PERSISTENT ORGANIC POLLUTANTS IN TURKEY'S ATMOSPHERE: SPATIAL VARIATION

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ABSTRACT

PERSISTENT ORGANIC POLLUTANTS IN TURKEY'S ATMOSPHERE: SPATIAL VARIATION

The objectives of this study was to measure ambient air levels of 43 PCBs and 22 OCPs in 16 cities at urban and background sites by using polyurethane foam discs (PUF) as passive air samplers (PAS), to investigate spatial variations, and to generate a baseline database which is the first large-scale nationwide database for POP residues in air of Turkey. Air sampling was conducted from May 2014 to April 2015 with three-month sampling periods. Samples were analyzed by gas chromatography - mass spectrometry after extraction, clean-up, and volume reduction.

The one-year overall average Σ_{43}PCBs concentration was 108±132 pg/m^3. The one-year average of Σ_{43}PCBs ranged from 14.5±14.3 pg/m^3 (Kayseri) to 403±428 pg/m^3 (İzmir) at urban sites with a mean of 116±141 pg/m^3, and from 19.0±22.7 pg/m^3 (Aksaray) to 217±353 pg/m^3 (Kastamonu) at rural sites with a mean of 101±122 pg/m^3. PCB 118 had the highest mean concentration (26.3±44.6 pg/m^3) among the 43 PCB congeners. The PCB homologue group with the highest contribution was penta-CBs with 54.3%. Overall one-year average Σ_{22}OCPs concentration was 341±870 pg/m^3 with a range of 55.3±36.5 pg/m^3 (Çankırı) and 1294±2153 pg/m^3 (Kırklareli). ΣDDT had the highest overall mean level with 134±296 pg/m^3 among the OCP groups. The highest concentration OCPs were *p'p*-DDE (97.6±236 pg/m^3), HCB (45.3±197 pg/m^3), *α*-HCH (22.0±92.8 pg/m^3), *β*-HCH (21.8±96.1 pg/m^3), and *p'p*-DDT (21.3±77.4 pg/m^3).

Principle Components Analysis showed that, in addition to the OCP with the highest concentration (*p'p*-DDE), parent OCP compounds such as *α*-endosulfan, *α*-HCH, HCB, and *p'p*-DDT differed from the others, and some of the remaining decay products were grouped together indicating similar behavior. Highly chlorinated PCBs were clustered together. Mann-Whitney U test indicated that the difference in the median concentrations of urban and rural sites was not significant. It was also used to test the significance of temperature effect on the median concentrations at a high and a low temperature range. The medians were significantly different for HCB, dieldrin, *p'p*-DDT, and *β*-endosulfan at urban sites but not significant for the remaining OCPs and ΣPCBs. The difference in the medians was significant for HCB, heptachlor, dieldrin, endrin, *p'p*-DDE, Mirex, and ΣPCBs at rural sites.

ÖZET

TÜRKİYE ATMOSFERİNDE KALICI ORGANİK KİRLETİCİLER: YERSEL DEĞİŞKENLİK

Bu çalışmada, yersel değişkenliği incelemek ve Türkiye atmosferinde bulunan KOK kalıntılarını gösteren ilk büyük ölçekli ulusal veri tabanını oluşturmak amacıyla seçilen 16 şehirdeki kentsel ve kırsal alanlara yerleştirilen pasif hava örnekleyicileri ile 43 adet PCB ve 22 adet OKP'nin atmosferdeki derişimleri incelenmiştir. Örnekleme dönemi 3 aylık periyotlar ile gerçekleştirilmiş ve Mayıs 2014 – Nisan 2015 tarihleri arasında 1 yıl sürmüştür. PÜK disklerin ekstraksiyonu, temizlenmesi ve hacim azaltılması işlemlerinden sonar elde edilen numuneler gaz kromatografisi - kütle spektrometresi ile analiz edilmişlerdir.

Yıllık ortalama Σ_{43}PCB derişimi 108±132 pg/m^3'dür. Değerler kentsel alanlar için 14,5±14,3 pg/m^3 (Kayseri) ve 403±428 pg/m^3 (İzmir) aralığında (ortalama 116±141 pg/m^3) değişirken, kırsal alanlar için 19,0±22,7 pg/m^3 (Aksaray) ve 217±353 pg/m^3 (Kastamonu) aralığında (ortalama 101±122 pg/m^3) değişkenlik göstermiştir. PCB 118, 26,3±44,6 pg/m^3 ile en yüksek ortalama derişime sahip olan PCBdir. Penta-CBler %54,3 ile en yüksek katkısı olan gruptur. Yıllık ortalama Σ_{22}OKP derişimi 341±870 pg/m^3'tür. Değerler 55,3±36,5 pg/m^3 (Çankırı) - 1294±2153 pg/m^3 (Kırklareli) aralığında değişmiştir. ΣDDT, 134±296 pg/m^3'lük yıllık ortalama ile en yüksek derişime sahip grup olmuştur. *p'p*-DDE (97,6±236 pg/m^3), HCB (45,3±197 pg/m^3), α-HCH (22,0±92,8 pg/m^3), β-HCH (21,8±96,1 pg/m^3) ve *p'p*-DDT (21,3±77,4 pg/m^3) en yüksek ortalamalara sahip olan OKPlerdir.

Asal Bilesen Analizi sonucunda en yüksek derişime sahip olan *p'p*-DDE ile α-endosulfan, α-HCH, HCB ve *p'p*-DDT gibi ana kirleticilerler oldukça farklı bir patern izlemiş olup kalan OKPlerden bazı bozunma ürünleri ise beraber kümelenmiştir. Yüksek klorlu PCBler birlikte kümelenmiştir. Mann-Whitney U test sonucunda kentsel ve kırsal alanlarda ölçülen ortanca değerler arasında istatistiksel olarak bir fark bulunmamıştır. Örnekler yüksek ve düşük sıcaklık grubu olarak ayrıldıklarında, kentsel alanlarda HCB, dieldrin, *p'p*-DDT ve β-endosulfan derişimlerinin ortanca değerleri arasındaki farklılık istatistiksel olarak anlamlı bulunmuştur. Kırsal alanlarda ise HCB, heptaklor, dieldrin, endrin, *p'p*-DDE, Mirex ve Σ_{43}PCB derişimlerinin ortanca değerleri arasındaki farklılık istatistiksel olarak anlamlıdır.

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CHAPTER 1

INTRODUCTION

Persistent organic pollutants (POPs) are a group of compounds, known to be persistent to degradation in the environmental compartment e.g. air, soil, and organisms capable of having long range atmospheric transport, causing global pollution due to having long half-time, have affinity to fatty tissues. Two main groups of POPs investigated in this thesis; Polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) which have been manufactured intentionally in the past and unintentionally in the present (Jones and de Voogt 1999). However, they are still produced in some developing countries in Asia and Africa (Harrad 2010).

POPs especially draw attention because of their particular bioaccumulation characteristics in fatty tissues resulting in bioaccumulation and biomagnification in food chain (Qing Li et al. 2006), low aqueous solubility, and moderate vapor pressure (Castro-Jiménez et al. 2008, Wick et al. 2011). These compounds released into air, soil, and water from different sources such as industry, waste disposal sites, and agricultural areas. Because of the unique transport property so called as “grasshopper effect”, these compounds can slowly evaporate into the air from low latitudes at warm days and then, they can travel for long distances through a series of short and relatively long hops until they reach cold arctic regions (high latitudes) and deposited. This behavior helps explaining how some of the POPs are detected in pristine environments such as Arctic and Antarctic although there is not any production in these areas (Bowes and Jonkel 1975). Additionally, they may be very toxic, and can cause adverse health effects because of being carcinogen, endocrine disrupting, and some other effects on immune system (Weber and Greim 1997).

Even though bans taken into account around 1980s, after awareness of the hazardous effects of POPs and detection in the remote areas, Stockholm Convention was coordinated by the UNEP (United Nations Environment Programme) around world to eliminate POPs from environment and protect from the potential adverse health effects. It was signed in 22 May 2001 and came into force in 17 May 2004. Among a large number of POPs, 12 were named as dirty dozen, and were banned because of their adverse health effects. These POPs were pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, Mirex, toxaphene), industrial chemicals (hexachlorobenzene, PCBs), and by-products (hexachlorobenzene, PCDD/PCDF, and PCBs). Turkey signed the convention in 23 May 2001 and date of ratification was 14 October 2009. Turkey will completely comply with the requirements by 2025. The requirements within the scope of convention were determination of POP sources and building inventory for all listed chemicals, and prohibition of the POPs from use and production. Additional 9 POPs (chlordecone, lindane (γ-HCH), α-HCH, β-HCH, perfluorooctane sulfonate, hexabromobiphenyl, commercial PBDE, pentachlorobenzene) have been added to the list in 2010.

Despite the fact that Turkey is a part of the Stockholm Convention, only a few studies are available in the literature and their sampling locations are either hot-spots (industrial areas) or urban locations (such as Esen 2013, Kaya et al. 2012). Additionally, there is no comprehensive study showing spatial variation in concentrations and profiles in Turkey.

The aims of this study were to measure ambient air concentrations of PCBs and OCPs at 16 cities with urban and background sites by passive air samplers (PAS), to observe spatial variations and to create the first large scale nationwide database for POPs residues in air of Turkey. The following chapters provide a literature review on concentrations of PCBs and OCPs measured by PAS around the world and Turkey (Chapter 2). Materials and methods are presented in Chapter 3, followed by Results and discussions (Chapter 4). Finally, conclusions and recommendations are stated in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

After it was established fact that POPs can be detected in the pristine environments and lead to dreadful adverse health effects, POP levels in the atmosphere became one of the most investigated topics. Therefore, there are many studies conducted around the world with both active and passive air samplers. However, there are a limited number of studies in Turkey compared to those in the world. In this chapter, general information about PCBs and OCPs, and ambient air concentrations measured by PAS throughout the world and Turkey are stated.

2.1. PCBs

PCBs are a class of POPs having 209 possible congeners with the general structure formed by attachment of chlorine atoms to biphenyl as given in Figure 2.1 where m and n denote number of chlorine atoms in two benzene rings. Number of chlorine atoms in the structure can vary from 1 to 10.

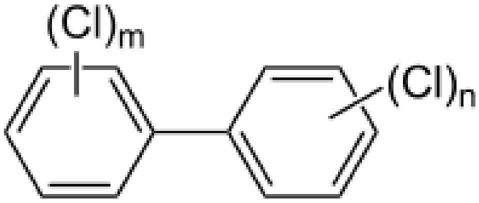

Figure 2.1. General structure of PCBs

PCBs are named both by International Union of Pure and Applied Chemistry (IUPAC) by indicating chlorine attachment sites to the phenyl ring and by the Chemical Abstracts Service (CAS) by giving a registry number. PCBs synthesized as a mixture of 209 congeners with different chlorine weight. Therefore, based on the countries manufactured PCBs, they have some difference in congener contents such as Aroclor (USA), Pyranol, Pyroclor, Phenochlor, Pyralene, Clophen, Elaol, Kanechlor (Japan), Santotherm, Fenchlor, Apirolioi Sovol (USSR), etc, among which Aroclor is the most commonly mixture produced and used between 1930 and 1979.

Two benzene rings in the PCB molecule can rotate around the bond formed. Additionally, the formed structure can be affected from the repulsion between nearby chlorine atoms resulting in either coplanar (rings in the same or different planes) structure or non-planar structure (rings in the perpendicular planes). Those located in the same plane are assumed to be the most toxic because of combined health effects. These PCBs are known as dioxin-like PCBs (ATSDR, 2014).

PCBs were mostly used in industrial and commercial applications because of their non-flammability, chemical stability, high boiling point so resistance to heat, and electrical insulation properties. PCBs are liquid at room temperature, not very soluble in water but highly soluble in organic solvents, and have low electric conductivity. Some of the properties which vary among homolog groups are presented in Table 2.1. It can be seen that increasing number of chlorine atom increases molecular weight and boiling point but decreases vapor pressure and water solubility. The compounds with higher vapor pressure and water solubility tend to be in gas phase and dissolve in water so possibility to detect in the atmosphere increases. However, other compounds tend to deposit on different surfaces.

Table 2.1. Chemical and physical properties of PCB homolog groups

Homolog Group	**MW[a] (g/mol)**	**Boiling Point (°C)**	**Vapor Pressure (Pa) at 25 °C**	**Water Solubility (g/m^3) at 25 °C**
monoCB	189	285	1.10	4.00
diCB	233	312	0.24	1.60
triCB	257	337	0.05	0.65
tetraCB	292	360	0.01	0.26
pentaCB	326	381	2.6×10^{-3}	0.10
hexaCB	361	400	5.8×10^{-4}	0.04
heptaCB	395	417	1.3×10^{-4}	0.01
octaCB	430	432	2.8×10^{-5}	5.5×10^{-3}

(Cont. on next page)

Table 2.1. (Cont.)

Homolog Group	**MW[a] (g/mol)**	**Boiling Point (°C)**	**Vapor Pressure (Pa) at 25 °C**	**Water Solubility (g/m^3) at 25 °C**
nonaCB	464	445	6.3×10^{-6}	2.0×10^{-3}
decaCB	499	456	1.4×10^{-6}	7.6×10^{-4}

[a] MW: Molecular weight

PCBs were extensively used in the industry as dielectric fluid in transformers/capacitors and heat exchange fluids, in carbonless copy paper, paint additives, adhesives, and plastics. Therefore, today the major possible sources of PCBs are volatilization from and combustion of PCB containing materials such as capacitors and transformers, and volatilization from PCB contaminated waste disposal sites (Simcik et al. 1997).

PCBs can lead to a wide variety of health effects and they are classified as probable human carcinogens (Groups 2A) by International Agency for Research on Cancer (IARC) (USEPA 2010). Non-carcinogenic effects can be listed as immune, reproductive, neurological, and endocrine effects.

2.2. OCPs

OCPs are also organic compounds with five or more chlorine atoms (Figure 2.2). Organochlorinated pesticides vary within the group based on how they were synthesized. Some have benzene rings; some of them have aliphatic compounds. They are persistent and lipophilic compounds hence not good soluble in water. Additionally, OCPs are stable to photo-oxidation reactions so they are persistent in the environment (Kim and Smith 2001).

The aim of usage of the OCP compounds was to prevent, control or destroy pests including vectors during diseases and insects causing harm to plants and animals. OCPs are also named similarly to PCBs by IUPAC and CAS. Pesticides can be classified based on mode of action such as contact and systemic pesticides such as clothianidin, imidacloprid, dinotefuran; targeted pest species such as insecticide, herbicide, fungicide algaecide; chemical composition of the pesticide such as organochloride insecticides, organophosphates, carbamates, pyrethrins and pyrethroids; and new groups such as imidazolinones, isothiazolinones, pyridines (Drum 1980, USEPA 2015). The contact pesticides become active when they contact with the targeted species, while the systematic pesticides penetrate into plant tissues to give the desired effect or they are taken up from soil via roots.

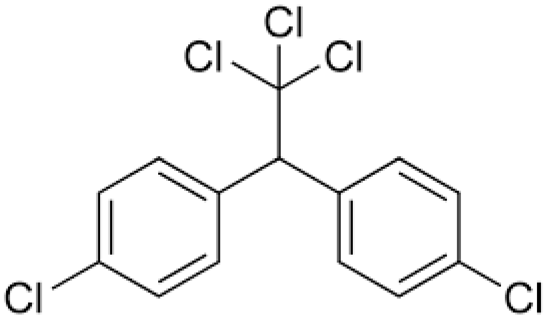

Figure 2.2. Chemical structure of *p,p'*-DDT as an example of pesticides

They are mainly emitted to the environment as a result of application as pesticides in agricultural practices. Chemical and physical properties of OCPs vary depending on the chemical structure and formulation (Table 2.2). Those with higher vapor pressure tend to be in gas phase. Although it seems to be an advantage for effectiveness to the target species, it is a disadvantage from environmental pollution point of view. The ones with low vapor pressure accumulate in the environment and can affect aquatic and soil ecosystem.

OCPs can be transformed into their isomers as a result of chemical and biological degradation. Oxidation reaction is the most important way of chemical degradation. For example, *p,p'*-DDT can be degraded to *p,p'*-DDE and then to *p,p'*-DDD.

Some of the possible health effects of OCPs are memory loss, loss of coordination, reduced motor skills, asthma, and hormone disruption. Some of them such as DDTs, heptachlor, HCB, toxaphene, chlordane, and Mirex are classified as possible human carcinogens (Group 2B) by IARC (UNEP 1995).

Table 2.2. Chemical and physical properties of some OCPs

Pollutant	**MW[a] (g/mol)**	**Boiling Point (°C)**	**Vapor Pressure (Pa) at 25 °C**	**Water Solubility (g/m^3) at 25 °C**
α-HCH	291	288	4.7×10^{-3}	2.00
o,p'-DDT	354	368	1.8×10^{-4}	0.08
Aldrin	365	330	0.02	0.02
Dieldrin	381	330	4.0×10^{-4}	0.19
Endo-I	407	401	8.0×10^{-5}	0.51
CC[b]	410	351	1.3×10^{-3}	0.06

[a] MW: Molecular weight [b] CC: Cis-chlordane

2.3. Ambient Air Concentrations of PCBs and OCPs

Atmospheric concentrations of PCBs and OCPs have been drawing attention around the world for last decades because of their harmful effects on health and environment. Sampling of POPs have been performed by high volume active sampling but after awareness that pristine environments might also been contaminated by long range atmospheric/marine transport, it was required an alternative technique that allows easy access, less labor and operation cost, and more importantly no electricity requirement. In this manner, passive air samplers (PAS) were developed to determine gas phase pollutant concentration, which are only suitable for relatively longer term measurements. Advantages of passive sampling are no requirement for electrical power and daily maintenance, and being inexpensive. However, particulate phase cannot be sampled by this technique and they are not sensitive to short term fluctuations in concentrations. Although there are many studies around the world that determined the ambient air concentrations of POPs by PAS, there is a limited database in Turkey, with only 4 studies published between 1983 and 2014. In the part below, some examples from the literature performed by PAS are presented.

Wania et al. (2003) assessed a study to gather data on atmospheric concentration of selected OCPs in Great Lakes region at Point Petre, Burnt Island, and Canadian High Arctic, Alerton Ellesmere Island in 2000. The most detected OCP in these regions was HCB with the levels of 26, 36, and 62 pg/m^3, respectively.

Farrar et al. (2004) presented the air concentrations of target POPs in Toronto, Canada in October 2001. The sampling was performed by polymer-coated glass passive samplers located at different heights in CN Tower. The levels of $\sum_9$PCBs, α-HCH, γ-HCH, *cis*-chlordane (CC), and *trans*-chlordane (TC) were 2170, 340, 292, 4.5, and 7.4 pg/m^3, respectively. PCB concentrations decreased gradually with height, which indicated the dynamic nature of the sources and mixing of the POPs in the atmosphere.

Harner et al. (2004) measured PCB and OCP concentrations at eight sites (rural + urban) in Toronto during summer of 2000 for a 4-month duration. The range of measured value of $\sum_{13}$PCBs was 116-547 and 70.7-104 pg/m^3 for urban and rural sites, respectively. The reason for higher PCB concentrations in urban areas was claimed to be the industrialization. Endosulfan-I (Endo-I) was dominating the 11 OCPs with a maximum concentration of 817 pg/m^3 at a rural site (Egbert). At urban sites, TC/CC ratios were > 1 (1.08-1.10) indication fresh input from building foundations. *p,p'*-DDT/*p,p'*-DDE ratio was < 1 (0.17-0.45) probably as a result of early usage of DDT.

Jaward et al. (2004) presented concentration data of PCBs and OCPs measured in remote, rural, and urban cities across Europe from June to July 2002. $\sum_{29}$PCBs were in the range of 20-1700 pg/m^3. The lowest levels were measured in rural and remote areas. The highest level OCP was γ-HCH (9-390 pg/m^3), while the lowest one was *p,p'*-DDE (<0.4-25 pg/m^3). α-HCH and HCB concentrations showed a uniform distribution throughout Europe but higher levels of γ-HCH, *p,p'*-DDT, and *p,p'*-DDE were observed in southern and eastern sites.

