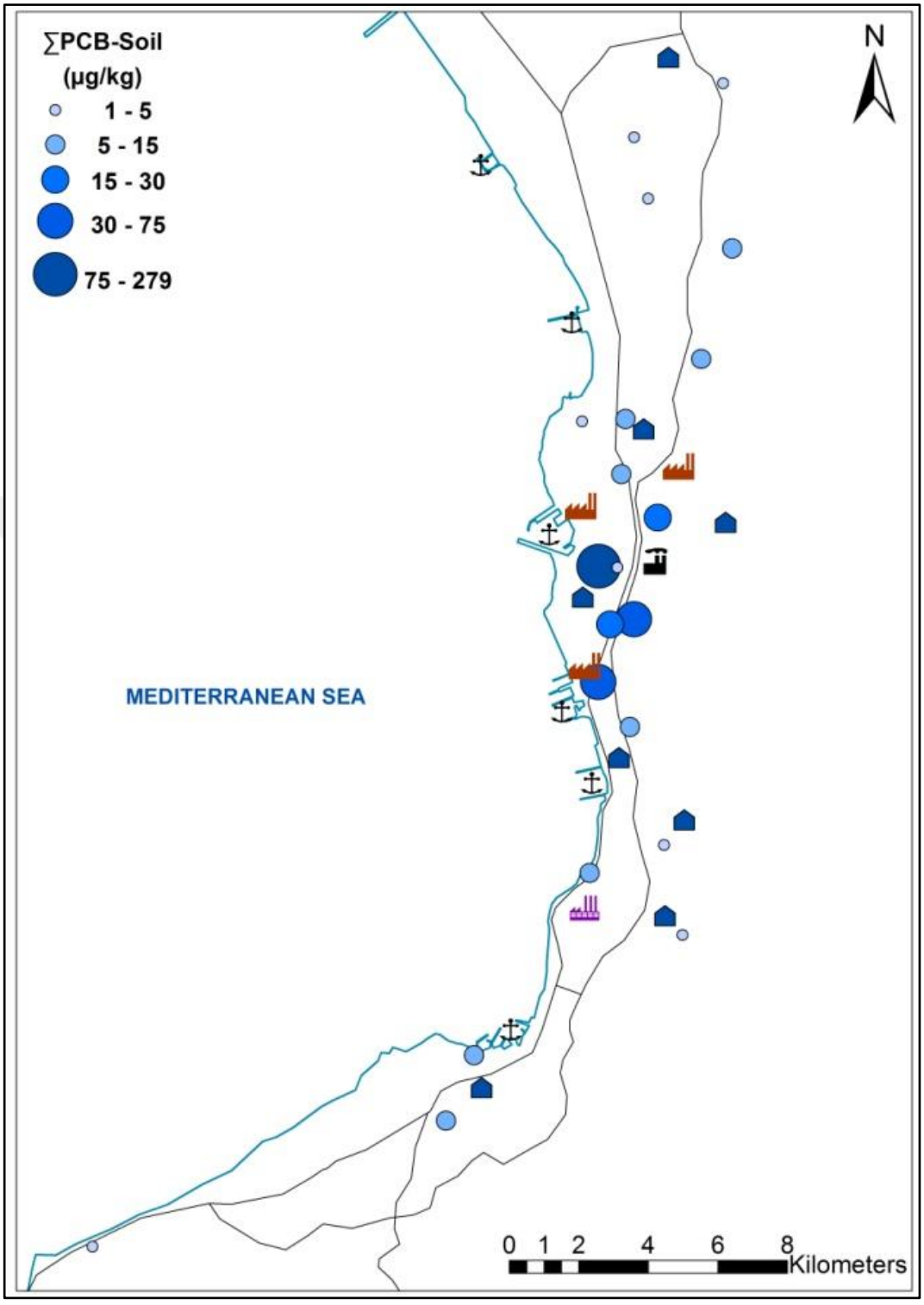


Figure 4.30 Spatial variations of soil Σ_{41}PCB concentrations in Iskenderun

4.4 Correlations of POP Concentrations in Different Media

The relationships between the total concentrations of POPs (Σ_{16}PAHs and Σ_{41}PCBs) observed in different sample types were investigated (Tables 4.3 - 4.4). The statistically significant correlations ($p < 0.01$) between ambient air, soil, tree components and litter showed that POPs are exchanged between atmosphere and these components. The correlations were also generally significant ($p < 0.01$) for individual compounds/congeners. POPs in soil, litter, needle, bark and branch samples (except the stem samples) were well correlated with ambient air for both sampling regions. This suggested that these components (soil, litter, needle, bark and branch) reflect the level of atmospheric pollution. They could be used as viable passive sampling alternatives to determine the spatial variation of atmospheric POPs in a region.

The low correlations of stem samples with other compartments could be described to the fact that POP concentrations in stem are those integrated over the ages of sampled trees and therefore they might not represent the recent conditions. However, some low correlations observed for branch samples are surprising since their ages are much lower than the stem samples. The best relationship was observed between 1-year needles and 2-year needles in tree components. Significant correlations ($p < 0.01$) were also observed between different POP groups, further suggesting that the measured PAHs and PCBs in two sampling regions were emitted by common sources (iron-steel plants, petroleum refining, ship-breaking, petrochemical plants) (Tables 4.3 - 4.4).

Table 4.3 Correlation matrixes of PAH concentrations (significant values in bold, $p < 0.01$)

ISKENDERUN-PAH	Air	Soil	Bark	Litter	1-Year needle	2-Year needle	Branch	Stem
Air	1.00							
Soil	**0.49**	1.00						
Bark	**0.50**	**0.73**	1.00					
Litter	**0.63**	**0.56**	**0.77**	1.00				
1-Year needle	**0.65**	**0.53**	**0.73**	**0.79**	1.00			
2-Year needle	**0.74**	**0.54**	**0.57**	**0.68**	**0.88**	1.00		
Branch	0.44	0.42	**0.48**	**0.57**	0.22	0.31	1.00	
Stem	0.23	0.26	0.14	0.12	0.15	0.003	-0.15	1.00
ALIAGA-PAH	**Air**	**Soil**	**Bark**	**Litter**	**1-Year needle**	**2-Year needle**	**Branch**	**Stem**
Air	1.00							
Soil	**0.53**	1.00						
Bark	**0.54**	**0.64**	1.00					
Litter	**0.57**	**0.69**	**0.63**	1.00				
1-Year needle	**0.80**	**0.67**	**0.60**	**0.79**	1.00			
2-Year needle	**0.76**	**0.63**	**0.78**	**0.75**	**0.88**	1.00		
Branch	**0.69**	**0.68**	**0.53**	**0.73**	**0.85**	**0.72**	1.00	
Stem	0.003	0.18	-0.08	**0.46**	0.13	0.134	0.02	1.00

Table 4.4 Correlation matrixes of PCB concentrations (significant values in bold, $p < 0.01$)

ISKENDERUN-PCB	Air	Soil	Bark	Litter	1-Year needle	2-Year needle	Branch	Stem
Air	1.00							
Soil	**0.73**	1.00						
Bark	**0.67**	**0.94**	1.00					
Litter	**0.85**	**0.89**	**0.81**	1.00				
1-Year needle	**0.86**	**0.73**	**0.72**	**0.85**	1.00			
2-Year needle	**0.76**	**0.66**	**0.52**	**0.76**	**0.78**	1.00		
Branch	**0.52**	**0.71**	**0.66**	**0.61**	**0.50**	**0.54**	1.00	
Stem	**0.62**	0.44	0.14	**0.54**	0.45	**0.70**	0.31	1.00
ALIAGA-PCB	**Air**	**Soil**	**Bark**	**Litter**	**1-Year needle**	**2-Year needle**	**Branch**	**Stem**
Air	1.00							
Soil	**0.70**	1.00						
Bark	**0.73**	**0.76**	1.00					
Litter	**0.69**	**0.57**	**0.81**	1.00				
1-Year needle	**0.58**	**0.53**	**0.64**	**0.76**	1.00			
2-Year needle	**0.56**	0.44	**0.63**	**0.72**	**0.82**	1.00		
Branch	**0.56**	**0.55**	**0.59**	**0.63**	**0.71**	**0.71**	1.00	
Stem	0.27	0.27	0.39	**0.50**	**0.65**	0.34	0.26	1.00

4.5 Historical Trends of POPs in Sampling Regions

POPs measured in annual growth rings provide a possibility to reveal historical trends of the atmospheric concentrations in Aliaga and Iskenderun. Historical variations of all POP concentrations indicated an increasing trend with time in parallel to industrialization for both regions. PAHs have several sources related to combustion. Therefore, they were present in air long before the industrialization in both regions. PCBs were manufactured between 1929 and 1979. They have been widely used throughout the world. PCBs are also emitted from combustion of fossil fuels and biomass (Odabasi et al., 2009, 2012; Aydın et al., 2014) The observed historical variations of PAHs and PCBs are in agreement with their production, use, and known local sources emitting substantial amounts in both regions (Odabasi et al., 2009; 2010). Although PCBs are not produced and their use was banned more than three decades ago, their concentrations continued to rise due to the increasing number of ongoing local sources (especially scrap processing iron-steel plants and ship breaking yards) (Cetin & Odabasi, 2007; Cetin et al., 2007; Bozlaker et al., 2008a, 2008b; Odabasi et al., 2009, 2010, 2012; Kaya et al., 2012).

Numbers of industries, population amount and vehicular traffic have substantially increased during the past few decades in Aliaga and Iskenderun. The establishment of major industries began in the 1970s (refinery and ship-breaking plants) and continued through the 1980s (1 petrochemical plant and 4 iron-steel plants) in Aliaga. Six more industries (iron-steel plants and steel rolling mills) were established between 1990 and 1995. Three steel rolling mills and a natural gas power plant were started to operate after 2000. Historical variations of POPs concentration measured in dated stem core samples for all sampling sites in Aliaga are presented in Figures 4.31 – 4.32. POPs concentration at industrial sites were relatively low and stable until the 1960s and increased onward. Concentrations sharply increased between 1980 and 1995, corresponding to establishment of most of the major industries in Aliaga (Figures 4.31 – 4.32). However, the increase in PAH concentrations was relatively less sharp since several PAH sources were present in the area (they are byproducts of combustion of fossil fuels) before the establishment of major industries. Although

POP concentrations at background sites showed increasing trends, their fluctuations were not similar to those observed at industrial sites, probably due to their distance from major sources (Figures 4.31 – 4.32). Thus, it could be concluded that the observed historical distribution patterns of POPs in the tree ring samples are representative for the variations in anthropogenic emissions and resulting atmospheric concentrations in Aliaga.

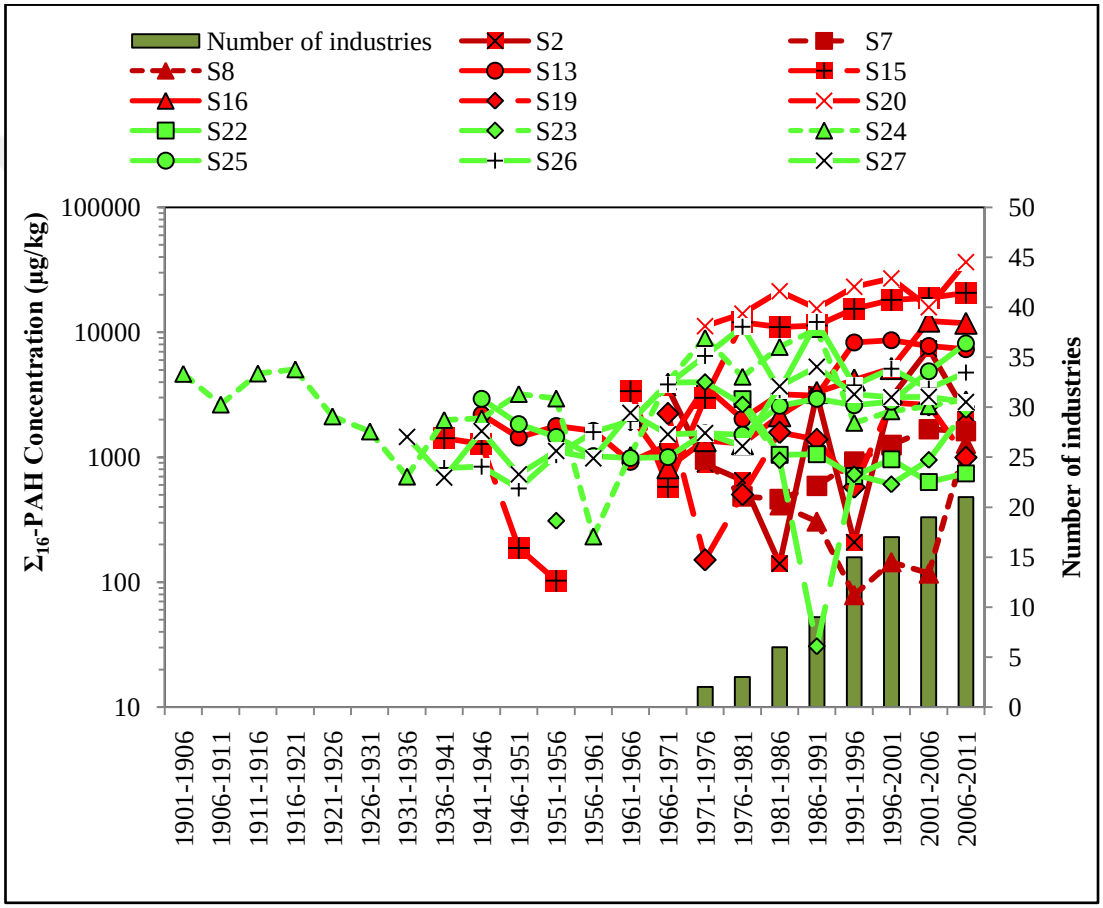


Figure 4.31 Historical variations of Σ_{16}PAH concentrations measured in dated stem core samples for all sampling sites in Aliaga (red color: industrial, green color: background)

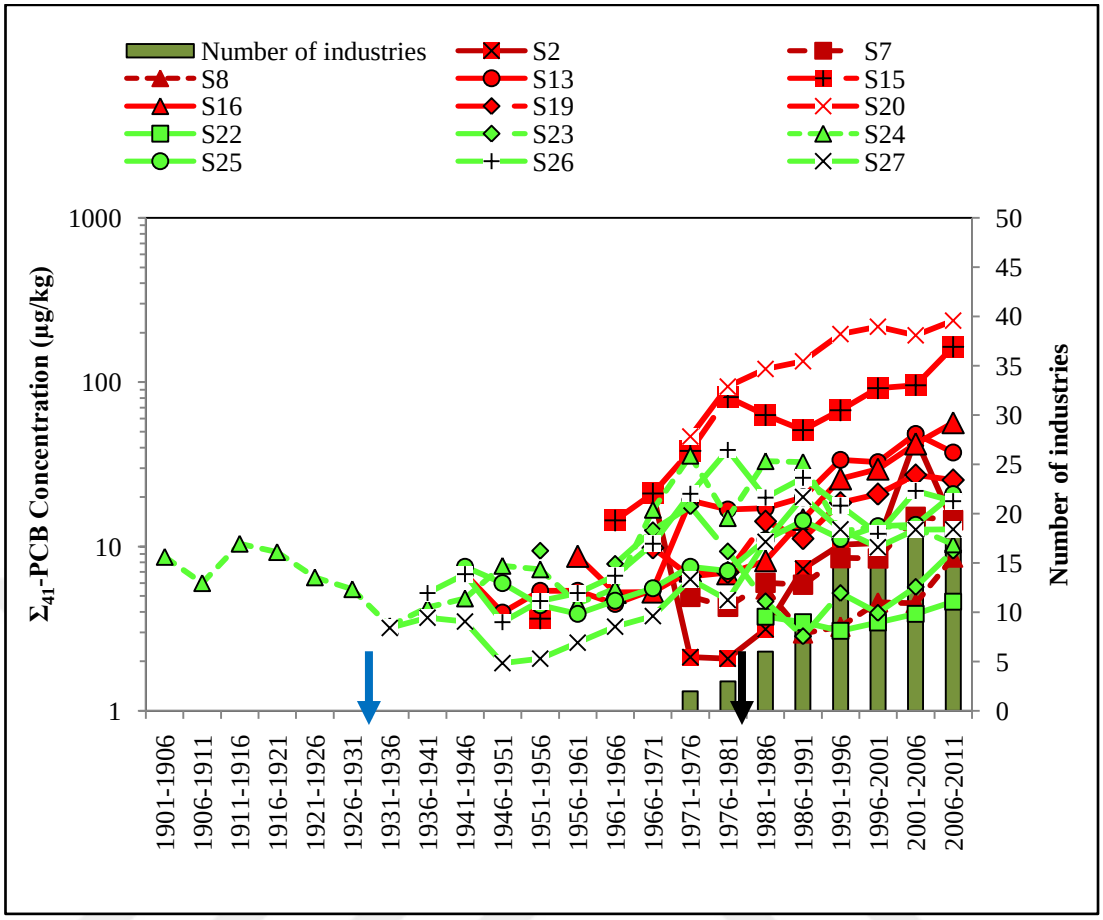


Figure 4.32 Historical variations of Σ_{41}PCB concentrations measured in dated stem core samples for all sampling sites in Aliaga (red color: industrial, green color: background). Blue and black arrows indicate the start and stop dates of commercial production of PCBs

Similar to the other plant components, highest stem POPs concentration were measured at industrial sites like 13, 15, and 20 while concentrations were substantially lower in the background sites like 25 and 27 in Aliaga. Historical trends of PAHs and PCBs concentration in selected industrial and background sites as an example are shown in Figures 4.33 – 4.37. Sampling Site-13 was situated in the Bozköy and it was very close to the iron-steel plants region. Total POP concentrations slightly started to increase from 1971 to 1976. After 1991, it was observed that nearly 2 times higher increase in POP concentrations in this site (Figure 4. 33). TUPRAS and PETKIM began operations in 1972 and 1984, respectively. In addition, iron-steel plants began operations in the 1980s and increased their numbers in 1990s. It is thought that, iron-steel plants, TUPRAS refineries and PETKIM caused this increase in stem POP concentrations.

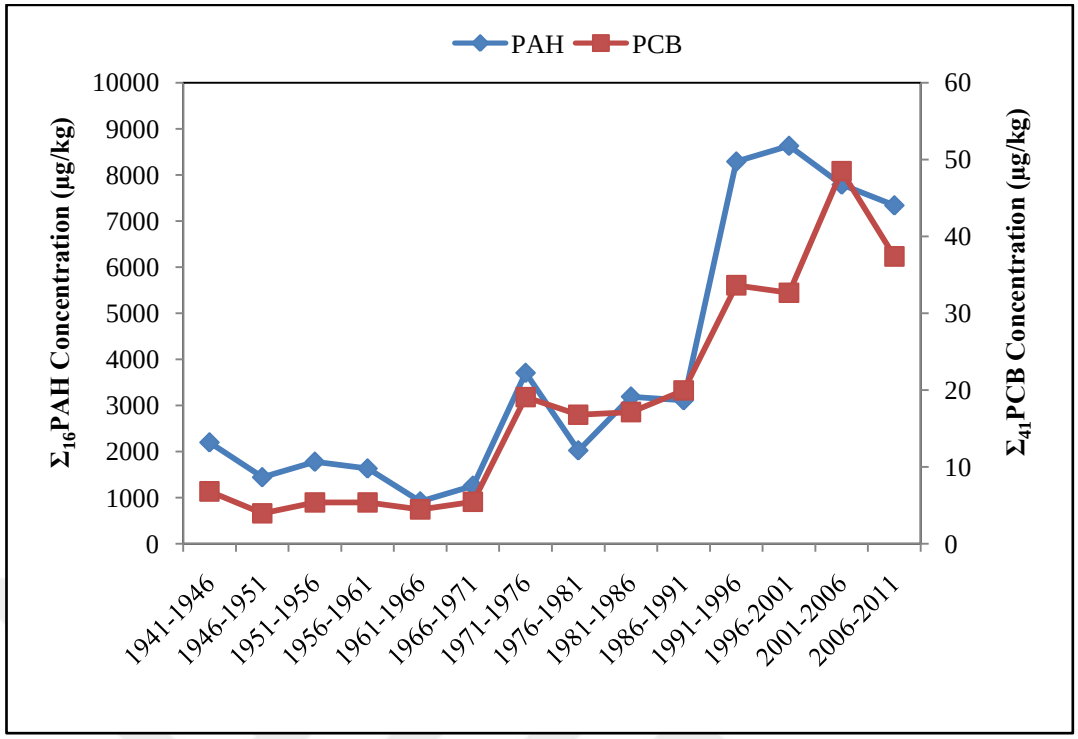


Figure 4.33 Historical variations of POP concentrations in Sampling Site-13 (industrial site) in Aliaga

Sampling Site-15 was situated in Kozbeyli and it was close to the Bozköy. Similar to Sampling Site-13, POP concentrations were started to increase since the 1970s and larger increases were observed after 1990s in Sampling Site-15 (Figure 4.34). The highest PAH concentrations were measured in Sampling Site-20 in Aliaga. This site was situated very close to Nemrut Bay and there were many ports in this site. POP concentrations were tending to a steady increase and the highest values were found in the last 5-year period (2006 - 2011) in this site (Figure 4.35). It is thought that Sampling Site-20 was under the effect of ports, TUPRAS refineries and PETKIM.

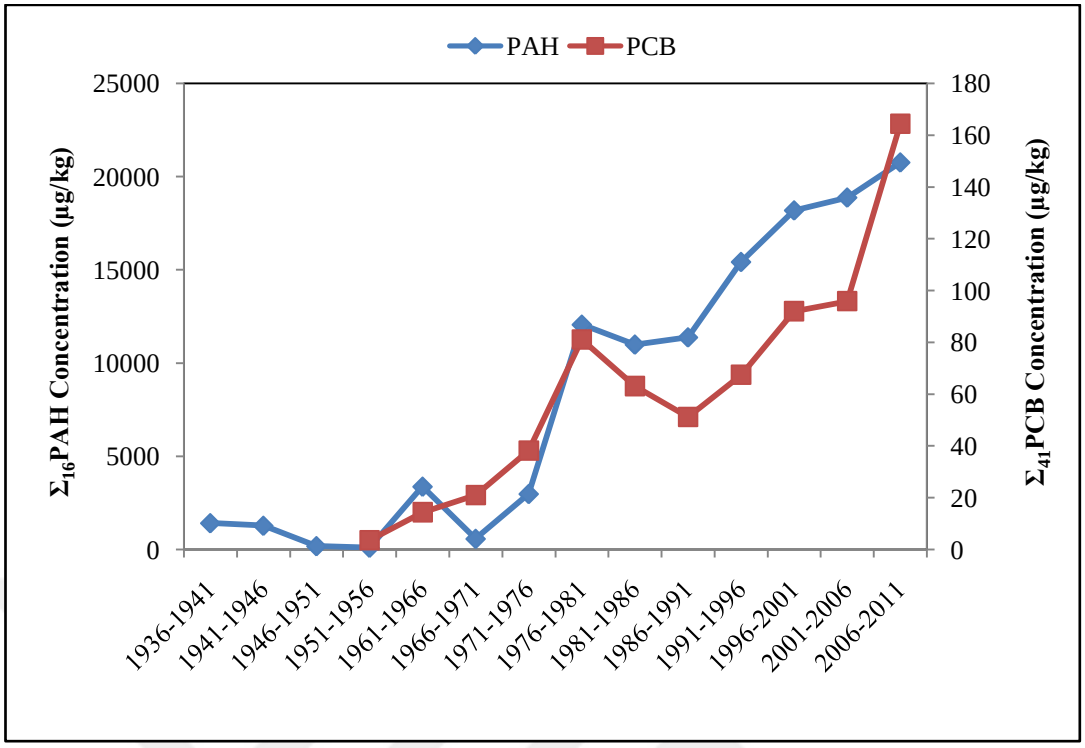


Figure 4.34 Historical variations of POP concentrations in Sampling Site-15 (industrial site) in Aliaga

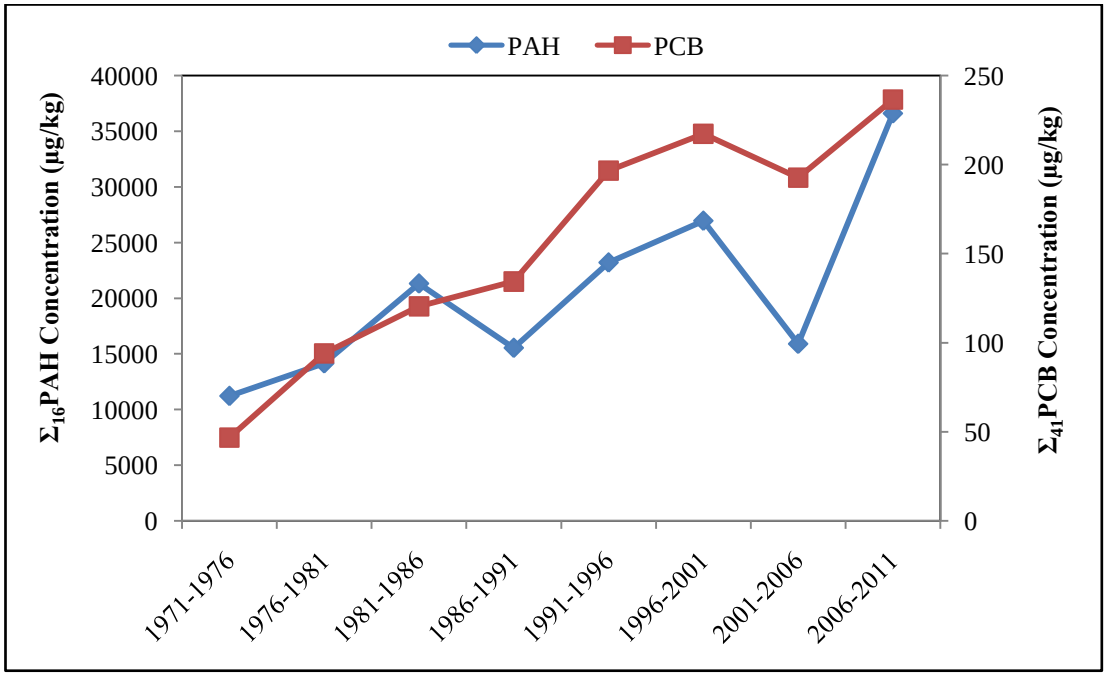


Figure 4.35 Historical variations of POP concentrations in Sampling Site-20 (industrial site) in Aliaga

After the 1980s, there was a slight tendency to increase in POP concentrations in Sampling Sites 25 and 27 (Figures 4. 36 – 4.37) in Aliaga. These sites were the background sites and they were far from the pollutant sources and residential areas. Therefore, it was not known possible POP resources and activities between 1970 and 1990 years in these sites. All PAH and PCB congeners showed similar historical variations at all sites as illustrated as an example at Site-13 in Aliaga (Figures 4.38−4.39). Stem concentrations showed similar patterns among the sampling sites and among different POP groups, suggesting that they were affected by similar sources in Aliaga.