Gouin et al. (2005) also conducted a study to determine PCB and OCP concentrations at 15 sites around Laurentian Great Lakes from July 2002 to June 2003. Annual average concentration of $\sum_{11}$PCBs was in the range of 15-960 pg/m^3 with higher concentrations at urban sites than remote areas. Additionally, maximum air concentrations occurred in warmer periods. α-HCH had a uniform distribution among the sampling points because of high volatilization characteristic and being persistent (15-73 pg/m^3) whereas higher γ-HCH concentrations were observed in agricultural and rural areas (13-100 pg/m^3). Endo-I and dieldrin (Dield) concentrations ranged between 33-430 and 15-165 pg/m^3, respectively. Endo-I was commonly used in insecticides at early times and high concentrations were detected in summer and spring due to agricultural activities. The source of dieldrin was also agricultural activities, but its level increased in gas phase with warmer air in spring and disperses around in summer period.

PCB and OCP concentrations were quantified at four locations in the inoperative coal tar and mixed tar oils processing plant (DEZA Valasske Mezirici, primary source of PAHs) by PAS on January 2004 in Czech Republic (Klánová et al. 2006). $\sum_7$PCBs, ΣDDTs (*p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD), and ΣHCHs ($\alpha + \beta + \gamma + \delta$- isomers) were in the range of 60-200, 30-120, and 20-90 ng/m^3, respectively. Although the factory was the source of PAHs, PCBs and OCPs were also detected in the area because PCBs were released to the environment by disposal of products or wastes, and/or as a result of volatilization of previously used POPs.

RůŽičková et al. (2007) conducted a study to determine concentration profile of PCBs and OCPs in different locations of Central and South Europe between July and December 2005. The mean concentrations of $\sum_7$PCBs at background, residential-rural-urban, industrial, and heavily contaminated sites were 0.11, 0.20, 0.29, and 7.56 ng/m^3, respectively. The mean concentrations of $\sum_6$OCPs (*p,p'*-DDT, DDE, DDD, and *α-β-γ*-HCH) were 0.22, 0.23, 0.29, and 1.88 ng/m^3, respectively.

Chaemfa et al. (2009) measured air concentrations of PCBs in Lancaster, United Kingdom at the time period of October-December 2007, resulted in the average levels of $\sum_{13}$PCBs 3.13 and 2.15 pg/m^3 due to sampling with two different types of PUF: high and low density foams.

Choi et al. (2008) reported the levels of OCPs and PCBs at Korean Arctic and Antarctic Research Stations (Ny-Ålesund, Norway (2005-2006) and King George Island, Antarctica (2004-2005)). PCB-11 was the dominant PCB, which has higher mobility, with a mean concentration of 60 pg/m^3 in Antarctica. The average amount of $\sum_{205}$PCBs (three mono-CBs and PCB-11 not included) was 95 and 19 pg/m^3 for Arctic and Antarctic, respectively. Using back-trajectory analysis, the source of PCB contamination in Arctic was determined to be Russia and Northern European Countries where South America was the source area for Antarctic. The study indicated that the remote sites without POP production can also be affected from other local sources. Most of the OCPs were not observed at the sampling points. The detected OCPs were in the range of ND-67.1 (*α*-HCH) for Arctic and ND-27.4 (Endo-I) for Antarctic. TC/CC ratio, 0.54 and *p,p'*-DDT/DDE ratio, 0.16 signed the usage of these compounds in the past.

Klanova et al. (2009) monitored concentrations of PCBs and OCPs at 26 sites of Africa in 2008. The median range of PCB levels was 500 pg/m^3-1 ng/m^3 and the maximum level was detected in Dakar, Senegal. The median range of HCHs was 10-20 ng/m^3. DDTs, HCHs, and HCB were in high levels in Kitengela, Kenya as a result of a formerly used as a waste disposal site. The ratio of *p,p'*-DDE/*p,p'*-DDT was low as an indication of recent usage of DDT. It was generalized that urban sites indicated a potential risk because of being highly polluted.

Levels of $\sum_{15}$PCB and four OCPs were determined between July 2007-June 2008 at the Tibetan Plateau for 16 locations (Wang et al. 2010). $\sum_{15}$PCB were between 1.8 and 8.2 pg/m^3. The high level of PCB concentrations were related to forest fires in the areas. ΣDDTs (*o,p'*-DDT *o,p'*-DDE, *p,p'*-DDT, *p,p'*-DDE), ΣHCHs (α + γ -isomers), Endo-I, and HCB were quantified in the range of 5-75, 0.1- 36, 0.1-10, and 2.8-80 pg/m^3, respectively. High DDT concentration was resulted from agricultural lands at Qamda where HCHs were detected at sites >4000 m in consequence of atmospheric transport.

Baek, Choi, and Chang (2011) studied on Korean Polar and the South Pacific research stations focused on PCB and OCP concentrations in air from 2005 to 2009. The highest total Σ_{19}OCPs and Σ_{206}PCBs concentrations were measured at Ny-Alesund with varying concentrations from 68.8 to 176 pg/m^3 and 80.1 pg/m^3, respectively. High amount of OCPs and PCBs in these remote areas were inclined from the sources in other countries in the Northern Hemisphere.

Pozo et al. (2011) examined concentrations of PCBs and OCPs at agricultural areas of India in 2006-2007. The mean concentration of $\sum_{48}$PCBs was 12,100 pg/m^3 with an extremely high value in 2007 but the value decreases to 972 pg/m^3 when the data was excluded. The mean concentrations of α-, γ-HCH, Endo-I, Endo-II, *p,p'*-DDE, and *p,p'*-DDT were 292, 812, 2770, 902, 247, and 931 pg/m^3, respectively. The potential resources of PCBs were the utilization in urban sites and waste yards. High amount of OCPs were related to wide of OCPs in agriculture and disease prevention. Furthermore, long range atmospheric transportation of OCPs was the other possible source.

Halse et al. (2012) determined PCBs and OCPs levels in ambient air throughout Norwegian coast and found out average $\sum_7$PCBs as 21 pg/m^3. The main conclusion was higher PCB levels in larger cities than other sites. OCPs were ranged from 0.2 pg/m^3 (*p,p'*-DDD and *cis*-nonachlor) to 58 pg/m^3 (HCB). The source of HCB was banned insecticides in the environment. In addition, α-HCH was a prevalent OCP originated from vaporization from coastal waters.

The study of Li, Geng, Hu, et al. (2012) was important due to the covering all PCB congeners. He and coworkers (2012) investigated PCB levels at Chinese Great Wall Station, Antarctica from 2009 – 2010. $\sum_{209}$PCB concentrations ranged between 26.74 and 45.08 pg/m^3 with the mean of 36.84 pg/m^3. Similar to the all literature, the dominating PCBs were tetra-CBs, tri-CBs, except di-CBs. Although local sources in this region were neglected in the study, it was found that long range atmospheric transport affected the ambient air PCB concentrations when the congeners' mobility was taken into account.

Kaya et al. (2012) reported $\sum_{41}$PCBs concentration that was measured between 2009 and 2010 for four seasons at 40 locations of an industrial region in Aliağa, Turkey which is the area could be unintentional source. The level of $\sum_{41}$PCBs was in the range of 134-230,958 pg/m^3. Since iron-steel plants, oil and petroleum refineries, and ship demolition areas were located in this region, high level of PCBs were released to environment. The reason of high PCB concentration in summer was elevated volatilization rate of contaminants from soil due to high temperatures.

Bogdal et al. (2013) measured PCB and OCP concentrations in 31 countries which are located in Africa, America, and Pacific regions. The highest median concentrations (84 pg/m^3) of $\sum_7$PCBs were measured in Africa followed by Latin America (21 pg/m^3). However, the maximum concentration (7281 pg/m^3) was recorded at an urban site (La Habana, Cuba) in Latin America because the samplers were placed near a harbor and a petrol refinery. A wide range was observed in Africa, 8-2074 pg/m^3 in contrast to Pacific Islands, 4-108 pg/m^3. The median values of ΣDDT (*p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, o,*p'*-DDD) were ranged from 306 pg/m^3 (Pacific Islands) to < 1 pg/m^3 (Latin America). Africa (27-2255 pg/m^3) and Pacific Islands (8-2178 pg/m^3) had the largest concentration ranges where Latin America (< 1-5 pg/m^3) had the narrowest range. Usage of DDT containing insecticides for malaria control gave rise to increase in concentration of DDT in the Pacific Islands.

Esen (2013) performed a study to determine PCBs and OCPs concentration around a landfill in Bursa, Turkey between June 2008 and June 2009. A total of 12 samples were collected. Average concentrations of $\sum_{29}$PCBs and $\sum_{14}$OCPs were 311 pg/m^3 and 198 pg/m^3, respectively.

Érseková et al. (2014) collected air samples from March to August 2006 from Eastern Europe-Slovakia, Lithuania, Romania, and Serbia, all of which contained one background and one polluted site. The highest concentrations of $\sum_7$PCBs were detected at the urban sites of Slovakia (366.9 pg/m^3), Serbia (346.1 pg/m^3), and Romania (337.1 pg/m^3). These locations were contaminated by the way of traffic pollution (Slovakia, Serbia), chemical industry, and oil refinery (Romania). Urban sites of Romania, Serbia, and Slovakia had the highest ΣHCH ($\alpha + \beta + \gamma + \delta$- isomers) levels with concentrations of 110652, 1631.9, and 1079.6 pg/m^3, respectively. Additionally, urban sites of Serbia (986.4 pg/m^3) and Romania (448.2 pg/m^3), and rural site of Romania (329.9 pg/m^3) had the highest ∑DDT levels.

PCBs and OCPs levels were measured in Buenos Aires, Argentina in two sampling periods, 2006 and 2007 (Tombesi, Pozo, and Harner 2014). The highest average level of $\sum_{46}$PCBs was detected in Bahia Blanca, urban site (200±130 pg/m^3), where the lowest level was measured in Buenos Aires, agricultural site (20±20 pg/m^3). The most abundant OCP was Σendosulfan (-I, -II, -SO_4) with the maximum value of 16000 pg/m^3 in an agricultural area. In general, OCP levels were higher in Bahia Blanca and amount of OCPs in warmer periods were increasing.

Other studies related to atmospheric concentrations of PCBs and OCPs found in the literature are given in Table 2.3 and Table 2.4 in addition to the studies summarized above. In the light of the literature reviewed, it can be said that PCBs are mostly found to be higher in urban and industrialized areas than suburban and agricultural areas. The reason of this trend is mainly utilization of PCB containing materials in the industry and spread from waste disposal areas. To add more, concentration of PCBs in the atmosphere becomes higher in summer than other seasons as a result of volatilization in warmer temperature. Different pollutants can be dominant according to sampling sites and seasons in the case of OCPs. Since OCPs are the main content of both pesticides and insecticides, they have generally high concentrations in both urban and agricultural areas. According to agricultural activities, OCPs can reach high levels in non-heating or heating periods. Long range atmospheric transportation is also affecting the distribution of these pollutants.

Table 2.3. Ambient air ΣPCB concentrations around the World

Reference	**Sampling Points**	**Sampling Period**	**Mean Concentration**
Aliyeva et al. (2012)	Azerbaijan	October - November 2008 (n=13)	[a]Urban + rural area Σ_7PCB = 0.046
Estellano et al. (2012)	Tuscany Region/ Italy	April - July 2008 (n=16)	Urban area Σ_5PCBs = 80 Rural area Σ_5PCBs = 18
Estellano et al. (2014)	Puglia Region/ Italy	January 2009 - February 2010 (n=16)	Urban area spring Σ_{26}PCB = 109 Urban area summer Σ_{26}PCB = 132 Urban area autumn Σ_{26}PCB = 51 Urban area winter Σ_{26}PCB = 68 Sub-urban area spring Σ_{26}PCB = 50 Sub-urban area summer Σ_{26}PCB = 90 Sub-urban area autumn Σ_{26}PCB = 36 Sub-urban area winter Σ_{26}PCB = 45
Vilavert et al. (2014)	Catalonia/ Spain	March - July 2010, September - December 2011 (n=16)	Waste disposal area 2010 spring Σ_7PCB = 27.2 Waste disposal area 2010 autumn Σ_7PCB = 25.6 Waste disposal area 2011 spring Σ_7PCB = 27.7 Waste disposal area 2011 autumn Σ_7PCB = 24.8
Zhang et al. (2008)	India	July - September 2006 (n=18)	Urban area $\sum_{28}$PCB = 662 Rural area $\sum_{28}$PCB = 464 Wetlands $\sum_{28}$PCB = 238
Ding et al. (2013)	Tientsin/ China	June 2008 (n=22) - October 2009 (n=22)	[b]Urban area summer Σ_{25}PCB = 1.56×10^5 [b]Urban area winter Σ_{25}PCB = 1.38×10^5
Syed et al. (2013)	Punjab Province/ Pakistan	January - March 2011 (n=10)	Industrial + agricultural area $\sum_{31}$PCB = 120
Zhang et al. (2013)	Yangtze River/ China	June 2010 - 2011 (n=368)	Industrial + urban area spring Σ_6PCB = 29.9 Industrial + urban area summer Σ_6PCB = 21.6 Industrial + urban area autumn Σ_6PCB = 44.1 Industrial + urban area winter Σ_6PCB = 44.4

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Table 2.3. (Cont.)

Reference	**Sampling Points**	**Sampling Period**	**Mean Concentration**
Mahmood et al. (2014)	River Chenab/ Pakistan	January - June 2013 (n=6)	$\sum_{33}$PCB = 150.8
Nasir et al. (2014)	Karachi and Lahore/ Pakistan	January - October 2011	Karachi (urban) $\sum_6$PCB[c] = 51-224 pg/m^3 Lahore (urban) $\sum_6$PCB[c] = 123-227 pg/m^3
Li, Geng, Liu, et al. (2012)	King George Island/ Antarctica	2009 – 2010	Remote area Σ_{20}PCB = 4.54 pg/m^3
Meire et al. (2012)	Southeast and South Brazil	December 2007- March 2008, June - August 2008	Remote area summer Σ_{30}PCB = 135 pg/m^3 Semi-rural area summer Σ_{30}PCB = 338 pg/m^3 Urban area summer Σ_{30}PCB = 215 pg/m^3 Rural area summer Σ_{30}PCB = 68 pg/m^3 Remote area winter Σ_{30}PCB = 161 pg/m^3 Sub-urban area winter Σ_{30}PCB = 450 pg/m^3 Urban area winter Σ_{30}PCB = 395 pg/m^3 Rural area winter Σ_{30}PCB = 144 pg/m^3
Pozo et al. (2012)	Bio Bio Region/ Chile	January - March 2007 (n=65)	Rural area Σ_{48}PCB = 40 pg/m^3 Urban area Σ_{48}PCB = 16 pg/m^3 Industrial areas Σ_{48}PCB = 195 pg/m^3

[a] ng/m^3
[b] fg/m^3
[c] Range of the concentrations

Table 2.4. Ambient air OCP concentrations around the World

Reference	Sampling Points/ Period	Mean Concentration	
Hayward, Gouin, and Wania (2010)	Ontario, Canada/ March 2006 - September 2007 (n=31)	OCP	Rural (pg/m^3)
		ENDO-I	52.5
Aliyeva et al. (2012)	Urban and rural, Azerbaijan/ October - November 2008 (n=13)	OCP	Urban + Rural (ng/m^3)
		α-HCH	0.46
		β-HCH	0.06
		γ-HCH	0.16
		o,p'-DDE	0.02
		p,p'-DDE	0.29
		o,p'-DDD	0.01
		p,p'-DDD	0.01
		o,p'-DDT	0.02
		p,p'-DDT	0.03

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Table 2.4. (Cont.)

Reference	**Sampling Points/ Period**	**Mean Concentration**			
Estellano et al. (2012)	Tuscany Region, Italy/ April - July 2008 (n=16)	OCP	Urban (pg/m^3)	Rural (pg/m^3)	
		α-HCH	230	BDL	
		γ-HCH	380	90.0	
		ENDO-I	560	300	
		p,p'-DDT	50.0	80.0	
Zhang et al. (2008)	India/ July-September 2006 (n=18)	OCP	Urban (pg/m^3)	Rural (pg/m^3)	Wetlands (pg/m^3)
		α-HCH	451	53	25
		β-HCH	36.0	16	17
		γ-HCH	909	174	61
		o,p'-DDT	268	88	52
		p,p'-DDT	110	79	25
		p,p'-DDE	554	81	13
		p,p'-DDD	33	18	9
		TC	62	15	7
		CC	89	28	7
		ENDO-I	264	262	5
		ENDO-II	76	53	6

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Table 2.4. (Cont.)

Reference	**Sampling Points/ Period**	**Mean Concentration**								
		OCP	Imphal (urban) (pg/m^3)				Thoubal (rural) (pg/m^3)			
			Cold season	Hot season	Rainy season	Retreating monsoon season	Cold season	Hot season	Rainy season	Retreating monsoon season
Devi et al. (2011)	India/ January - December 2009	*α*-HCH	49	11	130	31	78	165	127	42
		β-HCH	18	37	12	0	0	21	5	0
		γ-HCH	71	90	105	30	46	122	106	39
		o,p'-DDE	10	58	45	6	84	23	55	20
		p,p'-DDE	40	76	19	5	7	151	64	26
		o,p'-DDD	18	55	34	2	0	18	40	9
		p,p'-DDD	43	11	14	9	69	22	10	6
		o,p'-DDT	13	61	66	3	0	38	45	17
		p,p'-DDT	55	119	102	24	84	132	103	45
		ENDO-I	32	34	31	20	51	155	90	43
		ENDO-II	27	45	13	13	24	92	48	18
		ENDOSULP	4	14	5	1	6	13	12	5
		CC	16	17	21	2	0	29	47	4
		TC	26	19	28	13	0	40	69	13

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Table 2.4. (Cont.)

Reference	**Sampling Points/ Period**	**Mean Concentration**						
		OCP^a	Paranaque (urban) (pg/m^3)	Valenzuela (urban) (pg/m^3)	Quezon city (urban) (pg/m^3)	Laguna (rural) (pg/m^3)	Rizal (rural) (pg/m^3)	Bulacan (rural) (pg/m^3)
Santiago and Cayetano (2011)	Philippines/ May - December 2005 (n=24)	HEPT	ND	ND	ND-275	ND	ND-125	ND
		CC	364-578	88-288	85-168	ND-49	BDL-82	ND-83
		TC	414-743	68-191	62-108	ND-33	25-52	ND-51
		ALD	ND-96	ND-76	ND-121	ND-127	ND-118	ND
		DIELD	ND-94	ND-61	ND-129	ND	41-234	ND
		ENDR	ND-90	BDL-64	ND-14	ND-90	ND-20	ND-16
		ENDO-I	ND	ND	ND-139	ND	ND-55	ND-686
		ENDO-II	ND-142	ND-440	ND-387	ND-49	ND-148	112-375
		ENDOSULP	ND	ND	ND	ND-47	ND	ND-52
		o,p'-DDD	ND	ND	ND-28	ND	ND	ND
		o,p'-DDT	ND	ND	ND	ND-64	ND-BDL	ND-66
		p,p'-DDT	ND-29	ND-23	ND	ND	ND	ND-BDL

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Table 2.4. (Cont.)

Reference	**Sampling Points/ Period**	**Mean Concentration**				
Pozo et al. (2012)	Bio Bio Region, Chile/ January - Mach 2007 (n=65)	OCP	Rural (pg/m^3)	Urban (pg/m^3)	Industrial sites[a] (pg/m^3)	
		γ-HCH	40	80	5-120	
		TC	1.2	2.2	BDL-1.1	
		CC	BDL	BDL	BDL-1	
		DIELD	20	15	BDL-20	
		ENDO-I	14	BDL	BDL-20	
		p,p'-DDE	BDL	30	BDL-30	
Zhang et al. (2013)	Yangtze River/ China (Industrial + urban site)/ June 2010 - 2011 (n=368)	OCP	Spring (pg/m^3)	Summer (pg/m^3)	Autumn (pg/m^3)	Winter (pg/m^3)
		∑DDE	150	121	178	105
		∑DDT	176	175	215	106
		∑HCH	5.19	BDL	38.5	31.6
		TC+CC	BDL	99.1	331	12.1

[a] Range of the concentrations

CHAPTER 3

MATERIALS AND METHODS

In this section, sampling locations and periods, sample preparation, processing, and instrumental analysis, quality assurance and quality control, and determination of air volume passed through PUF-discs are presented.