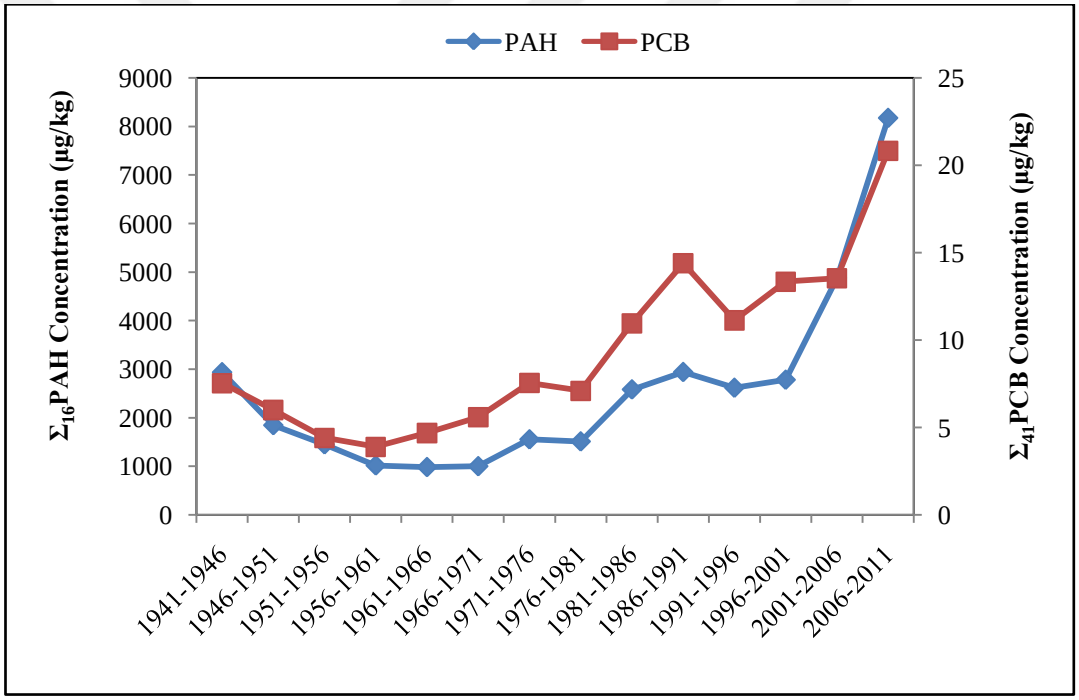


Figure 4.36 Historical variations of POP concentrations in Sampling Site-25 (background site) in Aliaga

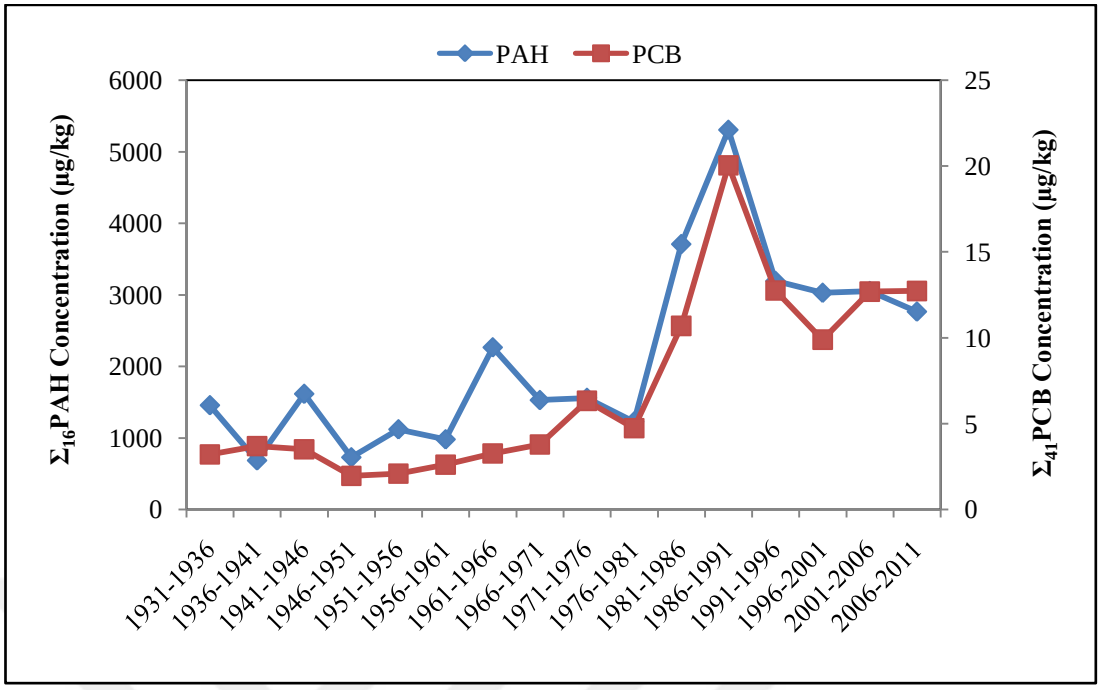


Figure 4.37 Historical variations of POP concentrations in Sampling Site-27 (background site) in Aliaga

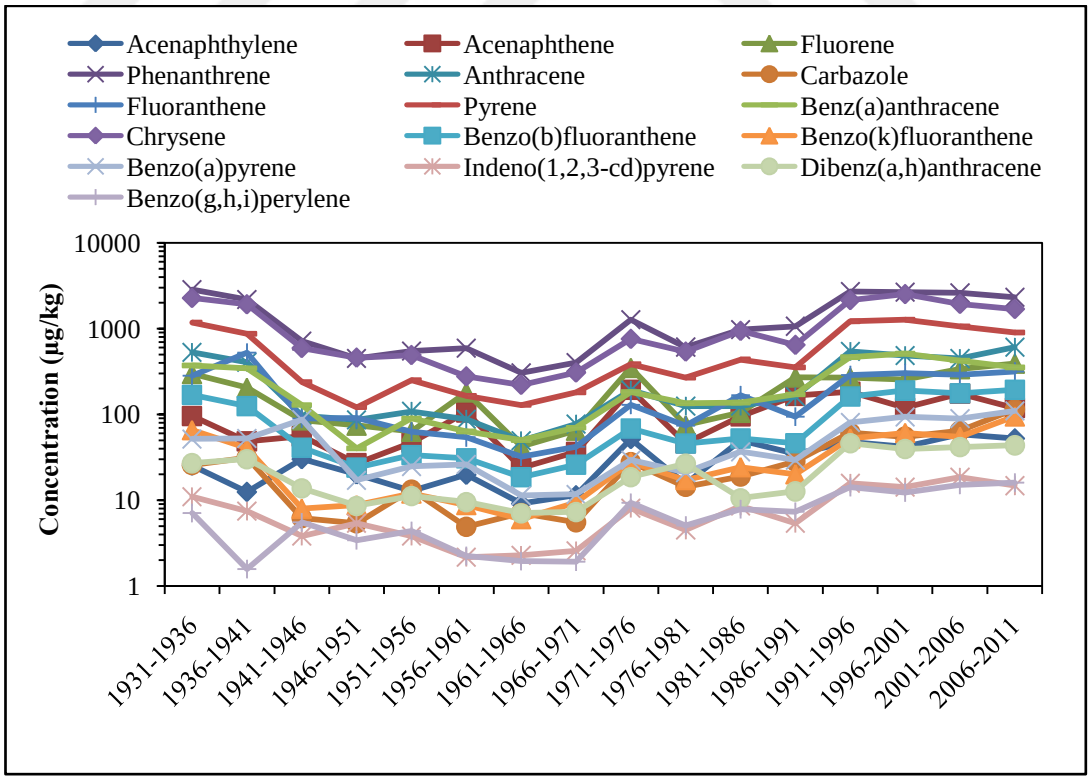


Figure 4.38 Historical variations of PAH congeners in Sampling Site-13 (industrial site) in Aliaga

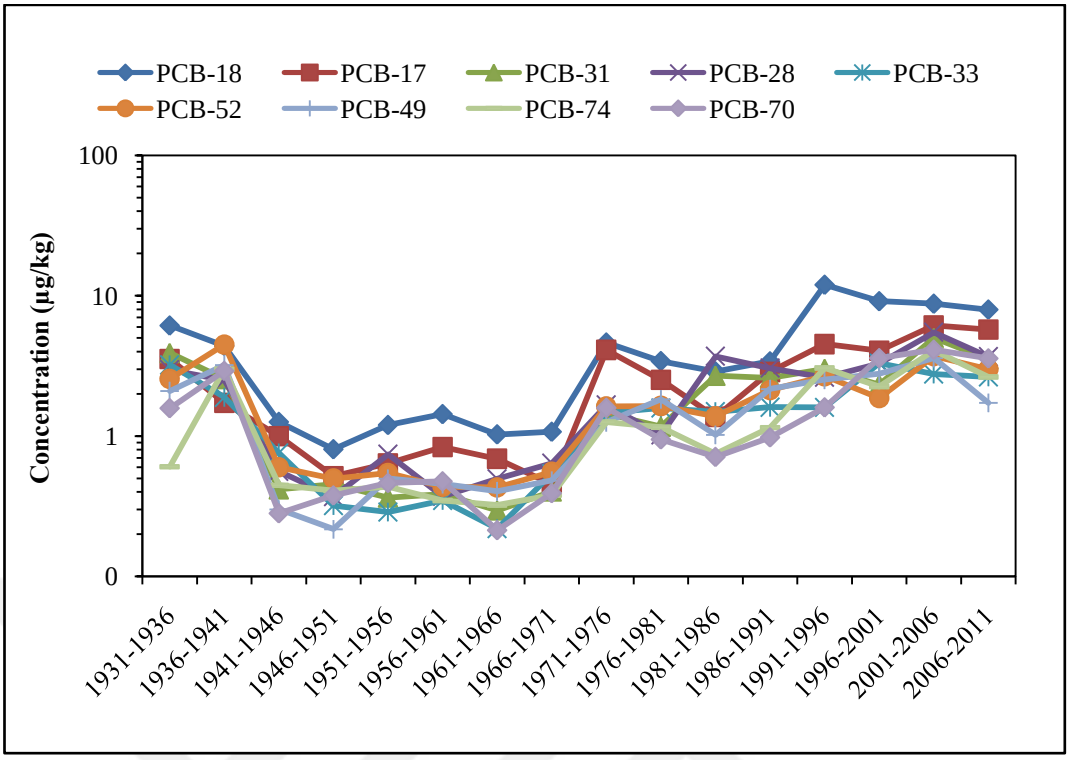


Figure 4.39 Historical variations of PCB congeners in Sampling Site-13 (industrial site) in Aliaga

The establishment of major industries began in the 1949 (rolling mill plant) and continued through the 1970s and 1980s (cement plant, steel rolling mills) in Iskenderun. Four steel rolling mills were established between 1980 and 1995. Many of the industrial plants were started to operate after 2005. In Iskenderun, most of the trees were young and they were developed intensive industrialization period starting after the mid-1970s. Therefore, evaluation of pre-pollution period was not been possible in the most sampling sites in this region. Historical variations of PAH and PCB concentrations measured in dated stem core samples for all sampling sites in Iskenderun are presented in Figures 4.40 – 4.41. POP concentrations at industrial sites were started to increase after 1970s and stable until the 1980s. Concentrations sharply increased after 1985, corresponding to establishment of most of the major industries in the region (Figures 4.40 – 4.41). Similar to the Aliaga, the increase in PAH concentrations were relatively less sharp due to the PAHs were byproducts of combustion of fossil fuels and they were present in the area before the establishment of major industries. POP concentrations at background sites showed increasing trends (Figures 4.40 – 4.41). Similar to Aliaga, it could be concluded that the

observed historical distribution patterns of POPs in the tree ring samples are representative for the variations in anthropogenic emissions and resulting atmospheric concentrations in Iskenderun.

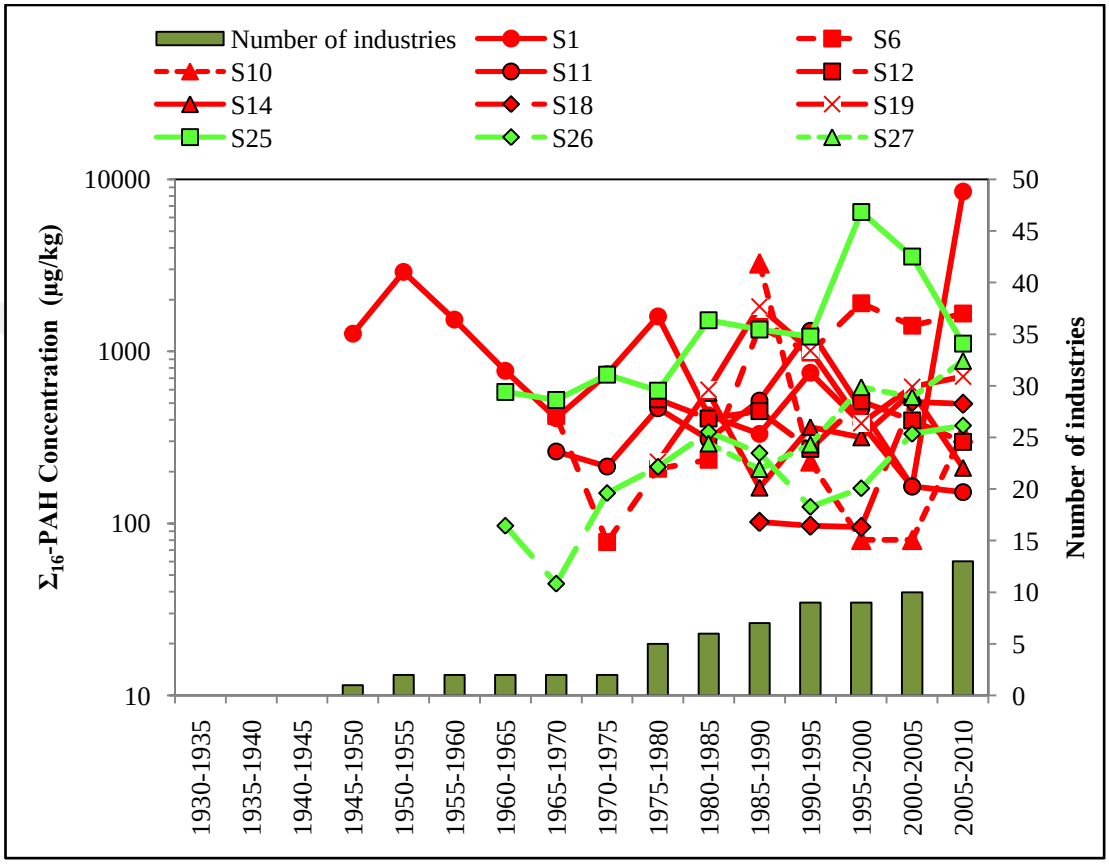


Figure 4.40 Historical variations of Σ_{16}PAH concentrations measured in dated stem core samples for all sampling sites in Iskenderun (red color: industrial, green color: background)

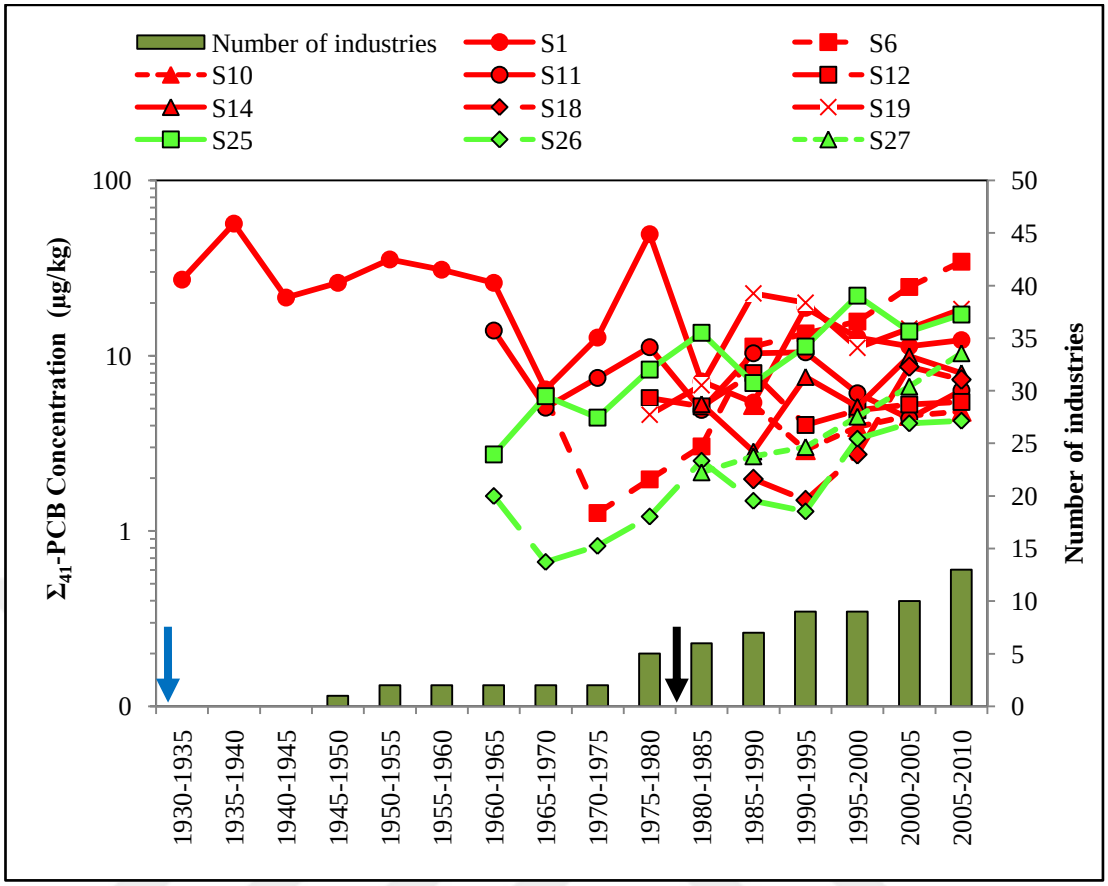


Figure 4.41 Historical variations of Σ_{41}PCB concentrations measured in dated stem core samples for all sampling sites in Iskenderun (red color: industrial, green color: background). Blue and black arrows indicate the start and stop dates of commercial production of PCBs

Highest stem POP concentrations were measured at industrial sites like 1 and 6 while concentrations were substantially lower in the background sites like 26 and 27 in Iskenderun. Historical trends of PAH and PCB concentrations in selected sites as an example are shown in Figures 4.42 – 4.45. Sampling Site-1 was located in the middle of the iron-steel plant area in Iskenderun. This site was under the influence of iron-steel plants due to the dominant winds in the region. The first plant (rolling mill) in Iskenderun was started to operate in 1949. Then, steel mill and cement plant began operations in 1977. Many of the plants were opened after 2005. The highest POP concentrations were measured between the years 1950-1955, 1975-1980 and 1990-1995 in Sampling Site-1 (Figure 4.42). These changes in POP concentrations were consistent with the starting years of industrial activities in the region. It is thought

that POP concentrations of annual tree rings in Sampling Site-1 could be reflecting pollution in the region.

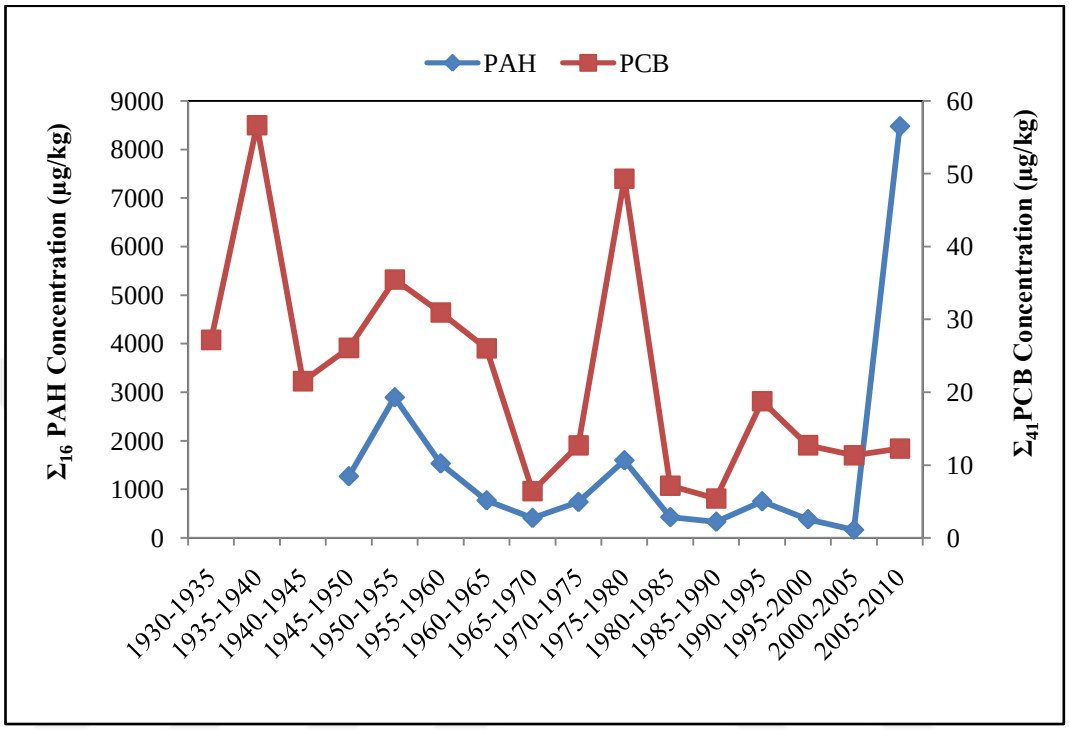


Figure 4.42 Historical variations of POP concentrations in Sampling Site-1 (industrial site) in Iskenderun

Sampling Site-6 was located near the residential area in the Denizciler Municipality. Denizciler Municipality was established in 1987 and since then the population was increased. Therefore, it is thought that the Sampling Site-6 may reflect pollution from domestic-based PAH concentrations. There was a continuous increase in POP concentrations after 1985 in this site (Figure 4.43). It is thought that this situation was occurred due to the increase of population and industrial plants since the 1990s in this site.

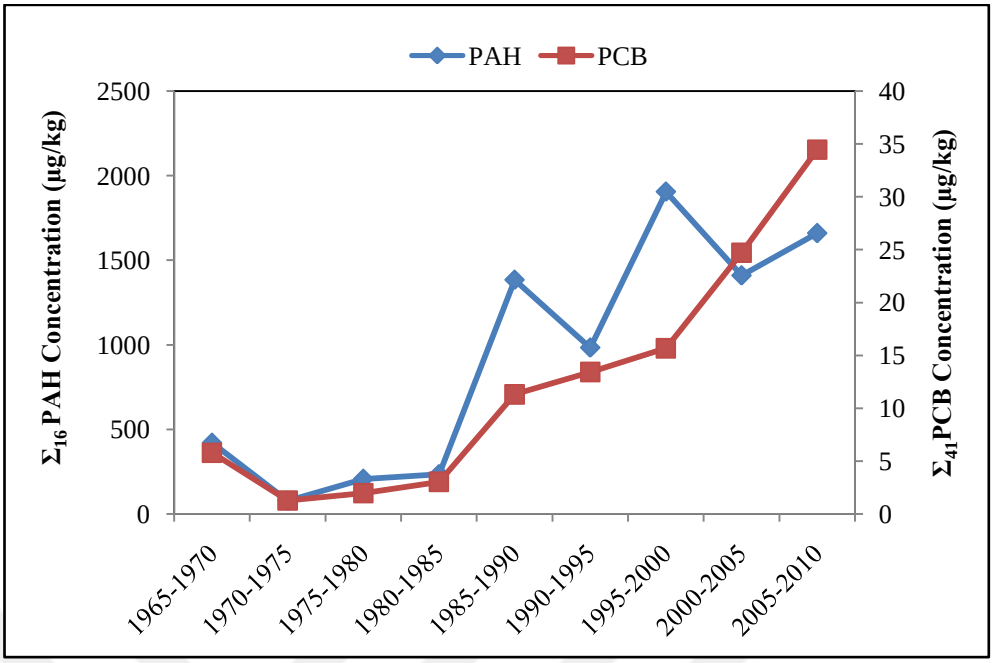


Figure 4.43 Historical variations of POP concentrations in Sampling Site-6 (industrial site) in Iskenderun

Sampling Sites 26 and 27 were the background sites and they were far from major pollutant sources. Historical trends of POP concentrations in these background sites were similar to each other (Figures 4.44 – 4.45). At the Sampling Sites 26 and 27, POP concentrations were increased slightly after 1995 (Figures 4.44 – 4.45). As previously described, it was not known possible POP resources and activities after 1995 in these sites. All PAH and PCB congeners showed similar historical variations at all sites as illustrated as an example at Site-1 in Iskenderun (Figures 4.46−4.47). Stem concentrations showed similar patterns among the sampling sites and among different POP groups in Iskenderun, suggesting that they were affected by similar sources as in Aliaga.

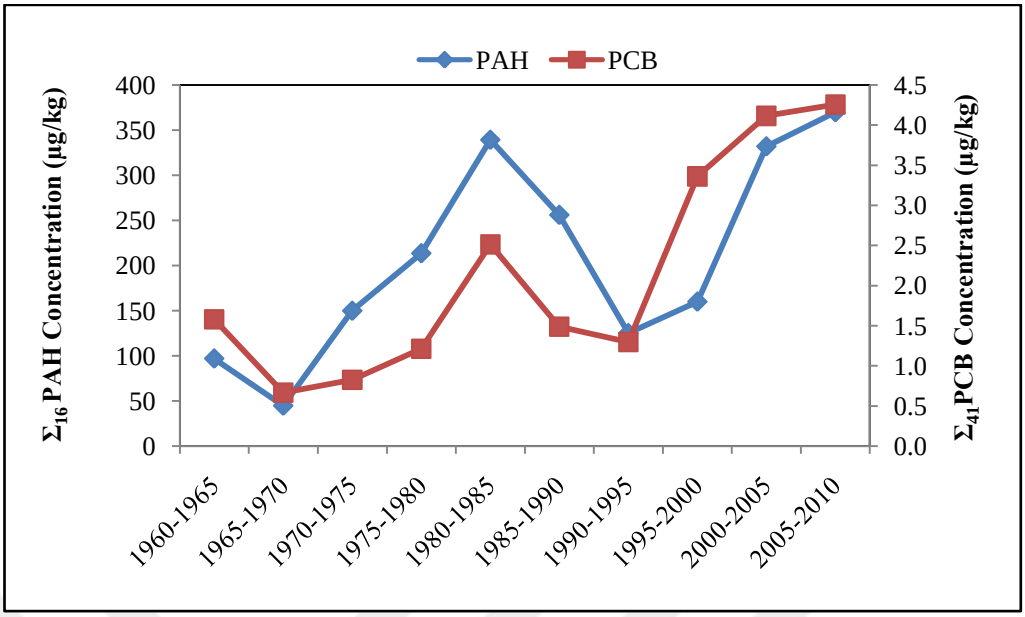


Figure 4.44 Historical variations of POP concentrations in Sampling Site-26 (background site) in Iskenderun

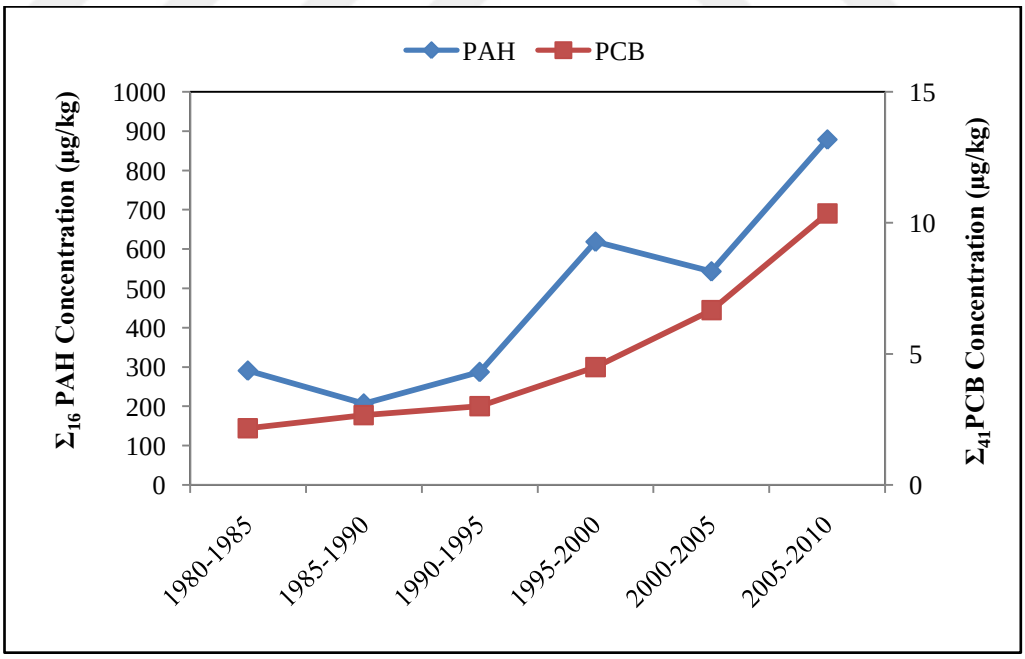


Figure 4.45 Historical variations of POP concentrations in Sampling Site-27 (background site) in Iskenderun

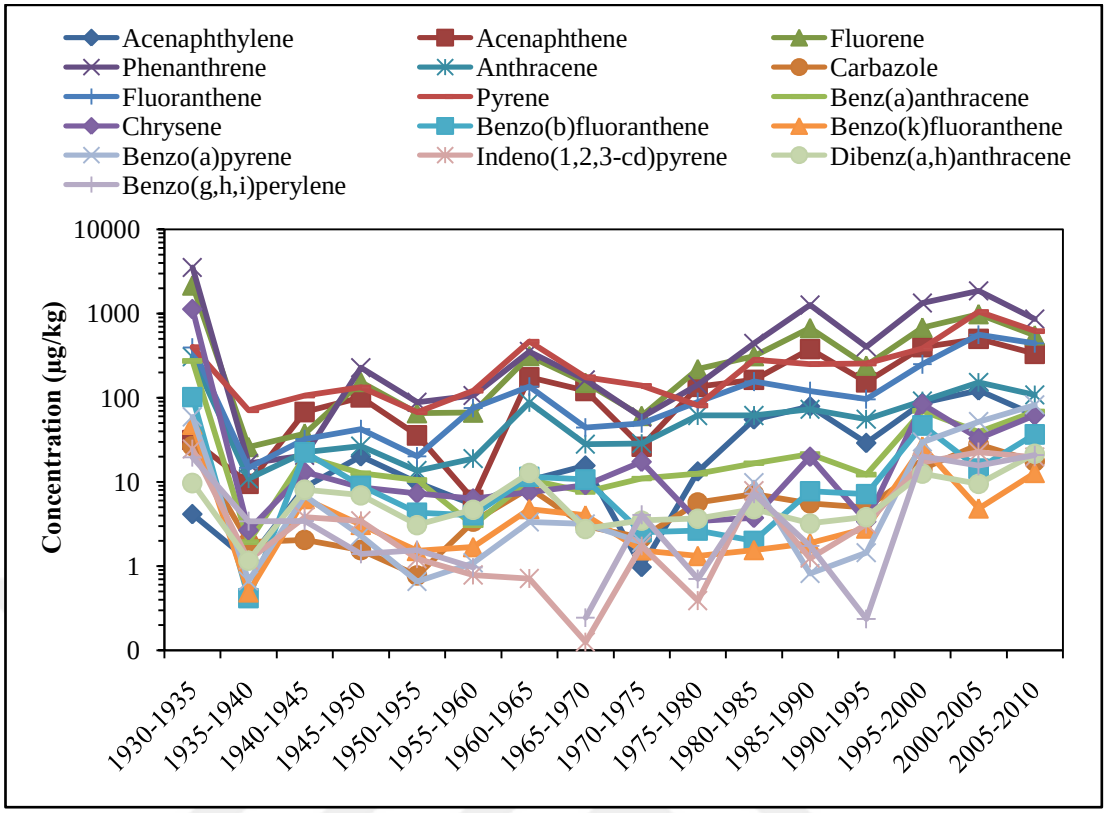


Figure 4.46 Historical variations of PAH congeners in Sampling Site-1 (industrial site) in Iskenderun

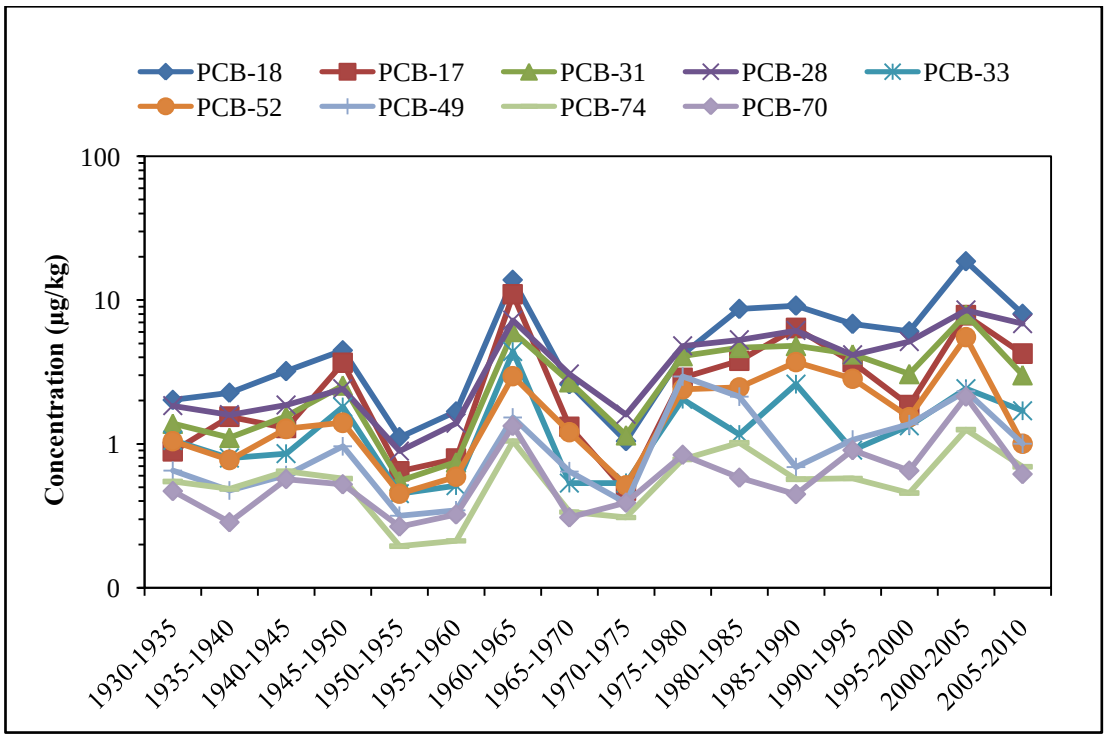


Figure 4.47 Historical variations of PCB congeners in Sampling Site-1 (industrial site) in Iskenderun

4.6 Results of Modeling Ambient Air POP Concentrations

Modeled and observed average concentrations of individual POP compounds are given in Tables 4.5 - 4.6. The modeled/observed ratios of individual POP compounds are close to 1.0 for several compounds and especially low molecular compounds are substantially overestimated by the model up to a factor of 6.67 in Iskenderun. In addition, these ratios higher than 1.0 for several compounds that are overestimated by the model up to a factor of 9.04 in Aliaga (Tables 4.5 - 4.6). The model was estimated the ambient air PAH concentrations within factors of 0.23 - 3.07 and 0.08 - 6.88 in Iskenderun and Aliaga, respectively. PCB concentrations were estimated by the model within factors of 1.02 – 6.67 and 1.52 – 9.04 in Iskenderun and Aliaga, respectively. However, the modeled/observed ratios of total PAH and PCB concentrations are 1.17, 3.36 and 1.23, 4.78 in Iskenderun and Aliaga, respectively. Although these ratios were obtained from two different regions, they were very close to each other.

Table 4.5 Modeled and observed average concentrations of individual PAH compounds (ng/m^3)

PAH	ISKENDERUN			ALIAGA		
	Modeled	Observed	(M/O)[a]	Modeled	Observed	(M/O)[a]
Acenaphthylene	8.81	2.86	3.07	6.76	5.10	1.32
Acenaphthene	4.01	2.32	1.73	14.17	2.06	6.88
Fluorene	12.92	20.39	0.63	13.59	15.03	0.90
Phenanthrene	114	71.03	1.61	90.81	53.97	1.68
Anthracene	7.18	4.75	1.51	2.96	2.71	1.09
Carbazole	1.14	2.47	0.46	0.58	0.85	0.67
Fluoranthene	17.77	26.25	0.68	11.14	20.50	0.54
Pyrene	9.48	15.25	0.62	7.19	13.64	0.53
Benz(a)anthracene	0.86	1.43	0.61	0.37	0.67	0.55
Chrysene	1.72	3.03	0.57	1.13	1.85	0.61
Benzo(b)fluoranthene	1.19	1.29	0.92	0.73	0.56	1.30
Benzo(k)fluoranthene	0.94	1.18	0.80	0.42	5.37	0.08
Benzo(a)pyrene	0.87	0.73	1.18	0.51	0.23	2.22
Indeno(1.2.3-cd)pyrene	0.78	0.92	0.85	0.28	0.29	0.98
Dibenz(a.h)anthracene	0.18	0.79	0.23	0.11	0.08	1.33
Benzo(g.h.i)perylene	0.75	1.21	0.62	0.41	0.34	1.21
Total	**183**	**156**	**1.17**	**151**	**123**	**1.23**

a: Modeled / Observed

Table 4.6 Modeled and observed average concentrations of individual PCB compounds (ng/m^3)

PCB	ISKENDERUN			ALIAGA		
	Modeled	**Observed**	**(M/O)[a]**	**Modeled**	**Observed**	**(M/O)[a]**
PCB-18	0.956	0.241	3.963	1.678	0.335	5.013
PCB-17	0.329	0.080	4.117	0.655	0.123	5.341
PCB-31	0.681	0.163	4.186	1.292	0.216	5.975
PCB-28	1.014	0.189	5.372	2.337	0.281	8.329
PCB-33	0.981	0.147	6.671	1.348	0.207	6.513
PCB-52	0.272	0.120	2.271	0.490	0.144	3.402
PCB-49	0.232	0.073	3.192	0.400	0.100	4.009
PCB-44	0.206	0.096	2.150	0.314	0.116	2.704
PCB-74	0.090	0.040	2.218	0.198	0.052	3.834
PCB-70	0.209	0.080	2.613	0.389	0.093	4.165
PCB-95	0.076	0.052	1.443	0.164	0.060	2.719
PCB-101	0.125	0.074	1.687	0.250	0.089	2.816
PCB-99	0.053	0.024	2.247	0.081	0.027	3.000
PCB-87	0.034	0.034	1.023	0.076	0.043	1.774
PCB-110	0.072	0.051	1.400	0.172	0.064	2.666
PCB-82	n.d.	0.012	n.d.	0.021	0.014	1.516
PCB-151	0.015	0.010	1.482	0.032	0.013	2.449
PCB-149	0.045	0.029	1.540	0.114	0.042	2.737
PCB-118	0.070	0.036	1.907	0.148	0.049	3.018
PCB-153	0.050	0.026	1.872	0.154	0.043	3.560
PCB-132	0.021	0.012	1.688	0.053	0.017	3.043
PCB-105	0.028	0.020	1.387	0.061	0.030	2.055
PCB-138	0.050	0.030	1.643	0.149	0.047	3.177
PCB-158	0.009	0.004	2.062	0.021	0.006	3.389
PCB-187	0.017	0.007	2.542	0.042	0.014	3.008
PCB-183	0.018	0.006	2.933	0.025	0.008	3.205
PCB-128	0.025	0.009	2.695	0.045	0.015	2.937
PCB-177	n.d.	0.005	n.d.	0.033	0.008	4.053
PCB-171	n.d.	0.005	n.d.	0.016	0.005	3.269
PCB-156	0.014	0.005	2.884	0.029	0.007	4.043
PCB-180	0.020	0.008	2.556	0.115	0.020	5.751
PCB-191	n.d.	n.d.	n.d.	0.014	0.002	9.042
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	n.d.	0.007	n.d.	0.072	0.012	6.269
PCB-199	n.d.	0.004	n.d.	0.031	0.005	5.967
PCB-208	n.d.	n.d.	n.d.	0.004	0.002	1.977
PCB-195	n.d.	n.d.	n.d.	0.023	0.004	6.387
PCB-194	n.d.	n.d.	n.d.	0.029	0.005	6.209
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	0.009	0.002	4.214
PCB-209	n.d.	n.d.	n.d.	0.004	0.002	2.643
Total	**5.710**	**1.699**	**3.360**	**11.087**	**2.320**	**4.779**

a: Modeled / Observed
n.d.: Not detected

The octanol-air partitioning coefficient (K_{OA}), and it is temperature dependence are important descriptors for the partitioning of hydrophobic chemicals between air and environmental lipids (Simonich & Hites, 1995). Statistically significant correlations were found between bark-air partitioning coefficients (log K_{BA}) and octanol-air partitioning coefficients (log K_{OA}) with good correlation coefficients (r^2) of 0.72, 0.86 and 0.85, 0.95 ($p < 0.01$) for PAHs and PCBs in Iskenderun and Aliaga, respectively. It is suggested that the octanol is a good representative surrogate for bark lipids (Figures 4.48 - 4.49).

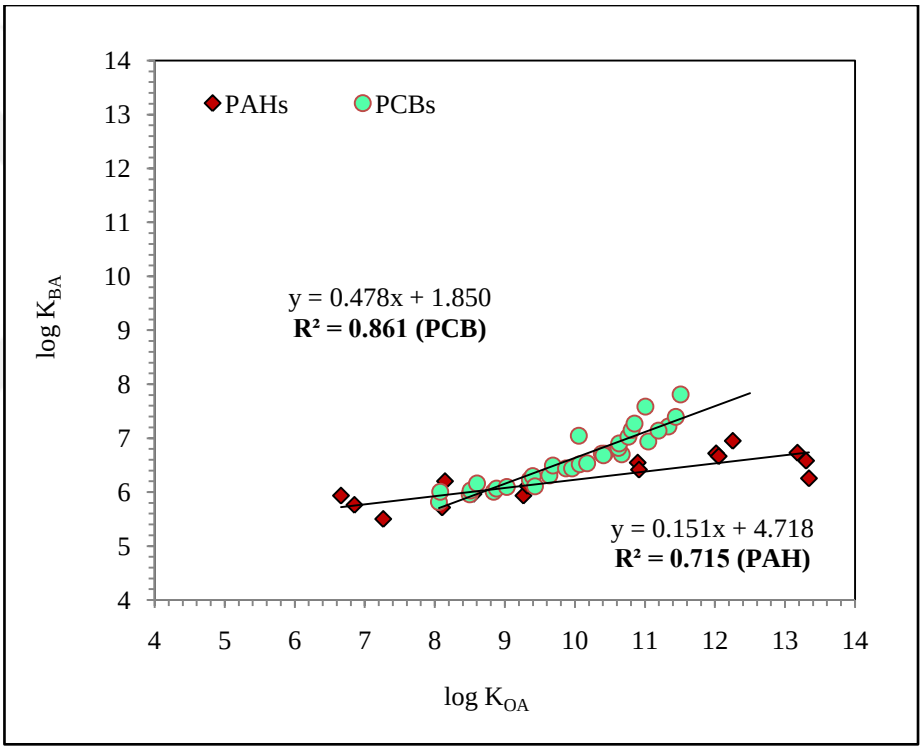


Figure 4.48 Relationships between bark-air partitioning coefficients (K_{BA}) and octanol-air partition coefficients (K_{OA}) in Iskenderun

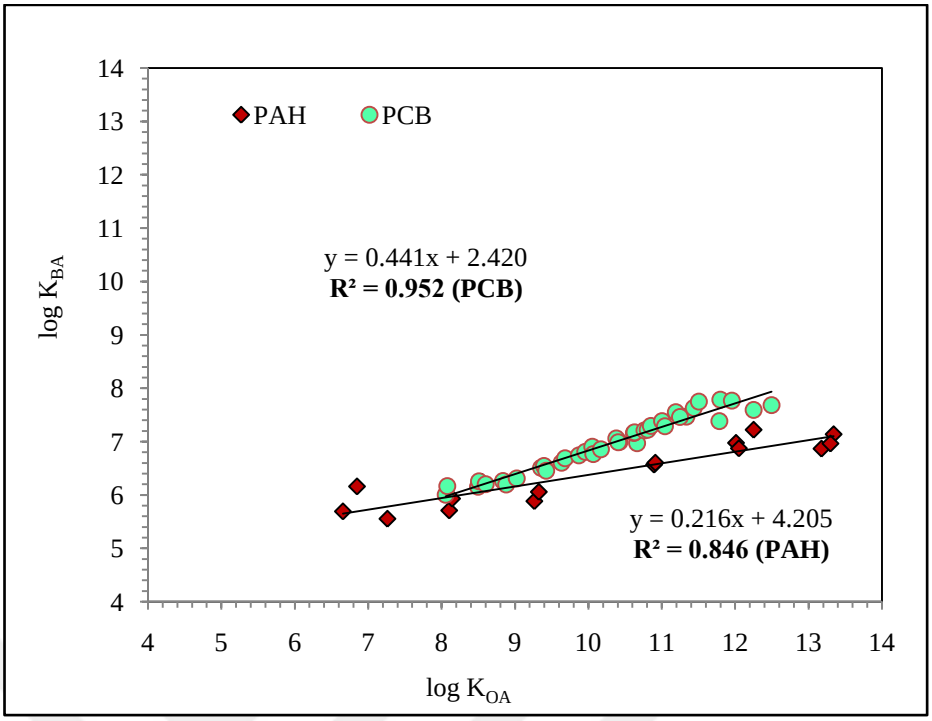


Figure 4.49 Relationships between bark-air partitioning coefficients (K_{BA}) and octanol-air partition coefficients (K_{OA}) in Aliaga

The relationship between modeled and observed average ambient air concentrations of individual POP compounds are compared in Figures 4.50 - 4.53. Statistically significant correlations were found between modeled and observed air POP concentrations with excellent correlation coefficients (r^2) of 0.92, 0.87 and 0.89, 0.90 ($p < 0.01$) for PAHs and PCBs in Iskenderun and Aliaga, respectively. The results indicated that the bark-air partitioning model could be used to estimate the ambient air concentrations of POPs from the bark measurements without any direct air-sampling event. In addition, it is suggested that bark could be used as a passive sampler to estimate the atmospheric POP levels in a region. Significant correlations between air and bark POP concentrations were also reported in recent studies (Salamova & Hites, 2010; Peverly et al., 2015).

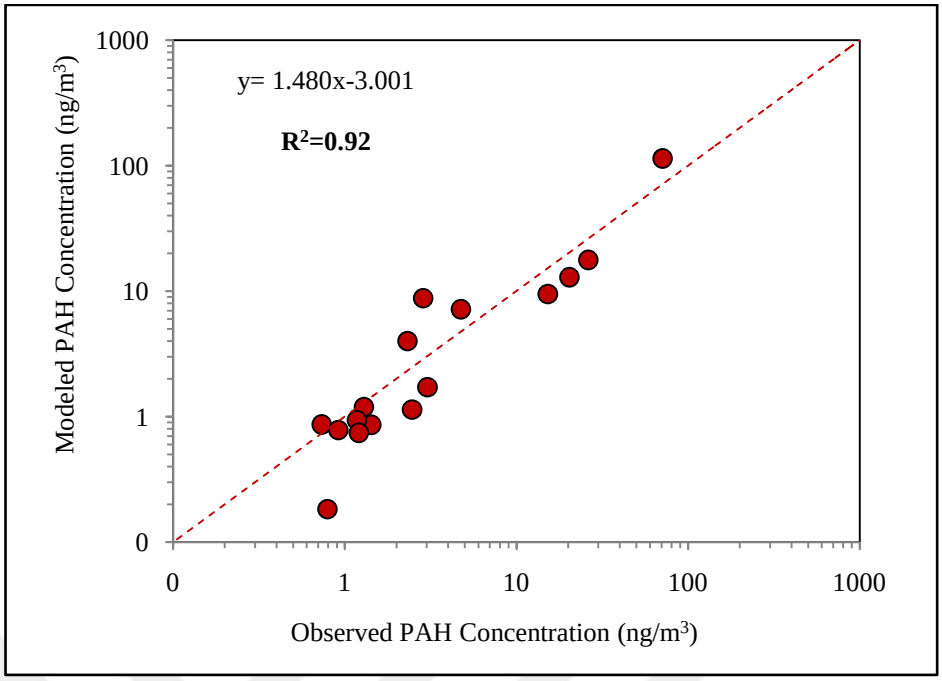


Figure 4.50 Relationships between observed and modeled average PAH concentrations in Iskenderun (Dashed diagonal line shows the 1:1 relationship)

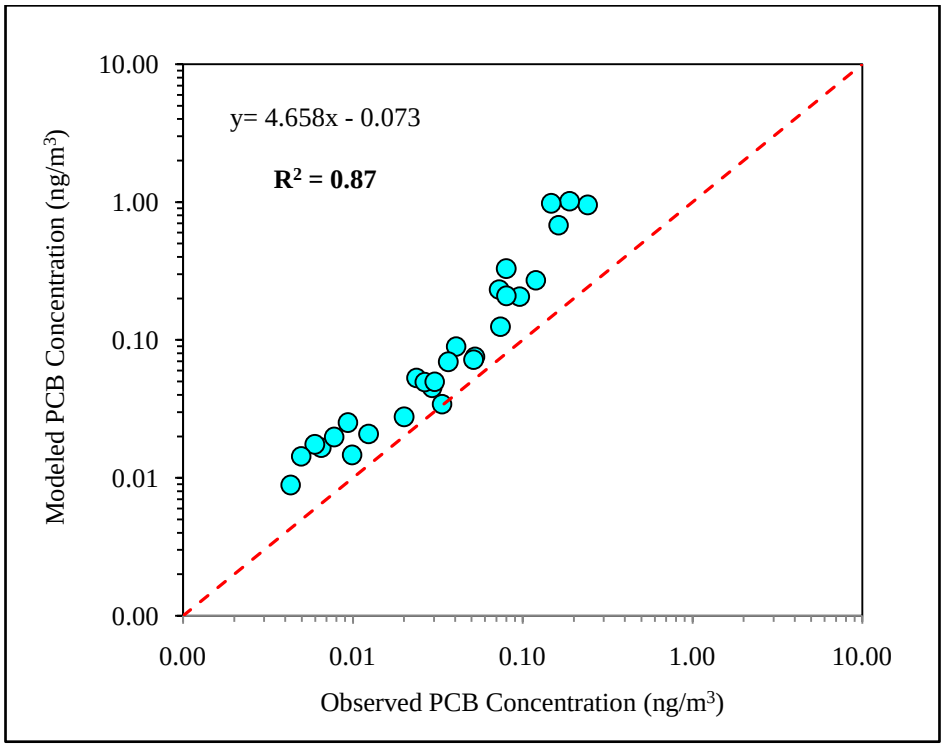


Figure 4.51 Relationships between observed and modeled average PCB concentrations in Iskenderun (Dashed diagonal line shows the 1:1 relationship)

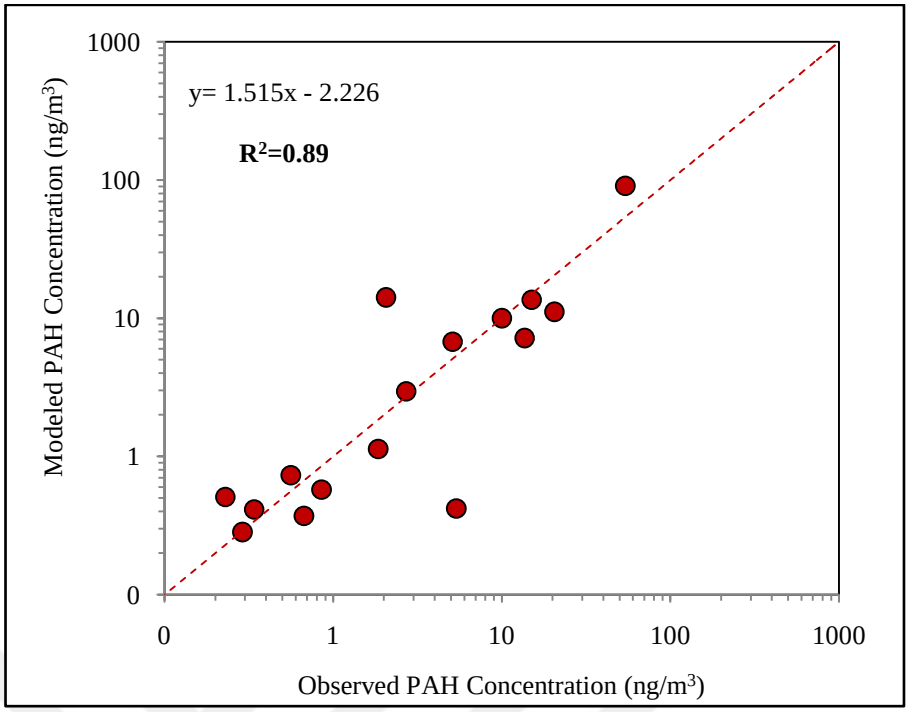


Figure 4.52 Relationships between observed and modeled average PAH concentrations in Aliaga (Dashed diagonal line shows the 1:1 relationship)

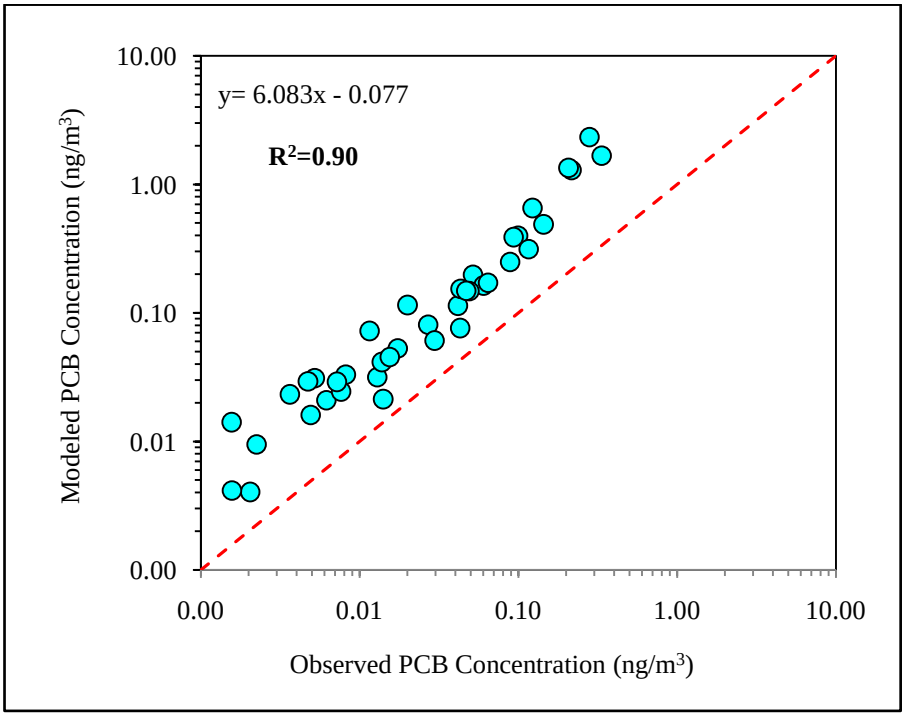


Figure 4.53 Relationships between observed and modeled average PCB concentrations in Aliaga (Dashed diagonal line shows the 1:1 relationship)

4.7 Inventory of POPs

4.7.1 Biomass Amount of Tree Components

Vegetation is an important compartment that scavenges and accumulates the atmospheric POPs and transfers them to the soil via falling litter. Therefore, vegetation is a globally significant reservoir for POPs (Su et al., 2007; Bartrons et al., 2016). POP amounts accumulated in soil, litter, and different tree components were inventoried to assess the relative importance of different POP accumulating mediums. POP amounts accumulated per unit area (mg/ha) were calculated using the measured concentrations in tree components (mg/kg), litter and soil, and the amounts of these components per unit area (kg/ha). Properties (diameter, height, number, and volume) of trees and biomass amount of tree components in two sampling regions are presented in Tables 4.7 - 4.8.

Aboveground mass of trees in sampling regions were varied 1.2 - 433 tons/ha to 16.7 - 642 tons/ha in Iskenderun and Aliaga, respectively. Biomass amount of per unit area in Iskenderun was lower because of the trees were single in residential areas. Therefore, it was accepted that there were 10 trees per hectare in Iskenderun (Table 4.7). There are a few studies on plant biomass amount of per unit area in Turkey (Balat, 2005; Gokcol et al., 2009; Comez, 2011). Aboveground mass of *Pinus sylvestris* was changed between 26 tons/ha and 479 tons/ha in one of the recent studies (Comez, 2011).

Table 4.7 Tree properties and biomass amount of tree components in Iskenderun

Sampling Site	Avg. Diameter (cm)	Avg. Height (m)	Tree number (number/ha)	Tree Volume (m^3/ha)	Needle (t/ha)	Branch (t/ha)	Bark (t/ha)	Stem (t/ha)	Above ground mass (t/ha)
1	24.0	13.2	733	226	10.2	24.5	16.9	91.4	142.9
2	15.4	7.8	325	21	0.9	2.2	2.0	7.9	13.1
3	22.8	11.0	900	188	8.4	20.3	14.2	75.5	118.4
4	22.5	11.7	10	2	0.1	0.2	0.2	0.7	1.2
5	26.0	10.0	10	2	0.1	0.2	0.2	0.9	1.5
6	51.9	11.9	10	10	0.5	1.1	0.5	4.4	6.5
7	17.0	12.1	1100	137	6.2	14.8	13.5	51.9	86.3
8	19.1	11.0	700	102	4.6	11.0	9.1	39.5	64.2
9	18.7	8.7	1300	161	23.6	15.4	13.0	88.9	140.9
10	46.2	13.6	10	10	0.4	1.0	0.5	4.0	6.0
11	23.0	9.2	1600	311	14.0	33.6	25.7	122.9	196.1
12	38.5	17.2	10	8	0.3	0.8	0.5	3.2	4.9
13	25.8	10.3	10	3	0.4	0.3	0.2	1.6	2.5
14	43.4	14.1	10	8	0.4	0.9	0.5	3.5	5.3
15	17.9	13.4	1000	133	6.0	14.3	13.6	49.9	83.8
16	20.0	10.8	800	108	4.9	11.7	10.6	41.2	68.5
17	25.9	12.9	600	163	7.3	17.6	14.1	63.8	102.8
18	48.7	17.4	10	13	0.6	1.4	0.7	5.4	7.9
19	41.0	16.9	10	9	0.4	1.0	0.7	3.5	5.6
20	34.1	8.9	10	3	0.2	0.4	0.2	1.3	2.1
21	21.9	6.3	600	65	2.9	7.0	6.0	25.1	41.0
22	22.38	9.07	250	37	1.6	4.0	3.5	14.0	23.1
23	21.4	7.3	625	82	14.8	10.5	7.0	58.7	90.9
24	29.8	8.1	300	84	14.7	15.1	5.8	68.1	103.7
25	40.2	11.8	300	210	9.5	22.7	12.2	88.2	132.5
26	74.1	16.1	100	362	39.0	102.5	11.1	280.1	432.6
27	35.0	11.8	300	136	6.1	14.6	9.9	54.9	85.6

Table 4.8 Tree properties and biomass amount of tree components in Aliaga

Sampling Site	Avg. Diameter (cm)	Avg. Height (m)	Tree number (number/ha)	Tree Volume (m^3/ha)	Needle (t/ha)	Branch (t/ha)	Bark (t/ha)	Stem (t/ha)	Above ground mass (t/ha)
1	25.3	7.8	300	66	11.0	10.7	4.7	49.7	76.1
2	30.9	10.3	275	107	14.8	16.3	6.4	70.2	107.7
3	23.8	5.9	150	22	4.7	4.1	1.8	20.4	31.0
4	28.9	7.4	500	123	23.5	24.5	9.0	109.8	166.7
5-1[a]	35.0	10.4	300	151	21.2	26.4	8.5	106.6	162.7
5-2[b]	20.7	9.8	600	81	3.7	8.8	7.8	31.1	51.4
6	21.6	10.0	700	107	4.8	11.5	12.5	38.5	67.4
7	54.8	16.1	200	433	43.2	97.5	14.6	284.6	439.9
8	43.9	13.4	200	203	23.8	37.8	9.0	133.1	203.8
9	18.2	6.2	375	31	6.2	3.6	3.0	22.7	35.5
10-1[a]	31.5	7.9	500	165	28.7	33.5	10.8	140.8	213.8
10-2[b]	18.7	7.9	600	64	2.9	6.9	6.0	24.4	40.2
11	18.1	8.3	525	48	2.1	5.1	4.8	18.0	30.0
12	11.7	6.2	900	27	1.2	2.9	3.0	9.7	16.7
13	42.4	16.8	200	209	9.4	22.6	12.0	87.9	131.9
14	21.5	10.0	667	101	4.5	10.9	9.6	38.6	63.6
15	29.5	8.6	500	158	7.1	17.0	11.2	64.2	99.5
16	33.3	13.4	175	85	3.8	9.2	6.1	34.4	53.5
17	22.0	7.0	625	87	15.9	12.0	7.2	64.7	99.9
18	27.9	6.8	350	75	15.3	15.6	5.8	71.0	107.7
19	23.1	9.1	375	102	4.6	11.0	7.3	41.4	64.3
20	27.7	15.1	600	219	9.8	23.6	18.0	86.6	138.1
21	30.6	11.0	800	326	42.2	45.9	18.9	198.3	305.3
22	38.3	10.6	600	551	61.3	121.9	23.3	385.3	591.8
23	50.1	18.8	175	279	12.6	30.1	13.7	119.6	176.0
24	39.0	13.9	500	795	65.3	136.4	25.2	414.6	641.5
25	47.6	20.2	200	323	14.5	34.8	16.2	138.1	203.6
26	46.3	18.1	125	224	17.1	35.5	6.7	107.8	167.1
27	59.7	21.4	300	693	31.2	74.9	30.8	300.7	437.5

a: Stone Pine
b: Red Pine

Properties (diameter, height, number, and volume) of trees and biomass amount of tree components in industrial and background sites of two sampling regions are given in Table 4.9. The average biomass amounts of tree components were low in industrial areas of Aliaga and Iskenderun. This situation is consisted due to the number of trees in the city center was less and the forest was occurred mostly young plantations in the industrial areas. Biomass amount of stem samples had the highest values in all tree components. The biomass amounts of stem samples were followed by branch, needles and bark samples (Table 4.9).

Table 4.9 Tree properties and biomass amount of tree components in industrial and background sites of two sampling regions

Tree Properties	**Industrial**		**Background**	
	Mean	**SD**	**Mean**	**SD**
ISKENDERUN				
Avg. Diameter (cm)	29.1	11.7	35.0	18.7
Avg. Height (m)	12.1	2.8	10.0	3.4
Tree number (number/ha)	458	524	354	191
Tree Volume (m^3/ha)	81	93	139	113
Needle (t/ha)	4.5	6.1	12.7	12.7
Branch (t/ha)	8.6	10.0	25.2	34.6
Bark (t/ha)	6.8	7.8	7.9	3.2
Stem (t/ha)	33.1	38.3	84.1	90.0
Aboveground Mass (t/ha)	53.0	61.0	130	139
ALIAGA				
Avg. Diameter (cm)	27.9	9.7	46.8	7.9
Avg. Height (m)	9.8	3.2	17.2	4.1
Tree number (number/ha)	453	213	317	192
Tree Volume (m^3/ha)	130	98.1	478	237
Needle (t/ha)	13.2	12.1	33.7	23.9
Branch (t/ha)	19.9	20.4	72.3	47.1
Bark (t/ha)	8.6	4.5	19.3	8.7
Stem (t/ha)	75.9	65.2	244	140
Aboveground Mass (t/ha)	118	99.6	370	216

4.7.2 Total Pollutant Amounts Stored in Unit Area

Total accumulated PAH and PCB levels of litter, soil and tree components per unit area are presented in Tables 4.10 - 4.11. Although the higher POP concentrations were measured in industrial areas, the total POP levels of stem samples in background sites were higher than the industrial sites. It was consisted due to there was a higher amount of stem per unit area in the background sites. Total amount of accumulated PCBs per unit area was less than the total amount of accumulated PAHs per unit area (Tables 4.10 - 4.11).

Table 4.10 Total accumulated PAH amounts per unit area in two sampling regions (mg/ha)

Σ_{16}PAH (mg/ha)	**Industrial**		**Background**	
	Mean	**SD**	**Mean**	**SD**
ISKENDERUN				
Litter	23876	40229	1746	1960
Soil	1230887	3334912	59892	19849
1-Year needle	2363	4276	904	884
2-Year needle	4781	7399	1458	1049
Branch	1459	1828	1416	778
Bark	2266	4183	436	314
Stem	16456	35567	44170	33364
Aboveground Mass	18539	27033	56196	31753
Tree Components+Litter+Soil	1280894	3329148	111165	47214
ALIAGA				
Litter	34625	39347	2767	1765
Soil	98073	112969	18812	5829
1-Year needle	6041	6039	5922	4573
2-Year needle	10017	8183	9058	7490
Branch	4737	8052	3249	1974
Bark	1977	2655	1778	1296
Stem	192060	330826	429217	327838
Aboveground Mass	214830	337995	449223	336679
Tree Components+Litter+Soil	347528	448071	470801	337839

Table 4.11 Total accumulated PCB amounts per unit area in two sampling regions (mg/ha)

Σ_{41}PCBs (mg/ha)	Industrial		Background	
	Mean	SD	Mean	SD
ISKENDERUN				
Litter	687	668	47	75
Soil	8354	21560	324	144
1-Year needle	55	118	12	7
2-Year needle	132	251	20	16
Branch	31	41	23	16
Bark	87	198	11	8
Stem	210	337	277	240
Aboveground Mass	514	822	343	251
Tree Components+Litter+Soil	9521	21666	720	307
ALIAGA				
Litter	3442	4442	86	75
Soil	12934	19381	422	207
1-Year needle	51	63	49	79
2-Year needle	220	279	39	64
Branch	84	89	78	57
Bark	192	234	28	15
Stem	1192	2381	1558	1048
Aboveground Mass	1740	2771	1752	1109
Tree Components+Litter+Soil	18115	22472	2260	1167

Generally, the highest POP quantities were accumulated in the stem followed by needles. Overall, the highest POP quantities were accumulated in soil followed by trees and litter in Iskenderun while the highest POP amounts were stored in soil for PCBs and in trees for PAHs in Aliaga region. It is showing that vegetation is also an important reservoir accumulating the POPs in addition to soil. These results have significant implications regarding the partitioning of POP compounds in the environment and the potential of vegetation to clean the atmosphere.

The distributions of total accumulated PAH amount per unit area in two sampling regions are shown in Figures 4.54 - 4.61. Considering the tree components in the industrial areas, generally, the highest PAH quantities were accumulated in the stem (60% and 89%) followed by needles (27% and 8%) in Iskenderun and Aliaga, respectively (Figures 4.54 - 4.55). PAH contribution of stem (91% and 96%) was considerably higher in the background sites of Iskenderun and Aliaga, respectively (Figures 4.56 - 4.57).