3.1. Sampling Locations and Collection

Air samples were collected from both urban and background sites of 16 cities in Turkey that have been selected on the central axes that passes Anatolia east to west and north to south in addition to the three corner locations of Turkey (Figure 3.1). The sampling points were selected by considering the specified criteria in UNEP (2007), and ease of transportation. It was suggested that the background sites should represent a diameter of a circular area of at least 100 km, therefore the distance between the sampling points was about 250-300 km. Additionally, the sampling locations were chosen to reflect a mixture of rural, industrial, and agricultural areas. Sampling was performed in 3-month periods in 4 phases; May-July 2014 (Phase-I), August-October 2014 (Phase-II), November 2014-January 2015 (Phase-III), and February-April 2015 (Phase-IV). The deployment and collection dates of PUFs, and average temperature during the sampling periods are given in Table 3.1. The sampling durations varied between 80 and 118 days depending on the field work conditions availability. Range of average temperatures in each sampling periods were 10.6-24.2˚C (Phase-I), 12.9-25.6˚C (Phase-II), -3.6-12.8˚C (Phase-III), and 3.5-15.6˚C (Phase-IV), respectively.

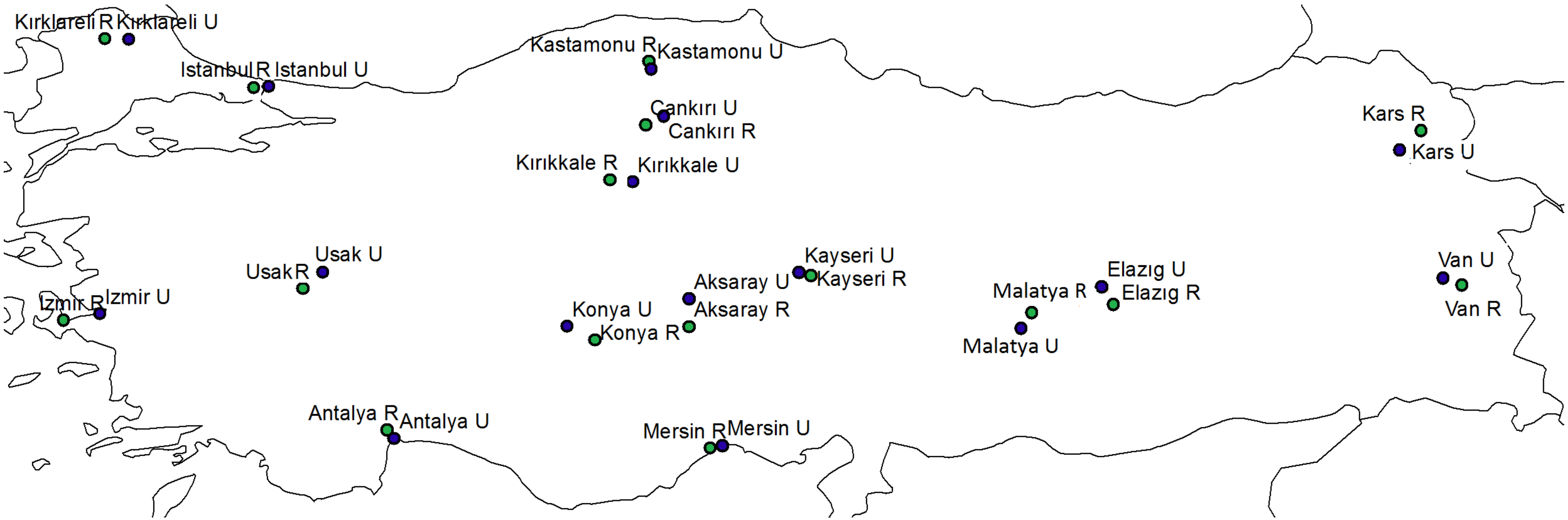

Figure 3.1. Sampling locations (Blue: urban site, green: background site)

Table 3.1. Deployment and collection dates of PAS

Sampling Point	**Phase-I Deployment/ Collection**	**Phase-I Average T[a] (˚C)**	**Phase-II Deployment/ Collection**	**Phase-II Average T (˚C)**	**Phase-III Deployment/ Collection**	**Phase-III Average T (˚C)**	**Phase-IV Deployment/ Collection**	**Phase-IV Average T (˚C)**
Aksaray (U[b], R[c])	27.04.2014/ 09.08.2014	19.2	09.08.2014/ 07.11.2014	16.4	07.11.2014/ 15.02.2015	3.2	15.02.2015/ 17.05.2015	6.9
Antalya (U, R)	22.04.2014/ 08.08.2014	24.2	08.08.2014/ 04.11.2014	24.8	04.11.2014/ 13.02.2015	12.8	13.02.2015/ 28.05.2015	15.6
Çankırı (U, R)	01.05.2014/ 06.08.2014	19.0	06.08.2014/ 13.11.2014	16.2	13.11.2014/ 23.02.2015	2.5	23.02.2015/ 18.05.2015	7.8
Elazığ (U, R)	29.04.2014/ 14.08.2014	23.5	14.08.2014/ 08.11.2014	19.2	08.11.2014/ 16.02.2015	3.5	16.02.2015/ 20.05.2015	9.0
İstanbul (U, R)	05.05.2014/ 01.08.2014	22.8	01.08.2014/ 04.11.2014	22.0	04.11.2014/ 26.02.2015	9.2	26.02.2015/ 27.05.2015	13.4
İzmir (U, R)	01.05.2014/ 01.08.2014	23.6	01.08.2014/ 04.11.2014	23.3	04.11.2014/ 15.02.2015	10.3	15.02.2015/ 25.05.2015	14.1
Kars (U, R)	22.04.2014/ 07.08.2014	15.2	07.08.2014/ 08.11.2014	12.9	08.11.2014/ 23.02.2015	-3.6	23.02.2015/ 29.05.2015	3.5
Kastamonu (U, R)	01.05.2014/ 05.08.2014	19.0	05.08.2014/ 08.11.2014	16.8	08.11.2014/ 13.02.2015	3.3	13.02.2015/ 18.05.2015	7.4
Kayseri (U, R)	28.04.2014/ 09.08.2014	10.6	09.08.2014/ 09.11.2014	16.9	05.11.2014/ 28.02.2015	3.0	28.02.2015/ 30.05.2015	9.3

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Table 3.1. (Cont.)

Sampling Point	Phase-I Deployment/ Collection	Phase-I Average T[a] (˚C)	Phase-II Deployment/ Collection	Phase-II Average T (˚C)	Phase-III Deployment/ Collection	Phase-III Average T (˚C)	Phase-IV Deployment/ Collection	Phase-IV Average T (˚C)
Kırıkkale (U, R)	30.04.2014/ 07.08.2014	19.1	07.08.2014/ 06.11.2014	17.7	06.11.2014/ 16.02.2015	3.3	16.02.2015/ 17.05.2015	6.8
Kırklareli (U)	24.06.2014/ 04.08.2014	22.9	04.08.2014/ 06.11.2014	19.1	06.11.2014/ 25.02.2015	6.4	25.02.2015/ 01.06.2015	14.4
Kırklareli (R)	Sampler was lost		04.08.2014/ 06.11.2014	19.1	06.11.2014/ 25.02.2015	6.4	25.02.2015/ 01.06.2015	14.4
Konya (U, R)	27.04.2014/ 20.08.2014	20.3	20.08.2014/ 07.11.2014	17.7	07.11.2014/ 06.03.2015	3.3	06.03.2015/ 17.05.2015	9.1
Malatya (U, R)	29.04.2014/ 06.08.2014	23.1	06.08.2014/ 08.11.2014	19.7	08.11.2014/ 12.02.2015	3.6	12.02.2015/ 20.05.2015	8.8
Mersin (U, R)	21.04.2014/ 04.08.2014	24.7	04.08.2014/ 08.11.2014	25.6	08.11.2014/ 14.02.2015	12.2	14.02.2015/ 18.05.2015	14.7
Uşak (U, R)	26.04.2014/ 12.08.2014	19.1	12.08.2014/ 08.11.2014	17.0	08.11.2014/ 22.02.2015	3.0	22.02.2015/ 16.05.2015	8.3
Van (U, R)	21.04.2014/ 06.08.2014	16.8	06.08.2014/ 08.11.2014	15.4	08.11.2014/ 21.02.2015	0.8	20.02.2015/ 28.05.2015	5.7

[a] T: Temperature
[b] U:Urban
[c] R:Rural

3.2. Sampling Preparations

3.2.1. Cleaning of Laboratory Equipment

The laboratory equipment used for sampling and analyses were cleaned according to methods described in USEPA (2007) to eliminate contamination of the materials, and to minimize the error caused by laboratory equipment. All equipment was washed with technical alcohol and dried. The dried materials were waited in wash water prepared by mixing hot water and Alconox detergent (a spoonful for 1.5 liter water) until water cools down. Then, they were brushed and cleaned by tap water. After this step, equipment was divided into two groups. The first group (glass materials) was firstly cleaned by chromic acid, tap water, and distilled water, respectively. However, the second group materials (teflon tap, cover, etc.) were only washed with distilled water. Then, they were dried in open-air. The heat-resistant glass materials were dried in oven at 300 ˚C after covering with aluminum foil. All solvents used in the laboratory were in the purity of HPLC grade.

3.2.2. Preparation of Sampling Devices

3.2.2.1. Preparation of Passive Air Sampling (PAS) Devices

The metal parts of the PAS (Figure 3.2) device was washed with warm water and dried. Then, they were cleaned with acetone and hexane. Finally, the device was wrapped with the aluminum foil and transported to the sampling points in zip lock bags.

PUF discs were waited in warm tap water for 4 hours, and then waited in pure water approximately for 2 hours. After PUFs were dehydrated, soxhlet extraction with solvent was applied for final cleaning of PUFs. PUF discs were firstly extracted with acetone, then with hexane:acetone (1:1) mixture, and finally with hexane. Each of the extractions was performed for 12 hours. After soxhlet extraction, PUFs were dried in a desiccator for at least 4 hours at 70 °C, and wrapped with aluminum foil that was conditioned minimum of 2 hours at 450 °C in a muffle furnace. The wrapped PUFs were placed into zip log bags, put into tin cans, and kept in the refrigerator until deployment to the sampling locations (Figure 3.2). Polyurethane foam (PUF) disc placed into passive sampling device as in Figure 3.3.

Figure 3.2. Cleaning and storage procedures of PUF discs

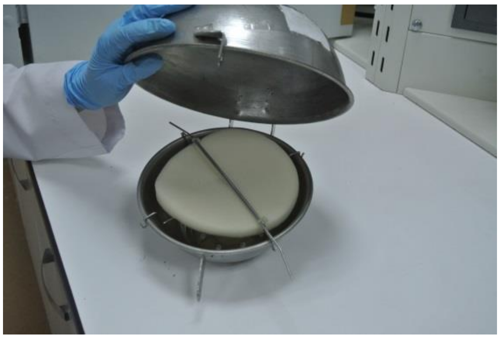


Figure 3.3. Passive sampling device

3.2.2.2 Spike of PUFs with Depuration Chemicals

Depuration chemicals can be selected among the compounds which are in trace amounts or not available in air and isotope labelled. The depuration chemicals, listed in Table 3.2, were selected according to range of octanol-air partition coefficients (K_{OA}) of target chemicals. Solvent cleaned PUF discs were placed into a pyrex previously cleaned by pure water, hexane, and acetone. A solution containing 400 pg/µL of $^{13}C_{12}$-labelled and unlabeled PCBs and 800 pg/µL of d_6 γ-HCH was prepared and two ml of petroleum ether was added to 0.5 ml of the mixture of depuration chemicals. These chemicals were injected on to PUFs approximately 3-4 days prior to travelling for placement into PAS. One surface of PUF was spiked with the mixture by pasteur pipette and petroleum ether was blown by gentle N_2 stream for approximately 15 minutes. Then, same procedure was applied to other side with the remaining mixture. The prepared PUFs were wrapped with baked aluminum foil and placed into tin cans. Connection point of the cans was covered with teflon tape and the boxes were again kept in refrigerator. The scope of blowing of acetone and keeping the boxes in refrigerator was penetration of the depuration chemicals into the PUFs. All the steps were shown in Figure 3.4.

Table 3.2. Depuration chemicals injected on to PUFs

Chemicals	**logK$_{OA}$**	**Spiked amount (ng)**
$^{13}C_{12}$PCB9	7.04	200
$^{13}C_{12}$PCB15	7.63	200
$^{13}C_{12}$PCB32	7.48	200
PCB30	7.71	200
PCB107	9.59	200
PCB198	10.9	200
$d_6\gamma$HCH	7.85	400

Figure 3.4. Injection of depuration chemicals on to PUFs and storage of boxes

3.3. Analyses of the PUFs and Instrumental Analyses

3.3.1. Extraction of PUF Discs

3.3.1.1. Preparation before Extraction

Soxhlet extraction was used for transfer of PCBs and OCPs from PUFs into solvent. Impurities must be removed from samples to be able to transfer the target chemicals from PUFs to solvent completely. One of the impurities, moisture can be removed from samples by anhydrous sodium sulfate (Na_2SO_4). Na_2SO_4 was dried at 400 °C for purification for 4 hours, and waited in desiccator. If water is noticed in the samples at any step further, Na_2SO_4 is added and waited for a while.

Any other organic compounds that are undesired can be kept by neutral alumina (Al_2O_3). It is also used for fractionation of PCBs and OCPs after volume reduction by rotary evaporator. Alumina, particle size of 0.063-0.30 mm was dried at 400 °C for at least 12 hours. After cooling in a desiccator, alumina was deactivated with 6% deionized water. The deactivated alumina was poured into a brown glass jar and closed with a teflon cover. The jar was kept in a desiccator.

3.3.1.2. Extraction of PUFs and Clean-up

PUFs kept in the refrigerator were conditioned in the room conditions, and then prepared for soxhlet extraction. Firstly, PUF was placed into the extractor, and glass weights were put on the PUF to minimize solvent usage. Five ng from each of the surrogate chemicals ($^{13}C_{12}$-PCB 28, $^{13}C_{12}$-PCB 52, $^{13}C_{12}$-PCB 101, $^{13}C_{12}$-PCB 138, $^{13}C_{12}$-PCB 153, $^{13}C_{12}$-PCB 180, and PCB 209) equal to 50 µL was injected onto PUFs in the extractor to calculate method recovery efficiencies. Extraction was done using approximately 180 ml of hexane:acetone (1:1) mixture and 3 or 4 glass beads were also added. The aim of glass beads was to increase heat transfer in the solvent. Allihn condenser, extractor, and flask were connected to each other and connection points were wrapped with teflon band to prevent any solvent loss. Heater and cooler were adjusted to 110 °C and 19 °C, respectively. The extraction was performed for 18 hours.

After extraction of PUFs, solvent was cooled down to room temperature. If water is escaped from cooler to the solvent in flasks in this step, Na_2SO_4 is added to solvent. Volume of the cooled solvent was reduced by a rotary evaporator. Temperature of heater and cooler of the rotary evaporator was adjusted to 36 °C and 19 °C, respectively. Solvent exchange was conducted by washing evaporator column with dichloromethane (DCM), and then 1 ml of isooctane was added to the solvents to transfer target into isooctane to decrease volatilization during storage and analysis. Pressure of the system was selected according to vapor pressure of the solvents used in the extraction. The pressure at the beginning was selected from library of rotary evaporator around 550-600 mbar. Flask was connected to the rotating head and immersed to water bath. Speed was regulated to 2.5 rpm. Then, the system was started, and dripping of the solvent into a collecting bottle was observed. If dripping becomes quick, target chemicals can be lost. The process was continued until reaching a final volume of 3 ml. Then, volume of remaining sample was concentrated to 0.5 ml by N_2 stream, and solvent was exchanged to isooctane.

Figure 3.5. Alumina column

The next step was clean-up and fractionation of PCBs and OCPs by alumina column. The column was prepared by locating a piece of glass wool was placed to bottom of a glass column (10 mm inner diameter × 200 mm height) to prevent loss of particles. One cm height of oven dried Na_2SO_4 was added on 3 g of deactivated alumina (Figure 3.5). The column and collecting bottles were washed two times with 0.5 ml hexane. The extracts were applied to column and 35 ml of elution solution (1:4, DCM: Hexane) was added to collect PCBs and OCPs as one fraction.

Volume of the samples obtained from column was finally reduced to 1 ml, and solvent was exchanged to isooctane again by rotary evaporator-N_2 stream applications.

Fifty ng $^{13}C_{12}$PCB 105 (10 µL) internal standard was injected to the resulting sample, and then the extract was transferred to a GC vial for GC-MS analysis.

3.3.2. Instrumental Analyses

3.3.2.1. Preparation of PCB/OCP/$^{13}C_{12}$ Labeled Surrogate Standards

PCB (Protocol Analytical Supplies, New Jersey, USA), pesticide (Protocol Analytical Supplies, New Jersey, USA), PBDE (Cambridge Isotope Laboratories), $^{13}C_{12}$ labelled PCB (Cambridge Isotope Laboratories), $^{13}C_{12}$-g-HCH (Cambridge Isotope Laboratories), and $^{13}C_{12}$PCB105 standards were used for preparation of calibration and synthetic solutions.

Main stock solution was prepared by using related stock solutions of target POPs (Table 3.3). Then, main stock solution was diluted to obtain 8 different calibration standard concentrations ranged between 0.1 pg/µL and 100 pg/µL. All standards were prepared in isooctane and kept in deep-freeze at -18 °C.

3.3.2.2. GC-MS Analysis

Analysis of PCBs and OCPs were performed by a GC (Agilent 7890B GC) coupled with an MSD (5977A) at research laboratory in Department of Environmental Engineering Department at Bursa Technical University.

PCB analysis was carried out by the GC-MS system operated with electron impact (EI) - selective ion monitoring (SIM) mode. After splitless injection of 2 µL extract, sample was sent to the column (DB-5, 30 m, 0.25 mm i.d., 0.25 µm film thickness) by a carrier gas, Helium (1.1 ml/min). Injector, ion source (70 eV), quadrupole, and auxiliary were operated at 200 °C, 230 °C, 150 °C, and 310 °C, respectively. Temperature programme for PCBs was 1 min at 90°C, 15 °C/min to 160 °C, 3 °C/min to 210 °C, and 10 °C/min to 310 °C (wait 10 min).

OCP analysis was also performed by the GC-MS system operated with negative chemical ionization (NCI) - selective ion monitoring (SIM) mode, and methane was used as ionization gas. After splitless injection of 2 µL extract, it was sent to the column

(DB-5, 15 m, 0.25 mm i.d., 0.1 film thickness) by a carrier gas, Helium (1.1 ml/min). Injector, ion source (70 eV), quadrupole, and auxiliary were operated at 200 °C, 150 °C, 150 °C, and 310 °C, respectively. Temperature programme for OCPs was 2 min at 80°C, 10 °C/min to 285 °C (wait 5 min), and 25 °C/min to 315 °C (wait 5 min). Detailed information about GC-MS analyses is given in Table A.1 in the Appendix.