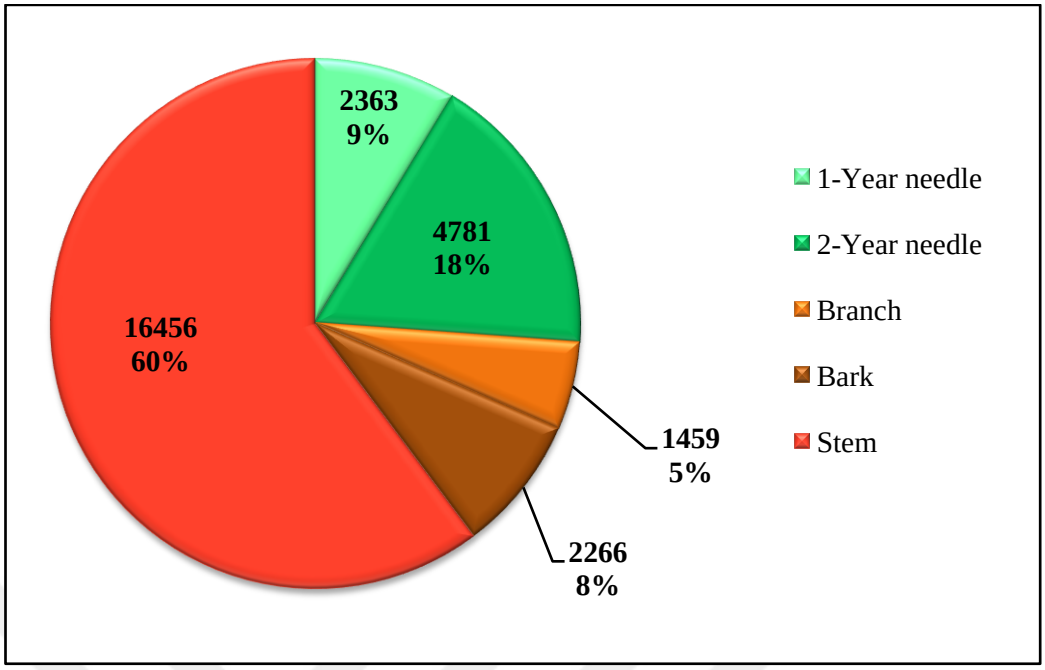


Figure 4.54 Contribution (%) of tree components to total accumulated PAH amounts per unit area (mg/ha) in industrial sites of Iskenderun

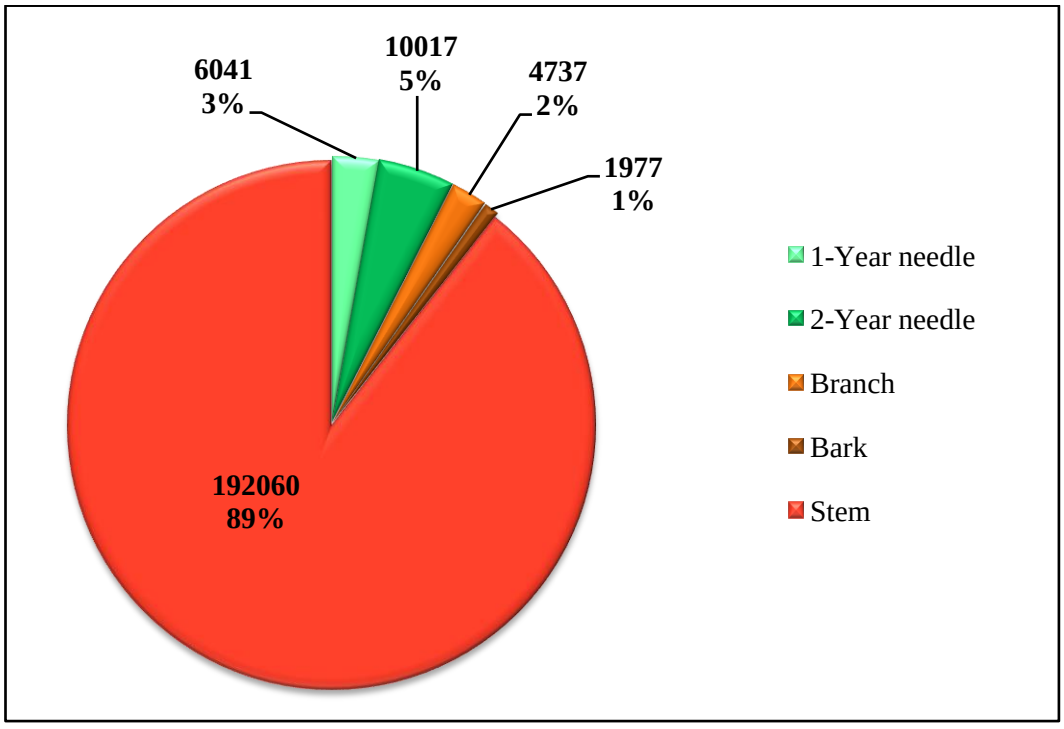


Figure 4.55 Contribution (%) of tree components to total accumulated PAH amounts per unit area (mg/ha) in industrial sites of Aliaga

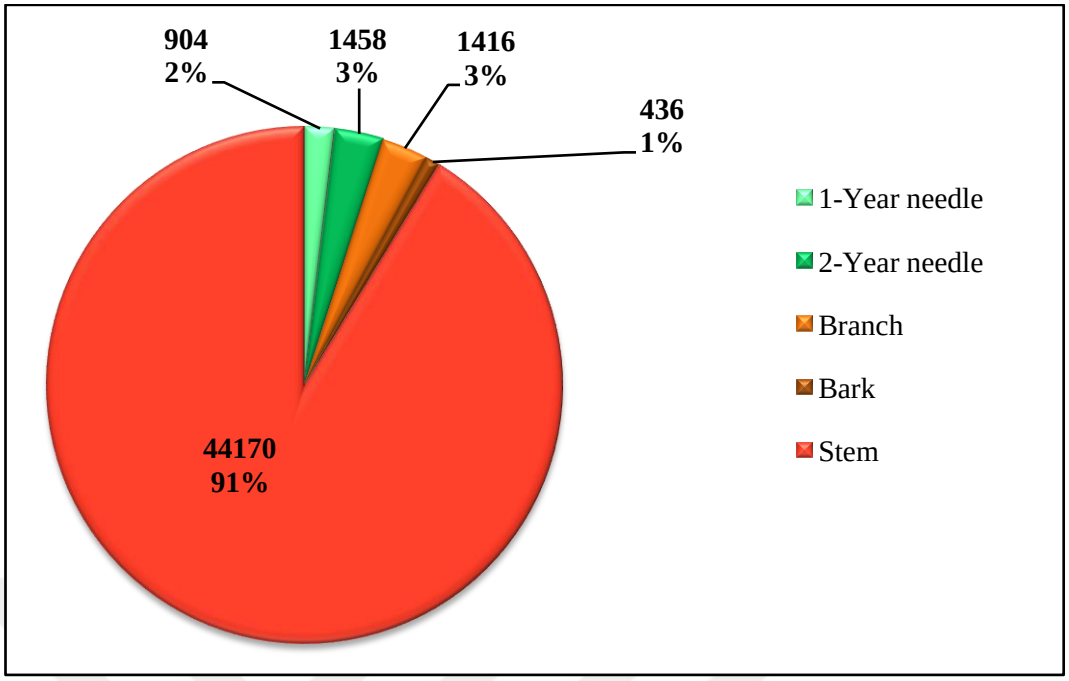


Figure 4.56 Contribution (%) of tree components to total accumulated PAH amounts per unit area (mg/ha) in background sites of Iskenderun

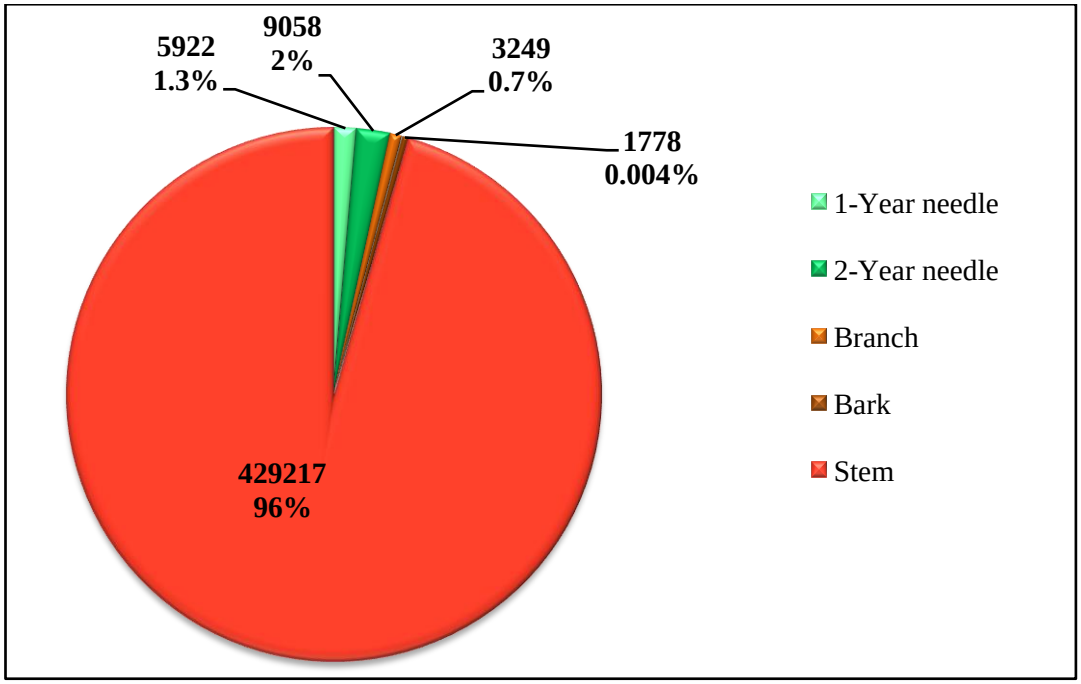


Figure 4.57 Contribution (%) of tree components to total accumulated PAH amounts per unit area (mg/ha) in background sites of Aliaga

Overall, the considerably higher PAH levels were observed in soil (97%) in the industrial sites of Iskenderun (Figure 4.58). This situation was occurred due to both PAH concentrations of soil were higher and the mass of tree per unit area was less in this region. Highest PAH quantities were accumulated in trees (62%) followed by soil (28%) in the industrial sites of Aliaga (Figure 4.59). In the background areas, highest PAH levels were observed in soil (51%) followed by trees (48%) in Iskenderun (Figure 4.60) while PAH contribution by trees was considerably higher (95%) in Aliaga (Figure 4.61).

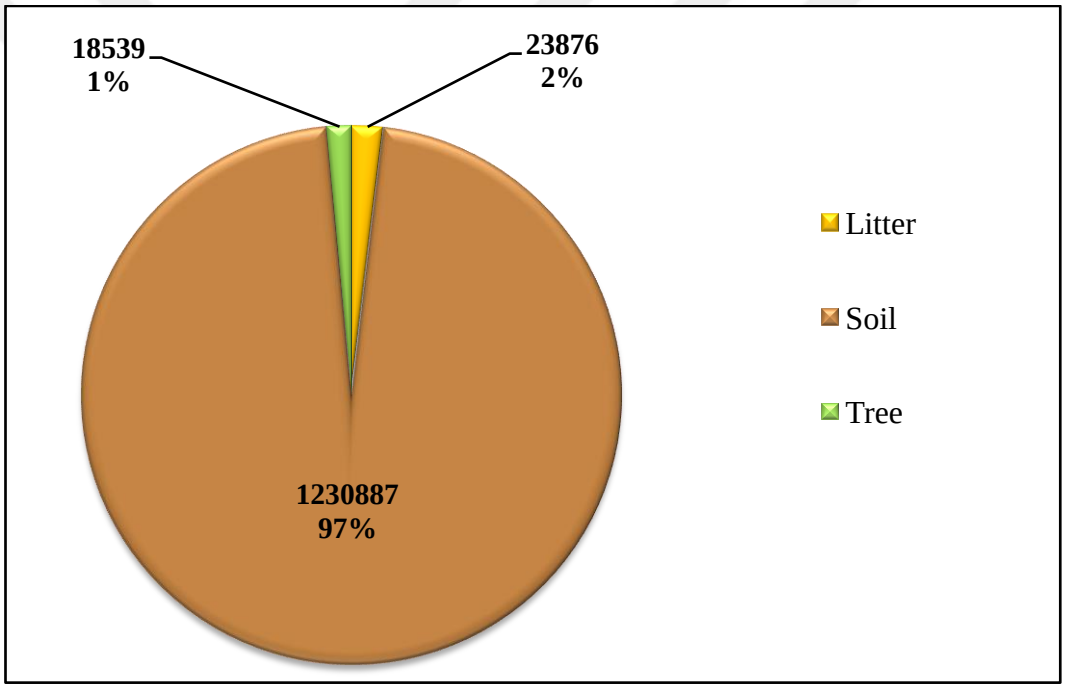


Figure 4.58 Contribution (%) of compartments to total accumulated PAH amounts per unit area (mg/ha) in industrial sites of Iskenderun

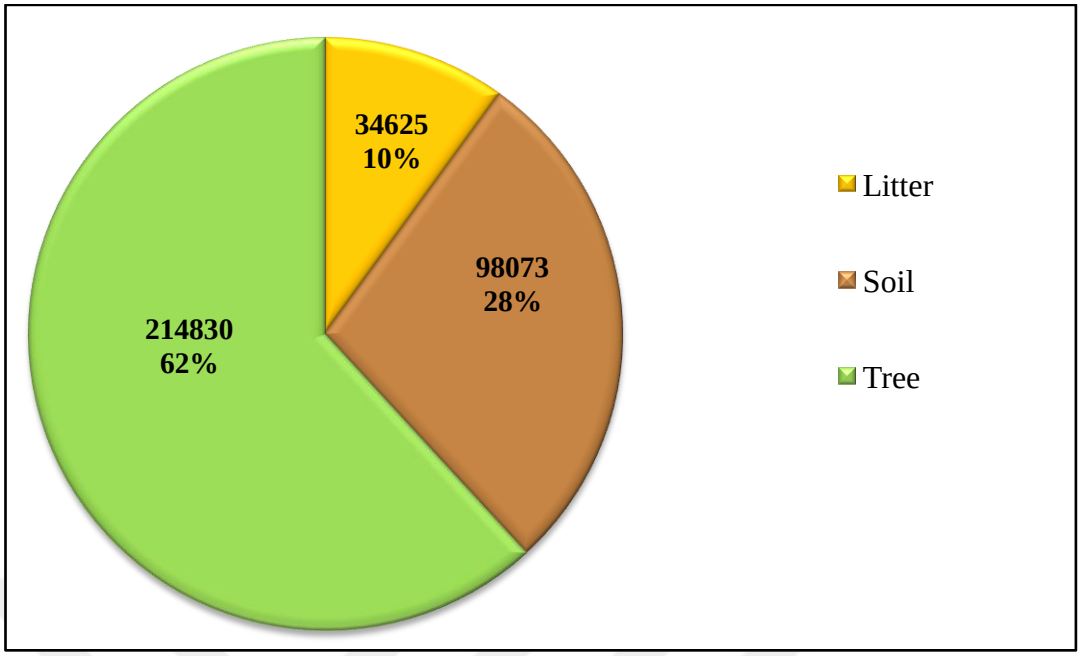


Figure 4.59 Contribution (%) of compartments to total accumulated PAH amounts per unit area (mg/ha) in industrial sites of Aliaga

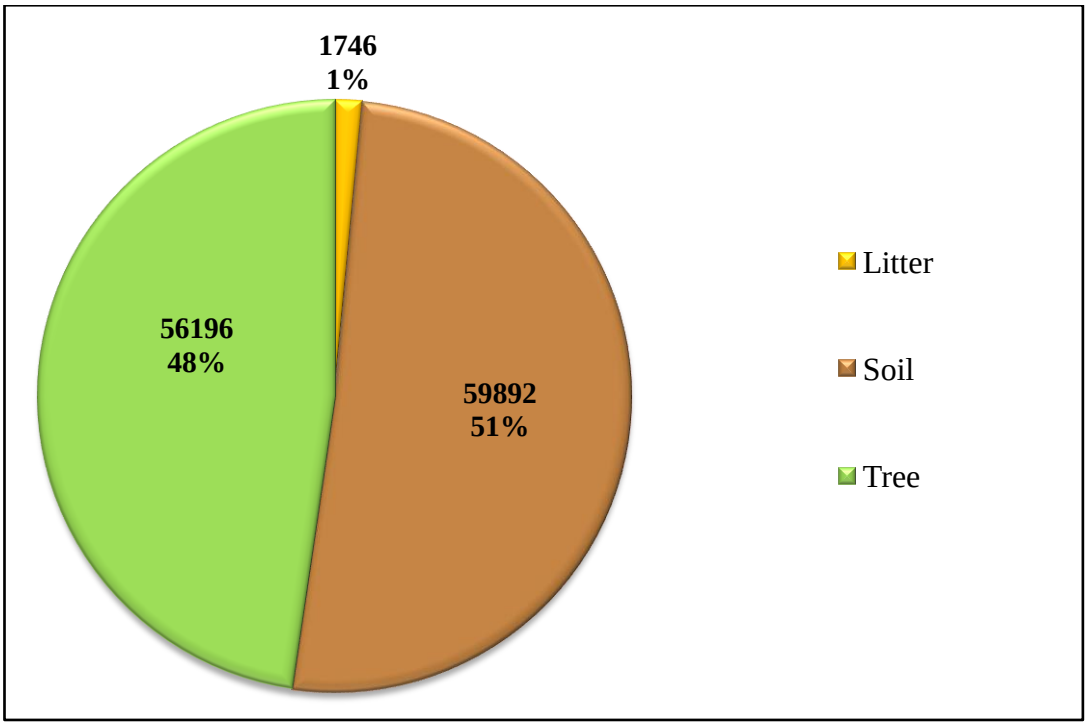


Figure 4.60 Contribution (%) of compartments to total accumulated PAH amounts per unit area (mg/ha) in background sites of Iskenderun

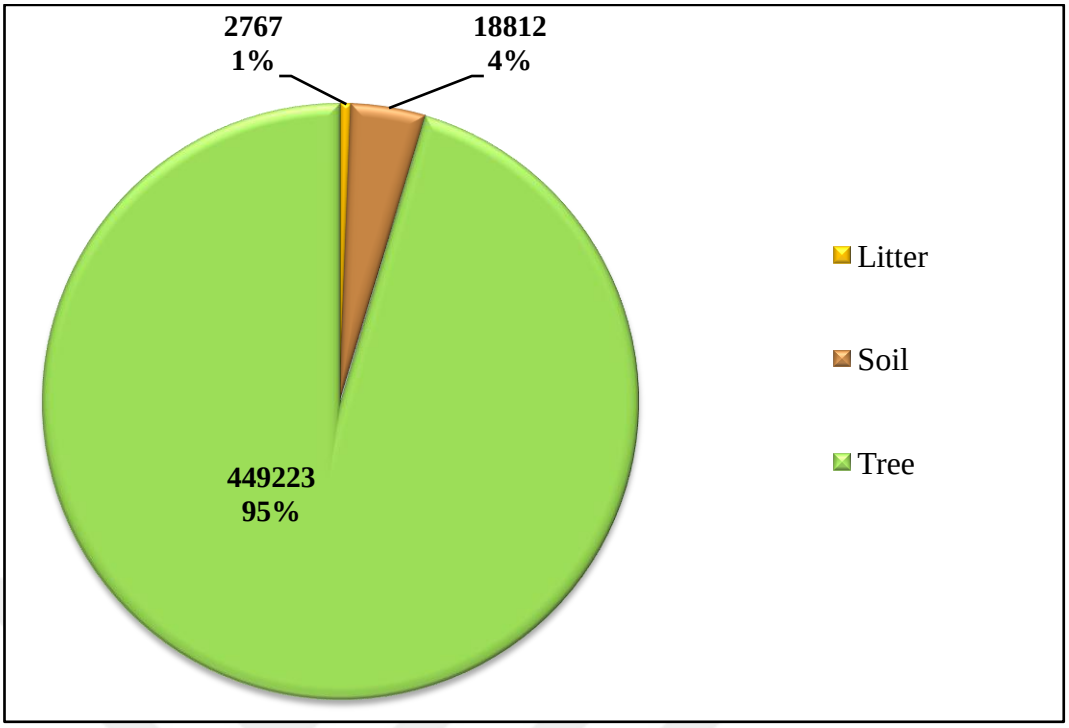


Figure 4.61 Contribution (%) of compartments to total accumulated PAH amounts per unit area (mg/ha) in background sites of Aliaga

The distributions of total accumulated PCB amounts per unit area in two sampling regions are shown in Figures 4.62 - 4.69. Among tree components, generally, the highest PCB amounts were stored in the stem (41% and 68%) followed by needles (36% and 16%) in the industrial areas of Iskenderun and Aliaga, respectively (Figures 4.62 - 4.63). The PCB contribution of stem (80% and 89%) was substantially higher in the background areas of both regions (Figures 4.64 - 4.65).

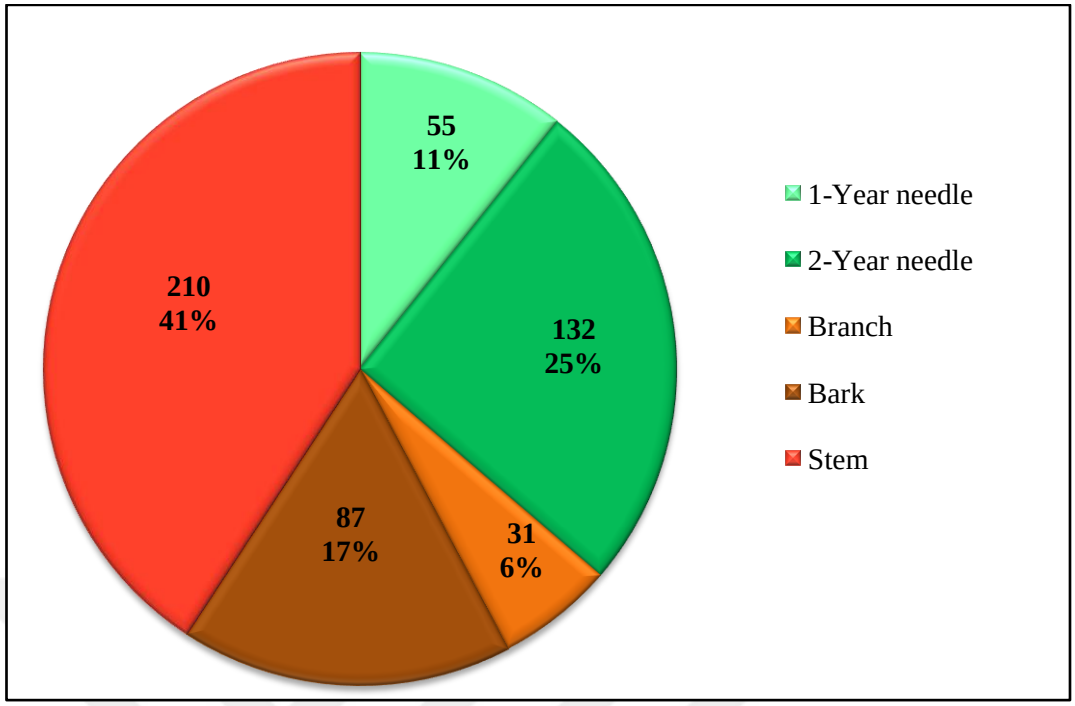


Figure 4.62 Contribution (%) of tree components to total accumulated PCB amounts per unit area (mg/ha) in industrial sites of Iskenderun

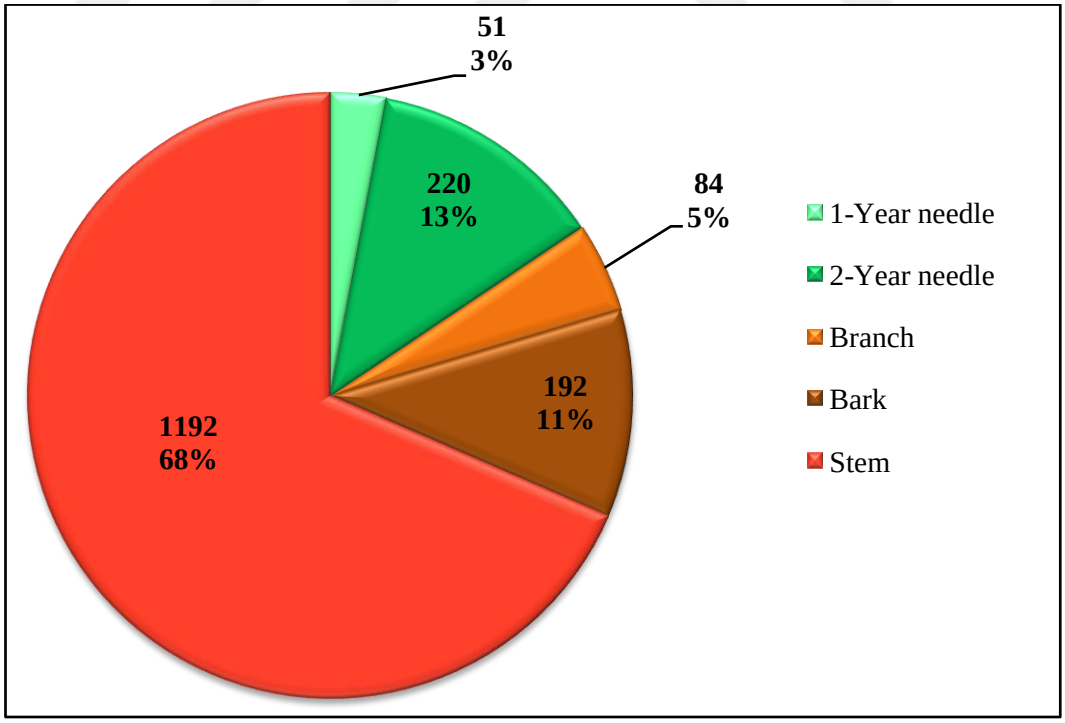


Figure 4.63 Contribution (%) of tree components to total accumulated PCB amounts per unit area (mg/ha) in industrial sites of Aliaga

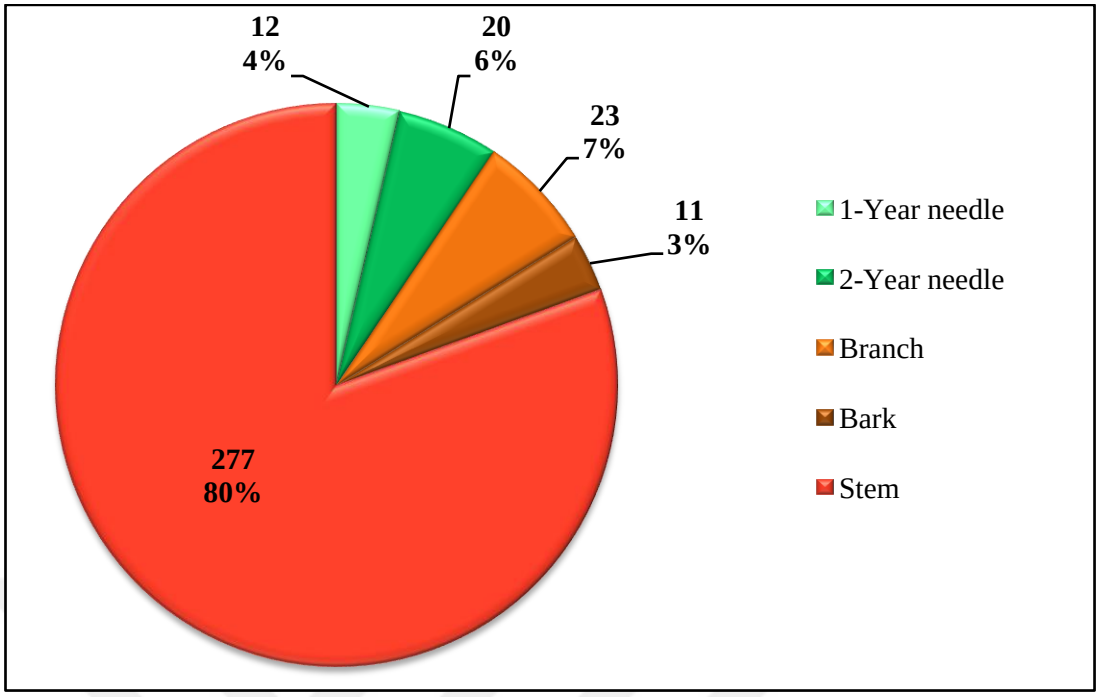


Figure 4.64 Contribution (%) of tree components to total accumulated PCB amounts per unit area (mg/ha) in background sites of Iskenderun

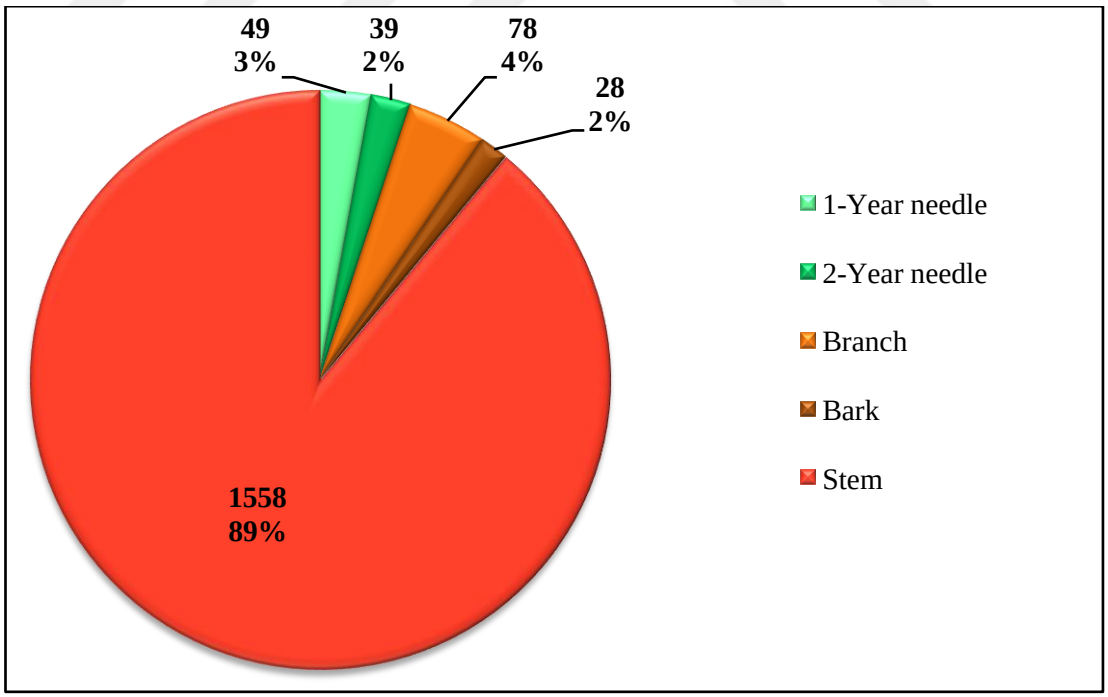


Figure 4.65 Contribution (%) of tree components to total accumulated PCB amounts per unit area (mg/ha) in background sites of Aliaga

For the overall inventory, the highest PCB amounts were stored in soil (88% and 71%) followed by litter (7% and 19%) in the industrial areas of Iskenderun and Aliaga, respectively (Figures 4.66 - 4.67). PCB contribution of trees was substantially higher (48% and 77%) in the background areas of Iskenderun and Aliaga, respectively (Figures 4.68 - 4.69).