Table 3.3. Target chemicals

PCBs		**OCPs**	
PCB18	PCB123	ALD	Aldrin
PCB22	PCB132	*α*-HCH	*α*-hexachlorocyclohexane
PCB28	PCB138	*β*-HCH	*β*-hexachlorocyclohexane
PCB31	PCB141	*γ*-HCH	Lindane
PCB41/64	PCB149	*δ*-HCH	*β*-hexachlorocyclohexane
PCB44	PCB151	*o,p'*-DDT	Ortho-para dichlorodiphenyltrichloroethane
PCB49	PCB153	*p,p'*-DDT	Para-para dichlorodiphenyltrichloroethane
PCB52	PCB156	*o,p'*-DDD	Ortho-para dichlorodiphenyldichloroethane
PCB54	PCB157	*p,p'*-DDD	Para-para dichlorodiphenyldichloroethane
PCB56	PCB158	*o,p'*-DDE	Ortho-para dichlorodiphenyldichloroethylene
PCB60	PCB167	*p,p'*-DDE	Para-para dichlorodiphenyldichloroethylene
PCB70	PCB170	DIELD	Dieldrin
PCB74	PCB174	HEPT	Heptachlor
PCB87	PCB180	HEPX	Heptachlor epoxide
PCB90/101	PCB183	TC	*Trans* (alfa)-chlordane
PCB95	PCB187	CC	*Cis* (gamma)- chlordane
PCB99	PCB188	ENDO-I	*α*-Endosulfan
PCB104	PCB189	ENDO-II	*β*-Endosulfan
PCB105	PCB194	ENDOSULP	Endosulfan Sulfate
PCB110	PCB199	ENDR	Endrin
PCB114	PCB203	Mirex	mirex
PCB118		HCB	hexachlorobenzene

3.3.3. Quality Assurance and Quality Control

Instrumental detection limit (IDL) was specified for concentrations determined by internal standard calibration method. IDL was estimated by lowering the signal/noise ratio down to 3 to reach target analyte concentration, and by considering sample extracted and air volume. IDL was determined to be 2/3 of the smallest calibration concentration. Limit of detection (LOD) was calculated by addition of three standard deviations to the average concentration of blank samples. For chemicals not detected in the blanks, LOD was assumed to be equal to IDL. LOD of the target chemicals are given in Table 3.4.

3.3.3.1. Laboratory Control Samples and Field Blanks

PUF disks previously cleaned and kept in aluminum foil, metal box, and zip lock bag were chosen as samples for quality assurance for PAS. One blank PUF disk for soxhlet setup with 6 columns or two blank PUF disks for soxhlet setup with 12 columns were used for laboratory quality control. Results of laboratory control samples are given in Table A.2 in the Appendix.

For field blanks, one of the depuration chemicals injected PUF disk was taken to the selected sampling point and exposed to air approximately 10 seconds. Then PUF disk was wrapped with aluminum foil and put into a tin can to bring back to the laboratory. The PUF disk, field blank was analyzed similar to other PUFs. Three field blanks were prepared in each of the sampling periods but target chemicals were in negligible amounts in the field blanks.

Table 3.4. LOD of chemicals of interest

Analyte	**PAS (pg/m^3)**	**Analyte**	**PAS (pg/m^3)**	**Analyte**	**PAS (pg/m^3)**
pcb30	4.33	pcb114	3.81	HCB	2.16
pcb18	4.13	pcb105	3.44	*α*-HCH	2.22
pcb31	1.21	pcb155	7.32	*β*-HCH	2.22
pcb28	3.33	pcb151	3.06	*γ*-HCH	4.68
pcb22	5.41	pcb149	4.08	*δ*-HCH	2.22
pcb54	3.83	pcb153	1.41	HEPT	3.05
pcb52	2.09	pcb132	2.27	ALD	2.22
pcb49	3.35	pcb141	2.53	HEPX	3.93
pcb44	7.73	pcb138	4.62	CC	2.22
pcb41/60	3.32	pcb158	3.46	TC	2.22
pcb74	4.29	pcb167	2.13	*o,p'*-DDE	9.86
pcb70	2.54	pcb156	2.33	ENDO-I	2.03
pcb60	3.58	pcb157	4.3	DIELD	2.40
pcb56	2.80	pcb188	4.56	*o,p'*-DDD	2.70
pcb104	3.73	pcb187	4.29	*p,p'*-DDE	2.87
pcb95	3.61	pcb183	2.20	END	7.79
pcb90/101	5.69	pcb174	2.08	ENDO-II	2.62
pcb99	4.17	pcb180	1.07	*o,p'*-DDT	4.20
pcb87	3.21	pcb170	1.62	*p,p'*-DDD	5.07

(Cont. on next page)

Table 3.4. (Cont.)

Analyte	PAS (pg/m^3)	Analyte	PAS (pg/m^3)	Analyte	PAS (pg/m^3)
pcb110	3.14	pcb189	5.06	ENDOSULP	2.22
pcb123	3.23	pcb199	3.72	*p,p'*-DDT	5.01
pcb118	4.57	pcb203	3.63	Mirex	6.40

3.3.3.2. Calibration Control Standards

Third level calibration standard, usually 50-60 pg/µL was chosen as quality assurance standard (QA/QC) to test the validation of calibration during GC-MS analyses. This standard was passed through column every 25 samples and analyzed in GC-MS as one of the usual samples. Table A.3 in the Appendix lists the calibration control results.

3.3.3.3. Recovery Efficiencies for Different Steps of the Analyses

To determine loss rate of the target chemicals, target analyte was firstly injected into 250 ml acetone: hexane mixture. Then the samples were processed with the steps; rotary evaporator, volume reduction by N_2 stream, clean-up with alumina column, and final volume reduction and solvent exchange to isooctane, respectively. The obtained samples were analyzed by GC-MS and results are given in Table 3.5. The average recovery efficiencies of PCBs (n=6) vary from 64.7% (PCB 153) to 100% (PCB 138) and vary from 64% (*p,p′*-DDD) to 103% (endrin) for OCPs (n=6).

Table 3.5. Recovery efficiencies

Analyte	Avg.[a]	S. D.[b]	Min.[c]	Max.[d]	Analyte	Avg.	S. D.	Min.	Max.
PCBs									
PCB30	87.14	8.72	75.42	101.08	PCB114	80.90	9.86	68.08	91.42
PCB18	68.17	6.79	59.83	76.67	PCB105	77.65	19.75	62.50	114.92
PCB31	81.43	11.03	64.83	98.42	PCB155	73.35	7.53	65.17	83.08
PCB28	65.17	6.56	59.08	77.08	PCB151	76.15	8.70	65.75	86.25
PCB22	71.56	8.30	61.75	82.75	PCB149	76.97	8.21	68.25	86.25

(Cont. on next page)

Table 3.5. (Cont.)

Analyte	**Avg.**[a]	**S. D.**[b]	**Min.**[c]	**Max.**[d]	**Analyte**	**Avg.**	**S. D.**	**Min.**	**Max.**
PCBs									
PCB54	70.32	8.09	59.58	81.67	PCB153	64.71	7.63	56.42	74.33
PCB52	72.57	8.13	61.17	82.25	PCB132	72.28	8.81	62.58	82.50
PCB49	70.58	6.70	63.33	80.50	PCB141	79.54	8.77	67.58	88.58
PCB44	72.68	8.44	63.00	81.75	PCB138	100.11	13.00	74.08	108.25
PCB41/60	71.64	7.70	61.75	81.58	PCB158	76.97	7.37	68.33	84.33
PCB74	77.47	8.75	66.92	91.17	PCB167	84.57	11.66	69.92	98.25
PCB70	73.85	8.76	64.25	87.58	PCB156	87.58	9.83	76.92	99.08
PCB60	79.35	5.99	71.42	85.42	PCB157	84.33	9.58	73.75	96.75
PCB56	72.49	6.47	66.33	81.83	PCB188	78.07	8.29	68.33	86.50
PCB104	70.01	8.18	59.42	79.17	PCB187	86.08	10.74	75.75	99.50
PCB95	74.10	8.50	64.08	82.92	PCB183	86.46	10.09	73.92	97.00
PCB90/101	73.33	6.91	63.92	82.50	PCB174	86.31	8.80	77.58	96.42
PCB99	77.78	7.95	68.17	88.17	PCB180	87.68	10.66	75.58	99.58
PCB87	74.74	5.97	67.33	81.17	PCB170	93.24	15.44	76.33	112.17
PCB110	76.64	8.13	67.17	85.92	PCB189	85.32	11.48	70.17	96.75
PCB123	82.15	9.09	70.42	93.42	PCB199	90.58	12.79	75.83	104.58
PCB118	75.78	8.67	65.33	86.67	PCB203	92.51	8.23	79.50	104.08
OCPs									
HCB	81	10	65	93	TC	88	10	72	99
α-HCH	74	13	59	90	DIELD	71	17	54	96
β-HCH	69	8	57	78	*o.p'*-DDD	76	16	60	101
γ-HCH	70	8	63	85	*p.p'*-DDE	93	6	87	102
δ-HCH	99	24	70	137	ENDR	103	13	84	115
HEPT	67	5	59	73	ENDO-II	99	21	69	127
ALD	77	5	69	83	*o.p'*-DDT	70	6	61	76
HEPX	80	13	66	100	*p.p'*-DDD	64	9	54	76
CC	90	13	77	109	ENDOSULP	92	10	75	105
o,p'-DDE	72	11	52	83	*p.p'*-DDT	66	13	53	87
ENDO-I	98	13	78	111	Mirex	74	14	55	95

[a] Avg.: Average [b] S.D.: Standard deviation [c] Min.: Minimum [d] Max.: Maximum

3.3.3.4. Recovery Efficiencies of the Surrogate Chemicals

PUF disks were injected with 5 ng ^{13}C labelled PCB mixture (200 ng of each) to determine surrogate chemical recovery efficiencies and the results are shown in Table 3.6. The mean of recovery efficiencies of the surrogate chemicals was 86.7% with the range of 57.6% - 140%.

Table 3.6. Recovery efficiencies of the surrogate chemicals

	Minimum	**Maximum**	**Average**	**S.D.**
$^{13}C_{12}PCB28$	60.2	137	87.0	15.7
$^{13}C_{12}PCB52$	60.2	140	89.8	19.2
$^{13}C_{12}PCB101$	60.4	124	87.4	15.1
$^{13}C_{12}PCB153$	60.2	134	85.8	14.1
$^{13}C_{12}PCB138$	57.6	137	90.3	14.6
$^{13}C_{12}PCB180$	59.4	140	87.2	16.0
$^{13}C_{12}PCB209$	58.8	139	79.4	15.4

S.D.: Standard Deviation

3.4. Calculation of Air Volume Passed Through PAS Device

Since PAS operates without a pump, it is required to calculate an uptake rate of air passed through PUF disk. The uptake rate is controlled by air side mass transfer coefficient (k_A) which weakly depends on temperature but a strong function of wind speed. However, the effect of wind speed is minimized by keeping PUF disk in a metal chamber (Harner et al. 2004).

Since PUF disks used for PAS are placed into a protective chamber, mass transfer from bulk air to PUF disk occurred step by step (Figure 3.6). First transport occurs from bulk air to the air inside the chamber, and then at the air-sampler interface followed by transport from interface to sampler bulk.

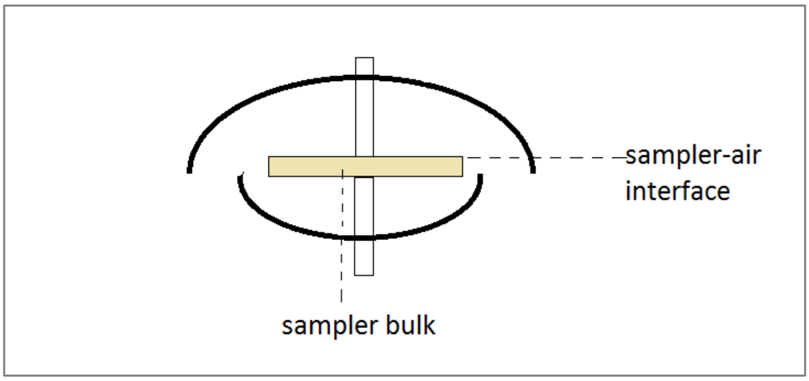


Figure 3.6. Schematic representation of mass fluxes between air and PAS

Estimation of air volume passed through PUF disk was performed as explained in the study of Harner et al. (2004). Accumulation of compounds of interest depends on the PUF-air partition coefficient ($K_{PUF\text{-}air}$) at equilibrium (Eq 3.1) where $K_{PUF\text{-}air}$ is a function of K_{OA}. The compounds with higher K_{OA} accumulate in high amounts in samplers than those with the lower K_{OA} so PCBs, and OCPs with low molecular weight reach equilibrium faster than the heavier ones (Chaemfa et al. 2008). Pollutants tend to transfer from air to PUF disc because of concentration gradient, and calculations are as follows.

$$K_{PUF\text{-}air}=\frac{C_{PUF,equilibrium}}{C_{air,equilibrium}} \tag{3.1}$$

where $C_{PUF,equilibrium}$ and $C_{air,equilibrium}$ stand for concentration of pollutants in PUF disk and in air (mol/volume). Total sampling profile of passive sampling material is calculated as in Eq 3.2 (Pozo et al. 2004).

$$C_{PUF\text{-}equilibrium}=K'_{PUF\text{-}air} \times C_{air\text{-}equilibrium}\left\{1\text{-}\exp\text{-}\left[\left(\frac{A_{PUF}}{V_{PUF}}\right) \times \left(\frac{k_A}{K'_{PUF\text{-}air}}\right)\right] \times t\right\} \tag{3.2}$$

where A_{PUF} is the surface area of PUF disk (m^2), V_{PUF} is the volume of PUF disc, k_A is the transmission rate of POPs from air at the sampling location to PUF (m/day), $K'_{PUF\text{-}air}$ is a unitless parameter of the sampling material, and t is the exposure time (days). In the above equation, $K'_{PUF\text{-}air}$, an unknown parameter, calculated as in Equation 3.3 (Shoeib and Harner 2002a), and $\log K_{OA}$ values used in Equation 3.4 were taken from literature

(Harner and Bidleman (1996), Shoeib and Harner (2002b)). For chemicals with $\log K_{OA}$ >8.5, the sampling rate becomes linear for the first 100 days but for lower compounds PUF discs reaches saturation point before 100 days. It can be resulted that time required to reach saturation inversely proportional to K_{OA} values (Pozo et al. 2004). k_A is calculated by Equation 3.8 derived from Equation 3.5 (Gouin et al. 2005).

$$K'_{PUF\text{-}air}=K_{PUF\text{-}air} \times \text{Density of PUF} \qquad (3.3)$$

$$\log K_{PUF\text{-}air}=0.6366 \times \log K_{OA}-3.1774 \qquad (3.4)$$

$$\frac{C_o \times A \times k_A}{K_{PUF\text{-}air}}=-V\frac{dC}{dt} \qquad (3.5)$$

$$\frac{dC}{dt}=-\frac{C_o \times k_A}{D_{film} \times K_{PUF\text{-}air}}=-Co \times k_d \qquad (3.6)$$

$$C_t=C_o \times \exp(-k_d \times t) \qquad (3.7)$$

$$k_A=\frac{\ln\left(\frac{C}{C_o}\right) \times D_{film} \times K'_{PUF\text{-}air}}{t} \qquad (3.8)$$

where C_O is the initial concentration of spiked depuration chemicals, and C is the final concentration after sampling period. The calculated values of C/C_O are given in Table B.1 and Table B.2 in the Appendix. Daily effective air sampling rate (R, m^3/day) is calculated by using k_A (Eq 3.9).

$$R=k_A \times \text{Surface area of PUF} \qquad (3.9)$$

After calculation of all these parameters, volume of total air passed through PUF (V_{air}, m^3) is calculated by using Equation 3.10. The properties of PUF used in the study are given in Table 3.7 (Pozo et al. 2004).

$$V_{air}=K'_{PUF\text{-}air} \times V_{PUF}\left\{1-\exp\left[-\left(\frac{A_{PUF}}{V_{PUF}}\right)\left(\frac{k_A}{K'_{PUF\text{-}air}}\right)\right] \times t\right\} \qquad (3.10)$$

Table 3.7. The properties of PUF discs

Effective film thickness of PUF, D_{film},	5.67×10^{-3}
Density (g/m^3)	2.1×10^{4}
Surface area (m^2)	3.7×10^{-2}
Volume (m^3)	2.1×10^{-4}

The calculated air volumes were divided into total sampling date for each of the periods and the uptake rate of air was determined (Table 3.8).

Table 3.8. Uptake rate of air for sampling periods

Sampling Point	**Phase-I Uptake Rate of Air (m^3/day)**		**Phase-II Uptake Rate of Air (m^3/day)**		**Phase-III Uptake Rate of Air (m^3/day)**		**Phase-IV Uptake Rate of Air (m^3/day)**	
	Urban	**Rural**	**Urban**	**Rural**	**Urban**	**Rural**	**Urban**	**Rural**
Aksaray	7.75	10.46	11.26	9.18	4.55	7.91	5.64	7.65
Antalya	5.95	6.88	7.57	6.81	3.59	1.18	4.20	3.65
Çankırı	8.19	8.54	9.53	9.94	3.03	4.10	4.08	6.78
Elazığ	5.66	7.08	7.68	7.46	3.30	7.15	4.46	6.64
İstanbul	6.99	7.89	6.47	7.65	2.20	2.56	3.10	2.64
İzmir	9.07	8.30	6.87	9.87	1.61	4.94	3.87	6.54
Kars	9.87	11.08	11.86	12.15	2.56	3.28	4.29	7.44
Kastamonu	9.36	6.43	9.63	9.62	3.27	2.34	3.89	4.58
Kayseri	9.85	12.74	11.11	8.89	2.05	4.28	4.22	5.53
Kırıkkale	7.88	8.75	10.04	9.46	4.33	3.73	6.13	3.94
Kırklareli	7.22	Sampler was lost	8.58	8.13	1.88	3.98	4.10	6.08
Konya	8.89	6.80	10.93	9.74	3.16	5.49	5.12	8.69
Malatya	6.46	5.77	8.05	7.71	3.32	3.86	3.01	4.04
Mersin	5.34	7.79	5.83	5.61	3.17	1.33	4.62	2.67
Uşak	7.36	10.21	9.45	9.63	4.39	2.90	4.49	4.34
Van	8.09	8.34	10.42	8.78	3.50	2.62	4.96	5.92

3.5. Statistical Analysis

3.5.1. Multivariate Analysis

Principle Component Analysis (PCA) is a multivariate method to analyze and represent a data set by principle components, and to indicate the similarity of observations (Abdi and Williams 2010). In this study, PCA was used to investigate if variation in concentrations of 21 OCPs (o,*p'*-DDD excluded because it was not detected) could be represented with a fewer number of components. The components would include compounds with similar variations that might indicate source similarities. Hence, it could be used as a receptor oriented source apportionment tool. PCA analysis was performed by Minitab 16 software and the data were standardized. Initially, PCA models were built with 10 PCs. Then, according to the breaking point in the scree plots, 5 PC models were built with 81.4% and 84.8% cumulative Eigen value proportion for urban and rural sites, respectively (Figure 3.7a and Figure 3.7b, respectively). PCA was also applied for 43 PCB congeners. Similar to procedure applied to OCPs, the program was run by 10 PC initially and then run by 4 PC for urban and rural sites (Figure 3.7c and Figure 3.7d, respectively) with 79.0% and 80.5% cumulative Eigen value proportion, respectively. Finally, the program was run for all targeted PCBs and OCPs together initially with 10 PC and then by 5 PC for urban and rural sites with 77.5% and 81.6% cumulative Eigen value proportion, respectively (Figure 3.8).