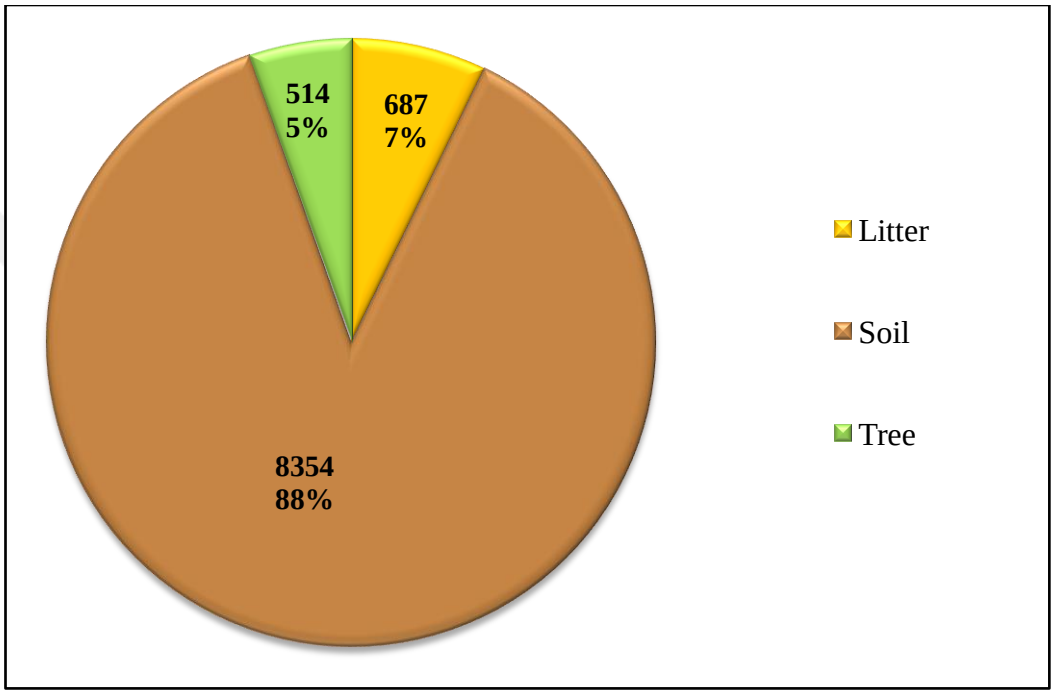


Figure 4.66 Contribution (%) of compartments to total accumulated PCB amounts per unit area (mg/ha) in industrial sites of Iskenderun

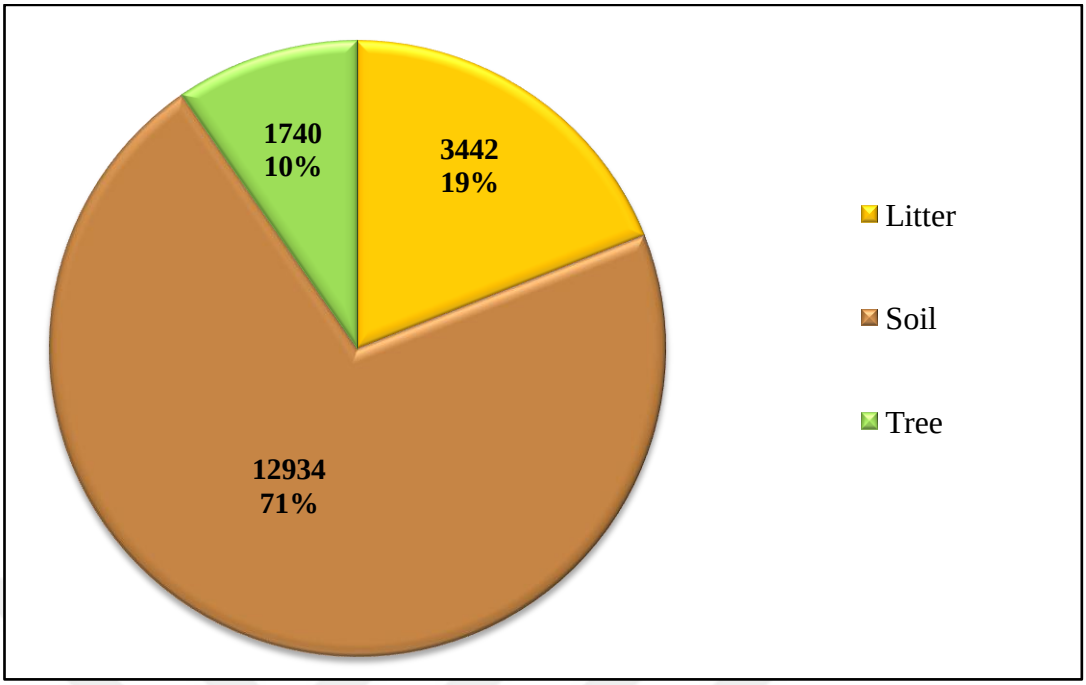


Figure 4.67 Contribution (%) of compartments to total accumulated PCB amounts per unit area (mg/ha) in industrial sites of Aliaga

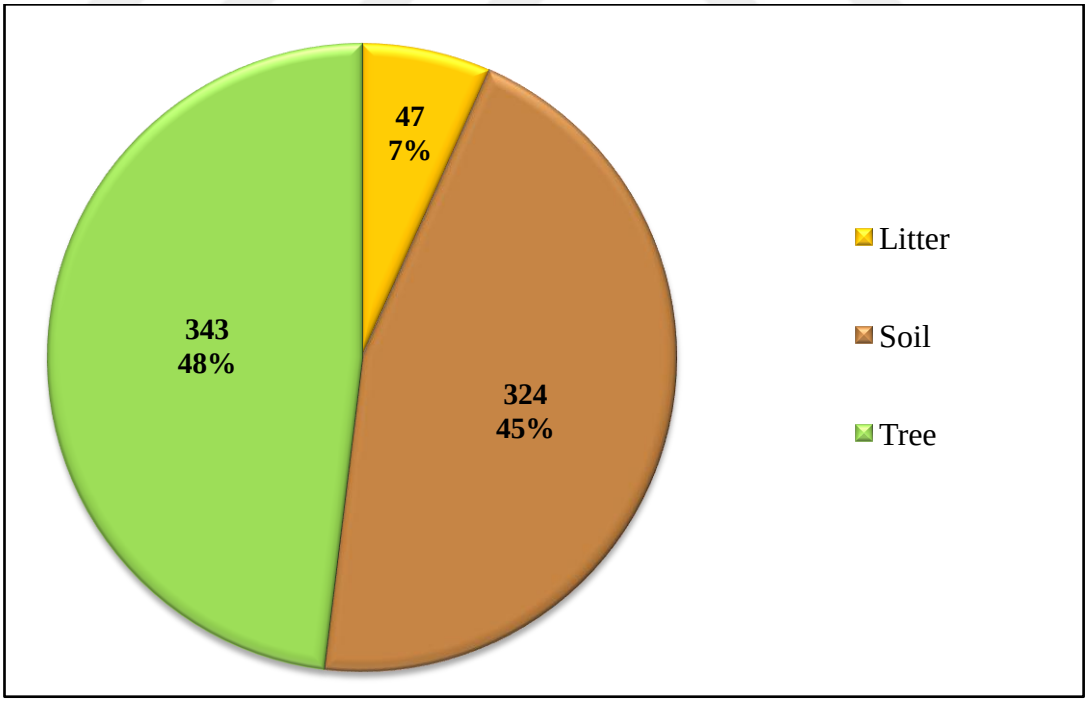


Figure 4.68 Contribution (%) of compartments to total accumulated PCB amounts per unit area (mg/ha) in background sites of Iskenderun

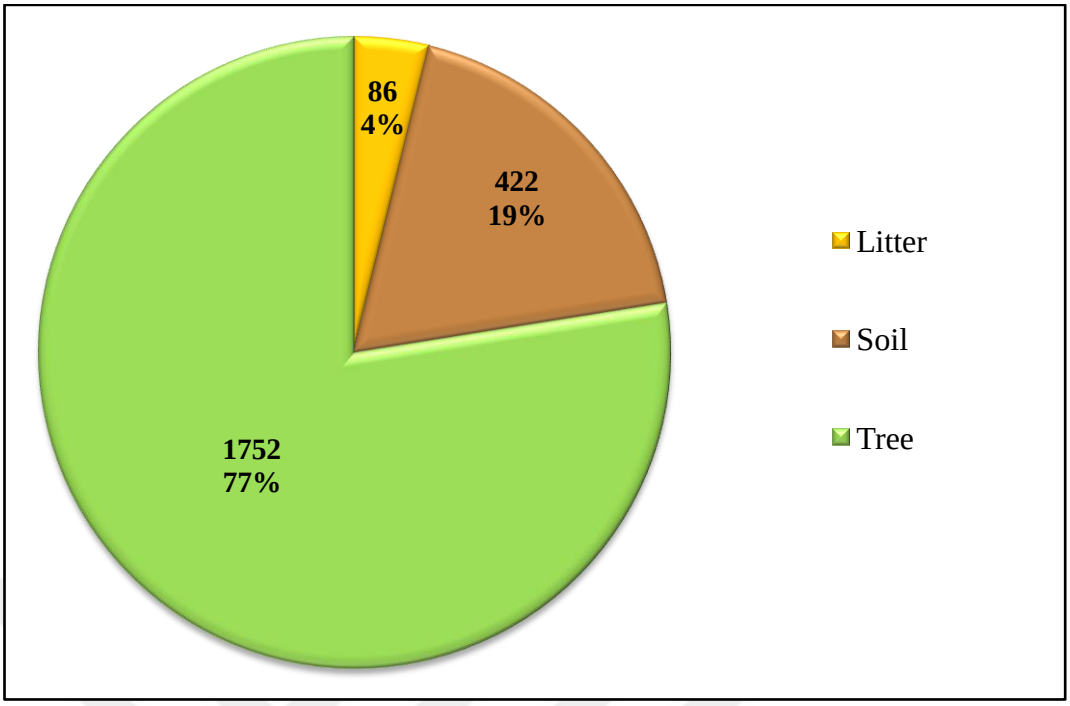


Figure 4.69 Contribution (%) of compartments to total accumulated PCB amounts per unit area (mg/ha) in background sites of Aliaga

Stored POP amounts (mg/ha) were higher in the industrial area except those in stem. The difference between industrial and background areas in stored amounts and relative contribution of different compartments is due to (i) POP concentrations in all compartments were higher in the industrial area, (ii) biomass amounts (kg/ha) in the background area were higher because of higher number of trees per unit area, having higher stem diameters and heights.

It should be noted that the soil inventory could be underestimated in some extent since only the upper 5 cm soil layer was analyzed and this depth was considered for the calculations. Recent studies have indicated that the majority of POPs are found in the upper soil layer (0-5 cm) (Armitage et al., 2006; Aichner et al., 2015) and therefore it could be suggested that the underestimation in soil POP inventory may not be substantial. However, it is not possible to determine the degree of underestimation since the depth profiles of POPs were not determined in the present study.

4.8 Results of Statistical Analysis

Data analysis is the process of systematically examining data with the purpose of spotlighting useful information. There are wide ranges of statistical tests. Statistical tests can be divided into two groups called as "parametric tests" and "non-parametric tests". The decision of which statistical test to use depends on the research design, the distribution of the data, and the type of variable. In general, parametric tests are used for normally distributed data while non-parametric tests are used for non-normally distributed data. The most common kind of statistical inference is hypothesis testing. In statistical hypothesis testing, a *p*-value (probability value) is used to decide whether the sample provides strong evidence against the null hypothesis.

The *p*-value is a numerical measure of the statistical significance of a hypothesis test. It is told that how likely it could have gotten sample data even if the null hypothesis is true. By convention, if the *p*-value is less than 5% ($p < 0.05$) the null hypothesis can be rejected. In other words, the results are statistically significant when p-values are lower than 5% ($p < 0.05$). It is mean that there is strong evidence to suggest the null hypothesis is false.

Σ_{16}PAH and Σ_{41}PCB concentrations in all samples (tree components, litter, air and soil) of background and industrial sites for both regions were statistically analyzed by using a non-parametric test. Mann Whitney U test were used because of the data sets were non-normally distributed. This test was used to examine the equality of the medians of the POP concentrations for each region. The test results are presented in Tables 4.12 – 4.13 – 4.14 – 4.15. As seen in the tables, there are statistically significant differences with 95% confidence ($p < 0.05$) between the medians of all samples (except stem samples, $p > 0.05$) POP concentrations in industrial and background sites for both regions. It is shown that ambient air, soil, litter and tree component samples (needle, branch, and bark) can be used for determine the spatial distribution of atmospheric POP levels in a region.

Table 4.12 Test results of Σ_{16}PAH concentrations in Iskenderun (*p* values are shown in bold)

Test Statistics[a]								
Iskenderun-PAH	**Air**	**Bark**	**Litter**	**1-year needle**	**2-year needle**	**Branch**	**Soil**	**Stem**
Mann-Whitney U	4.000	6.000	0.001	1.000	1.000	29.000	0.001	48.000
Wilcoxon W	32.000	34.000	28.000	29.000	29.000	57.000	28.000	258.000
Z	-3.615	-3.542	-3.846	-3.818	-3.818	-2.269	-3.874	-1.217
Asymp. Sig. (2-tailed)	**0.0003**	**0.0004**	**0.0001**	**0.0001**	**0.0001**	**0.0233**	**0.0001**	**0.2235**

a: Grouping Variable: Industrial - Background

Table 4.13 Test results of Σ_{41}PCB concentrations in Iskenderun (*p* values are shown in bold)

Test Statistics[a]								
Iskenderun-PCB	**Air**	**Bark**	**Litter**	**1-year needle**	**2-year needle**	**Branch**	**Soil**	**Stem**
Mann-Whitney U	0.001	8.000	0.001	3.000	0.001	7.500	0.001	20.000
Wilcoxon W	28.000	36.000	28.000	31.000	28.000	35.500	28.000	48.000
Z	-3.852	-3.430	-3.846	-3.707	-3.875	-3.460	-3.874	-2.766
Asymp. Sig. (2-tailed)	**0.0001**	**0.0006**	**0.0001**	**0.0002**	**0.0001**	**0.0005**	**0.0001**	**0.0567**

a: Grouping Variable: Industrial - Background

Table 4.14 Test results of Σ_{16}PAH concentrations in Aliaga (*p* values are shown in bold)

Test Statistics[a]								
Aliaga-PAH	**Air**	**Bark**	**Litter**	**1-year needle**	**2-year needle**	**Branch**	**Soil**	**Stem**
Mann-Whitney U	4.000	30.000	1.000	7.500	4.000	15.000	5.000	67.000
Wilcoxon W	25.000	51.000	22.000	28.500	25.000	36.000	26.000	343.000
Z	-3.444	-2.100	-3.661	-3.311	-3.499	-2.908	-3.446	-0.108
Asymp. Sig. (2-tailed)	**0.0006**	**0.0357**	**0.0003**	**0.0009**	**0.0005**	**0.0036**	**0.0006**	**0.9143**

a: Grouping Variable: Industrial - Background

Table 4.15 Test results of Σ_{41}PCB concentrations in Aliaga (*p* values are shown in bold)

Test Statistics[a]								
Aliaga-PCB	**Air**	**Bark**	**Litter**	**1-year needle**	**2-year needle**	**Branch**	**Soil**	**Stem**
Mann-Whitney U	2.000	2.000	2.000	22.000	3.000	6.000	0.001	36.000
Wilcoxon W	23.000	23.000	23.000	43.000	24.000	27.000	21.000	57.000
Z	-3.559	-3.607	-3.607	-2.530	-3.553	-3.392	-3.715	-1.777
Asymp. Sig. (2-tailed)	**0.0004**	**0.0003**	**0.0003**	**0.0114**	**0.0004**	**0.0007**	**0.0002**	**0.0756**

a: Grouping Variable: Industrial - Background

Modeled and observed ambient air POP concentrations were also statistically analyzed by using Mann Whitney U test. Confidence level of model was determined by using this test. The test results are presented in Table 4.16. As seen in Table 4.16, there are statistically significant differences with 95% confidence ($p < 0.05$) between the medians of modeled and observed ambient air POP concentrations for both regions. It is shown that this model can be used for estimation of ambient air POP concentrations by using measured bark POP concentrations.

Table 4.16 Test results of modeled and observed ambient air POP concentrations in both regions (*p* values are shown in bold)

Test Statistics[a]				
Ambient Air	**ISKENDERUN**		**ALIAGA**	
	PAH	**PCB**	**PAH**	**PCB**
Mann-Whitney U	173.000	51.000	178.000	78.000
Wilcoxon W	363.000	241.000	409.000	309.000
Z	-0.819	-3.906	-0.069	-3.585
Asymp. Sig. (2-tailed)	**0.0266**	**0.0001**	**0.0349**	**0.0003**

a: Grouping Variable: Observed - Modeled

CHAPTER FIVE

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

The main objective of this study is to investigate the spatial variations and historical trends of air pollution in two severely polluted industrial regions (Aliaga and Iskenderun) in Turkey by measuring persistent organic pollutants (POPs) sorbed in tree components. Several POPs like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were measured in needle, branch, bark, and stem samples from two pine tree species (*Pinus brutia* and *Pinus pinea*) commonly grown in these regions. Samples were collected at 27 different sites (industrial and background sites) in each industrial region representing the spatial distribution of pollutants. Soil, litter, and ambient air samples were also collected and analyzed to explore the relationships between the POP concentrations measured in air, soil, litter, and tree components.

POP concentrations in air, soil, litter and tree component samples decreased with distance from the major sources. The lowest POP levels in tree components, soil, litter, and ambient air samples were measured in background sites, away from specific local sources. Highest levels of POPs were observed at the industrial sites with industrial/background concentration ratios varying between 1.3 (stem) to 23.0 (soil) for PAHs and 2.2 (stem) to 29.6 (soil) for PCBs in Iskenderun. In Aliaga, this ratio was varied from 1.5 (stem) to 9.3 (litter) for PAHs and 2.3 (stem) to 48.0 (soil) for PCBs. Among all POP groups, the highest concentrations were measured for PAHs followed by PCBs in both regions. Correlations among the ambient air and soil, litter, and tree components POP levels were significant, showing that POPs are exchanged between atmosphere and these compartments. The results of the present study have suggested that tree components (needle, bark, branch), litter, and soil could be utilized to determine the spatial variations of atmospheric POPs.

Spatial variation of POP concentrations measured in all sample types showed that the iron-steel plants, ship-breaking, petrochemical industries, and the petroleum refinery are the major POP emitting sources in both regions. Compound profiles were similar for ambient air and some tree component samples (needles, branch, and stem). However, medium to high molecular weight compounds dominated the POP profiles in soil while their contributions to total POPs were relatively higher for litter and bark compared to branch, stem, and needles. Industrial sampling sites were relatively close to the local sources. Therefore, the difference in POP profiles can be due to the high molecular weight compounds are mainly associated with particle phase and deposited more easily close to the point sources compared to the lower molecular weight ones, which are mainly in the gas phase and could be transported to relatively longer distances. Measured POP profiles also suggest that particle phase deposition is an effective mechanism for accumulation in soil, litter, and bark while gas phase uptake and translocation is relatively more important for accumulation in needles, branch, and stem.

POPs measured in annual growth rings provide a possibility to reveal historical trends of the atmospheric concentrations in Aliaga and Iskenderun. Historical variations of all POP concentrations indicated an increasing trend with time in parallel to industrialization for both regions. The results of this study indicated that tree components (needle, branch, bark), litter and soil could be used to determine the spatial variations while tree rings could be used to investigate the historical trends of atmospheric POPs in a region.

Ambient air POP concentrations were also modeled using those measured in bark samples. The modeled/observed ratios were close to 1.0 for several compounds and the results indicated that the bark-air partitioning model is able to estimate atmospheric POP concentrations from bark measurements. The model was estimated the ambient air PAH concentrations within factors of 0.23 - 3.07 and 0.08 - 6.88 in Iskenderun and Aliaga, respectively. PCB concentrations were estimated by the model within factors of 1.02 – 6.67 and 1.52 – 9.04 in Iskenderun and Aliaga,

respectively. The results of modeling also indicated that tree bark could be used as passive samplers to estimate the ambient air POP concentrations in a region.

Amounts of POPs (mg/ha) accumulated in soil, litter and tree components were inventoried. Generally, the highest POP quantities were accumulated in the stem followed by needles. Overall, the highest POP quantities were accumulated in soil followed by trees and litter in Iskenderun while the highest POP amounts were stored in soil for PCBs and in trees for PAHs in Aliaga region. It is showing that vegetation is also an important reservoir accumulating the POPs in addition to soil. These results have significant implications regarding the partitioning of POP compounds in the environment and the potential of vegetation to clean the atmosphere.

5.2 Suggestions

The results of the present study have indicated that iron-steel plants, ship-breaking, petrochemical industries, and the petroleum refinery are potential PAH and PCB sources in the regions. In addition to PAHs and PCBs, other persistent organic pollutant concentrations could be measured and their possible sources could be determined in the regions.

According to results, especially iron-steel plants are one of the most considerable sources in two regions for PAH and PCB emissions. It could be suggested that establishment of new iron-steel plants should not be allowed and control measurements should be applied to reduce PAH and PCB emissions in the regions.

The various plant species are ideal for biomonitoring (especially mosses). They play an important role in the global cycling of persistent organic pollutants. PAHs and PCBs were measured in tree components of two pine tree species (*Pinus brutia* and *Pinus pinea*) in this study. In addition, tree components of other tree species grown in these regions could be sampled and analyzed. Then, amounts of total POPs accumulated in these tree components could be inventoried.

Ambient air POP concentrations were modeled using a bark-air partitioning model. Statistically significant correlations were found between bark-air partitioning coefficients (K_{BA}) and octanol-air partitioning coefficients (K_{OA}) for all POP groups suggesting that the octanol is a representative surrogate for bark lipids. However, slopes were substantially lower than 1.0 indicating non-equilibrium conditions. This may be considered as a limitation of the equilibrium model used in the present study. A dynamic model could be used for the estimation of POP levels uptake by environmental compartments.

Finally, very little information is known about the magnitude of vegetation as a sink and its effect on the atmospheric residence times of lipophilic organic pollutants. The role of vegetation as a sink will be influenced by time of the year, lipophilicity of the organic pollutant, and whether the pollutant is present in the atmosphere gas or particle phase. Additional studies are required to investigate this issue.

Vegetation is the link between the atmosphere and the human food supply. The results of the present study have showed that vegetation can be used as an indicator for regional contamination levels. It is important to determine the POP levels in the atmosphere and vegetation to evaluate public health risks. The findings obtained open up new possibilities for the estimation of regional and global contamination levels in pollution monitoring, and the assessment of the importance of vegetation as a pollutant sink.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR). (1995). *Toxicological profile for polycyclic aromatic hydrocarbons (PAHs)*. Retrieved November 15, 2013 from http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf.

Agency for Toxic Substances and Disease Registry (ATSDR). (2000). *Toxicological profile for polychlorinated biphenyls (PCBs).* Retrieved September 3, 2013 from http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=142&tid=26

Aichner, B., Bussian, B.M., Lehnik-Habrink, P., & Hein, S. (2015). Regionalized concentrations and fingerprints of polycyclic aromatic hydrocarbons (PAHs) in German forest soils. *Environmental Pollution, 203,* 31-39.

Albuquerque, M., Coutinho, M., & Borrego, C. (2016). Long-term monitoring and seasonal analysis of polycyclic aromatic hydrocarbons (PAHs) measured over a decade in the ambient air of Porto, Portugal. *Science of the Total Environment, 543,* 439–448.

Alcock, R.E., Sweetman, A.J., Prevedouros, K., & Jones, K.C. (2003). Understanding levels and trends of BDE-47 in the UK and North America: An assessment of principal reservoirs and source inputs. *Environment International, 29,* 691-698.

Alfani, A., Maisto, G., Prati, M.V., & Baldantoni, D. (2001). Leaves of Quecus ilex L. as biomonitors of PAHs in air of Naples. *Atmospheric Environment, 35,* 3553–3559.

Amigo, J.M., Ratola, N., & Alves, A. (2011). Study of geographical trends of polycyclic aromatic hydrocarbons using pine needles. *Atmospheric Environment, 45,* 5988-5996.

Armitage, J.M., Hanson, M., Axelman, J., & Cousins, I.T. (2006). Levels and vertical distribution of PCBs in agricultural and natural soils from Sweden. *Science of the Total Environment, 371,* 344-352.

Augusto, S., Maguas, C., Matos, J., Pereira, M. J., & Branquinho, C. (2010). Lichens as an integrating tool for monitoring PAH atmospheric deposition: A comparison with soil, air and pine needles. *Environmental Pollution, 158* (2), 483-489.

Augusto, S., Maguas, C., Matos, J., Pereira, M. J., Soares, A., & Branquinho, C. (2009). Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. *Environmental Science & Technology, 43*(20), 7762-7769.

Aydin, Y. M., Kara, M., Dumanoglu, Y., Odabasi, M., & Elbir, T. (2014). Source apportionment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in ambient air of an industrial region in Turkey. *Atmospheric Environment, 97,* 271−285.

Aydın, Y.M. (2013). S*ource apportionment of persistent organic pollutants in Aliaga industrial region*. M.Sc Thesis, Dokuz Eylül University, İzmir.

Backe, C., Cousins, I.T., & Larsson, P. (2004). PCB in soils and estimated soil-air exchange fluxes of selected PCB congeners in the south of Sweden. *Environmental Pollution, 128,* 59-72.

Balat, M. (2005). Use of biomass sources for energy in Turkey and a view to biomass potential. *Biomass and Bioenergy, 29* (1), 32–41.

Barber, J.L., Thomas, G.O., Kerstiens, G., & Jones, K.C. (2004). Current issues and uncertainties in the measurement and modelling of air-vegetation exchange and within plant processing of POPs. *Environmental Pollution, 128,* 99-138.

Bartrons, M., Catalan, J., & Penuelas, J. (2016). Spatial and temporal trends of organic pollutants in vegetation from remote and rural areas. *Scientific Reports, 6*, 25446.

Basha, S., Gaur, P.M., Thorat, R.B., Trivedi, R.H., Mukhopadhyay, S.K., Anand, N., et al. (2007). Heavy metal content of suspended particulate matter at world's largest ship-breaking yard, Alang-Sosiya, India. *Water Air and Soil Pollution, 178*, 373-384.

Bayram, A., Odabasi, M., Elbir, T., Seyfioglu, R., Dumanoglu, Y., Demircioglu, H., et al. (2008). *Air pollutants from iron-steel plants with electric arc furnaces I: gaseous pollutants and particulate matter (in Turkish)*. Proceedings of National Air Pollution and Control Symposium-2008, October 22-25, 2008, Hatay, Turkey, 121-132.

Blasco, M., Domeno, C., & Nerin, C. (2008). Lichens biomonitoring as feasible methodology to assess air pollution in natural ecosystems: Combined study of quantitative PAHs analyses and lichen biodiversity in the Pyrenees Mountains. *Analytical and Bioanalytical Chemistry, 391* (3), 759-771.

Blasco, M., Domeno, C., & Nerin, C. (2006). Use of lichens as pollution biomonitors in remote areas: Comparison of PAHs extracted from lichens and atmospheric particles sampled in and around the Somport Tunnel (Pyrenees). *Environmental Science & Technology*, *40* (20), 6384-6391.

Bohlin, P., Jones, K.C., Tovalin, H., & Strandberg, B. (2008). Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers, *Atmospheric Environment, 42*, 7234-7241.

Bozlaker, A., Muezzinoglu, A., & Odabasi, M. (2008a). Atmospheric concentrations, dry deposition and air-soil exchange of polycyclic aromatic hydrocarbons (PAHs) in an industrial region in Turkey. *Journal of Hazardous Material, 153*, 1093-1102.

Bozlaker, A., Odabasi, M., & Muezzinoglu, A. (2008b). Dry deposition and soil–air gas exchange of polychlorinated biphenyls (PCBs) in an industrial area. *Environmental Pollution, 156,* 784-793.

Braekevelt, E., Tittlemier, S.A., & Tomy, G.T. (2003). Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere, 51,* 563-567.

Breivik, K., Gioia, R., Chakraborty, P., Zhang, G., & Jones, K.C. (2011). Are reductions in industrial organic contaminants emissions in rich countries achieved partly by export of toxic wastes?. *Environmental Science & Technology, 45,* 9154-9160.

Breivik, K., Sweetman, A., Pacyna, J.M., & Jones, K.C. (2007). Towards a global historical emission inventory for selected PCB congeners - A mass balance approach 3. An update. *Science of the Total Environment, 377,* 296-307.

Breivik, K., Sweetman, A., Pacyna, J.M., & Jones, K.C. (2002a). Towards a global historical emission inventory for selected PCB congeners - A mass balance approach 1. Global production and consumption. *Science of the Total Environment, 290,* 181-198.

Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M. & Vighi, M. (1991). Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. *Environmental Science & Technology, 25,* 1489-1495.

Castro-Jimenez, J., Mariani, G., Vives, I., Skejo, H., Umlauf, G., Zaldivar, J.M., et al. (2011). Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). *Environmental Pollution, 159,* 1948-1956.

Castro-Jimenez, J., Dueri, S., Eisenreich, S.J., Mariani, G., Skejo, H., Umlauf, G., et al. (2009). Polychlorinated biphenyls (PCBs) in the atmosphere of sub-alpine northern Italy. *Environmental Pollution, 157,* 1024-1032.

Catal, Y. (2009). *Batı Akdeniz Bölgesi Kızılçam (Pinus brutia Ten.) Meşcerelerinde Artım ve Büyüme*. PhD Thesis, Süleyman Demirel University, Isparta.

Cetin, B., Ozturk, F., Keles, M., & Yurdakul, S. (2017). PAHs and PCBs in an Eastern Mediterranean megacity, Istanbul: Their spatial and temporal distributions, air-soil exchange and toxicological effects. *Environmental Pollution, 220,* 1322 – 1332.

Cetin, B. (2016). Investigation of PAHs, PCBs and PCNs in soils around a heavily industrialized area in Kocaeli, Turkey: Concentrations, distributions, sources and toxicological effects. *Science of the Total Environment 560–561*, 160–169.

Cetin, B., & Odabasi, M. (2008). Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Chemosphere, 71* (6), 1067−1078.

Cetin, B., & Odabasi, M. (2007). Particle-phase dry deposition and air-soil gas exchange of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Environmental Science & Technology, 41,* 4986-4992.

Cetin, B., & Odabasi, M. (2005). Measurement of Henry's law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature. *Atmospheric Environment, 39,* 5273-5280.

Cetin, B., Yatkin, S., Bayram, A., & Odabasi, M. (2007). Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey. *Chemosphere, 69,* 1267-1277.

Chaney, W. R. (2000). *Water and chemical movement beneath the bark.* Retriewed March 12, 2014
from http://woodlandsteward.squarespace.com/storage/pastissues/htm.

Chau, K.W. (2005). Characterization of transboundary POP contamination in aquatic ecosystems of Pearl River delta. *Marine Pollution Bulletin, 51,* 960-965.

Chen, P., Mei, J., Peng, P., Hu, J., & Chen, D. (2012). Atmospheric PCDD/F concentrations in 38 cities of China monitored with pine needles, a passive biosampler. *Environmental Science & Technology, 46,* 13334−13343.

Chen, L.G., Mai, B.X., Bi, X.H., Chen, S.J., Wang, X.M., Ran, Y., et al. (2006). Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environmental Science & Technology, 40,* 1190-1196.

Choi, S.D. (2014). Time trends in the levels and patterns of polycyclic aromatic hydrocarbons (PAHs) in pine bark, litter, and soil after a forest fire. *Science of the Total Environment, 470-471,* 1441-1449.

Choi, S.D., Kwon, H.O., Lee, Y.S., Park, E.J., & Oh, J.Y. (2012). Improving the spatial resolution of atmospheric polycyclic aromatic hydrocarbons using passive air samplers in a multiindustrial city. *Journal of Hazardous Material, 241–242,* 252–258.

Choi, S.D., Staebler, R. M., Li, H., Su, Y., Gevao, B., Harner, T., et al. (2008). Depletion of gaseous polycyclic aromatic hydrocarbons by a forest canopy. *Atmospheric Chemistry and Physics, 8,* 4105-4113.