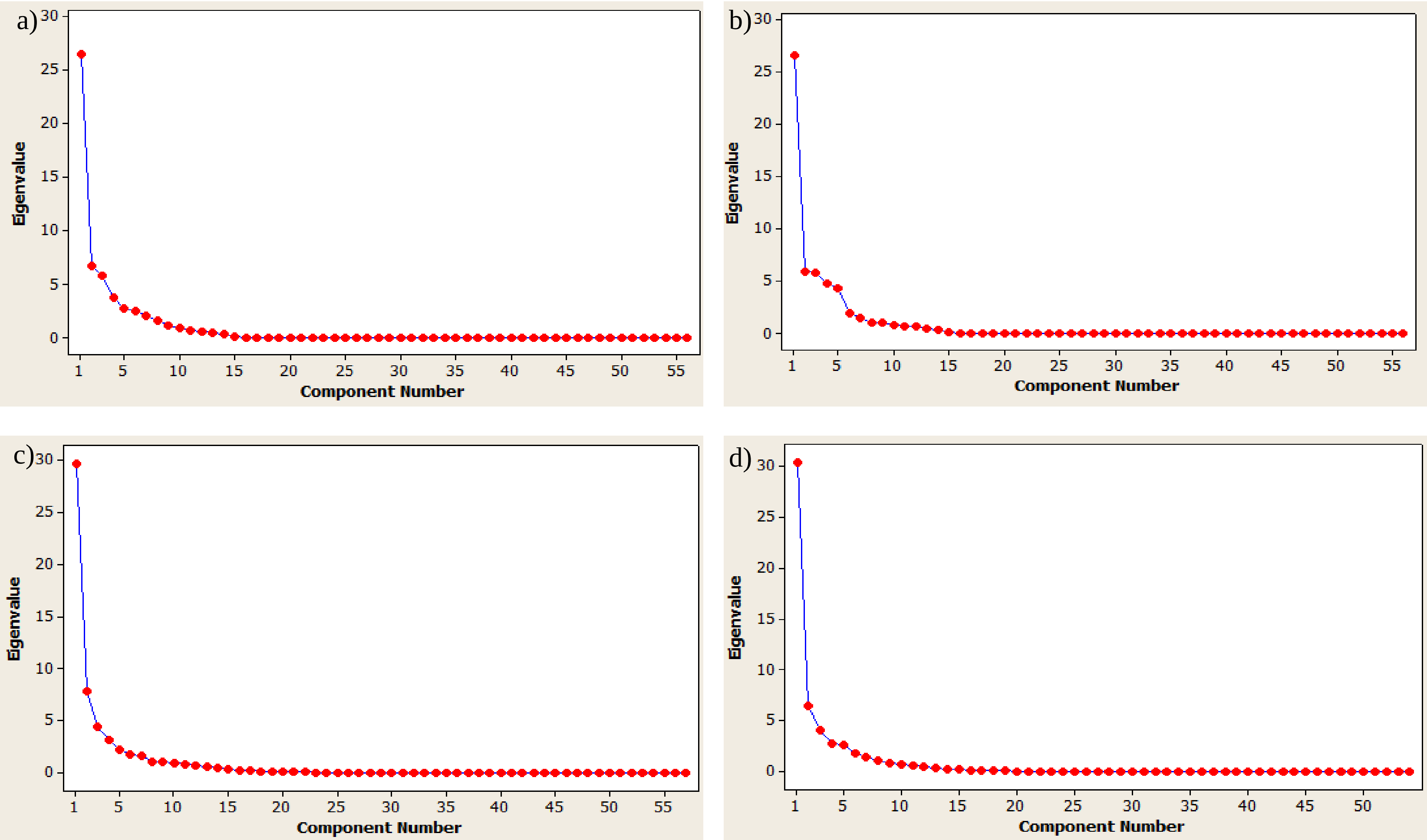


Figure 3.7. Scree plot with 10 PC of a) OCPs for urban sites b) OCPs for rural sites c) PCBs for urban sites d) PCBs for rural sites

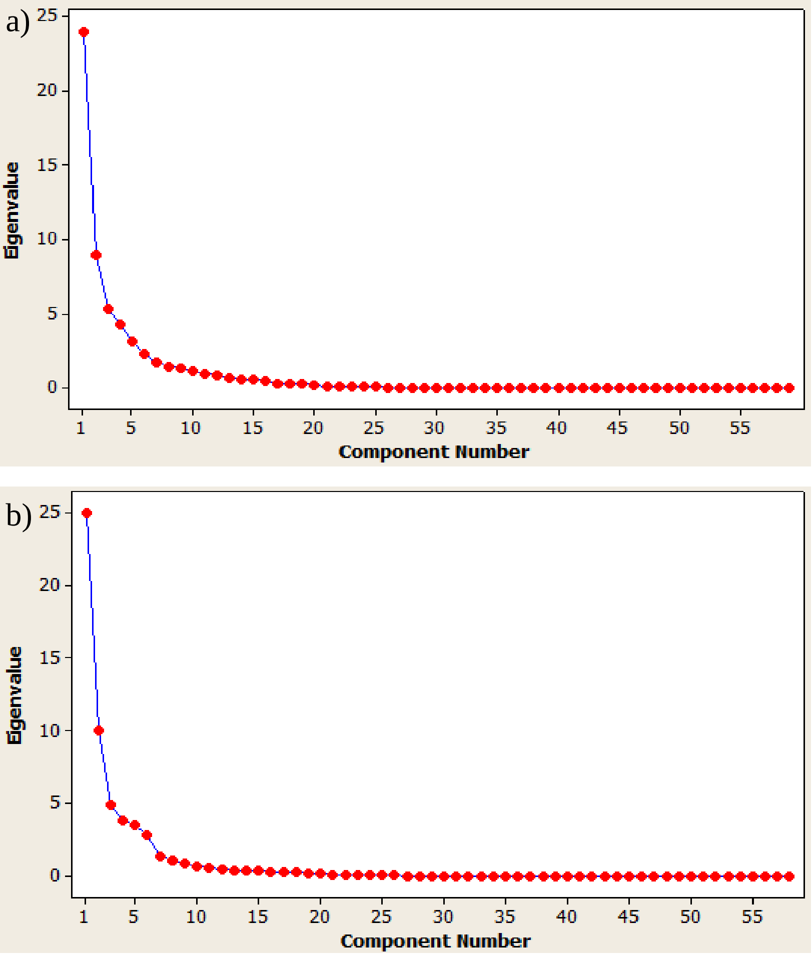


Figure 3.8. Scree plot with 10 PC for a) urban sites b) rural sites for PCBs and OCPs

3.5.2. Univariate Analysis

Mann-Whitney U test is a non-parametric test used to compare the median of two independent samples if distribution of the data set is not normal. In this thesis, it was used to determine the differences in median pollutant concentrations between urban and rural sites, and to investigate the effects of temperature on pollutant concentrations using Minitab v16 software. The samples were divided into two groups as for the analysis of temperature effect: low (range: -3.6 – 14.1˚C) and high temperature ranges (range: 14.4 – 25.6˚C) by choosing mid-point (14.2˚C) of the temperature range of the one-year sampling period.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Ambient Air Concentrations of Targeted POPs

In this part, ambient air concentrations of 43 PCBs and 22 OCPs are discussed. To be able to visualize the results better; the annual concentrations of POPs measured at urban and rural sites were plotted both as bar graphs and maps. Since the extreme results on the bar graphs suppressed others, y-axis was plotted as log-scale. Additionally, bar plots were divided into three regions for the sake of easier spatial comparison: region 1 (sampling locations placed from West to East), region 2 (sampling locations placed from North to South), and region 3 (three corner locations and Istanbul).

4.1.1. Ambient Air Concentrations of PCBs

Annual average of Σ_{43}PCBs was 108±132 pg/m^3. The average levels of Σ_{43}PCBs varied from 39.2±34.2 pg/m^3 (Aksaray) to 278±304 pg/m^3 (İzmir) (Figure 4.1a). The sampling points with the lowest and highest average concentrations at rural sites were 19.0±22.7 pg/m^3 (Aksaray) and 217±353 pg/m^3 (Kastamonu), respectively, whereas at urban sites they were 14.5±14.3 pg/m^3 (Kayseri) and 403±428 pg/m^3 (İzmir), respectively (Figure 4.1b). Spatial variation of Σ_{43}PCBs is shown on a map in Figure 4.1c. Inspection of Figure 4.1a reveals that the concentrations differed only at Izmir on the W-E axis, and only in Aksaray on the N-S axis, indicating a general similarity. The reason for some highest levels occurring in Izmir may be due to the effect of ferrous scrap processing steel plants with electric arc furnaces in Aliağa (Odabasi et al. 2009). In fact, Σ_{48}PCB concentration measured in Izmir was the second highest among the 41 sites around the globe (Pozo et al. 2006), and the second highest (Σ_7 indicator PCBs) after Thessaloniki among the 10 sites around the Aegean (Lammel et al. 2015). Tombesi, Pozo, and Harner (2014) monitored PCBs levels in Buenos Aires, Argentina in two sampling periods, 2006 and 2007. The highest mean level of $\sum_{46}$PCBs measured in Bahia Blanca (urban site: 200 pg/m^3) was 1.9 times lower than the highest concentration detected at urban site of İzmir (402 pg/m^3) in this study. The one-year average concentration of the urban sites was 118±140 pg/m^3, whereas it was 100±122 pg/m^3 at rural sites. Pozo et al. (2012) reported Σ_{48}PCBs at urban sites (16 pg/m^3) and rural sites (40 pg/m^3) in Chile between January and March 2007, the concentrations were elevated at urban/suburban sites measured in The Global Atmospheric Passive Sampling (GAPS) study (Pozo et al., 2006). Although the opposite behavior was noticed in the study conducted in Chile, concentrations measured at urban sites were higher than those of rural sites in this study, in agreement with the global study.

Among the targeted PCB congeners, PCB 118 (penta-CB) had the highest annual average with the value of 26.3±44.6 pg/m^3. However, PCB54, PCB156, and PCB188 were not detected in the samples. PCB104, PCB114, PCB118, PCB123, PCB151, PCB167, and PCB203 had the higher average levels at rural sites compared to urban sites. The others were found to be higher at urban sites. Although PCB118 was higher at urban sites in the study of Aliyeva et al. (2012); PCB101, PCB138, and PCB153 were similarly higher at urban sites. Annual average contributions of tri-, tetra, penta-, hexa-, hepta-, and octa-CBs are indicated in Figure 4.2a. Homologue groups from the highest to lowest contributions were listed as penta-CBs > tetra-CBs > tri-CBs > hepta-CBs > octa-CBs > hexa-CBs. The parameters effecting contribution of the groups can be composition of PCB mixtures, partitioning, vapor pressure, and water solubility. Additionally, tri- and tetra-CBs may travel to long distances because of being lighter than others and heavier groups (hexa-, hepta-, and octa-CBs) can deposit on the soil. However, penta-CBs cannot go a lot further away from the starting point so they can have higher contribution. Among the indicator PCBs (28, 51, 101, 118, 138, 153, and 180), PCB 118 (penta-CB) was the dominant congener in cold periods (3rd and 4th sampling periods) whereas some variability was observed in 1st and 2nd periods (Figure 4.3). High penta-CB contribution was in agreement with the study of Du et al. (2009) conducted in Philadelphia metropolitan area. Ogura, Masunaga, and Nakanishi (2004) stated that penta-CB levels are directly proportional to temperature. The homologue group with the lowest contribution was hexa-CBs (3.2%). In general, the contribution of homolog groups with lower molecular weight/lower number of chlorine atom (tri-, tetra, and penta-CBs) was higher compared to those with higher molecular weight/higher number of chlorine atom (hexa-, hepta-, and octa-CBs) because increasing number of chlorine atom decreases vapor pressure and water solubility. Therefore, PCBs with higher vapor pressure and water solubility (≤ penta-CBs) tend to be in gas phase and dissolve in water so possibility to detect in the atmosphere increases (Yeo et al. 2003). However, higher number of chlorinated compounds tends to deposit on different surfaces. The congeners with low molecular weight were generally found to be higher at background sites, whereas those with high molecular weight were detected at suburban and urban sites (Du et al. 2009). However, the results obtained in this study were not in agreement with Pozo et al. (2004) because not only urban sites but also rural sites were dominated by penta-CBs, and lighter groups (such as tri- and tetra-CBs) had lower percentages at rural sites (Figure 4.2b).

The main sources of PCBs can be listed as emission from PCB-containing products, volatilization from deposited surfaces such as soil and water, incineration, and from steel and petrochemical manufacturing plants (Baek et al. 2008, Baek et al. 2010, Ishikawa et al. 2007). Since usage of PCBs was forbidden in 1996 in Turkey (Aydın 2004), it is not possible to use PCBs legally. The lighter congeners can be degraded during long range atmospheric transportation (LRAT) and those with high molecular weight can be deposited on the surfaces. Therefore, one of the potential PCB sources can be LRAT from countries including point sources (Wania et al. 2003). Additionally, rising temperature during sampling periods can lead to evaporation of PCBs from deposited surfaces (Cleverly et al. 2007).

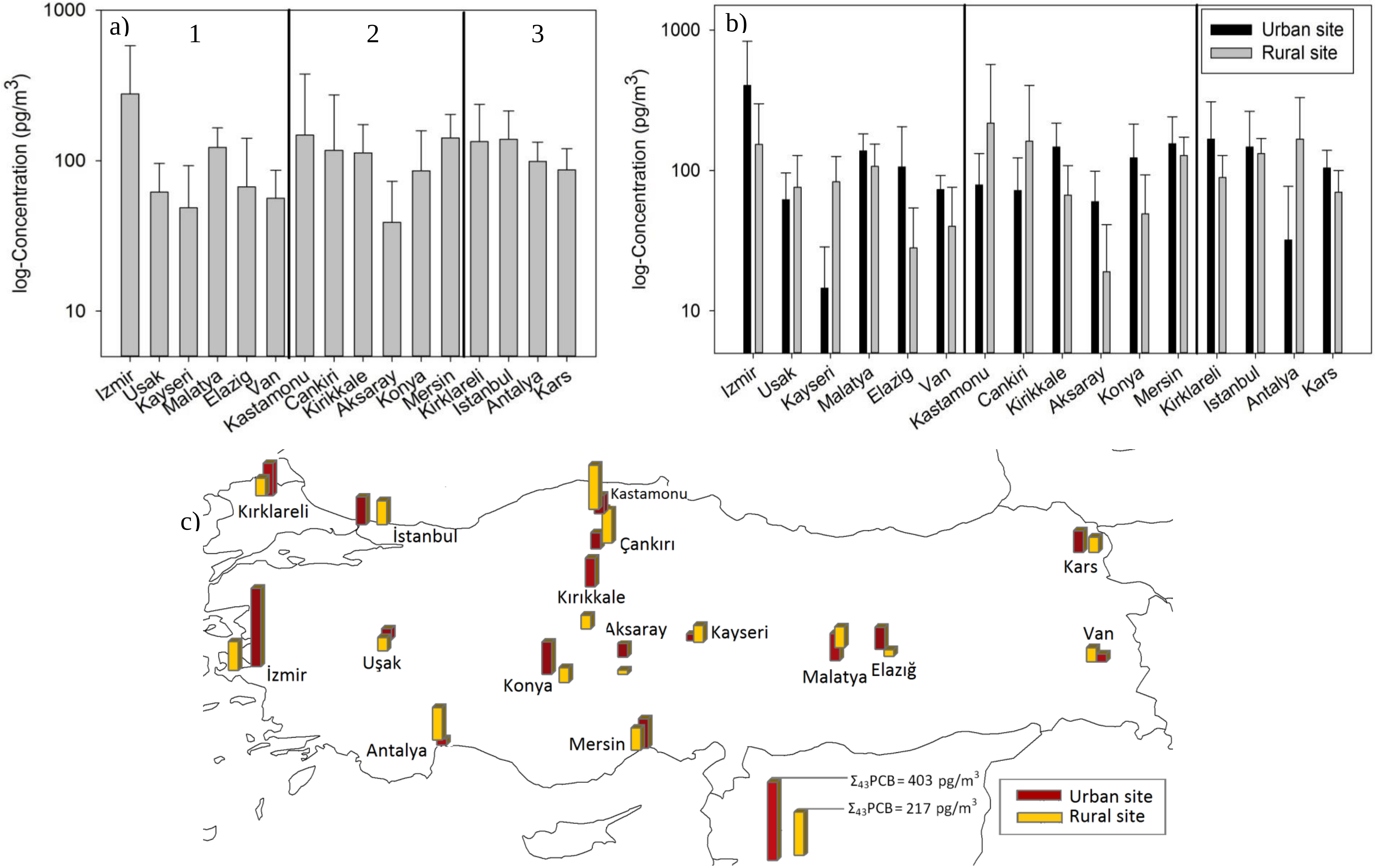


Figure 4.1. Annual average concentrations of a) Σ_{43}PCBs b) Σ_{43}PCBs at urban and rural sites c) Spatial variation of Σ_{43}PCBs

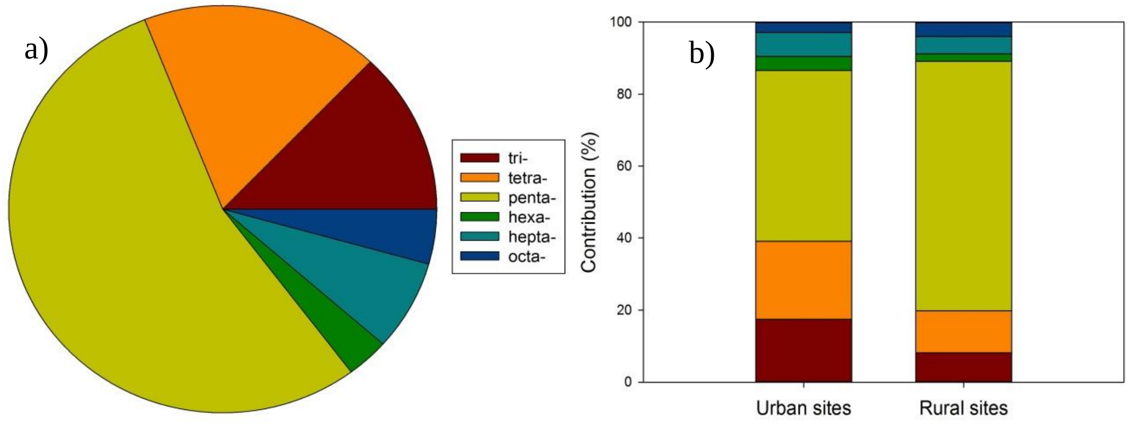
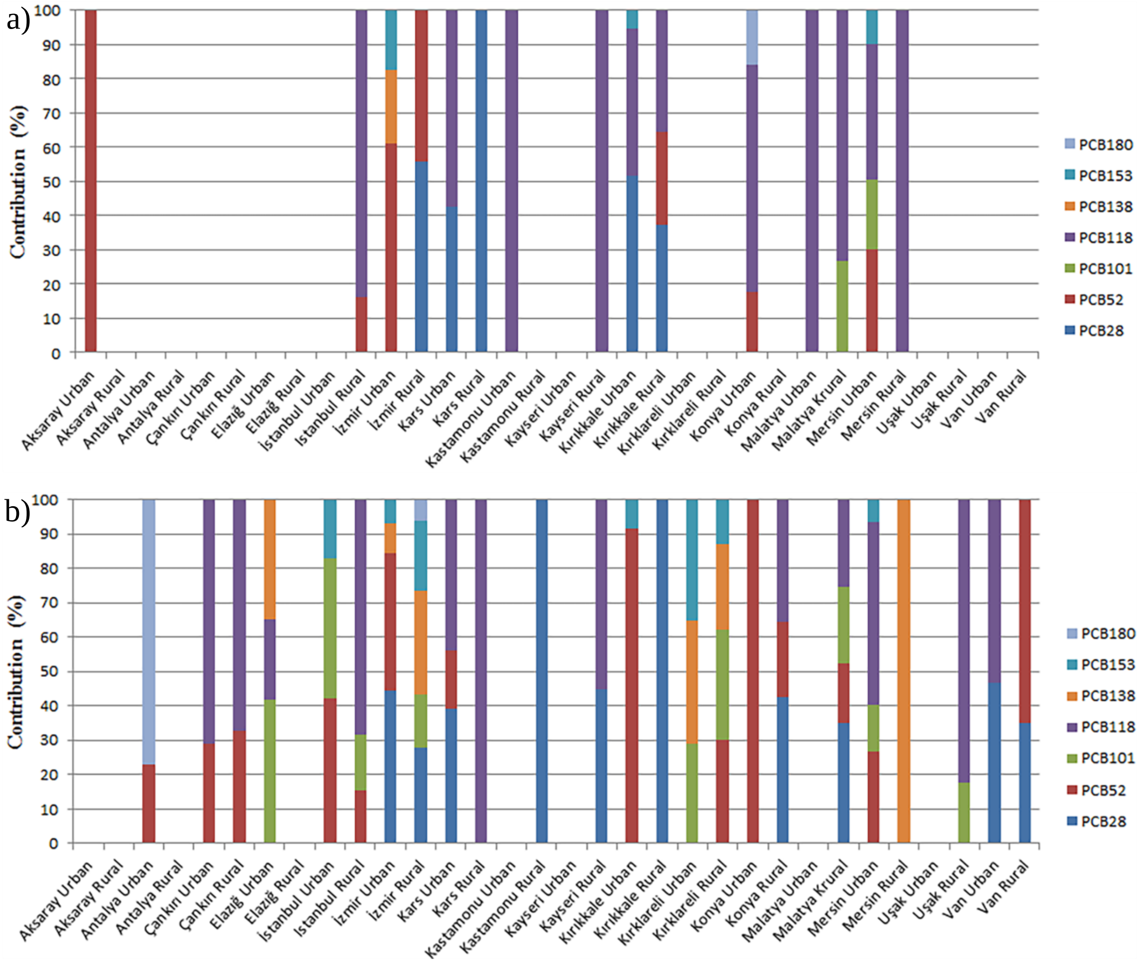


Figure 4.2. Percentage of PCB homologue groups for a) one-year average b) urban and rural sites



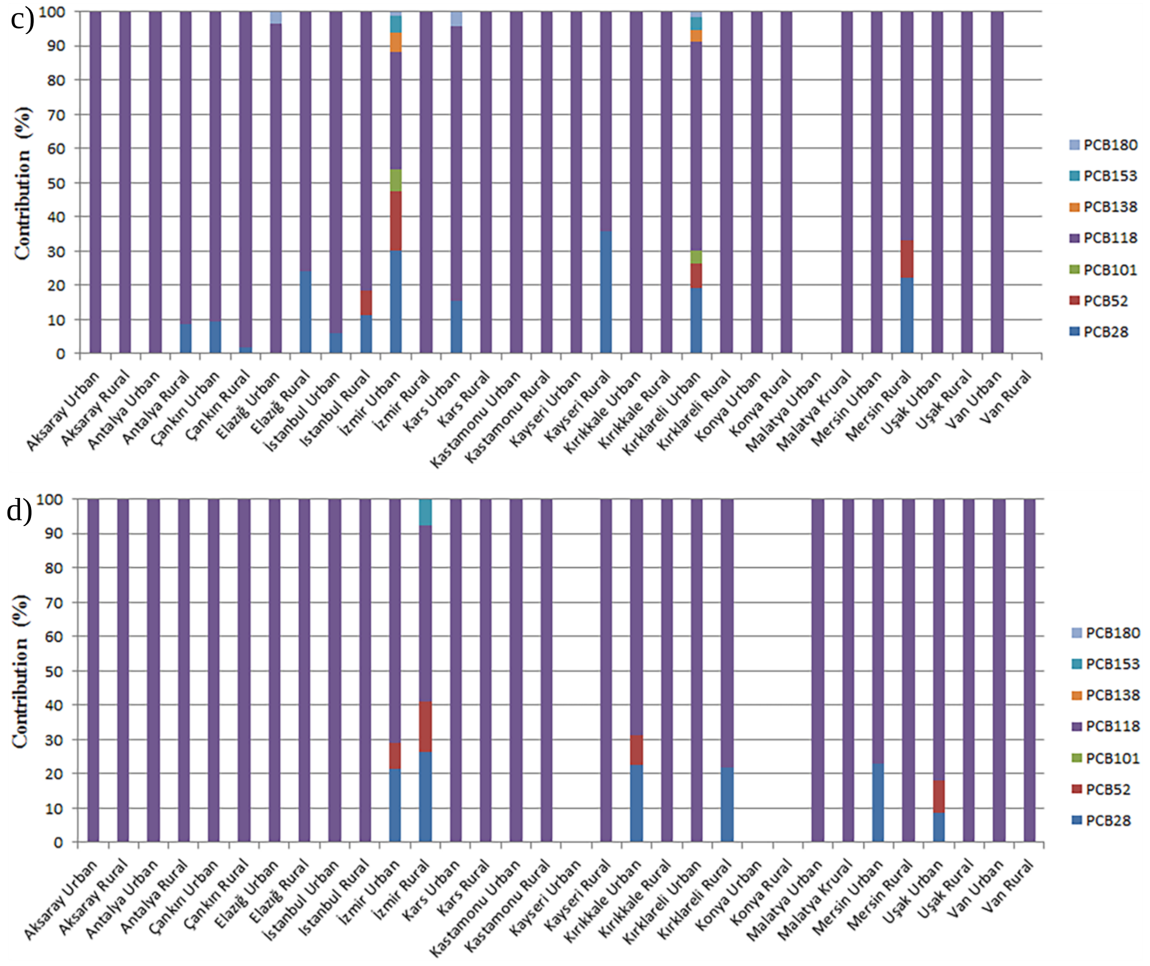


Figure 4.3. Contribution (as %) of indicator PCBs for one-year average a) 1st period b) 2nd period c) 3rd period d) 4th period

4.1.2. Ambient Air Concentrations of OCPs

Annual average concentration of Σ_{22}OCPs was 341±870 pg/m^3 (range: 55.3±36.5 pg/m^3 (Çankırı) and 1294±2153 pg/m^3 (Kırklareli)). Average concentrations at urban and rural sites were 415±1012 pg/m^3 and 266±690 pg/m^3, respectively. Average level of pollutants were ranked as ΣDDT (*p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD) (134 pg/m^3) > ΣHCH ($\alpha + \beta + \gamma + \delta$- isomers) (64.4 pg/m^3) > HCB (45.1 pg/m^3) > Σendrin+dieldrin (30.4 pg/m^3) > Σendosulfan (α-, β-, -SO_4) (27.2 pg/m^3) > Σheptachlor+heptachlorepoxide (24.1 pg/m^3) > mirex (13.4 pg/m^3) > Σchlordane (*cis*- + *trans*-chlordane) (2.14 pg/m^3). *o,p'*-DDD was not detected in the samples. ΣDDT was the pollutant group with the highest average concentration. Among the listed pollutant groups, ΣHCH, HCB, ΣDDT, and Σendosulfan were generally found to be higher at urban sites than rural sites.

HCHs are chemicals composed of different isomers. For example, *γ*-HCH was developed as a pesticide to protect vegetables and animals (ATSDR 2005). Technical HCH is a mixture abound in *α*-isomer (*α*: 55-80%, *β*: 5-14%, *γ*: 8-15%, *δ*: 2-16% *Ɛ*: 3-5%) whereas *γ*-isomer (> 90%) dominates lindane (Vijgen et al. 2006). Lindane was forbidden in 1979 in Turkey (Ahioğlu 2008). Mean ΣHCH concentration (64.5±288 pg/m^3) comprised 19.1% of the total OCP concentration. Figure 4.4a indicates that the average levels measured on the W-E axis and except Kastamonu on the N-S axis seems to be similar. The levels were in the range of 3.13±4.347 pg/m^3 (Van) - 511±40.0 pg/m^3 (Kırklareli). The averages at urban sites varied from BDL (Van) to 867 pg/m^3 (Kırklareli) and from 4.45 pg/m^3 (Çankırı) to 134 pg/m^3 (İstanbul) at rural sites (Figure 4.4b). One-year averages at urban sites (93.6±397 pg/m^3) were 2.5 folds higher than those of rural sites (35.1±73.1 pg/m^3). Spatial variation of ΣHCH is shown on a map in Figure 4.4c. Zhang et al. (2008) measured average HCH levels in India between July and September 2006 at urban (1471 pg/m^3) and rural sites (259 pg/m^3) with an average of 865 pg/m^3 which was much higher than the mean value (64.5 pg/m^3) measured in this study. Tombesi, Pozo, and Harner (2014) also found higher concentrations at urban sites as in the case of this study. The dominating HCH isomers were *α*- (22.0±92.8 pg/m^3) and *β*-HCH (21.8±96.1 pg/m^3). The mean levels of *γ*- and *δ*- isomers were 7.34±45.7 and 13.4±86.8 pg/m^3, respectively. Aliyeva et al. (2012) and Devi et al. (2011) were also found that *α*-HCH was the dominating isomer. Detailed isomer information for urban and rural sites is given in Figure 4.5a and it is obvious that all isomers were higher at urban sites. Additionally, coefficient of variation values (CV) for each HCH isomer at urban and rural sites were > 237% show that variation in the samples was very high. Average *α*-HCH/*γ*-HCH ratios for urban and rural sites were 2.26 and 7.68, respectively. The ratios between 4 and 7 indicate that atmospheric concentrations were affected from usage of technical-HCH but the ratios < 4 suggest that levels were under the mixed influence of lindane and technical-HCH utilization (Su et al. 2006). The ratio for rural sites was > 7 probably because *γ*-HCH has a lower residence time in the atmosphere due to high reaction rate of hydroxyl radicals with *γ*- isomer and lower Henry’s Law constant than *α*- isomer (Brubaker and Hites 1998).

HCB was first presented in 1933 as a fungicide for seeds of onions, sorghums, and crops (Estellano et al. 2012). It is additionally produced as a by-product from chlorinated solvents, chlorinated compounds and pesticides, e.g., mirex, simazine, and atrazine production (EEA 2005). Annual average concentration of HCB was found to be

45.3±197 pg/m^3 with the minimum in Antalya and the maximum in Kırklareli (Figure 4.6a). A higher annual average concentration was recorded in the study of Zhang et al. (2013). The concentrations were similar on the both axes, whereas they were higher in the most northern sites. The sampling points with the lowest and highest average concentrations were Çankırı and Kars among urban sites, and Antalya and İstanbul among rural sites (Figure 4.6b). Spatial variation of HCB is demonstrated on a map in Figure 4.6c. Jaward et al. (2004) reported a lower range of HCB levels (1.4 - 8.9 pg/m^3) between June and July 2002 at urban, rural, and remote areas across Europe.

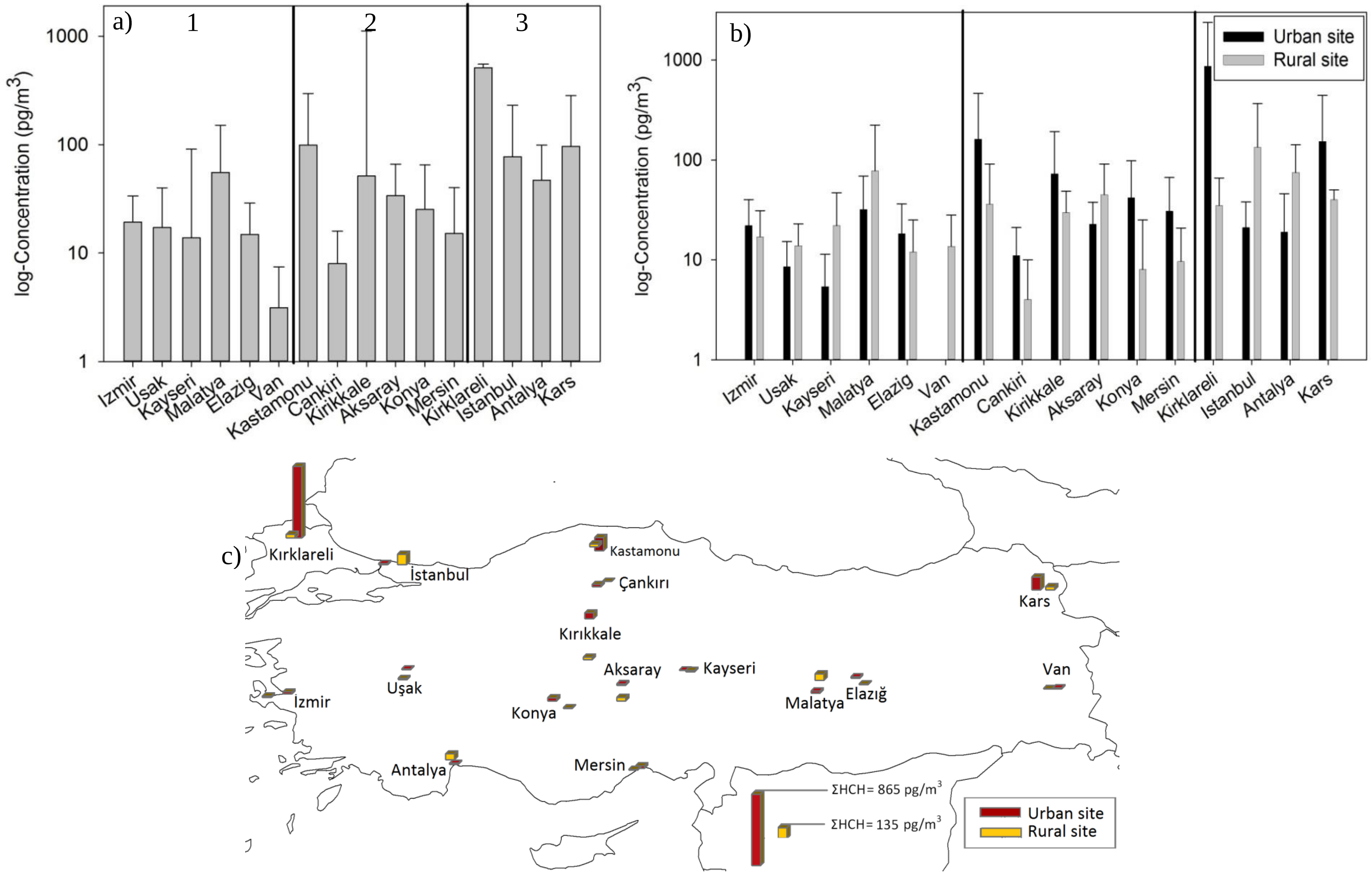


Figure 4.4. Annual average concentrations a) ΣHCHs b) ΣHCHs at urban and rural sites c) Spatial variation of ΣHCHs

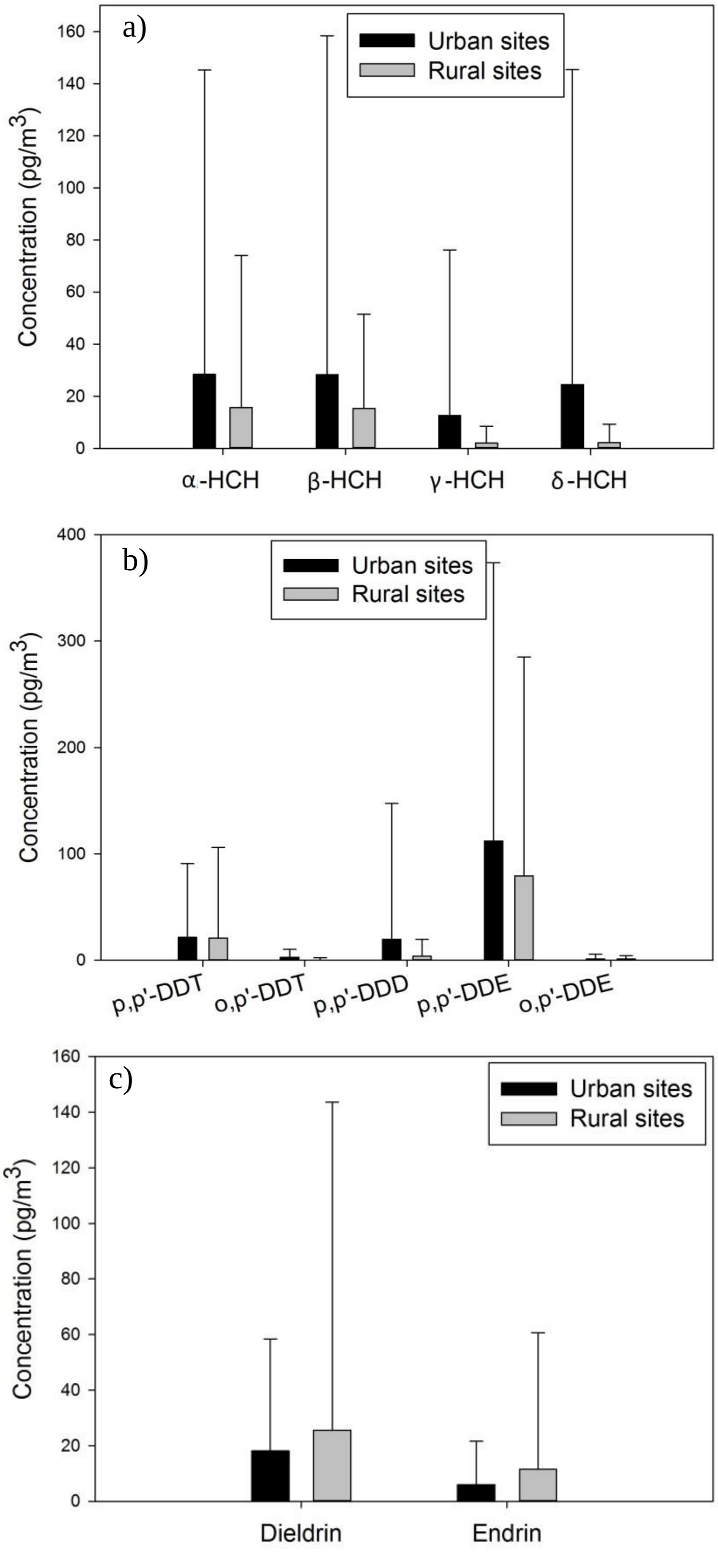


Figure 4.5. Annual average isomer levels of a) HCH b) DDT c) dieldrin and endrin

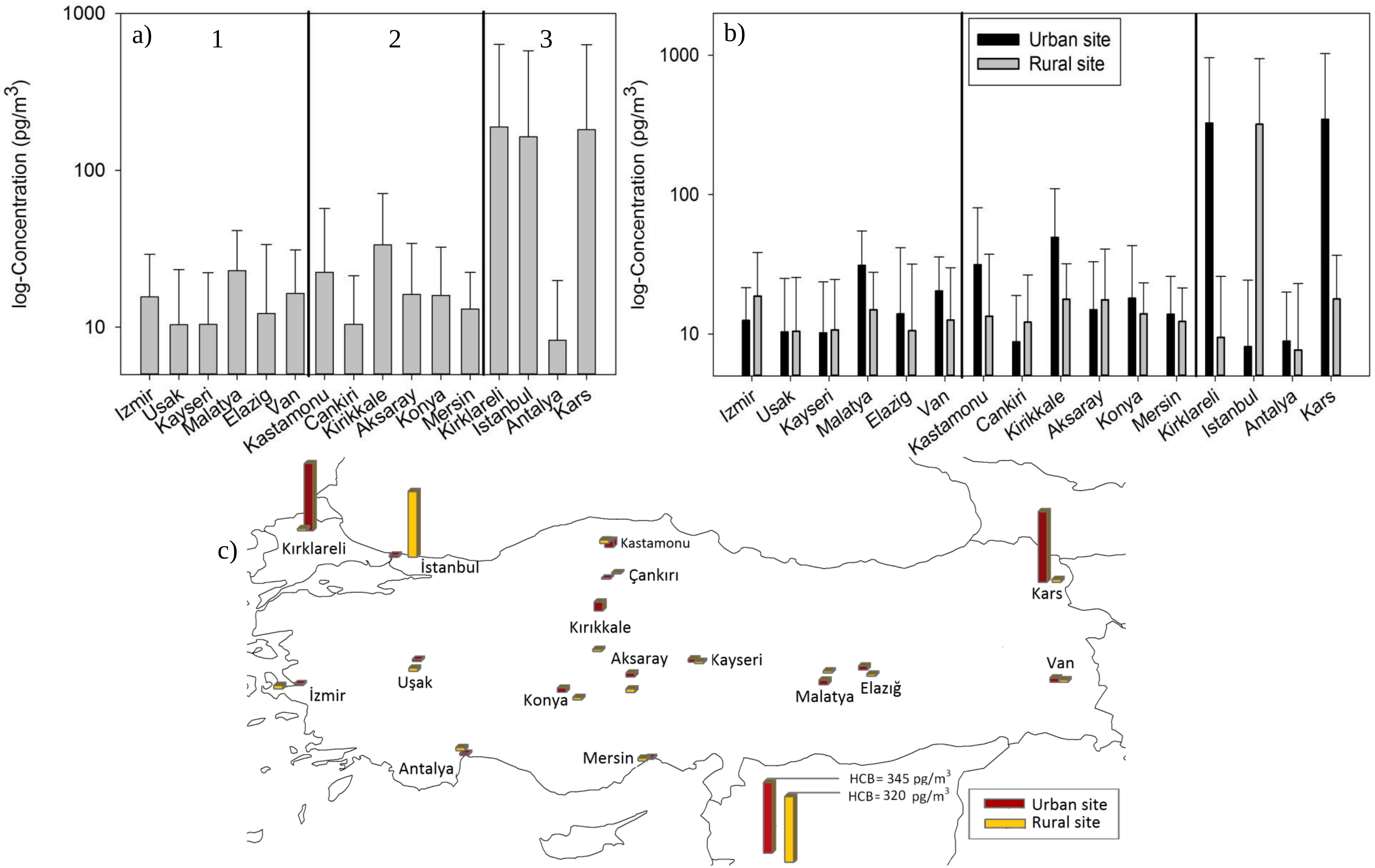


Figure 4.6. Annual average concentrations a) HCB b) HCB at urban and rural sites c) Spatial variation of HCB

DDT was used for agricultural products and to protect from illness-causing organisms such as malaria and typhus (ATSDR 2002). The production and selling of DDT was banned in 1978 and 1985 in Turkey, respectively (Ahioğlu 2008). The highest annual average of ΣDDT was detected at Kars whereas the lowest one was detected at Kastamonu (Figure 4.7a). Except annual averages measured at Kastamonu and Çankırı on the N-S axis and on the W-E axis, the data seems to be uniform. ΣDDT levels varied in the range of 12.5±15.6 - 686±754 pg/m^3 at urban sites and 11.7±8.62 - 484±789 pg/m^3 at rural sites (Figure 4.7b). The spatial variation of ΣDDT is shown in Figure 4.7c. Érseková et al. (2014) reported the highest levels of ΣDDT from March to August 2006 in urban sites of Serbia (986 pg/m^3) and Romania (448 pg/m^3), and rural site of Romania (330 pg/m^3) with the mean of 295 pg/m^3 which was 2.1 times higher than the average calculated in this study (134±296 pg/m^3) but there was a high variation in the samples. *p,p'*-DDE was the isomer with the highest average level among the listed isomers for all sampling periods whereas o,*p'*-DDD was not detected as in the study of Pozo et al. (2006). Additionally, *p,p'*-DDE had the highest average level among targeted OCPs similar to findings of Klánová et al. (2006). The elevated level of this isomer can be interpreted with the conversion of *p,p'*-DDT to *p,p'*-DDE by UV radiation during atmospheric transport (Atlas and Giam 1988). Additionally, most of DDT decomposes slowly into DDD and DDE in the soil by microorganisms and they also evaporate to air and deposit at other places (ATSDR 2002). The levels of all isomers are shown in Figure 4.5b, all of which were higher at urban sites. Additionally, CV values for DDT isomers at urban and rural sites were > 233% indicate that variation in the samples was very high. Contribution of p,p'-DDT to ΣDDT (16%) was a little bit higher than the study of Zhang et al. (2008) (12%). Average *p,p'*-DDE/*p,p'*-DDT ratios were found > 1 at urban (5.21) and rural sites (3.80) indicating aged usage of DDT in the sampling periods (Aliyeva et al. 2012).