Chropenova, M., Greguskova, E.K., Karaskova, P., Pribylova, P., Kukucka, P., Barakova, D., et al. (2016). Pine needles and pollen grains of *Pinus mugo* Turra – A biomonitoringtool in high mountain habitats identifying environmental contamination. *Ecological Indicators, 66*, 132–142.

Collins, C., Fryer, M., & Grosso, A. (2006). Plant uptake of non-ionic organic chemicals. *Environmental Science & Technology, 40* (1), 45−52.

Comez, A. (2011). *Sündiken Dağları'nda Sarıçam (pinus sylvestris l.) meşcerelerinde karbon birikiminin belirlenmesi*". PhD. Thesis, İstanbul University, İstanbul.

Correia, A., Faias, S., Tome, M., Evangelista, M., Freire, J., & Carvalho, P.O. (2008). Simultaneous fitting of biomass equations for Pinus pinea L. in Portugal. *Silva Lusitana, 16*, 197-205.

Crimmins, B.S., & Baker, J.E. (2006). Improved GC/MS methods for measuring hourly PAH and nitro-PAH concentrations in urban particulate matter. *Atmospheric Environment, 40*, 6764-6779.

Cutini, A., Chianucci, F., & Manetti, M.C. (2013). Allometric relationships for volume and biomass for stone pine (Pinus pinea L.) in Italian coastal stands. *iForest, 0*, 331-335.

Dabestani, R., & Ivanov, I. N. (1999). A compilation of physical, spectroscopic and photophysical properties of polycyclic aromatic hydrocarbons. *Photochemistry and Photobiology, 70*, 10-34.

Dassler, H.G. (1986). *Hava kirliliğinin vejetasyon üzerindeki etkileri, nedenler-etkiler-önlemler* (3. Basım). VEB Gustav Jena: Fischer Yayınevi.

De Nicola, F. Grana, C.E., Mahía, L. P., Lorenzo, S.M., Rodríguez, D.P., Retuerto, R., et al. (2016). Evergreen or deciduous trees for capturing PAHs from ambient air? A case study. *Environmental Pollution doi: http://dx.doi.org/10.1016/j.envpol.2016.11.074*

De Nicola, F., Baldantoni, D., & Alfani, A. (2014). PAHs in decaying *Quercus ilex* leaf litter: Mutual effects on litter decomposition and PAH dynamics. *Chemosphere 114*, 35–39.

Dorr, G., Hippelein, M., Kaupp, H., & Hutzinger, O. (1996b). Baseline contamination assessment for a new resource recovery facility in Germany - Part VI: Levels and profiles of polycyclic aromatic hydrocarbons (PAH) in ambient air. *Chemosphere, 33*, 1569-1578.

Du, S.Y., & Rodenburg, L.A. (2007). Source identification of atmospheric PCBs in Philadelphia/Camden using positive matrix factorization followed by the potential source contribution function. *Atmospheric Environment, 41*, 8596-8608.

Estellano, V.H., Pozo, K., Harner, T., Corsolini, S., & Focardi, S. (2012). Using PUF disk passive samplers to simultaneously measure air concentrations of persistent organic pollutants (POPs) across the Tuscany Region, Italy. *Atmospheric Pollution Research, 3*, 88-94.

Falconer, R.L., & Bidleman, T.F. (1994). Vapor pressures and predicted particle gas distributions of polychlorinated biphenyl congeners as functions of temperature and orthochlorine substitution. *Atmospheric Environment, 28*, 547-554.

Farrar, N.J., Prevedouros, K., Harner, T., Sweetman, A.J., & Jones, K.C. (2006). Continental scale passive air sampling of persistent organic pollutants using rapidly equilibrating thin films (POPs). *Environmental Pollution, 144*, 423-433.

Gambaro, A., Manodori, L., Zangrando, R., Cincinelli, A., Capodaglio, G., & Cescon, P. (2005). Atmospheric PCB concentrations at Terra Nova Bay, Antarctica. *Environmental Science & Technology, 39*, 9406–9411.

Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S. et al. (2002). Use of moss (Tortula muralis Hedw.) for monitoring organic and inorganic air pollution in urban and rural sites in Northern Italy. *Atmospheric Environment, 36*, 4069–4075.

Gokcol, C., Dursun, B., Alboyaci, B., & Sunan, E. (2009). Importance of biomass energy as alternative to other sources in Turkey. *Energy Policy*, *37* (2), 424–431.

Gouin, T., Thomas, G. O., Cousins, I., Barber, J., Mackay, D., & Jones, K. C. (2002). Air-surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. *Environmental Science & Technology, 36*, 126–1434.

Graham, L.E., Graham, J.M., & Wilcox, L.W. (2004). *Bitki fizyolojisi*. Palme Yayınları No: 283, Ankara: Palme Yayıncılık.

Gueguen, F., Stille, P., & Millet, M. (2011). Air quality assessment by tree bark biomonitoring in urban, industrial and rural environments of the Rhine Valley: PCDD/Fs, PCBs and trace metal evidence, *Chemosphere, 85*, 195-202.

Halsall, C.J., Sweetman, A.J., Barrie, L.A., & Jones, K.C. (2001). Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmospheric Environment, 35*, 255-267.

Halsall, C.J., Coleman, P.J., Davis, B.J., Burnett, V., Waterhouse, K.S., Hardingjones, P., et al. (1994). Polycyclic aromatic hydrocarbons in U.K. urban air. *Environmental Science & Technology, 28*, 2380-2386.

Han, X. Y., Wang, Z. Y., Zhai, Z. C., & Wang, L. S. (2006). Estimation of n-octanol/water partition coefficients (K_{OW}) of all PCB congeners by Ab initio and a Cl substitution position method. *QSAR Combinatorial Science, 25*(4), 333−341.

Harner, T., Pozo, K., Gouin, T., Macdonald, A.M., Hung, H., Cainey, J., et al. (2006a). Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environmental Pollution, 144*, 445-452.

Harner, T., & Shoeib, M. (2002). Measurements of octanol-air partition coefficients (K_{OA}) for polybrominated diphenyl ethers (PBDEs): Predicting partitioning in the environment. *Journal of Chemical and Engineering, 47*, 228-232.

Harner, T., & Bidleman, T.F. (1998). Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. *Environmental Science & Technology, 32*, 1494-1502.

Harner, T., & Bidleman, T.F. (1996). Measurements of octanol-air partition coefficients for polychlorinated biphenyls. *Journal of Chemical and Engineering, 41*, 895-899.

Harner, T., & Mackay, D. (1995). Measurement of octanol-air partition coefficients for chlorobenzenes, PCBs, and DDT. *Environmental Science & Technology, 29*, 1599- 1606.

Hermanson, M.H., & Johnson, G.W. (2015). Chlorinated dibenzo-p-dioxin and dibenzofuran congener and homologue distributions in tree bark from Sauget, Illinois, U.S.A. *Environmental Science & Technology, 49*, 855-862.

Hermanson, M.H., & Johnson, G.W. (2007). Polychlorinated biphenyls in tree bark near a former manufacturing plant in Anniston, Alabama. *Chemosphere, 68*, 191-198.

Hogarh, J.N., Seike, N., Kobara, Y., Habib, A., Nam, J.J., Lee, J.S., et al. (2012a). Passive air monitoring of PCBs and PCNs across East Asia: A comprehensive congener evaluation for source characterization. *Chemosphere, 86*, 718-726.

Holoubek, I., Korinek, P., Seda, Z., Schneiderova, E., Holoubkova, I., Pacl, A., et al. (2000). The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales. *Environmental Pollution, 109* (2), 283-292.

Horstmann, M., & McLachlan, M.S. (1998). Atmospheric deposition of semivolatile organic compounds to two forest canopies. *Atmospheric Environment, 32*, 1799-1809.

Howsam, M., Jones, K. C., & Ineson, P. (2000). PAHs associated with the leaves of three deciduous tree species. I-Concentrations and profiles. *Environmental Pollution, 108* (3), 413-424.

Hulster, A., & Marschner, H. (1993). Transfer of PCDD/PCDF from contaminated soils to food and fodder crop plants. *Chemosphere, 27*, 439-446.

Integrated Pollution Prevention and Control (IPPC). (2001). *Best Available Techniques Reference Document on the Production of Iron and Steel;* European Commission, Seville, Spain.

Ishikawa, Y., Noma, Y., Mori, Y., & Sakai, S. (2007). Congener profiles of PCB and a proposed new set of indicator congeners. *Chemosphere, 67,* 1838-1851.

Jaward, F.M., Barber, J.L., Booij, K., & Jones, K.C. (2004a). Spatial distribution of atmospheric PAHs and PCNs along a north-south Atlantic transect. *Environmental Pollution, 132,* 173-181.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., & Jones, K.C. (2004b). Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe. *Environmental Toxicology and Chemistry, 23,* 1355-1364.

Jin, R.H., Park, S.U., Park, J.E., & Kim, J.G. (2012). Polychlorinated biphenyl congeners in river sediments: Distribution and source identification using multivariate factor analysis. *Archives of Environmental Contamination and Toxicology, 62*, 411-423.

Jones, K.C., & de Voogt, P. (1999). Persistent organic pollutants (POPs): State of the science. *Environmental Pollution, 100,* 209-221.

Kacar, B. (1989). *Bitki fizyolojisi* (3. Basım). Ankara Üniversitesi Basımevi, Ziraat Fakültesi Yayınları.

Kaya, E., Dumanoglu, Y., Kara, M., Altiok, H., Bayram, A., Elbir, T., et al. (2012). Spatial and temporal variation and air–soil exchange of atmospheric PAHs and PCBs in an industrial region. *Atmospheric Pollution Research, 3,* 435-449.

Kim, K.S., Masunaga, S., & Kim, J.G. (2002). Concentration and congener pattern of PCB in the air at Yokohama. *Korean Social Analitic Science & Technology,* 157.

Klanova, J., Matykiewiczova, N., Macka, Z., Prosek, P., Laska, K., & Klan, P. (2008). Persistent organic pollutants in soils and sediments from James ROSS Island, Antarctica. *Environmental Pollution, 152,* 416-423.

Krauss, M., & Wilcke, W. (2003). Polychlorinated naphthalenes in urban soils: Analysis, concentrations, and relation to other persistent organic pollutants. *Environmental Pollution, 122,* 75-89.

Krommer, V., Zechmeister, H. G., Roder, I., Scharf, S., & Hanus-Illnar, A. (2007). Monitoring atmospheric pollutants in the biosphere wienerwald by a combined approach of biomonitoring methods and technical measurements. *Chemosphere, 67* (10), 1956-1966.

Kuang, Y.W., Li, J., & Hou, E.Q. (2015). Lipid content normalized polycyclic aromatic hydrocarbons (PAHs) in the xylem of conifers can indicate historical changes in regional airborne PAHs. *Environmental Pollution, 196*, 53−59.

Kuang, Y.W., Li, Y., Li, J., & Wen, D.Z. (2014). Temporal patterns and potential sources of polycyclic aromatic hydrocarbons in xylem of Pinus kwangtungensis. *Atmospheric Pollution Research, 5*, 520-527.

Kuang, Y.W., Zhou, G.Y., Wen, D.Z., Li, J., & Sun, F.F. (2011). Analysis of polycyclic aromatic hydrocarbons in tree–rings of Masson pine (Pinus massoniana L.) from two industrial sites in the Pearl River Delta, south China. *Journal of Environmental Monitoring, 13*, 2630–2637.

Kuzu, L.S., Saral, A., Günes, G., & Karadeniz, A. (2016). Evaluation of background soil and air polychlorinated biphenyl (PCB) concentrations on a hill at the outskirts of a metropolitan city. *Chemosphere, 154*, 79 – 89.

Lang, Q., Hunt, F., & Wai, C.M. (2000). Supercritical fluid extraction of polycyclic aromatic hydrocarbons from white pine (Pinus strobus) needles and its implications. *Journal of Environmental Monitoring, 2* (6), 639-644.

Lehndorff, E., & Schwark, L. (2004). Biomonitoring of air quality in the Cologne Conurbation using pine needles as a passive sampler — Part II: Polycyclic aromatic hydrocarbons (PAH). *Atmospheric Environment, 38*, 3793-3808.

Lei, Y.D., Wania, P., & Shiu, W.Y. (1999). Vapor pressures of the polychlorinated naphthalenes. *Journal of Chemical Engineering Data, 44*, 577-582.

Li, Q.L., Xu, Y., Li, J., Pan, X.H., Liu, X., & Zhang, G. (2012). Levels and spatial distribution of gaseous polychlorinated biphenyls and polychlorinated naphthalenes in the air over the northern South China Sea. *Atmospheric Environment, 56,* 228-235.

Li, X., Li, Y., Zhang, Q., Wang, P., Yang, H., Jiang, G., et al. (2011). Evaluation of atmospheric sources of PCDD/Fs, PCBs and PBDEs around a steel industrial complex in northeast China using passive air samplers. *Chemosphere, 84,* 957-963.

Liu, X., Zhang, G., Jones, K. C., Li, X., Peng, X., & Qi, S. (2005). Compositional fractionation of polycyclic aromatic hydrocarbons (PAHs) in mosses (hypnum plumaeformae wils.) from the northern slope of Nanling Mountains, South China. *Atmospheric Environment, 39* (30), 5490-5499.

Loganathan, B.G., Kumar, K.S., Seaford, K.D., Sajwan, K.S., Hanari, N., & Yamashita, N. (2008). Distribution of persistent organohalogen compounds in pine needles from selected locations in Kentucky and Georgia, USA. *Archives of Environmental Contamination and Toxicology, 54,* 422-439.

Loppi, S., Pozo, K., Estellano, V.H., Corsolini, S., Sardella, G., & Paoli, L. (2015). Accumulation of polycyclic aromatic hydrocarbons by lichen transplants: Comparison with gas-phase passive air samplers. *Chemosphere 134,* 39–43.

Macek, T., Mackova, M., & Kas, J. (2000). Exploitation of plants for the removal of organics in environmental remediation. *Biotechnology Advances, 18,* 23-34.

Mamontova, E.A., Mamontov, A.A., Tarasova, E.N., Kuzmin, M.I., Ganchimeg, D., Khomutova, M.Y., et al. (2013). Polychlorinated biphenyls in surface soil in urban and background areas of Mongolia. *Environmental Pollution 182,* 424–429.

Manodori, L., Gambaro, A., Moret, I., Capodaglio, G., Cairns, W. R. L., & Cescon, P. (2006). Seasonal evolution of gas-phase PCB concentrations in the Venice Lagoon area. *Chemosphere, 62*, 449–458.

McLachlan, M.S. (1999). Framework for the interpretation of measurements of SOCs in plants. *Environmental Science & Technology, 33* (11), 1799−1804.

Meijer, S.N., Shoeib, M., Jantunen, L.M.M., Jones, K.C., & Harner, T. (2003). Air-soil exchange of organochlorine pesticides in agricultural soils. 1. Field measurements using a novel in situ sampling device. *Environmental Science & Technology, 37,* 1292-1299.

Morosini, M. J., Schreitmüller, U., & Reuter, B. (1993). Correlation between C-6/C-14 chlorinated hydrocarbons levels in the vegetation and in the boundary layer of the troposphere. *Environmental Science & Technology, 27*, 1517-1523.

Motelay-Massei, A., Ollivon, D., Garban, B., Teil, M.J., Blanchard, M., & Chevreuil, M. (2004). Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere, 55,* 555-565.

Nadal, M., Schuhmacher, M., & Domingo, J.L. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environmental Pollution, 132,* 1-11.

Nadal, M., Schuhmacher, M., & Domingo, J.L. (2007). Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: Temporal trend. *Chemosphere, 66,* 267-276.

Nagpal, N.K. (1992). Water quality criteria for polychlorinated biphenyls (PCBs), *Technical Appendix, Ministry of Environment, Lands and Parks Province of British Columbia*.

Nagpal, N.P. (1993). Ambient water quality criteria for polycyclic aromatic hydrocarbons (PAHs). *Technical Appendix, Ministry of Environment, Lands and Parks Province of British Columbia*.

Nakajima, D., Yoshida, Y., Suzuki, J., & Suzuki, S. (1995). Seasonal changes in the concentration of polycyclic aromatic hydrocarbons in azalea leaves and relationship to atmospheric concentration. *Chemosphere, 30,* 409-418.

Nam, J.J., Thomas, G.O., Jaward, F.M., Steinnes, E., Gustafsson, O., & Jones, K.C. (2008b). PAHs in background soils from Western Europe: Influence of atmospheric deposition and soil organic matter. *Chemosphere, 70,* 1596-1602.

National Library of Medicine (NLM). (2008). *Specialized Information Services (SIS), Toxnet, ChemIDplus Advanced.* Retriewed November 1, 2013 from http://chem.sis.nlm.nih.gov/chemidplus

Neser, G., Unsalan, D., Tekogul, N., & Stuer-Lauridsen, F. (2008). The ship-breaking industry in Turkey: Environmental, safety and health issues. *Journal of Cleaner Production, 16,* 350-358.

Netto, A.D.P., Barreto, R.P., Moreira, J.C., & Arbilla, G. (2007). Spatial distribution of polycyclic aromatic hydrocarbons in Terminalia catappa L. (Combretaceae) bark from a selected heavy road traffic area of Rio de Janeiro City, Brazil. *Journal of Hazardous Materials, 142,* 389-396.

Nizzetto, L., Cassani, C., & Di Guardo, A. (2006). Deposition of PCBs in mountains: The forest filter effect of different forest ecosystem types. *Ecotoxicology and Environmental Safety, 63,* 75–83.

Nost, T.H., Halse, A.K., Randall, S., Borgen, A.R., Schlabach, M., Paul, A., et al. (2015). High concentrations of organic contaminants in air from ship breaking activities in Chittagong, Bangladesh. *Environmental Science & Technology,* 49, 11372–11380.

Ockenden, W.A., Steinnes, E., Parker, C., & Jones, K.C. (1998). Observations on persistent organic pollutants in plants: Implications for their use as passive air samplers and for POP cycling. *Environmental Science & Technology, 32,* 2721-2726.

Odabasi, M., Ozgunerge Falay, E., Tuna, G., Altiok, H., Kara, M., Dumanoglu, Y., et al. (2015). Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region, *Environmental Scence & Technology, 49,* 2105−2114.

Odabasi, M., Bayram, A., Elbir, T., Dumanoglu, Y., Kara, M., Altiok, H., et al. (2012). Investigation of seasonal variations and sources of atmospheric polychlorinated naphthalenes (PCNs) in an urban area. *Atmospheric Pollution Research, 3,* 477-484.

Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., & Ornektekin, S. (2010). Investigation of soil concentrations of persistent organic pollutants, trace elements, and anions due to iron-steel plant emissions in an industrial region in Turkey. *Water Air and Soil Pollution, 213,* 375-388.

Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., & Bozlaker, A. (2009). Electric arc furnaces for steel-making: Hot spots for persistent organic pollutants. *Environmental Science & Technology, 43,* 5205-5211.

Odabasi, M., Cetin, B., Demircioglu, E., & Sofuoglu, A. (2008). Air-water exchange of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) at a coastal site in Izmir Bay, Turkey. *Marine Chemistry, 109,* 115-129.

Odabasi, M., Cetin E., & Sofuoglu A. (2006a). Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas/particle partitioning in an urban atmosphere. *Atmospheric Environment, 40*, 6615-6625.

Odabasi, M., Cetin, B., & Sofuoglu, A. (2006b). Henry's law constant, octanol-air partition coefficient and supercooled liquid vapor pressure of carbazole as a function of temperature: Application to gas/particle partitioning in the atmosphere. *Chemosphere, 62*, 1087-1096.

Odabasi, M., Cetin, E., & Sofuoglu, A. (2006). Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas-particle partitioning in an urban atmosphere. *Atmospheric Environment, 40* (34), 6615−6625.

Odabasi, M. (1998). *The measurement of PAH dry deposition and air-water exchange with the water surface sampler*, PhD Thesis, Illinois Institute of Technology, USA.

Oishi, Y. (2013). Comparison of pine needles and mosses as bio-indicators for polycyclic aromatic hydrocarbons. *Journal of Environmental Protection, 4,* 106-113.

Park, J.S. (2000). A*tmospheric deposition of PAHs, PCBs, and pesticides to the South Texas Bays, Galveston Bay and Corpus Christy Bay*. PhD Thesis, Texas A & M University, College Station, TX, USA.

Paterson, S., Mackay, D., & McFarlane, C. (1994). A model of organic chemical uptake by plants from soil and the atmosphere. *Environmental Science & Technology, 28* (13), 2259-2266.

Paterson, S., Mackay, D., & Gladman, A. (1991). A fugacity model of chemical uptake by plants from soil and air. *Chemosphere, 23* (4), 539-565.

Peverly, A.A., Salamova, A., & Hites, R.A. (2015). Locating POPs sources with tree bark. *Environmental Science & Technology, 49,* 13743-13748.

Piccardo, M.T., Pala, M., Bonaccurso, B., Stella, A., Redaelli, A., Paola, G., et al. (2005). Pinus nigra and Pinus pinaster needles as passive samplers of polycyclic aromatic hydrocarbons. *Environmental Pollution, 133,* 293-301.

Pozo, K., Mabilia, R., & Focardi, S. (2012). Survey of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of rural, urban and industrial areas of Concepcion, Chile, using passive air samplers. *Atmospheric Pollution Research, 3,* 426-434.

Pozo, K., Harner, T., Lee, S.C., Sinha, R.K., Sengupta, B., Loewen, M., et al. (2011). Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers. *Environmental Pollution, 159,* 646-653.

Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., & Parra, O. (2004). Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environmental Science & Technology, 38,* 6529-6537.

Pribylova, P., Kares, R., Boruvkova, J., Cupr, P., Prokes, R., & Kohoutek, J. (2012). Levels of persistent organic pollutants and polycyclic aromatic hydrocarbons in ambient air of Central and Eastern Europe. *Atmospheric Pollution Research, 3,* 494-505.

Ratola, N., Alves, A., Santos, L., & Lacorte, S. (2011a). Pine needles as passive bio-samplers to determine polybrominated diphenyl ethers. *Chemosphere, 85,* 247-252.

Ratola, N., Amigo, J.M., Oliveira, M.S.N., Araujo, R., Silva, J.A., & Alves, A. (2011b). Differences between Pinus pinea and Pinus pinaster as bioindicators of polycyclic aromatic hydrocarbons. *Environmental and Experimental Botany, 72*, 339-347.

Ratola, N., Amigo, J.M., & Alves, A. (2010a). Comprehensive assessment of pine needles as bioindicators of PAHs using multivariate analysis: The importance of temporal trends. *Chemosphere, 81*, 1517-1525.

Ratola, N., Amigo, J.M., & Alves, A. (2010b). Levels and sources of PAHs in selected sites from Portugal: Biomonitoring with Pinus pinea and Pinus pinaster needles. *Archives of Environmental Contamination and Toxicology, 58,* 631-647.

Ratola, N., Lacorte, S., Barcelo, D., & Alves, A. (2009). Microwave-assisted extraction and ultrasonic extraction to determine polycyclic aromatic hydrocarbons in needles and bark of *Pinus pinaster Ait*. and *Pinus pinea L*. by GC-MS. *Talanta, 77,* 1120-1128.

Ratola, N., Alves, A., Kalogerakis, N., & Psillakis, E. (2008). Hollow-fibre liquid-phase microextraction: A simple and fast cleanup step used for PAHs determination in pine needles. *Analytica Chimica Acta, 618,* 70-78.

Ratola, N., Lacorte, S., Alves, A., & Barcelo, D. (2006). Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography–mass spectrometry–comparison of different extraction and clean–up procedures. *Journal of Chromatography A, 1114*, 198–204.

Rauert, C., & Harner, T. (2016). A preliminary investigation into the use of Red Pine (*Pinus Resinosa*) tree cores as historic passive samplers of POPs in outdoor air. *Atmospheric Environment, 140*, 514-518.

Rhind, S.M., Kyle, C.E., Kerr, C., Osprey, M., Zhang, Z.L., Duff, E.I., et al. (2013). Concentrations and geographic distribution of selected organic pollutants in Scottish surface soils. *Environmental Pollution 182*, 15–27.

Ritter, L., Solomon, K.R., Forget, J., Stemeroff, M., & O'Leary, C. (2007). *Persistent organic pollutants.* United Nations Environment Programme. Retrieved September 09, 2007 from http://yosemite.epa.gov.

Ruge, Z., Muir, D., Helm, P., & Lohmann, R. (2015). Concentrations, trends, and air-water exchange of PAHs and PBDEs derived from passive samplers in Lake Superior in 2011. *Environmental Science & Technology*, 49, 13777–13786.

Ruzickova, P., Klanova, J., Cupr, P., Lammel, G., & Holoubek, I. (2008). An assessment of air-soil exchange of polychlorinated biphenyls and organochlorine pesticides across Central and Southern Europe. *Environmental Science & Technology, 42,* 179-185.

Salamova, A., & Hites, R.A. (2010). Evaluation of tree bark as a passive atmospheric sampler for flame retardants, PCBs, and organochlorine pesticides. *Environmental Science & Technology, 44*, 6196-6201.

Shoeib, M., & Harner, T. (2002). Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. *Environmental Toxicology and Chemistry, 21*, 984-990.

Schroll, R., Bierling, B., Cao, G., Dorfler, U., Lahaniati, M., Langenbach, T., et al. (1994). Uptake pathways of organic chemicals from soil by agricultural plants. *Chemosphere*, *28*, 297-303.

Schuhmacher, M., Nadal, M., & Domingo, J.L. (2004). Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation in an area with chemical and petrochemical industries. *Environmental Science & Technology, 38,* 1960-1969.

Schulz, H., Popp, P., Huhn, G., Stark, H.J., & Schuurmann, G. (1999). Biomonitoring of airborne inorganic and organic pollutants by means of pine tree barks. I. Temporal and spatial variations. *Science of the Total Environment, 232,* 49–58.

Simonich, S.L. & Hites, R.A. (1995). Organic pollutant accumulation in vegetation. *Environmental Science & Technology, 29,* 2905-2914.

Simonich, S.L., & Hites, R.A. (1994). Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. *Nature, 370*, 49-51.

Singh, D.P., Gadi, R., & Mandal, T.K. (2010). Emissions of polycyclic aromatic hydrocarbons in the atmosphere: An Indian perspective, *Human and Ecological Risk Assessment, 16,* 1145-1168.

Smith, K.E.C., & Jones, K.C. (2000). Particles and vegetation: Implications for the transfer of particle-bound organic contaminants to vegetation. *Science of the Total Environment, 246*, 207–236.

Sofuoglu, S.C., Sofuoglu, A., Holsen, T.M., Alexander, C.M., & Pagano, J.J. (2013). Atmospheric concentrations and potential sources of PCBs, PBDEs, and pesticides to Acadia National Park. *Environmental Pollution, 177,* 116-124.

Stockholm Convention, (2009). *The initial 12 POPs*. Retriewed October 10, 2013 fromhttp://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx

Strachan, W.M.J., Eriksson, G., Kylin, H. & Jensen, S. (1994). Organochlorine compounds in pine needles: Methods and trends. *Environmental Science & Technology, 13,* 443-451.

Su, Y., Wania, F., Harner, T., & Lei, Y.D. (2007). Deposition of polybrominated iphenyl ethers, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons to a boreal deciduous forest. *Environmental Science & Technology, 41*, 534–540.

Su, Y.S., Lei, Y.D., Daly, G.L., & Wania, F. (2002). Determination of octanol-air partition coefficient (K_{OA}) values for chlorobenzenes and polychlorinated naphthalenes from gas chromatographic retention times. *Journal of Chemical Engineering Data, 47,* 449-455.

Sun, O., Eren, M.E., & Orpak, M. (1978). T*emel ağaç türlerimizde tek ağaç ve birim alandaki odun çeşidi oranlarının saptanması*. Ankara: TUBITAK, Project Number: TOAG/288.

Taiz, L., & Zeiger, E. (2010). *Plant physiology* (Fifth Edition), ed. Sinauer Associates, USA.

Takasuga, T., Kumar, K.S., Noma, Y., & Sakai, S. (2005). Chemical characterization of polychlorinated biphenyls, -dibenzo-p-dioxins, and -dibenzofurans in technical kanechlor PCB formulations in Japan. *Archives of Environmental Contamination and Toxicology, 49*, 385-395.

Takasuga, T., Senthilkumar, K., Matsumura, T., Shiozaki, K., & Sakai, S.I. (2006). Isotope dilution analysis of polychlorinated biphenyls (PCBs) in transformer oil and global commercial PCB formulations by high resolution gas chromatography-high resolution mass spectrometry. *Chemosphere, 62*, 469-484.

Tang, L., Tang, X.Y., Zhu, Y.G., Zheng, M.H., & Miao, Q.L. (2005). Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. *Environment International, 31,* 822-828.

Tasdemir, Y., Vardar, N., Odabasi, M., & Holsen, T.M. (2004a). Concentrations and gas/particle partitioning of PCBs in Chicago. *Environmental Pollution, 131,* 35-44.

Tasdemir, Y., Odabasi, M., Vardar, N., Sofuoglu, A., Murphy, T.J., & Holsen, T.M. (2004b). Dry deposition fluxes and velocities of polychlorinated biphenyls (PCBs) associated with particles. *Atmospheric Environment, 38,* 2447-2456.

Thompson, P. L., Ramer, L. A., & Schnoor, J. L. (1998). Uptake and transformation of TNT by hybrid poplar trees. *Environmental Science & Technology*, *32* (7), 975−980.

Tolls, J., & McLachlan, M.S. (1994). Partitioning of semivolatile organic compounds between air and Lolium multiflorum (Welsh ray grass). *Environmental Science & Technology*, *28* (1), 159-166.

Tolunay, D. (2013). *Türkiye'de ağaç servetinden bitkisel kütle ve karbon miktarlarının hesaplamasında kullanılabilecek katsayılar*. Ormancılıkta Sektörel Planlamanın 50. Yılı Uluslararası Sempozyumu, Antalya.

Tolunay, D. (1992). Toprak kirlenmesi ve yanlış arazi kullanımının yarattığı sorunlar ile çözüm önerileri, *İ.Ü. Orman Fakültesi Dergisi, 42,* 57-71.

Trapp, S. (2000). Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. *Pest Management Science, 56,* 767–778.

Trapp, S., & McFarlane, J.C. (1995). *Plant contamination: Modeling and simulation of organic processes.* Lewis Publishers: Ann Arbor, MI.

Trapp, S., McFarlane, C., & Matthies, M. (1994). Model for uptake of xenobiotics into plants: Validation with bromacil experiments. *Environmental Toxicology Chemistry, 13* (3), 413-422.

Tremolada, P., Burnett, V., Calamari, D., & Jones, K.C. (1996). Spatial distribution of PAHs in the UK atmosphere using pine needles. *Environmental Science & Technology, 30* (12), 3570-3577.

United Nations Environmental Programme (UNEP), (1999). *Guidelines for the identification of PCBs and materials containing PCBs*. Retriewed September 6, 2013 from http://www.chem.unep.ch/pops/pdf/PCBident/pcbid1.pdf.

United States Environmental Protection Agency (U.S. EPA), (2008). C*ompilation of air pollutant emission factors, Volume 1: Stationary point and area sources*. Retriewed November 05, 2014 http://www.epa.gov/ttn/chief/ap42/index.html.

United States Environmental Protection Agency (U.S. EPA), (2005). *Portland harbor joint source control strategy.* Retriewed September 25, 2013 from http://www.deq.state.or.us/lq/cu/nwr/PortlandHarbor/jointsource.htm

United States Environmental Protection Agency (U.S. EPA), (2003). *Appendix A to 40CFR, Part 423-126 Priority pollutants.* Retriewed September 12, 2013 from http://www.epa.gov/region1/npdes/permits/generic/prioritypollutants.pdf.