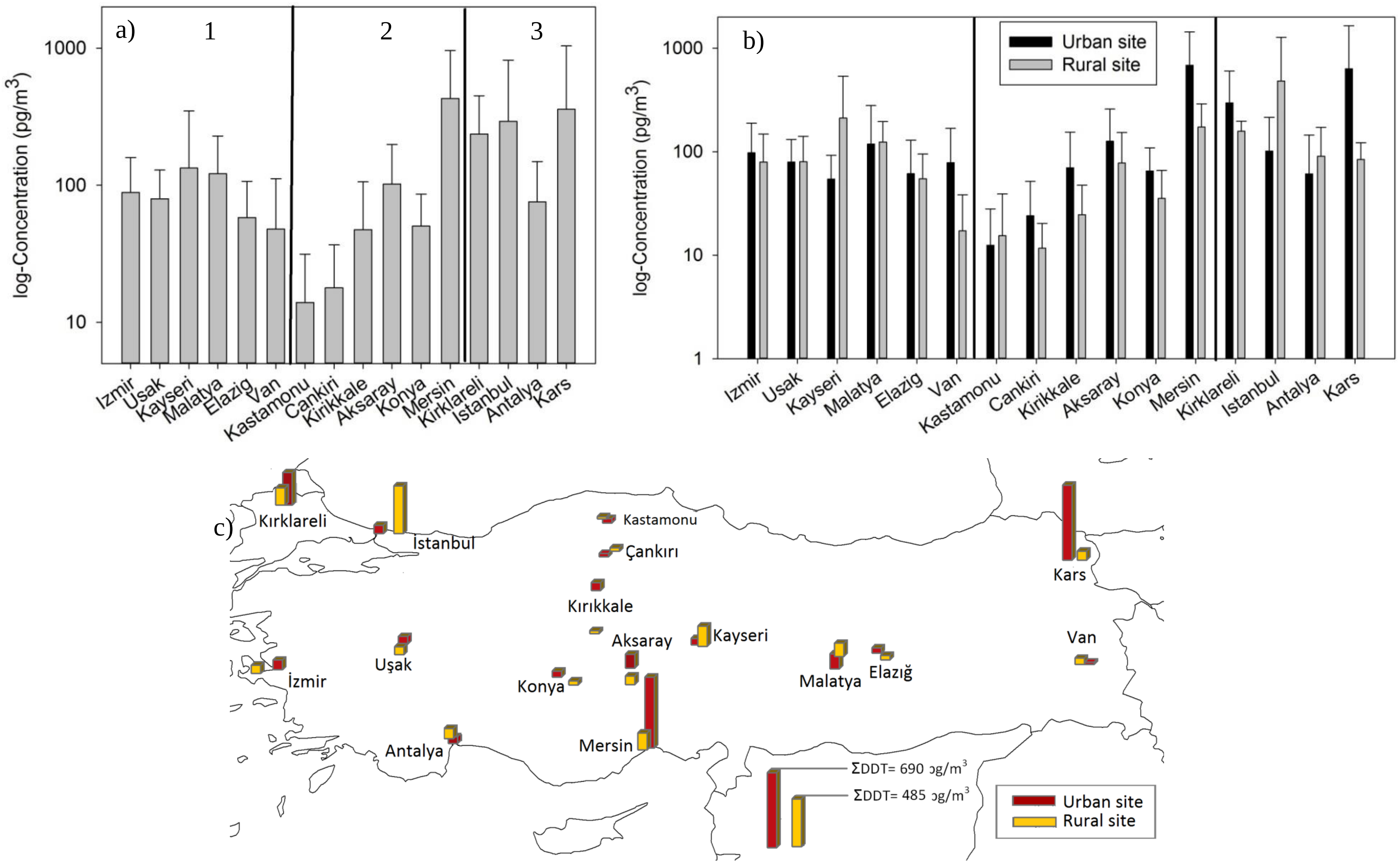


Figure 4.7. Annual average concentrations a) ΣDDT b) ΣDDT at urban and rural sites c) Spatial variation of ΣDDT

Dieldrin was generally applied to the soil to protect from ants as well as to corn and citrus trees and it is the main product of aldrin degradation (Aigner, Leone, and Falconer 1998). Dieldrin is the first prohibited OCP in Turkey (1971) (Ahioğlu 2008). It was detected only 2 out of 128 samples. One-year average of Σendrin+aldrin+dieldrin found as 30.4±121 pg/m^3 and average levels were ranked from 1.30±3.43 (Çankırı) pg/m^3 to 193±380 (İstanbul) pg/m^3 as shown in Figure 4.8a. The mean levels at urban and rural sites were in the range of BDL - 105±182 pg/m^3 and BDL - 366±617 pg/m^3, respectively (Figure 4.8b). The measured levels on the W-E axis and N-S axis show similarity in terms of the smallest and highest data. Spatial variation of Σendrin+aldrin+dieldrin is shown in Figure 4.8c. Santiago and Cayetano (2011) determined average concentrations of Σendrin+dieldrin at urban and rural sites as 70.6 and 54.9 pg/m^3, respectively, Philippines. Lower average levels but high variations in the data set were measured at urban sites (24.4±54.0 pg/m^3) and rural sites (36.5±163 pg/m^3) in this study. Dieldrin was the dominant isomer among the three OCPs for both urban and rural sites whereas the levels of aldrin were almost zero (Figure 4.5c). Since CV values > 99%, variation in the concentrations was very high. Dieldrin range measured in this study (BDL to 931 pg/m^3) was higher than the range (BDL to 115 pg/m^3) given in the study of Pozo et al. (2006).

Mirex was mostly used as an insecticide, and to control fire ants between 1960 and 1970 in USA because it has a good heat resistance. It was also used as a flame retardant in paint, paper, and electrical instruments (ATSDR 1995). Mirex usage was prohibited in Turkey with Stockholm Convention in 2001. It was detected in 19 out of 128 samples. Annual average of Mirex was 13.4±66.6 pg/m^3 with the range of BDL - 96.5±231 pg/m^3 (Konya) (Figure 4.9a). There is a similarity between the average concentrations except Izmir on the W-E axis, and Konya and Aksaray. The range at urban sites was BDL to 23.0±46.1 pg/m^3 (average: 5.62±17.7 pg/m^3) and BDL to 176±352 pg/m^3 (average: 21.4±92.2 pg/m^3) at rural sites (Figure 4.9b). The spatial variation of Mirex is shown on a map in Figure 4.9c. Detection rate of Mirex in the study of Santiago and Cayetano (2011) was 2/28 (urban site average: 14.8 pg/m^3, rural site: 7.3 pg/m^3). A similar annual average concentration was recorded in the study conducted in the Yangtze River Delta, China with the value of 17.9±56.4 pg/m^3 (Zhang et al. 2013). Mirex does not evaporate to air easily due to the fact that it mostly binds to soil particles or sediment in water (ATSDR 1995). This might be the reason of low detection rate of Mirex, however, the reason might just as well be that it was not used in Turkey and LRT may be the only source.

Endosulfan was used as insecticide and acaricide for fruits, vegetables, and grains, and the ratio of *α*- and *β*- isomer is 2.3 where endosulfan-SO_4 is formed as the reaction product in the mixture (ATSDR 2013). Annual average levels of endosulfan (*α*-, *β*-, -SO_4) is given in Figure 4.10a. Figure 4.10a reveals that the concentrations differed at Kayseri and Malatya on the W-E axis, and in Çankırı and Mersin on the N-S axis, indicating a general similarity. The measured levels varied from 5.79±4.34 pg/m^3 (Çankırı) to 102±203 pg/m^3 (Kars) with an average of 27.3±65.7 pg/m^3. Average concentration at urban sites (35.0±83.2 pg/m^3) was higher than the average at rural sites (19.4±39.2 pg/m^3). As shown in Figure 4.10b, maximum one-year average was measured in Kars among the urban sites (180±306 pg/m^3), while it was measured in İstanbul among the rural sites (81.6±147 pg/m^3). Spatial distribution of endosulfan is given in Figure 4.10c. Santiago and Cayetano (2011) investigated endosulfan levels in Philippines from May to December 2005. Endosulfan concentrations were in the range of BDL - 461 pg/m^3 at urban sites (average: 166 pg/m^3) and BDL - 904 pg/m^3 at rural sites (214 pg/m^3). Maximum concentrations recorded in this study were below those measured in the study conducted in Philippines and in Argentina (Tombesi, Pozo, and Harner 2014). Among the isomers, Endo-SO_4 was detected only 2 times out of 128 samples (average: 0.57±4.74 pg/m^3). Average *β*-endosulfan (15.2±59.8 pg/m^3) was > *α*-endosulfan (11.5±12.5 pg/m^3). Although urban sites were dominated by *β-e*ndosulfan (*α*-endosulfan: 12.4±13.8 pg/m^3, *β-e*ndosulfan: 22.8±79.2 pg/m^3), rural sites were enriched by *α*-endosulfan (*α*-endosulfan: 10.6±10.9 pg/m^3, *β-e*ndosulfan: 7.75±28.2 pg/m^3). *α*-endosulfan/*β-e*ndosulfan ratio for urban sites was 0.55 which means that *α*-endosulfan decomposed during atmospheric transportation (Shunthirasingham et al. 2010). However, the ratio was 1.38 for rural sites. *α*-endosulfan generally reached elevated levels at agricultural sites in literature (such as olives, sunflower, and vineyards) (Estellano et al. 2012) so it was reasonable that rural sites were dominated by *α*-endosulfan, which might indicate its fresh use.

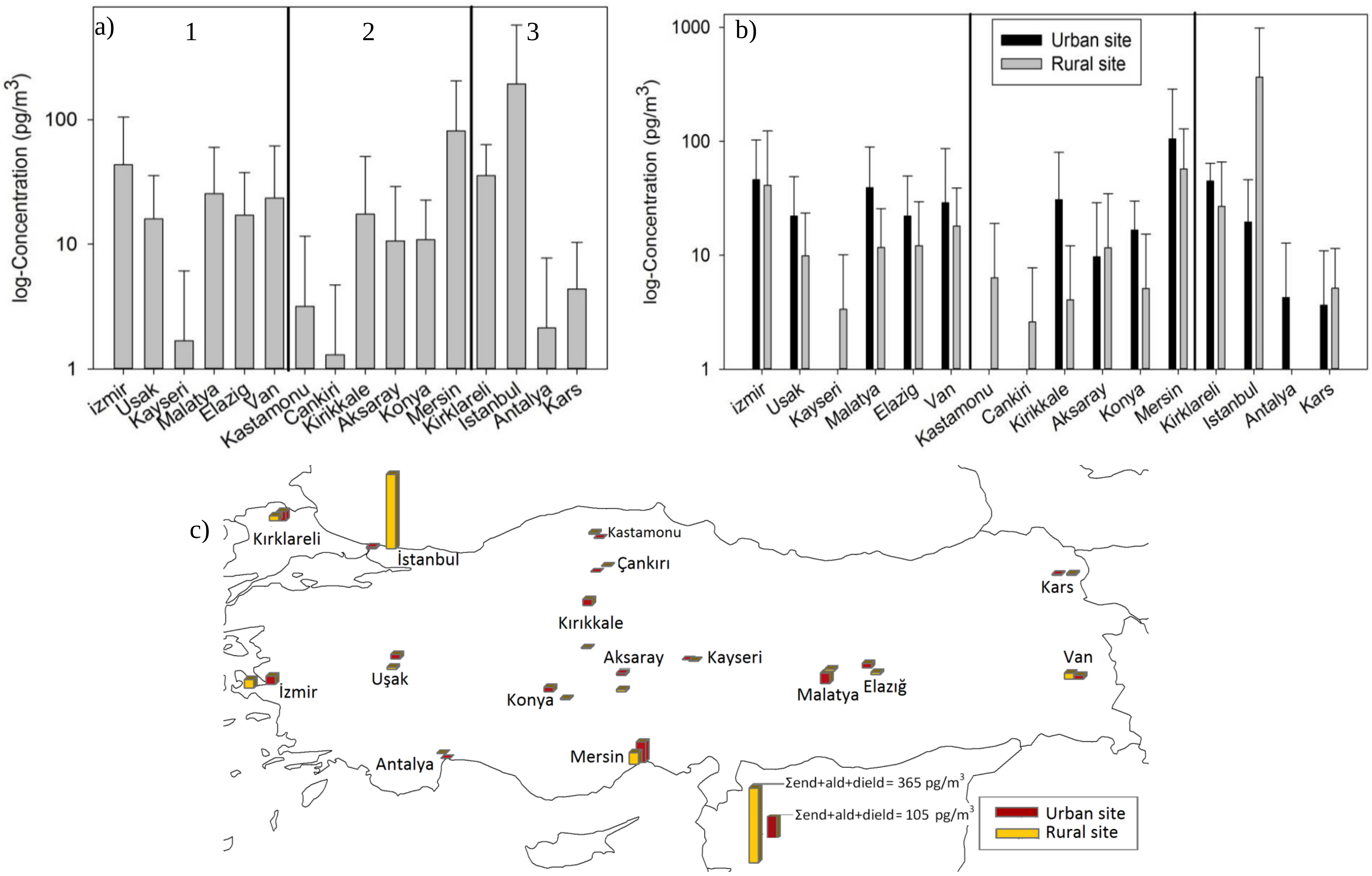


Figure 4.8. Annual average concentrations a) Σend+ald+dield b) Σend+ald+dield at urban and rural sites c) Spatial variation of Σend+ald+dield

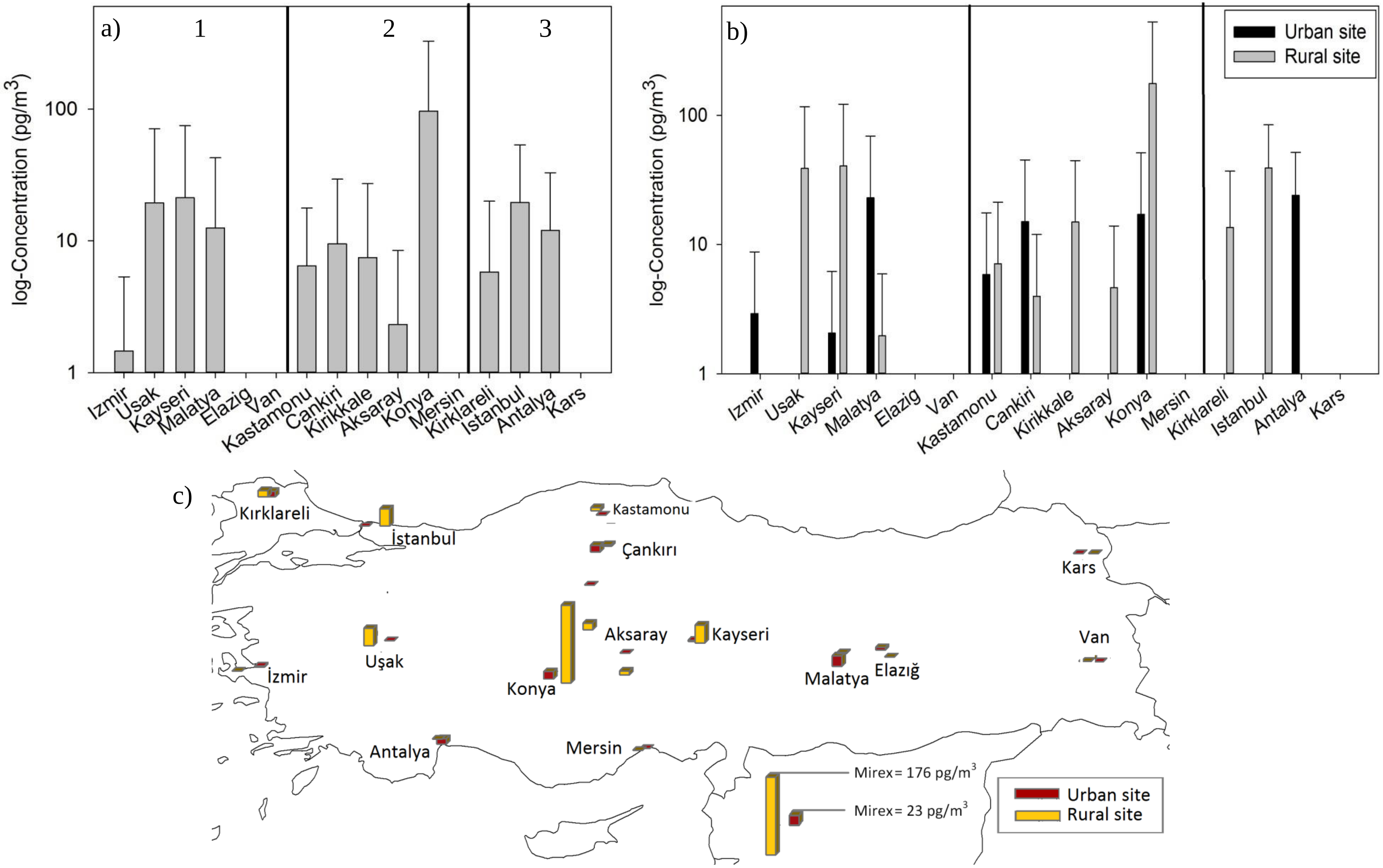


Figure 4.9. Annual average concentrations a) Mirex b) Mirex at urban and rural sites c) Spatial variation of Mirex