United States Environmental Protection Agency (U.S. EPA), (2002a). *The foundation for global action on persistent organic pollutants: A United States perspective. EPA/600/P-01/003F, NCEA-I-1200.* Retrieved March 2002, from http://www.epa.gov/NCEA/pdfs/pops/POPsa.pdf.

United States Environmental Protection Agency (U.S. EPA), (1996). *PCBs: Cancer dose response assessment and application to environmental mixtures* – Retriewed September 16, 2013 from http://www.epa.gov/pcb/pubs/pcb.pdf

Vallack, H.W., Bakker, D.J., Brandt, I., Brostrom-Lunden, E., Brouwer, A., Bull, K.R., et al. (1998). Controlling persistent organic pollutants - What next?, *Environmental Toxicology and Pharmacology, 6*, 143-175.

Vilavert, L., Nadal, M., Schuhmacher, M., & Domingo, J.L. (2014). Seasonal surveillance of airborne PCDD/Fs, PCBs and PCNs using passive samplers to assess human health risks. *Science of the Total Environment, 466–467,* 733-740.

Wagrowski, D.M., & Hites, R.A. (1997). Polycyclic aromatic hydrocarbon accumulation in urban, suburban, and rural vegetation. *Environmental Science & Technology, 31* (1), 279-282.

Wang, X.P., Sheng, J.J., Gong, P., Xue, Y.G., Yao, T.D., & Jones, K.C. (2012b). Persistent organic pollutants in the Tibetan surface soil: Spatial distribution, air-soil exchange and implications for global cycling. *Environmental Pollution, 170,* 145-151.

Wang, D.G., Tian, F.L., Yang, M., Liu, C.L., & Li, Y.F. (2009). Application of positive matrix factorization to identify potential sources of PAHs in soil of Dalian, China. *Environmental Pollution, 157,* 1559-1564.

Wang, Q.Q., Zhao, Y.L., Yan, D., Yang, L.M., Li, Z.J., & Huang, B.L. (2004). Historical records of airborne polycyclic aromatic hydrocarbons by analyzing dated corks of the bark pocket in a Longpetiole Beech tree. *Environmental Science & Technology, 38,* 4739-4744.

Wang, M., & Jones, K. C. (1994). Uptake of chlorobenzenes by carrots from spiked and sewage sludge-amended soil. *Environmental Science & Technology, 28,* 1260-1267.

Weiss, P., Offenthaler, I., Ohlinger, R., & Wimmer., J. (2003). Chapter 13: Higher plants as accumulative bioindicators. *Bioindicators & Biomonitors — Principles, Concepts and Applications, 6,* 465-500.

Weiss, P. (1998). *Umweltbundesamt, Bundesministerium für Umwelt, Jugend und Familie,* Vienna, Austria.

Welsch-Pausch, K., McLachlan, M.S., & Umlauf, G. (1995). Determination of the principal pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans to Lolium multiflorum (Welsh Ray Grass). *Environmental Science & Technology, 29*, 1090–1098.

Wen, S., Yang, F., Li, J.G., Gong, Y., Zhang, X.L., & Hui, Y. (2009). Polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs) monitored by tree bark in an e-waste recycling area. *Chemosphere, 74*, 981-987.

Wilcke, W., Krauss, M., Safronov, G., Fokin, A.D., & Kaupenjohann, M. (2006). Polychlorinated biphenyls (PCBs) in soils of the Moscow region: Concentrations and small-scale distribution along an urban-rural transect. *Environmental Pollution, 141,* 327-335.

Wilczynski, S. (2006). The variation of tree-ring widths of Scots pine (Pinus sylvestris L.) affected by air pollution. *European Journal of Forest Research*, *125,* 213-219.

Wild, S.R., & Jones, K.C. (1991). Studies on the polynuclear aromatic hydrocarbon content of carrots (Daucus carota). *Chemosphere, 23* (2), 243-251.

Wimmer, R. (1997). H*ava kirliliğinin ekolojisi, zararlı maddelerin bitkiler üzerindeki etkisi*. Ders notu, Toprak Kültürü Üniversitesi, Çevre ve Doğa Koruma Merkezi, Viyana.

Wong, A., Lei, Y.D., Alaee, M., & Wania, F. (2001). Vapor pressures of the polybrominated diphenyl ethers. *Journal of Chemical Engineering Data*, *46,* 239-242.

World Steel Association, (2015). Steel Statistical Yearbook 2015. Retriewed September 16, 2015 from http://www.worldsteel.org/

Wyrzykowska, B., Hanari, N., Orlikowska, A., Bochentin, I., Rostkowski, P., Falandysz, J., et al. (2007). Polychlorinated biphenyls and -naphthalenes in pine needles and soil from Poland: Concentrations and patterns in view of long-term environmental monitoring. *Chemosphere, 67* (9), 1877-1886.

Wyrzykowska, B., Bochentin, I., Hanari, N., Orlikowska, A., Falandysz, J., Yuichi, H., et al. (2006). Source determination of highly chlorinated biphenyl isomers in pine needles: Comparison to several PCB preparations. *Environmental Pollution, 143* (1), 46−59.

Xu, D.D., Deng, L.L., Chai, Z.F., & Mao, X.Y. (2004). Organohalogenated compounds in pine needles from Beijing city, China. *Chemosphere, 57*, 1343-1353.

Yin, H., Tan, Q., Chen, Y., Lu, G., & Hou, X.D. (2011a). Polycyclic aromatic hydrocarbons (PAHs) pollution recorded in annual rings of gingko (Gingko biloba L.): Determination of PAHs by GC/MS after accelerated solvent extraction. *Microchemical Journal, 97,* 138–143.

Yin, H., Tan, Q., Chen, Y., Lu, G., He, D.H., & Hou, X.D. (2011b). Polycyclic aromatic hydrocarbons (PAHs) pollution recorded in annual rings of gingko (Gingko biloba L.): Translocation, radial diffusion, degradation and modeling. *Microchemical Journal, 97,* 131–137.

Zhang, Y., Lin, Y., Cai, J., Liu, Y., Hong, L., Qin, M., et al. (2016). Atmospheric PAHs in North China: Spatial distribution and sources. *Science of the Total Environment, 565,* 994 – 1000.

Zhang, J., Yang, J.C., Wang, R.Q., Hou, H., Du, X.M., Fan, S.K., et al. (2013). Effects of pollution sources and soil properties on distribution of polycyclic aromatic hydrocarbons and risk assessment. *Science of the Total Environment, 463–464*, 1–10.

Zhang, H.B., Luo, Y.M., Wong, M.H., Zhao, Q.G., & Zhang, G.L. (2006). Distributions and concentrations of PAHs in Hong Kong soils. *Environmental Pollution, 141,* 107-114.

Zhao, Y.L., Yang, L.M., & Wang, Q.Q. (2008). Modeling persistent organic pollutant (POP) partitioning between tree bark and air and its application to spatial monitoring of atmospheric POPs in mainland China. *Environmental Science & Technology, 42,* 6046-6051.

Zhao, Y., Wang, Q., Satake, K., & Tsunoda, K.I. (2006). Alternative normalization method of atmospheric polycyclic aromatic hydrocarbons pollution level recorded by tree bark. *Environmental Science & Technology, 40,* 5853-5859.

Zhou, L., Dong, L., Huang, Y.R., Shi, S.X., Zhang, L.F., Zhang, X.L., et al. (2015). Tree bark as a biomonitor for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers from Southern Jiangsu, China: Levels, distribution, and possible sources. *Environmental Monitoring Assessment, 187,* 603.

Zhou, L., Dong, L., Huang, Y., Shi, S., Zhang, L., Zhang, X., et al. (2014). Spatial distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in Camphor (*Cinnamomum camphora*) tree bark from Southern Jiangsu, China. *Chemosphere 107,* 297–303.

Zhu, L.Y., & Hites, R.A. (2006). Brominated flame retardants in tree bark from North America. *Environmental Science & Technology, 40* (12), 3711−3716.

Zou, M.Y., Ran, Y., Gong, J., Maw, B.X., & Zeng, E.Y. (2007). Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: Occurrence, inventory, and fate. *Environmental Science & Technology, 41*, 8262-8267.

APPENDICES

APPENDIX-1: Moisture Contents of Samples

Table A1.1: Moisture contents of tree components, soil and litter samples in Iskenderun

Iskenderun	Tree species	Moisture Content (%)						
		1-year needle	2-year needle	Bark	Branch	Litter	Stem	Soil
N-1	*Pinus brutia*	53.2	50.6	6.6	52.7	10.6	28.5	16.0
N-2	*Pinus brutia*	51.8	48.5	6.3	53.5	8.9	32.5	13.4
N-3	*Pinus brutia*	53.0	50.8	7.5	55.1	12.1	37.8	15.6
N-4	*Pinus brutia*	52.8	48.8	6.2	50.4	8.4	18.1	10.5
N-5	*Pinus brutia*	52.2	49.3	8.1	53.6	13.1	45.2	13.1
N-6	*Pinus brutia*	53.6	51.2	7.3	51.7	10.0	32.6	5.0
N-7	*Pinus brutia*	56.9	55.6	7.5	51.8	16.0	35.9	14.5
N-8	*Pinus brutia*	51.8	47.9	6.8	55.2	8.7	33.2	11.1
N-9	*Pinus pinea*	61.6	58.4	9.1	56.0	11.1	39.4	9.3
N-10	*Pinus brutia*	49.7	50.1	7.0	54.1	9.9	37.4	8.9
N-11	*Pinus brutia*	53.2	49.6	6.3	53.0	8.5	26.3	15.7
N-12	*Pinus brutia*	54.6	52.9	5.5	51.6	9.7	29.0	8.9
N-13	*Pinus pinea*	59.8	56.0	5.5	55.9	- [a]	29.3	1.2
N-14	*Pinus brutia*	53.3	51.3	7.1	50.3	10.8	21.9	8.9
N-15	*Pinus brutia*	52.9	49.7	7.0	51.6	10.3	30.6	8.8
N-16	*Pinus brutia*	49.9	48.1	6.9	52.0	7.9	31.1	11.2
N-17	*Pinus brutia*	51.9	50.9	6.3	52.6	21.9	30.4	24.8
N-18	*Pinus brutia*	52.1	45.5	7.5	52.1	8.8	27.0	8.7
N-19	*Pinus brutia*	52.6	45.4	6.1	51.5	9.2	29.6	8.3
N-20	*Pinus brutia*	53.8	52.8	8.4	55.3	10.8	32.9	9.4
N-21 (B)	*Pinus brutia*	51.7	49.5	8.1	56.1	8.8	33.4	10.9
N-22 (B)	*Pinus brutia*	52.0	50.6	7.8	54.3	-	46.0	12.1
N-23 (B)	*Pinus pinea*	58.6	57.5	7.8	55.9	-	28.3	12.1
N-24 (B)	*Pinus pinea*	58.2	53.6	8.0	58.2	9.5	40.6	6.2
N-25 (B)	*Pinus brutia*	50.9	45.1	7.8	53.2	9.5	38.2	6.2
N-26 (B)	*Pinus pinea*	60.4	56.2	8.9	53.5	11.5	36.6	10.6
N-27 (B)	*Pinus pinea*	48.9	45.3	7.0	50.9	9.2	40.0	11.5
Mean		**53.8**	**50.8**	**7.2**	**53.4**	**10.6**	**33.0**	**10.9**
S.D.		**3.31**	**3.67**	**0.93**	**2.02**	**2.97**	**6.45**	**4.38**

B: Background sites

a: There was not litter sample at this sampling site

Table A1.2: Moisture contents of tree components, soil and litter samples in Aliaga

Aliaga	Tree species	Moisture Content (%)						
		1-year needle	2-year needle	Bark	Branch	Litter	Stem	Soil
N-1	*Pinus pinea*	63.1	58.7	10.1	58.8	25.8	36.9	15.6
N-2	*Pinus pinea*	61.1	56.5	9.9	55.3	8.9	22.4	6.4
N-3	*Pinus pinea*	62.6	58.2	9.0	55.4	11.6	42.6	14.4
N-4	*Pinus pinea*	59.2	56.1	10.9	55.7	14.9	29.4	10.4
N-5/1	*Pinus pinea*	56.1	51.6	10.7	52.7	16.7	34.8	11.6
N-5/2	*Pinus brutia*	58.7	58.0	9.8	54.3	13.4	40.2	11.8
N-6	*Pinus brutia*	56.2	51.1	9.2	55.7	14.1	42.5	18.1
N-7	*Pinus pinea*	62.5	57.6	9.7	50.4	10.5	20.6	9.1
N-8	*Pinus pinea*	64.4	59.2	9.8	52.4	10.4	23.6	13.2
N-9	*Pinus pinea*	60.8	56.6	9.8	57.0	1.5	43.3	12.1
N-10/1	*Pinus pinea*	55.1	50.9	8.3	52.5	10.8	42.9	10.0
N-10/2	*Pinus brutia*	61.2	58.5	9.6	56.3	8.3	45.1	10.9
N-11	*Pinus brutia*	55.1	51.0	7.1	53.8	7.5	44.8	11.2
N-12	*Pinus brutia*	57.2	54.1	7.9	55.9	9.5	46.7	11.2
N-13	*Pinus brutia*	58.2	51.8	6.3	50.6	10.3	36.7	14.2
N-14	*Pinus brutia*	57.5	52.8	9.7	54.0	15.9	45.7	16.4
N-15	*Pinus brutia*	56.7	53.8	7.3	48.9	13.9	20.1	15.8
N-16	*Pinus brutia*	54.7	49.5	7.2	49.4	9.2	26.4	16.8
N-17	*Pinus pinea*	63.2	58.6	8.4	57.9	13.7	50.7	13.6
N-18	*Pinus pinea*	64.4	59.0	9.9	58.9	10.1	38.7	13.8
N-19	*Pinus brutia*	56.4	50.2	7.0	50.6	15.4	38.8	11.8
N-20	*Pinus brutia*	57.9	55.1	8.5	44.0	11.0	25.1	18.4
N-21	*Pinus pinea*	81.7	58.7	10.0	54.9	9.7	60.6	4.4
N-22 (B)	*Pinus pinea*	63.3	59.0	8.4	55.5	11.8	21.2	3.5
N-23 (B)	*Pinus brutia*	55.1	53.7	8.6	51.2	9.8	38.0	4.4
N-24 (B)	*Pinus pinea*	62.3	58.1	8.0	53.7	9.1	17.6	5.0
N-25 (B)	*Pinus brutia*	58.0	53.9	8.5	51.5	8.7	36.6	12.1
N-26 (B)	*Pinus pinea*	61.5	57.6	8.9	53.5	11.2	46.8	10.2
N-27 (B)	*Pinus brutia*	57.9	54.2	8.5	52.5	7.8	20.8	6.8
Mean		**60.1**	**55.3**	**8.9**	**53.6**	**11.4**	**35.9**	**11.5**
S.D.		**5.2**	**3.2**	**1.2**	**3.2**	**4.2**	**11.0**	**4.1**

B: Background sites

APPENDIX-2: Lipid Contents of Samples

Table A2.1: Lipid contents of tree components and litter samples in Iskenderun

Iskenderun	Tree species	Lipid Content (%) (Dry Weight)					
		1-year needle	2-year needle	Bark	Branch	Litter	Stem
N-1	*Pinus brutia*	4.48	0.50	0.89	3.60	1.99	2.99
N-2	*Pinus brutia*	4.27	2.45	8.49	3.48	1.54	1.65
N-3	*Pinus brutia*	2.35	2.85	1.49	2.12	2.84	2.24
N-4	*Pinus brutia*	6.09	4.58	1.44	3.61	2.14	12.42
N-5	*Pinus brutia*	2.50	2.63	2.04	2.81	0.88	1.68
N-6	*Pinus brutia*	5.71	2.71	1.30	2.97	2.25	7.77
N-7	*Pinus brutia*	4.55	2.52	1.58	2.29	1.03	2.21
N-8	*Pinus brutia*	3.76	4.15	0.82	3.09	2.76	4.05
N-9	*Pinus pinea*	1.03	1.58	2.93	2.85	0.76	2.65
N-10	*Pinus brutia*	3.44	2.38	2.36	2.55	3.78	3.15
N-11	*Pinus brutia*	2.94	3.07	1.11	1.93	2.16	14.70
N-12	*Pinus brutia*	6.64	1.88	4.88	3.89	4.16	5.56
N-13	*Pinus pinea*	1.93	4.93	1.29	3.85	- [a]	2.56
N-14	*Pinus brutia*	4.38	1.42	0.87	2.68	1.63	3.07
N-15	*Pinus brutia*	3.06	2.55	0.95	2.46	4.83	18.49
N-16	*Pinus brutia*	3.21	3.16	1.14	2.85	2.61	2.06
N-17	*Pinus brutia*	5.26	4.70	0.63	2.91	1.56	1.60
N-18	*Pinus brutia*	6.47	5.50	1.15	3.39	1.44	8.58
N-19	*Pinus brutia*	5.65	4.50	0.88	2.95	3.22	1.97
N-20	*Pinus brutia*	3.16	5.82	1.34	3.98	3.65	11.23
N-21 (B)	*Pinus brutia*	6.94	1.05	1.67	2.90	2.77	3.33
N-22 (B)	*Pinus brutia*	3.50	5.27	1.93	1.92	1.71	2.02
N-23 (B)	*Pinus pinea*	3.14	0.11	0.77	2.30	1.71	7.89
N-24 (B)	*Pinus pinea*	2.37	0.76	0.96	1.93	1.77	4.36
N-25 (B)	*Pinus brutia*	5.42	6.07	0.80	2.20	1.77	1.72
N-26 (B)	*Pinus pinea*	1.47	0.89	0.54	2.27	1.40	2.23
N-27 (B)	*Pinus pinea*	3.57	4.29	0.64	2.44	1.94	3.60
Mean		**3.97**	**3.05**	**1.66**	**2.82**	**2.24**	**5.03**
S.D.		**1.62**	**1.73**	**1.63**	**0.63**	**1.02**	**4.48**

a: There was not litter sample at this sampling site

B: Background sites

Table A2.2: Lipid contents of tree components and litter samples in Aliaga

Aliaga	Tree species	Lipid Content (%) (Dry Weight)					
		1-year needle	2-year needle	Bark	Branch	Litter	Stem
N-1	*Pinus pinea*	1.46	2.01	1.62	3.54	1.39	4.23
N-2	*Pinus pinea*	2.71	0.86	1.48	2.29	2.03	19.52
N-3	*Pinus pinea*	1.28	1.29	6.46	3.39	1.08	3.86
N-4	*Pinus pinea*	1.61	4.66	14.17	4.54	1.14	19.43
N-5/1	*Pinus pinea*	1.10	1.55	0.66	3.18	1.57	13.24
N-5/2	*Pinus brutia*	5.60	7.22	15.57	2.98	0.81	2.32
N-6	*Pinus brutia*	7.16	5.71	1.68	2.56	0.83	2.80
N-7	*Pinus pinea*	1.02	1.20	2.05	1.31	1.22	24.92
N-8	*Pinus pinea*	4.81	1.60	1.34	5.13	2.94	1.05
N-9	*Pinus pinea*	1.02	1.73	1.86	4.66	0.84	2.62
N-10/1	*Pinus pinea*	1.52	1.37	2.00	3.93	1.52	2.86
N-10/2	*Pinus brutia*	5.45	5.88	1.47	3.15	2.79	3.89
N-11	*Pinus brutia*	4.67	3.67	1.33	2.14	1.10	2.17
N-12	*Pinus brutia*	6.18	5.53	1.39	4.50	1.63	2.12
N-13	*Pinus brutia*	5.40	4.03	1.58	1.87	1.59	51.83
N-14	*Pinus brutia*	4.24	5.49	1.37	2.37	2.77	3.12
N-15	*Pinus brutia*	7.97	6.27	0.74	4.40	2.46	8.61
N-16	*Pinus brutia*	5.31	3.74	0.95	3.86	2.58	16.87
N-17	*Pinus pinea*	0.57	1.24	7.15	2.95	3.12	1.69
N-18	*Pinus pinea*	1.96	1.36	4.27	3.48	1.43	4.14
N-19	*Pinus brutia*	6.02	3.44	1.39	3.13	0.83	17.60
N-20	*Pinus brutia*	7.21	8.41	1.22	2.61	0.98	13.13
N-21	*Pinus pinea*	1.07	3.40	1.15	1.65	0.97	16.84
N-22 (B)	*Pinus pinea*	1.24	1.99	1.54	4.34	12.09	4.70
N-23 (B)	*Pinus brutia*	5.88	5.47	0.88	3.18	3.20	11.26
N-24 (B)	*Pinus pinea*	5.36	0.73	1.60	2.00	1.47	44.91
N-25 (B)	*Pinus brutia*	4.58	3.36	2.98	3.19	2.34	16.58
N-26 (B)	*Pinus pinea*	0.95	1.27	0.94	3.50	4.24	31.80
N-27 (B)	*Pinus brutia*	5.62	4.10	0.66	6.15	2.64	32.64
Mean		**3.76**	**3.40**	**2.81**	**3.31**	**2.19**	**13.13**
S.D.		**2.36**	**2.15**	**3.68**	**1.11**	**2.10**	**13.36**

B: Background sites

APPENDIX-3: 16-PAH Congener's Concentrations of Samples

Table A3.1: 16-PAH congener's concentrations of ambient air samples in Iskenderun and Aliaga (ng/m^3)

AMBIENT AIR	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	3.1	2.5	0.4	0.3	5.1	10.9	1.7	1.7
Acenaphthene	2.7	1.7	0.7	0.4	2.1	1.1	1.2	1.3
Fluorene	20.4	10.6	7.1	2.8	15.0	8.9	6.7	2.7
Phenanthrene	71.0	44.3	13.1	5.3	54.0	50.2	14.5	8.9
Anthracene	4.8	4.9	0.3	0.2	2.7	4.9	0.6	0.8
Carbazole	2.5	1.3	0.3	0.2	0.9	1.1	0.1	0.02
Fluoranthene	26.3	16.1	3.9	1.4	20.5	25.2	3.4	1.6
Pyrene	15.3	11.5	1.7	0.7	13.6	20.4	1.8	1.2
Benz(a)anthracene	3.2	4.2	0.2	0.1	0.7	0.5	0.1	0.1
Chrysene	5.2	4.9	0.5	0.2	1.8	1.2	0.3	0.1
Benzo(b)fluoranthene	2.8	3.6	0.3	0.1	0.6	0.3	n.d.	n.d.
Benzo(k)fluoranthene	3.0	4.5	0.2	0.1	5.4	15.7	n.d.	n.d.
Benzo(a)pyrene	2.4	4.1	0.1	0.04	0.2	0.1	0.1	0.1
Indeno(1,2,3-cd)pyrene	2.6	4.1	0.1	0.1	0.3	0.2	0.1	0.02
Dibenz(a,h)anthracene	2.4	3.8	0.2	0.1	0.1	0.1	0.02	0.02
Benzo(g,h,i)perylene	3.0	4.0	0.3	0.1	0.3	0.3	0.1	0.02
ΣPAHs	170	101	29	12	120	123	31	18

n.d. : Not detected

Table A3.2: 16-PAH congener's concentrations of 1-year needle samples in Iskenderun and Aliaga (μg/kg)

1-YEAR NEEDLE	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	22.0	16.9	9.2	7.8	8.4	12.3	1.5	0.9
Acenaphthene	41.7	27.0	10.7	14.6	15.2	13.0	2.6	1.7
Fluorene	83.6	78.1	17.5	13.8	38.1	26.5	13.2	7.1
Phenanthrene	457	434	39.9	26.3	349	215	156	50.5
Anthracene	31.7	64.5	3.7	1.5	22.1	13.7	7.0	2.8
Carbazole	17.8	40.3	1.1	1.2	4.2	6.1	1.1	0.5
Fluoranthene	184	262	16.1	12.3	97.7	145	11.4	6.8
Pyrene	116	151	20.4	13.6	138	134	12.8	7.8
Benz(a)anthracene	34.9	77.8	4.0	2.3	42.6	24.4	14.4	10.5
Chrysene	113	162	9.8	5.9	241	107	123	26.9
Benzo(b)fluoranthene	24.0	29.3	2.5	1.1	22.0	17.2	3.9	2.0
Benzo(k)fluoranthene	20.1	31.5	1.6	0.8	10.3	10.2	1.7	0.6
Benzo(a)pyrene	6.5	6.2	2.6	0.7	17.6	7.6	7.6	3.6
Indeno(1,2,3-cd)pyrene	4.1	4.3	1.1	0.4	4.5	3.9	1.0	0.3
Dibenz(a,h)anthracene	0.8	0.7	0.2	n.d.	2.3	1.4	0.9	0.3
Benzo(g,h,i)perylene	3.3	2.5	1.0	0.4	3.6	3.1	0.8	0.2
ΣPAHs	1158	1334	136	60	1016	684	358	101

n.d.: Not detected

Table A3.3: 16-PAH congener's concentrations of 2-year needle samples in Iskenderun and Aliaga (μg/kg)

2-YEAR NEEDLE	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	27.0	16.8	10.7	3.6	21.2	19.4	2.2	1.1
Acenaphthene	51.3	33.7	16.7	13.9	25.5	25.3	3.8	1.9
Fluorene	224	175	28.3	19.8	99.7	98.1	26.7	14.0
Phenanthrene	1214	1024	147	116	866	805	239	95.3
Anthracene	67.8	111	7.1	3.5	38.6	39.4	10.4	4.6
Carbazole	14.0	23.2	3.7	6.3	6.7	7.5	1.4	0.7
Fluoranthene	418	489	34.9	30.3	272	392	23.5	12.0
Pyrene	218	250	27.5	19.3	270	296	29.5	17.5
Benz(a)anthracene	47.4	85.1	5.3	3.0	67.1	60.8	15.4	8.1
Chrysene	210	250	21.5	16.9	391	362	137	54.9
Benzo(b)fluoranthene	31.0	38.2	3.6	2.2	37.3	40.6	4.9	2.4
Benzo(k)fluoranthene	26.1	33.0	2.5	1.2	19.2	22.8	2.0	0.8
Benzo(a)pyrene	7.4	7.3	4.5	1.3	24.2	11.2	8.8	3.0
Indeno(1,2,3-cd)pyrene	5.2	4.9	1.0	0.4	6.8	9.3	1.1	0.3
Dibenz(a,h)anthracene	1.2	1.2	0.4	0.1	3.8	3.1	1.3	0.4
Benzo(g,h,i)perylene	4.9	4.9	1.4	0.8	7.0	8.7	1.2	0.4
ΣPAHs	2567	2445	299	200	2157	2098	509	188

Table A3.4: 16-PAH congener's concentrations of bark samples in Iskenderun and Aliaga (μg/kg)

BARK	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	3.8	1.7	2.2	2.6	2.8	1.5	2.1	1.2
Acenaphthene	2.4	1.9	2.6	1.9	7.1	4.6	7.6	4.2
Fluorene	13.3	6.2	8.3	3.8	12.5	8.1	14.8	8.6
Phenanthrene	82.3	56.8	16.0	9.8	59.7	39.5	48.0	29.6
Anthracene	7.5	5.6	1.9	0.9	2.7	2.9	0.8	0.5
Carbazole	6.0	8.2	0.6	0.6	2.6	2.0	0.7	0.2
Fluoranthene	54.0	52.5	6.6	3.6	32.9	24.6	9.9	3.9
Pyrene	36.1	36.7	6.7	5.7	26.5	15.3	10.9	2.7
Benz(a)anthracene	15.2	22.9	0.9	0.7	5.9	7.6	0.2	0.3
Chrysene	28.0	35.5	1.5	1.5	17.2	17.8	0.9	0.5
Benzo(b)fluoranthene	24.2	35.3	1.6	1.2	10.3	11.3	1.0	0.3
Benzo(k)fluoranthene	18.8	29.4	1.4	1.3	6.3	6.9	0.6	0.2
Benzo(a)pyrene	18.0	28.8	1.0	1.0	8.7	10.3	1.1	0.5
Indeno(1,2,3-cd)pyrene	16.2	27.6	1.0	0.8	5.3	6.6	0.6	0.2
Dibenz(a,h)anthracene	3.9	5.7	0.4	0.3	2.2	3.3	0.2	0.1
Benzo(g,h,i)perylene	15.7	26.1	1.1	0.8	7.5	11.6	1.0	0.2
ΣPAHs	345	350	50.6	30.8	210	157	100	50.7

Table A3.5: 16-PAH congener's concentrations of branch samples in Iskenderun and Aliaga (μg/kg)

BRANCH	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	8.8	3.5	7.6	3.6	9.4	5.0	4.4	2.5
Acenaphthene	9.4	6.9	9.8	4.1	11.1	5.8	7.6	4.1
Fluorene	37.1	19.1	28.3	17.7	17.6	9.8	12.4	10.6
Phenanthrene	73.3	51.2	43.5	17.5	67.6	73.7	22.7	20.2
Anthracene	6.5	3.9	4.6	2.8	3.6	5.2	0.8	0.6
Carbazole	1.8	3.0	0.3	0.2	1.8	1.8	0.4	0.2
Fluoranthene	18.0	19.2	2.7	0.9	24.1	29.2	2.9	2.4
Pyrene	8.6	10.4	2.0	1.7	36.0	35.4	4.3	2.4
Benz(a)anthracene	1.5	0.9	0.7	0.4	5.7	10.6	0.7	0.5
Chrysene	5.0	4.4	1.3	1.1	25.6	56.0	2.5	1.1
Benzo(b)fluoranthene	1.3	0.8	0.4	0.03	2.5	1.7	0.6	0.1
Benzo(k)fluoranthene	1.1	0.6	0.5	0.2	1.3	0.8	0.3	0.04
Benzo(a)pyrene	0.7	0.4	0.2	0.1	1.7	0.9	0.6	0.2
Indeno(1,2,3-cd)pyrene	0.4	0.3	0.1	0.1	0.8	0.4	0.3	0.1
Dibenz(a,h)anthracene	0.3	0.1	0.1	n.d.	0.4	0.3	0.1	0.1
Benzo(g,h,i)perylene	0.6	0.4	0.2	0.1	1.2	0.6	0.4	0.1
ΣPAHs	174	104	92.4	54.9	204	193	55.8	40.4

n.d.: Not detected

Table A3.6: 16-PAH congener's concentrations of litter samples in Iskenderun and Aliaga (μg/kg)

LITTER	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	16.7	10.4	5.8	3.0	13.6	6.9	5.5	2.3
Acenaphthene	11.7	5.9	6.1	4.9	14.5	9.8	6.3	3.7
Fluorene	28.4	20.1	8.1	4.7	31.9	26.2	7.8	3.7
Phenanthrene	629	467	73.4	39.6	276	202	54.8	32.2
Anthracene	42.8	49.1	3.4	1.1	12.7	12.6	1.2	0.5
Carbazole	19.1	31.3	4.4	2.7	5.2	5.2	0.5	0.4
Fluoranthene	359	444	30.1	20.6	176	143	11.6	7.3
Pyrene	192	189	23.7	11.0	131	94.6	12.8	3.8
Benz(a)anthracene	71.3	94.8	4.4	3.6	35.0	40.1	2.0	1.4
Chrysene	254	284	19.8	14.4	159	149	4.0	1.9
Benzo(b)fluoranthene	75.1	89.6	7.1	6.4	51.4	57.0	1.6	0.8
Benzo(k)fluoranthene	57.3	69.0	6.1	4.8	31.8	31.6	0.9	0.5
Benzo(a)pyrene	39.9	48.9	2.9	3.4	35.6	44.0	1.9	1.1
Indeno(1,2,3-cd)pyrene	39.2	50.1	3.2	2.7	24.2	29.9	1.1	0.5
Dibenz(a,h)anthracene	8.6	12.9	0.7	0.5	7.5	13.6	0.3	0.1
Benzo(g,h,i)perylene	36.6	46.7	3.9	3.8	22.5	32.0	0.9	0.5
ΣPAHs	1881	1786	203	106	1027	795	111	31.0

Table A3.7: 16-PAH congener's concentrations of soil samples in Iskenderun and Aliaga (μg/kg)

SOIL	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	19.8	16.4	4.0	3.6	3.5	2.6	0.9	0.1
Acenaphthene	25.8	60.3	8.4	5.7	5.7	3.5	1.9	0.2
Fluorene	61.4	36.6	49.3	20.7	15.4	7.2	7.6	0.4
Phenanthrene	257	530	44.0	20.2	54.7	44.0	22.9	0.7
Anthracene	56.3	106	9.0	2.6	7.1	8.3	1.3	0.7
Carbazole	20.0	50.7	0.8	0.4	3.2	2.6	0.5	0.1
Fluoranthene	406	1085	6.0	4.3	42.4	46.0	3.3	0.9
Pyrene	333	909	3.9	3.6	35.0	41.1	1.9	0.6
Benz(a)anthracene	336	1008	2.6	3.3	25.5	35.0	0.9	0.2
Chrysene	381	1011	5.6	4.1	53.2	67.0	4.5	1.9
Benzo(b)fluoranthene	412	1123	6.2	3.7	42.7	50.1	5.0	1.8
Benzo(k)fluoranthene	301	811	4.5	3.0	28.6	31.4	3.7	1.3
Benzo(a)pyrene	334	950	3.4	3.2	29.6	40.0	1.7	0.4
Indeno(1,2,3-cd)pyrene	310	794	4.5	2.8	28.1	32.5	2.9	0.9
Dibenz(a,h)anthracene	88.7	198	1.1	0.8	10.1	16.8	0.5	0.1
Benzo(g,h,i)perylene	317	761	5.3	3.4	40.1	53.8	2.8	0.8
ΣPAHs	3660	9433	159	53.9	407	467	51.2	14.9

Table A3.8: 16-PAH congener's concentrations of stem samples in Iskenderun and Aliaga (μg/kg)

STEM	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Acenaphthylene	21.8	9.2	17.4	16.6	28.5	37.8	12.9	4.0
Acenaphthene	56.7	27.3	68.8	67.0	87.5	174	40.5	8.9
Fluorene	81.4	90.0	89.1	75.0	157	260	94.1	33.0
Phenanthrene	182	327	224	160	885	1262	619	257
Anthracene	25.2	50.5	23.5	18.3	131	201	90.4	34.2
Carbazole	3.1	3.8	3.5	1.8	20.6	20.6	10.1	4.4
Fluoranthene	29.8	37.6	28.9	20.6	94.2	126.2	70.9	28.8
Pyrene	57.2	109.2	50.4	46.9	336	500	237	94.2
Benz(a)anthracene	17.2	43.9	12.9	16.0	130	202	87.7	32.4
Chrysene	74.5	232.0	66.2	98.6	591	800	432	168
Benzo(b)fluoranthene	8.1	18.0	7.0	7.1	44.3	66.6	33.3	13.1
Benzo(k)fluoranthene	3.4	6.2	2.4	2.1	13.3	19.7	10.6	4.6
Benzo(a)pyrene	4.9	7.8	2.7	2.2	29.8	30.4	15.4	6.1
Indeno(1,2,3-cd)pyrene	2.1	1.6	1.5	1.3	3.6	5.6	3.0	1.1
Dibenz(a,h)anthracene	3.0	2.1	2.1	1.4	7.5	10.4	6.2	2.9
Benzo(g,h,i)perylene	2.5	1.9	1.5	1.4	5.4	7.1	3.0	0.8
ΣPAHs	573	908	602	384	2565	3686	1767	673

APPENDIX-4: 41-PCB Congener's Concentrations of Samples

Table A4.1: 41-PCB congener's concentrations of ambient air samples in Iskenderun and Aliaga (ng/m^3)

AMBIENT AIR	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	0.241	0.126	0.024	0.019	0.335	0.261	0.031	0.017
PCB-17	0.080	0.044	0.009	0.008	0.123	0.097	0.010	0.004
PCB-31	0.163	0.091	0.016	0.014	0.216	0.174	0.017	0.006
PCB-28	0.189	0.102	0.020	0.014	0.281	0.229	0.020	0.008
PCB-33	0.142	0.077	0.015	0.012	0.189	0.149	0.013	0.005
PCB-52	0.118	0.061	0.014	0.010	0.144	0.115	0.011	0.003
PCB-49	0.073	0.038	0.009	0.007	0.092	0.074	0.008	0.003
PCB-44	0.094	0.049	0.010	0.006	0.116	0.096	0.009	0.004
PCB-74	0.036	0.020	0.007	0.001	0.048	0.040	0.004	0.002
PCB-70	0.072	0.042	0.008	0.006	0.093	0.079	0.008	0.002
PCB-95	0.052	0.028	0.006	0.005	0.060	0.049	0.004	0.001
PCB-101	0.074	0.042	0.008	0.007	0.089	0.071	0.007	0.001
PCB-99	0.023	0.013	0.003	0.002	0.027	0.020	0.002	0.000
PCB-87	0.031	0.017	0.005	0.003	0.037	0.029	0.003	0.001
PCB-110	0.051	0.030	0.006	0.005	0.064	0.052	0.005	0.001
PCB-82	0.008	0.003	0.002	n.d.	0.010	0.007	n.d.	n.d.
PCB-151	0.008	0.004	0.002	0.000	0.012	0.011	0.002	0.001
PCB-149	0.028	0.016	0.004	0.003	0.042	0.036	0.003	0.001
PCB-118	0.035	0.021	0.008	0.002	0.049	0.040	0.004	0.001
PCB-153	0.025	0.015	0.004	0.003	0.043	0.038	0.003	0.001
PCB-132	0.012	0.007	0.002	0.002	0.017	0.014	0.002	0.001
PCB-105	0.016	0.009	0.003	n.d.	0.024	0.020	0.003	0.000
PCB-138	0.028	0.017	0.005	0.002	0.047	0.040	0.003	0.000
PCB-158	0.004	0.002	0.003	0.002	0.006	0.004	n.d.	n.d.
PCB-187	0.006	0.003	0.001	0.000	0.013	0.017	0.001	n.d.
PCB-183	0.004	0.002	0.001	n.d.	0.007	0.007	n.d.	n.d.
PCB-128	0.009	0.004	0.003	n.d.	0.014	0.011	n.d.	n.d.
PCB-177	0.003	0.002	0.001	n.d.	0.006	0.006	n.d.	n.d.
PCB-171	0.003	0.001	n.d.	n.d.	0.004	0.003	n.d.	n.d.
PCB-156	0.004	0.002	n.d.	n.d.	0.007	0.005	n.d.	n.d.
PCB-180	0.009	0.005	0.002	0.001	0.020	0.022	n.d.	n.d.
PCB-191	0.001	0.000	n.d.	n.d.	0.001	0.001	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.005	0.002	0.001	n.d.	0.010	0.009	n.d.	n.d.
PCB-199	0.003	0.001	n.d.	n.d.	0.005	0.006	n.d.	n.d.
PCB-208	0.002	0.001	n.d.	n.d.	0.002	0.001	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	0.003	0.001	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	0.005	0.004	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	0.002	0.001	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	0.002	0.001	n.d.	n.d.
ΣPCBs	1.639	0.889	0.181	0.144	2.249	1.742	0.170	0.062

n.d: Not detected

Table A4.2: 41-PCB congener's concentrations of bark samples in Iskenderun and Aliaga (μg/kg)

BARK	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	0.441	0.446	0.160	0.051	0.652	0.487	0.334	0.148
PCB-17	0.212	0.191	0.088	0.028	0.359	0.283	0.168	0.104
PCB-31	0.448	0.585	0.121	0.032	0.673	0.677	0.171	0.072
PCB-28	0.648	0.824	0.152	0.035	1.128	1.233	0.312	0.165
PCB-33	0.646	0.879	0.154	0.072	0.696	0.659	0.139	0.058
PCB-52	0.346	0.421	0.110	0.044	0.533	0.442	0.120	0.038
PCB-49	0.236	0.258	0.066	0.027	0.353	0.306	0.075	0.028
PCB-44	0.370	0.517	0.084	0.034	0.487	0.401	n.d.	n.d.
PCB-74	0.208	0.291	0.036	n.d.	0.364	0.341	0.050	n.d.
PCB-70	0.495	0.804	0.107	0.030	0.733	0.747	0.075	0.037
PCB-95	0.209	0.331	0.043	0.022	0.410	0.370	0.109	n.d.
PCB-101	0.471	0.733	0.129	0.119	0.860	0.773	0.088	0.032
PCB-99	0.210	0.281	0.048	0.037	0.291	0.224	0.037	n.d.
PCB-87	0.275	0.440	0.064	n.d.	0.538	0.418	n.d.	n.d.
PCB-110	0.457	0.833	0.070	0.041	0.976	0.883	0.078	0.026
PCB-82	0.385	0.367	n.d.	n.d.	0.252	0.111	n.d.	n.d.
PCB-151	0.093	0.137	0.033	n.d.	0.219	0.207	n.d.	n.d.
PCB-149	0.315	0.538	0.052	0.027	0.820	0.843	0.066	0.038
PCB-118	0.580	0.999	0.090	0.030	1.137	1.047	0.080	0.017
PCB-153	0.441	0.840	0.071	0.037	1.434	1.560	0.054	0.016
PCB-132	0.185	0.332	0.047	0.009	0.470	0.475	n.d.	n.d.
PCB-105	0.311	0.545	0.060	n.d.	0.651	0.560	n.d.	n.d.
PCB-138	0.656	1.315	0.101	0.049	1.932	2.052	0.089	0.032
PCB-158	0.101	0.174	0.040	0.013	0.260	0.255	n.d.	n.d.
PCB-187	0.209	0.327	n.d.	n.d.	0.637	0.709	n.d.	n.d.
PCB-183	0.220	0.280	0.078	n.d.	0.380	0.396	n.d.	n.d.
PCB-128	0.409	0.584	n.d.	n.d.	0.792	0.665	n.d.	n.d.
PCB-177	0.453	0.563	n.d.	n.d.	0.538	0.424	n.d.	n.d.
PCB-171	0.114	n.d.	n.d.	n.d.	0.273	0.212	n.d.	n.d.
PCB-156	0.235	0.347	n.d.	n.d.	0.474	0.340	n.d.	n.d.
PCB-180	0.327	0.451	0.088	n.d.	2.120	2.786	n.d.	n.d.
PCB-191	0.065	n.d.	n.d.	n.d.	0.115	0.051	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.393	0.536	n.d.	n.d.	1.452	1.480	n.d.	n.d.
PCB-199	0.373	0.333	n.d.	n.d.	0.657	0.681	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	0.131	0.111	n.d.	n.d.
PCB-195	0.209	n.d.	n.d.	n.d.	0.289	0.247	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	0.722	0.699	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	0.103	0.036	n.d.	n.d.
PCB-206	0.255	n.d.	n.d.	n.d.	0.311	0.314	n.d.	n.d.
PCB-209	0.086	0.065	n.d.	n.d.	0.115	0.135	n.d.	n.d.
ΣPCBs	8.645	14.229	1.315	0.687	22.659	21.172	1.535	0.635

n.d.: Not detected

Table A4.3: 41-PCB congener's concentrations of litter samples in Iskenderun and Aliaga (μg/kg)

LITTER	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	4.072	1.915	0.448	0.262	3.295	3.107	0.333	0.114
PCB-17	1.369	0.633	0.196	0.095	1.709	1.700	0.141	0.046
PCB-31	3.780	1.939	0.317	0.247	3.456	3.722	0.180	0.078
PCB-28	6.082	3.327	0.374	0.298	5.756	6.338	0.280	0.145
PCB-33	3.282	1.791	0.488	0.310	2.872	3.021	0.157	0.005
PCB-52	2.904	1.627	0.321	0.242	2.889	2.673	0.179	0.069
PCB-49	1.884	1.073	0.342	0.050	1.874	1.876	0.102	0.034
PCB-44	2.357	1.475	0.258	0.140	2.701	2.696	0.181	0.014
PCB-74	1.337	0.865	0.184	0.033	1.786	2.041	0.093	0.043
PCB-70	2.655	1.775	0.215	0.223	3.843	4.307	0.153	0.056
PCB-95	1.482	1.048	0.138	0.131	2.181	2.039	0.124	0.036
PCB-101	2.637	2.012	0.229	0.224	4.662	4.266	0.172	0.047
PCB-99	0.954	0.695	0.094	0.078	1.507	1.407	0.071	0.039
PCB-87	1.254	0.991	0.185	0.117	2.154	1.966	0.337	0.199
PCB-110	2.456	2.034	0.219	0.231	4.519	4.502	0.197	0.085
PCB-82	0.490	0.329	0.068	0.028	0.860	0.649	n.d.	n.d.
PCB-151	0.331	0.294	0.092	0.024	0.921	0.923	0.045	0.004
PCB-149	1.469	1.322	0.152	0.159	3.824	3.816	0.124	0.056
PCB-118	2.502	2.309	0.298	0.276	5.336	5.528	0.147	0.063
PCB-153	1.946	1.982	0.213	0.226	6.300	6.422	0.133	0.050
PCB-132	0.671	0.701	0.137	0.060	1.833	1.741	0.070	0.005
PCB-105	1.288	1.276	0.209	0.084	2.842	3.015	n.d.	n.d.
PCB-138	2.547	2.758	0.290	0.313	7.677	7.895	0.174	0.061
PCB-158	0.336	0.321	0.055	0.023	0.863	0.824	n.d.	n.d.
PCB-187	0.528	0.481	0.157	0.104	1.958	2.424	0.081	0.003
PCB-183	0.331	0.296	0.135	0.076	1.070	1.211	0.042	0.001
PCB-128	1.073	0.965	0.248	0.138	2.297	2.067	n.d.	n.d.
PCB-177	0.374	0.367	0.121	n.d.	1.134	1.216	n.d.	n.d.
PCB-171	0.287	0.358	0.110	n.d.	0.599	0.544	n.d.	n.d.
PCB-156	0.480	0.464	0.168	n.d.	1.151	1.007	n.d.	n.d.
PCB-180	1.186	1.314	0.375	0.231	5.745	6.599	0.138	0.022
PCB-191	0.081	0.030	n.d.	n.d.	0.209	0.129	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.852	0.940	0.257	n.d.	2.934	3.079	n.d.	n.d.
PCB-199	0.277	0.232	n.d.	n.d.	1.246	1.815	n.d.	n.d.
PCB-208	0.071	0.035	n.d.	n.d.	0.261	0.280	n.d.	n.d.
PCB-195	0.166	0.129	n.d.	n.d.	0.621	0.514	n.d.	n.d.
PCB-194	0.357	0.283	0.048	n.d.	1.420	1.609	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	0.188	0.109	n.d.	n.d.
PCB-206	0.164	0.150	n.d.	n.d.	0.668	0.754	n.d.	n.d.
PCB-209	0.216	0.398	n.d.	n.d.	0.347	0.619	n.d.	n.d.
ΣPCBs	54.385	37.765	4.668	4.682	93.190	87.527	2.883	1.605

n.d.: Not detected

Table A4.4: 41-PCB congener's concentrations of 1-year needle samples in Iskenderun and Aliaga (μg/kg)

1-YEAR NEEDLE	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	2.509	1.235	0.647	0.300	1.453	1.106	0.899	0.405
PCB-17	0.862	0.428	0.251	0.139	0.648	0.505	0.447	0.188
PCB-31	1.975	0.942	0.419	0.169	1.635	1.095	1.221	n.d.
PCB-28	2.167	0.960	0.447	0.230	2.077	1.433	1.054	n.d.
PCB-33	1.871	0.948	0.341	0.254	1.606	1.525	0.582	n.d.
PCB-52	1.342	0.653	0.436	0.151	0.991	0.312	1.278	n.d.
PCB-49	0.919	0.377	0.398	n.d.	1.130	0.371	n.d.	n.d.
PCB-44	1.056	0.484	0.632	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-74	0.894	0.269	0.171	n.d.	2.985	2.810	n.d.	n.d.
PCB-70	1.357	0.586	0.436	n.d.	1.092	0.520	n.d.	n.d.
PCB-95	0.530	0.236	0.129	0.098	0.440	0.250	n.d.	n.d.
PCB-101	1.113	0.482	0.254	n.d.	0.922	0.323	n.d.	n.d.
PCB-99	0.516	0.236	0.226	n.d.	0.699	0.216	n.d.	n.d.
PCB-87	n.d.	n.d.	n.d.	n.d.	1.487	n.d.	n.d.	n.d.
PCB-110	1.035	0.516	n.d.	n.d.	1.634	0.810	n.d.	n.d.
PCB-82	1.189	0.670	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-151	0.261	0.094	n.d.	n.d.	0.220	0.075	0.131	n.d.
PCB-149	0.722	0.383	0.175	n.d.	0.537	0.294	n.d.	n.d.
PCB-118	1.312	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-153	0.783	0.361	n.d.	n.d.	0.801	0.404	0.328	n.d.
PCB-132	0.394	0.160	n.d.	n.d.	0.391	0.144	n.d.	n.d.
PCB-105	0.757	0.686	0.128	n.d.	0.742	0.241	n.d.	n.d.
PCB-138	1.975	n.d.	n.d.	n.d.	1.091	0.506	n.d.	n.d.
PCB-158	0.275	n.d.	n.d.	n.d.	0.232	n.d.	n.d.	n.d.
PCB-187	0.245	0.199	n.d.	n.d.	0.289	0.106	n.d.	n.d.
PCB-183	0.421	n.d.	n.d.	n.d.	0.181	0.094	n.d.	n.d.
PCB-128	0.673	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-177	0.286	n.d.	n.d.	n.d.	0.127	n.d.	n.d.	n.d.
PCB-171	n.d.	n.d.	n.d.	n.d.	0.303	n.d.	n.d.	n.d.
PCB-156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-180	0.334	0.297	n.d.	n.d.	0.508	0.298	n.d.	n.d.
PCB-191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.717	n.d.	n.d.	n.d.	0.760	0.127	n.d.	n.d.
PCB-199	0.218	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPCBs	16.791	10.458	2.515	1.640	9.393	9.473	2.112	2.283

n.d.: Not detected

Table A4.5: 41-PCB congener's concentrations of 2-year needle samples in Iskenderun and Aliaga (μg/kg)

2-YEAR NEEDLE	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	5.729	3.497	0.814	0.501	6.361	7.785	0.742	0.441
PCB-17	1.803	1.025	0.299	0.152	2.392	2.699	0.337	0.138
PCB-31	4.297	2.421	0.602	0.404	5.831	6.503	0.769	n.d.
PCB-28	5.226	3.190	0.720	0.445	6.764	7.862	0.863	n.d.
PCB-33	3.889	2.151	0.612	0.609	4.270	5.253	n.d.	n.d.
PCB-52	3.293	2.112	0.790	0.113	4.112	4.110	1.178	n.d.
PCB-49	1.914	1.242	0.700	0.106	4.567	3.656	n.d.	n.d.
PCB-44	1.907	1.295	0.884	n.d.	2.469	2.264	n.d.	n.d.
PCB-74	1.472	0.967	0.554	n.d.	3.673	3.101	n.d.	n.d.
PCB-70	2.134	1.152	1.878	n.d.	3.844	3.276	0.558	n.d.
PCB-95	1.155	0.680	0.225	0.130	1.319	1.252	0.190	n.d.
PCB-101	1.715	1.186	n.d.	n.d.	3.076	2.569	n.d.	n.d.
PCB-99	0.780	0.525	0.150	0.039	1.450	0.747	n.d.	n.d.
PCB-87	1.209	1.115	n.d.	n.d.	3.167	1.538	n.d.	n.d.
PCB-110	1.644	0.921	0.700	n.d.	3.517	2.682	n.d.	n.d.
PCB-82	1.148	0.035	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-151	0.376	0.179	n.d.	n.d.	0.635	0.330	0.112	n.d.
PCB-149	0.988	0.652	n.d.	n.d.	1.508	1.241	0.152	n.d.
PCB-118	1.108	0.419	n.d.	n.d.	4.431	2.205	n.d.	n.d.
PCB-153	1.281	0.824	n.d.	n.d.	1.943	1.682	n.d.	n.d.
PCB-132	0.765	0.306	n.d.	n.d.	1.012	0.454	n.d.	n.d.
PCB-105	0.821	0.403	0.365	n.d.	1.996	1.226	n.d.	n.d.
PCB-138	1.565	1.127	n.d.	n.d.	2.626	1.955	n.d.	n.d.
PCB-158	0.590	0.062	n.d.	n.d.	0.759	0.235	n.d.	n.d.
PCB-187	0.240	0.168	n.d.	n.d.	0.792	0.372	n.d.	n.d.
PCB-183	0.254	0.164	n.d.	n.d.	0.514	0.247	n.d.	n.d.
PCB-128	1.454	0.578	n.d.	n.d.	1.108	0.356	n.d.	n.d.
PCB-177	0.360	0.168	n.d.	n.d.	0.476	0.151	n.d.	n.d.
PCB-171	0.286	n.d.	n.d.	n.d.	0.513	0.051	n.d.	n.d.
PCB-156	n.d.	n.d.	n.d.	n.d.	0.732	0.198	n.d.	n.d.
PCB-180	0.431	0.388	n.d.	n.d.	1.339	1.133	n.d.	n.d.
PCB-191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.844	n.d.	n.d.	n.d.	1.067	0.445	n.d.	n.d.
PCB-199	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPCBs	41.024	25.596	4.296	4.159	52.743	61.876	1.715	1.882

n.d.: Not detected

Table A4.6: 41-PCB congener's concentrations of branch samples in Iskenderun and Aliaga (μg/kg)

BRANCH	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	0.609	0.254	0.342	0.112	0.539	0.218	0.392	0.103
PCB-17	0.257	0.100	0.169	0.041	0.232	0.118	0.176	0.067
PCB-31	0.330	0.147	0.192	0.052	0.568	0.259	0.194	0.047
PCB-28	0.435	0.175	0.230	0.079	0.715	0.321	0.254	0.063
PCB-33	0.401	0.168	0.161	0.027	0.497	0.225	n.d.	n.d.
PCB-52	0.395	0.262	0.295	n.d.	0.333	0.161	0.266	n.d.
PCB-49	0.440	0.182	0.383	n.d.	0.321	0.142	n.d.	n.d.
PCB-44	n.d.	n.d.	n.d.	n.d.	0.435	n.d.	n.d.	n.d.
PCB-74	n.d.	n.d.	n.d.	n.d.	0.333	0.222	n.d.	n.d.
PCB-70	0.651	n.d.	n.d.	n.d.	0.533	0.285	n.d.	n.d.
PCB-95	0.163	0.044	n.d.	n.d.	0.197	0.079	n.d.	n.d.
PCB-101	0.195	0.070	0.144	n.d.	0.337	0.186	n.d.	n.d.
PCB-99	0.384	0.089	0.199	n.d.	0.161	0.080	n.d.	n.d.
PCB-87	n.d.	n.d.	n.d.	n.d.	0.247	0.153	n.d.	n.d.
PCB-110	0.464	0.267	n.d.	n.d.	0.395	0.272	n.d.	n.d.
PCB-82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-151	n.d.	n.d.	n.d.	n.d.	0.096	n.d.	n.d.	n.d.
PCB-149	0.219	n.d.	n.d.	n.d.	0.299	0.136	n.d.	n.d.
PCB-118	0.392	0.057	n.d.	n.d.	0.477	0.366	n.d.	n.d.
PCB-153	0.371	0.156	n.d.	n.d.	0.425	0.246	n.d.	n.d.
PCB-132	n.d.	n.d.	n.d.	n.d.	0.324	0.168	n.d.	n.d.
PCB-105	n.d.	n.d.	n.d.	n.d.	0.286	n.d.	n.d.	n.d.
PCB-138	0.624	n.d.	n.d.	n.d.	0.590	0.450	n.d.	n.d.
PCB-158	n.d.	n.d.	n.d.	n.d.	0.200	n.d.	n.d.	n.d.
PCB-187	0.128	0.071	n.d.	n.d.	0.219	0.098	n.d.	n.d.
PCB-183	0.074	n.d.	n.d.	n.d.	0.154	0.079	n.d.	n.d.
PCB-128	1.160	n.d.	n.d.	n.d.	0.532	n.d.	n.d.	n.d.
PCB-177	n.d.	n.d.	n.d.	n.d.	0.163	0.049	n.d.	n.d.
PCB-171	n.d.	n.d.	n.d.	n.d.	0.102	n.d.	n.d.	n.d.
PCB-156	n.d.	n.d.	n.d.	n.d.	0.284	n.d.	n.d.	n.d.
PCB-180	0.331	0.098	n.d.	n.d.	0.520	0.263	n.d.	n.d.
PCB-191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	n.d.	n.d.	n.d.	n.d.	0.381	0.076	n.d.	n.d.
PCB-199	n.d.	n.d.	n.d.	n.d.	0.221	n.d.	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	0.243	n.d.	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPCBs	3.295	1.923	1.171	0.573	4.475	3.449	1.060	0.199

n.d.: Not detected

Table A4.7: 41-PCB congener's concentrations of soil samples in Iskenderun and Aliaga (μg/kg)

SOIL	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	0.372	0.276	0.144	0.070	0.635	0.613	0.145	0.121
PCB-17	0.208	0.120	0.092	0.023	0.289	0.307	0.065	0.071
PCB-31	0.385	0.428	0.056	0.036	0.790	1.064	0.092	0.007
PCB-28	0.528	0.634	0.093	0.033	1.199	1.788	0.151	0.023
PCB-33	0.379	0.390	0.106	0.041	0.666	0.856	0.134	0.008
PCB-52	0.481	0.777	0.111	0.020	0.858	1.271	0.102	0.032
PCB-49	0.400	0.490	0.104	0.030	0.720	0.936	0.080	0.022
PCB-44	0.411	0.432	n.d.	n.d.	0.851	1.128	n.d.	n.d.
PCB-74	0.275	0.360	0.040	n.d.	0.607	0.848	n.d.	n.d.
PCB-70	0.617	0.724	n.d.	n.d.	1.424	2.153	0.065	n.d.
PCB-95	0.749	2.116	0.041	n.d.	1.218	2.106	0.039	0.007
PCB-101	1.306	3.353	0.062	0.031	2.639	4.710	0.051	0.025
PCB-99	0.557	1.288	0.032	0.004	0.827	1.184	0.034	0.010
PCB-87	0.739	1.863	0.051	n.d.	1.217	1.925	0.051	0.014
PCB-110	1.585	4.101	0.063	0.021	2.705	4.738	0.057	0.017
PCB-82	0.469	0.832	n.d.	n.d.	0.448	0.507	n.d.	n.d.
PCB-151	0.477	1.301	0.023	n.d.	0.681	1.405	0.026	0.005
PCB-149	1.477	4.169	0.063	0.042	3.080	6.674	0.064	0.028
PCB-118	1.609	3.376	0.072	0.039	3.296	5.347	0.049	0.020
PCB-153	2.361	6.359	0.075	0.040	4.818	10.023	0.091	0.043
PCB-132	0.626	1.511	n.d.	n.d.	1.308	2.726	0.055	n.d.
PCB-105	0.826	1.412	0.045	n.d.	1.780	2.697	0.042	0.011
PCB-138	2.811	6.974	0.098	0.052	6.213	12.528	0.096	0.041
PCB-158	0.389	0.722	0.182	n.d.	0.732	1.334	n.d.	n.d.
PCB-187	0.870	2.555	0.031	n.d.	1.886	3.891	0.051	0.012
PCB-183	0.423	1.163	n.d.	n.d.	1.001	2.014	n.d.	n.d.
PCB-128	0.780	1.322	n.d.	n.d.	1.980	3.178	n.d.	n.d.
PCB-177	0.518	1.254	n.d.	n.d.	1.161	2.403	n.d.	n.d.
PCB-171	0.289	0.534	n.d.	n.d.	0.537	1.074	n.d.	n.d.
PCB-156	0.502	0.720	n.d.	n.d.	0.986	1.574	n.d.	n.d.
PCB-180	2.039	5.728	0.097	0.002	5.114	10.593	0.077	0.034
PCB-191	0.126	0.152	n.d.	n.d.	0.198	0.269	0.004	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	0.967	2.125	n.d.	n.d.	2.854	5.848	0.057	n.d.
PCB-199	0.958	2.036	n.d.	n.d.	1.156	1.605	n.d.	n.d.
PCB-208	0.135	0.175	n.d.	n.d.	0.204	0.104	n.d.	n.d.
PCB-195	0.670	1.118	n.d.	n.d.	0.550	0.810	n.d.	n.d.
PCB-194	1.382	2.578	n.d.	n.d.	1.438	2.197	n.d.	n.d.
PCB-205	0.287	0.182	n.d.	n.d.	0.221	0.189	n.d.	n.d.
PCB-206	0.442	0.678	n.d.	n.d.	0.605	0.497	n.d.	n.d.
PCB-209	0.119	0.065	n.d.	n.d.	0.437	0.505	n.d.	n.d.
ΣPCBs	26.556	61.574	0.902	0.561	57.566	101.190	1.151	0.543

n.d.: Not detected

Table A4.8: 41-PCB congener's concentrations of stem samples in Iskenderun and Aliaga (μg/kg)

STEM	ISKENDERUN				ALIAGA			
	Industrial		Background		Industrial		Background	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PCB-18	1.438	1.390	0.960	0.906	3.016	4.951	1.795	0.763
PCB-17	0.745	0.645	0.492	0.431	1.714	2.706	1.003	0.402
PCB-31	0.738	0.684	0.362	0.350	1.526	2.689	0.579	0.173
PCB-28	0.906	0.623	0.426	0.384	1.664	2.859	0.621	0.173
PCB-33	0.419	0.339	0.218	0.124	1.281	2.549	0.515	0.186
PCB-52	0.631	0.462	0.230	0.093	1.137	1.728	0.520	0.183
PCB-49	0.433	0.412	0.120	0.074	1.216	1.961	0.507	0.162
PCB-44	0.156	0.102	n.d.	n.d.	0.176	0.108	0.020	n.d.
PCB-74	0.366	0.206	0.175	0.012	1.049	1.685	0.513	0.172
PCB-70	0.551	0.241	0.196	0.129	1.030	1.934	0.492	0.135
PCB-95	0.219	0.130	n.d.	n.d.	0.215	0.275	0.040	0.013
PCB-101	0.085	n.d.	n.d.	n.d.	0.133	0.092	0.025	0.001
PCB-99	0.032	0.002	n.d.	n.d.	0.040	0.001	n.d.	n.d.
PCB-87	0.056	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-110	0.039	0.004	n.d.	n.d.	0.266	0.136	0.015	n.d.
PCB-82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-151	n.d.	n.d.	n.d.	n.d.	0.178	0.303	n.d.	n.d.
PCB-149	0.125	0.129	n.d.	n.d.	0.393	0.607	0.046	0.042
PCB-118	0.179	0.197	n.d.	n.d.	1.407	2.576	0.208	0.148
PCB-153	0.144	0.082	n.d.	n.d.	0.270	0.196	n.d.	n.d.
PCB-132	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-105	n.d.	n.d.	n.d.	n.d.	0.015	n.d.	n.d.	n.d.
PCB-138	n.d.	n.d.	n.d.	n.d.	0.019	0.003	n.d.	n.d.
PCB-158	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-187	0.071	n.d.	n.d.	n.d.	0.221	0.287	0.034	n.d.
PCB-183	0.044	n.d.	n.d.	n.d.	0.225	0.275	0.027	n.d.
PCB-128	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-177	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-171	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-180	0.164	n.d.	n.d.	n.d.	0.372	0.553	n.d.	n.d.
PCB-191	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-170	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-199	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-208	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-195	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-194	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-205	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PCB-209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPCBs	6.434	4.849	2.914	2.219	15.628	26.796	6.716	2.141

n.d.: Not detected