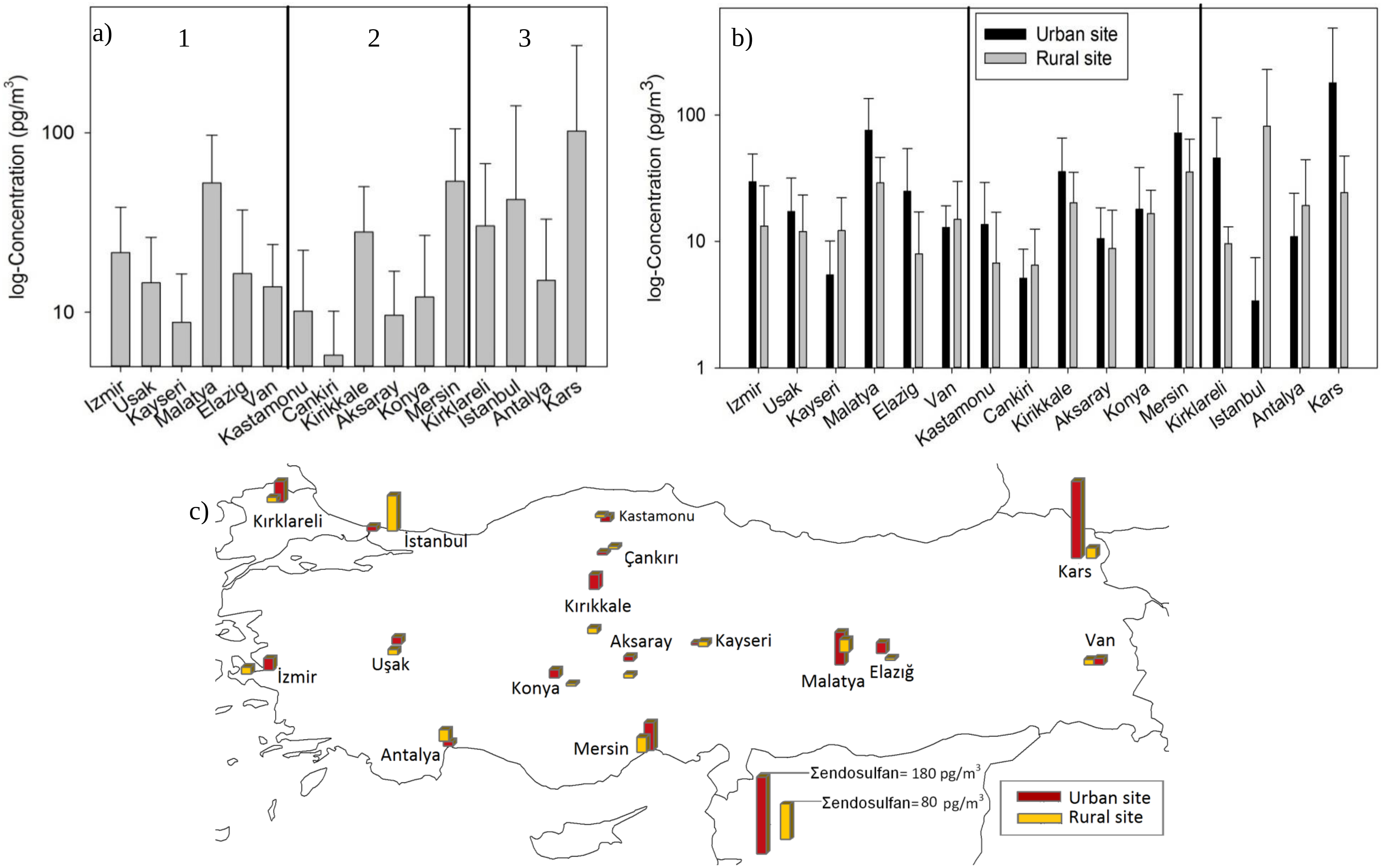


Figure 4.10. Annual average concentrations a) Σendosulfan b) Σendosulfan at urban and rural sites c) Spatial variation of Σendosulfan

Technical chlordane, a mixture of different types of isomers and chemicals, was used as an insecticide to protect agricultural products, grass, and vegetables (Pozo et al. 2012). Usage of chlordane was banned in 1979 in Turkey (Ahioğlu 2008). Annual average levels of chlordane (TC+CC) were very low (average: 2.15±13.3 pg/m^3) (Figure 4.11a) and detected only 9 out of 128 samples. Mean levels of chlordane at urban and rural sites were 3.44±17.8 pg/m^3 (maximum: 137 pg/m^3) and 0.85±5.76 pg/m^3 (maximum: 44.2 pg/m^3), respectively (Figure 4.11b). As it is seen from the figures, chlordane was not detected at region 1, and detected at three points at region 2. Spatial variation of chlordane is seen in Figure 4.11c. The level of chlordane was recorded as 1.2 and 2.2 pg/m^3 at urban and rural sites, respectively between January and March 2007 in Chile (Pozo et al. 2012). However, much higher levels were measured at urban (151 pg/m^3) and rural sites (43 pg/m^3) in the study of Zhang et al. (2008). The averages of chlordane during the sampling campaign at urban and rural sites were similar to those measured in Chile. Additionally, although level recorded at rural site was higher in Chile, an opposite behavior was observed in this study. Average of CC and TC were 2.11±10.9 pg/m^3 and 1.32±7.26 pg/m^3 at urban sites and 0.46±2.56 pg/m^3 and 0.39±3.09 pg/m^3 at rural sites, respectively. In the study of Tombesi, Pozo, and Harner (2014), urban sites were dominated by TC (58% of the total chlordanes). Similarly, urban sites were dominated by TC with 61.4% of TC+CC average in this study.

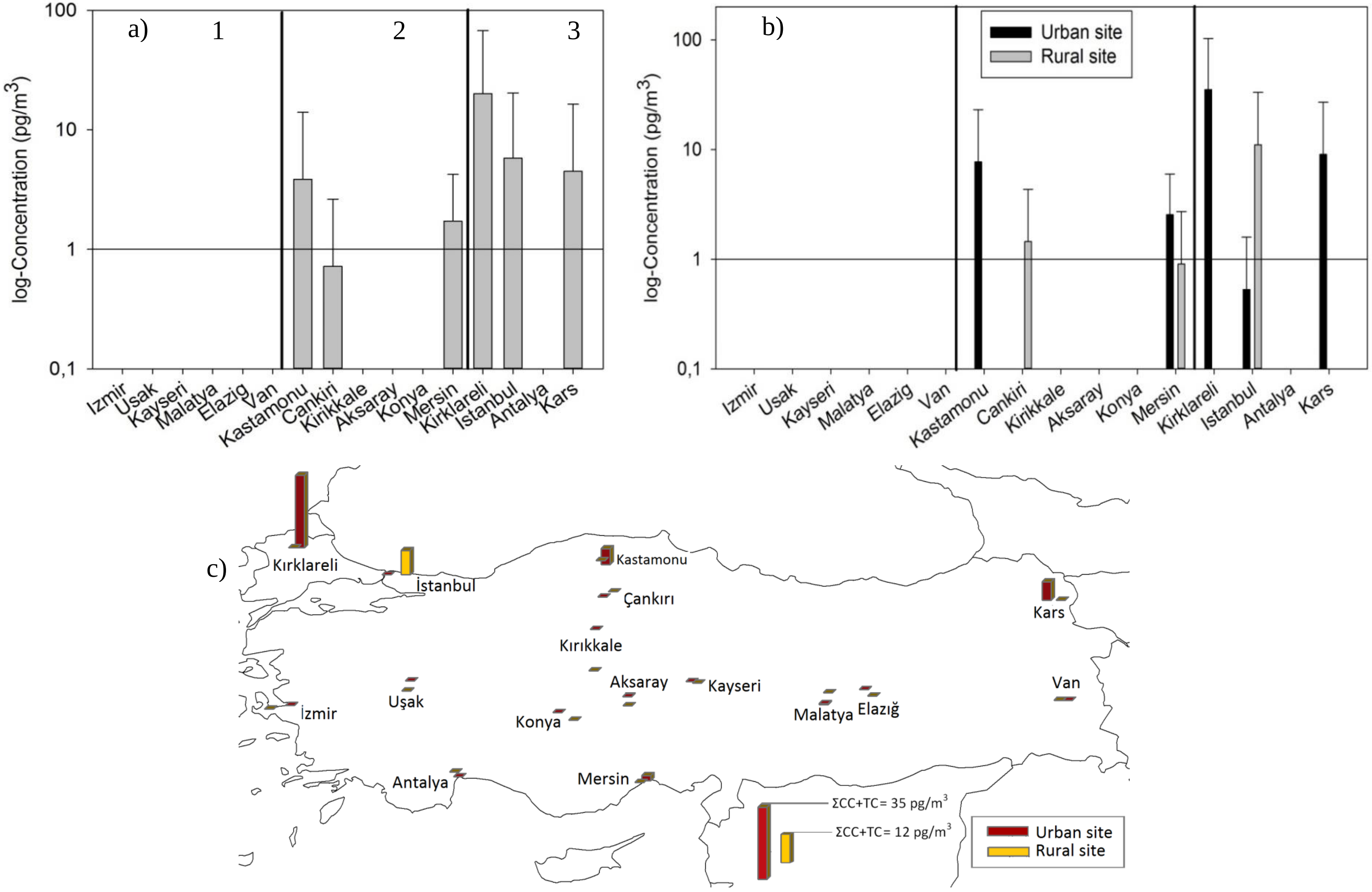


Figure 4.11. Annual average concentrations a) ΣCC+TC b) ΣCC+TC at urban and rural sites c) Spatial variation of ΣCC+TC

Heptachlor was used for insects and ants, cotton bugs, grasshoppers, and to control malaria carrying flies (Pozo et al. 2012). Heptachlor is converted to a more stable form, heptachlor epoxide when it is metabolized by animals and bacteria (ATSDR 2007). It was one of the prohibited OCPs in Turkey in 1979 (Ahioğlu 2008). Annual average levels of Σheptachlor+heptachlor epoxide were between BDL (Van) and 265 pg/m^3 (Kırklareli) (Figure 4.12a). This figure and the spatial variation map (Figure 4.12c) show that the concentrations measured at the two north-western sites were considerably higher than the rest. An extremely large value was recorded at the urban site of Kırklareli (1758 pg/m^3) so the average levels is greater than other locations in Figure 4.12b. Additionally, the concentrations measured on the W-E axis and N-E axis seems to be similar. Average levels were in the range of BDL - 103±191 pg/m^3 at rural sites. Mean heptachlor epoxide levels for both urban (29.3±2188 pg/m^3) and rural sites (8.50±48.9 pg/m^3) were higher than heptachlor concentrations measured at urban (5.89±14.9 pg/m^3) and rural sites (4.74±13.7 pg/m^3). Heptachlor and heptachlor epoxide levels were measured at urban sites of Argentine with an average of 10±7 pg/m^3 and 8±10 pg/m^3 (Tombesi, Pozo, and Harner 2014). Approximately 4 times higher heptachlor epoxide and 0.6 times lower heptachlor levels were recorded at urban sites compared to the study conducted in Argentine. However, variations in the samples especially for heptachlor epoxide were very high in this study. Additionally, Pozo et al. (2006) found lower heptachlor (0.1 - 40 pg/m^3) and heptachlor epoxide (0.7 - 338 pg/m^3) ranges than this study (heptachlor: 0 - 93.4, heptachlor epoxide: 0 - 1758 pg/m^3 pg/m^3).

As a general view, OCP groups reached extreme or higher annual average levels in Kırklareli, İstanbul, and Kars. One of the possible reasons can be LRAT because these are three of the four the most northern sites in this study. Dominant wind directions during the one-year sampling period can be seen as NNE for Istanbul and NE for Kars in Figure 4.13. NNE is also the dominant wind direction in Kırklareli (Vardar 2003). Therefore, transport of these legacy pollutants from the countries located in the northeast of Turkey may be the sources areas.

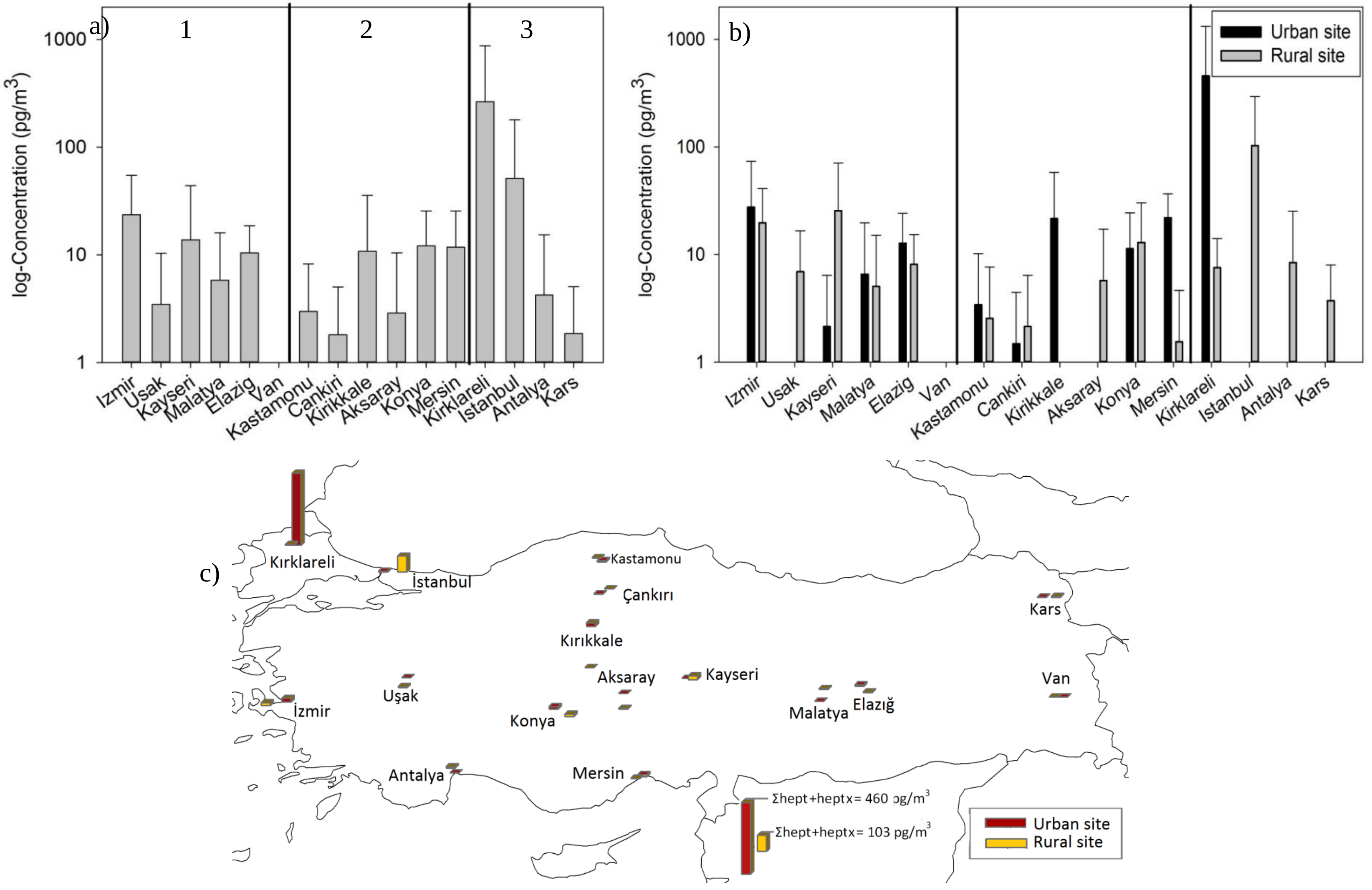


Figure 4.12. Annual average concentrations a) Σhept+hepx b) Σhept+hepx at urban and rural sites c) Spatial variation of Σhept+hepx

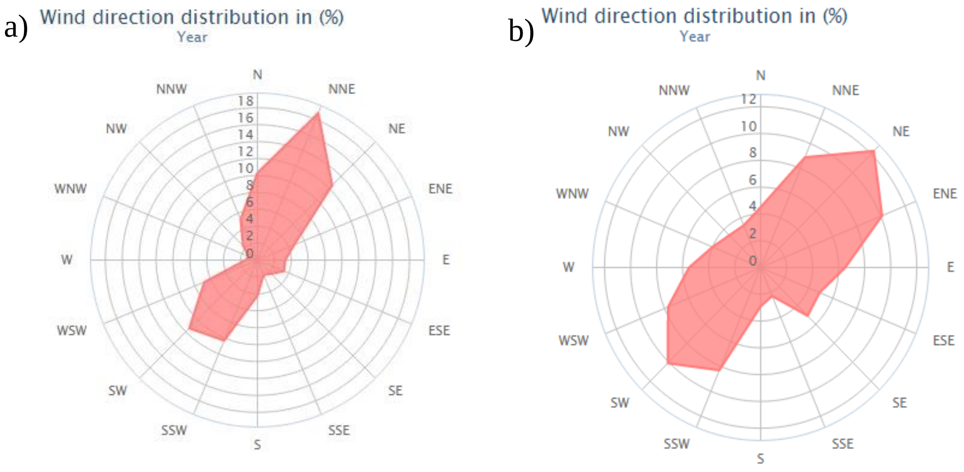


Figure 4.13. Dominant wind directions at a) İstanbul b) Kars

4.2. Statistical Analysis

4.2.1. Principle Component Analysis (PCA)

The score plots of OCPs at urban and rural sites using 5 PC are demonstrated in Figure 4.14. *p,p’*-DDE (the highest level OCP), *p,p’*-DDT and HCB at urban sites, and *p,p’*-DDE, *p,p’*-DDT, and β-HCH at rural sites were considered as outliers, so they were excluded from the data set. The outliers can suppress the score patterns. The score plots of a 6 PC model, after removal of the outliers are presented in Figure 4.14c and Figure 4.14d for urban and rural sites, respectively. Cumulative Eigen value proportions for urban and rural sites were 84.2% and 83.2%, respectively. α-HCH, α-endosulfan, and dieldrin at urban sites and additionally HCB and Mirex at rural sites beside the excluded OCPs had very different pattern than others. It may be speculated that the parent compounds such as α-HCH, α-endosulfan, *p,p’*-DDT, and HCB could be originated from separate sources, while the OCPs labelled in circles on the graphs, which were mostly decay products of the parent OCPs, were clustered together indicating similar behavior, therefore, probably similar secondary emission due to the meteorological factors. Devi et al. (2011) also showed a similar behavior because the parent compounds (α-HCH, α-endosulfan, *p,p’*-DDT) were clustered together whereas decay products (endo-SO_4, *p,p’*-DDE, and *o,p’*-DDE) were grouped together.

The score plots of PCBs at urban and rural sites using 4 PC are demonstrated in Figure 4.15a and Figure 4.15b, respectively. It can be seen that mostly highly-chlorinated PCB congeners were clustered together. These congeners were PCB-87, 90/101, 95, 99, 104, 105, 110, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 174, 180, 183, 187, 188, 189, 194, and 199 with the exceptions 41/64 and 54. The score plots of PCB and OCPs at urban and rural sites by 5 PC are shown in Figure 4.15c and 4.15d, respectively. PCBs and OCPs in the circles (except *p'p*-DDE, *p'p*-DDT, Endo-I, Endo-II, α-HCH, β -HCH, Mirex, heptachlorepoxide, HCB, PCB19, PCB74, PCB118, and PCB123 for urban sites; and additionally endrin, dieldrin, heptachlor, pcb170, and pcb203 for rural sites) can be thought to have originated from LRAT from similar sources with similar atmospheric conditions.

4.2.2. Hypothesis tests

As a result of Man-Whitney U test, the difference in the median concentrations were found to be significant at urban sites for HCB (p<0.0001), dieldrin (p=0.023), *p'p*-DDT (p=0.039), and β-endosulfan (p=0.001). Endo-SO_4 was not detected at urban sites, and the median concentrations of the remaining OCPs and Σ_{43}PCBs were not significantly different with temperature at urban sites. The difference in the median concentrations with temperature was significant at rural sites for HCB (p<0.0001), heptachlor (p=0.002), dieldrin (p=0.002), endrin (p=0.007), *p'p*-DDE (p=0.010), Mirex (p=0.044), β-endosulfan (p=0.012), and Σ_{43}PCBs (p=0.047), whereas the median concentrations of the remaining OCPs were not significantly different at rural sites. Median concentrations of the pollutants at urban sites were not significantly different than those measured at rural sites (p>0.05).

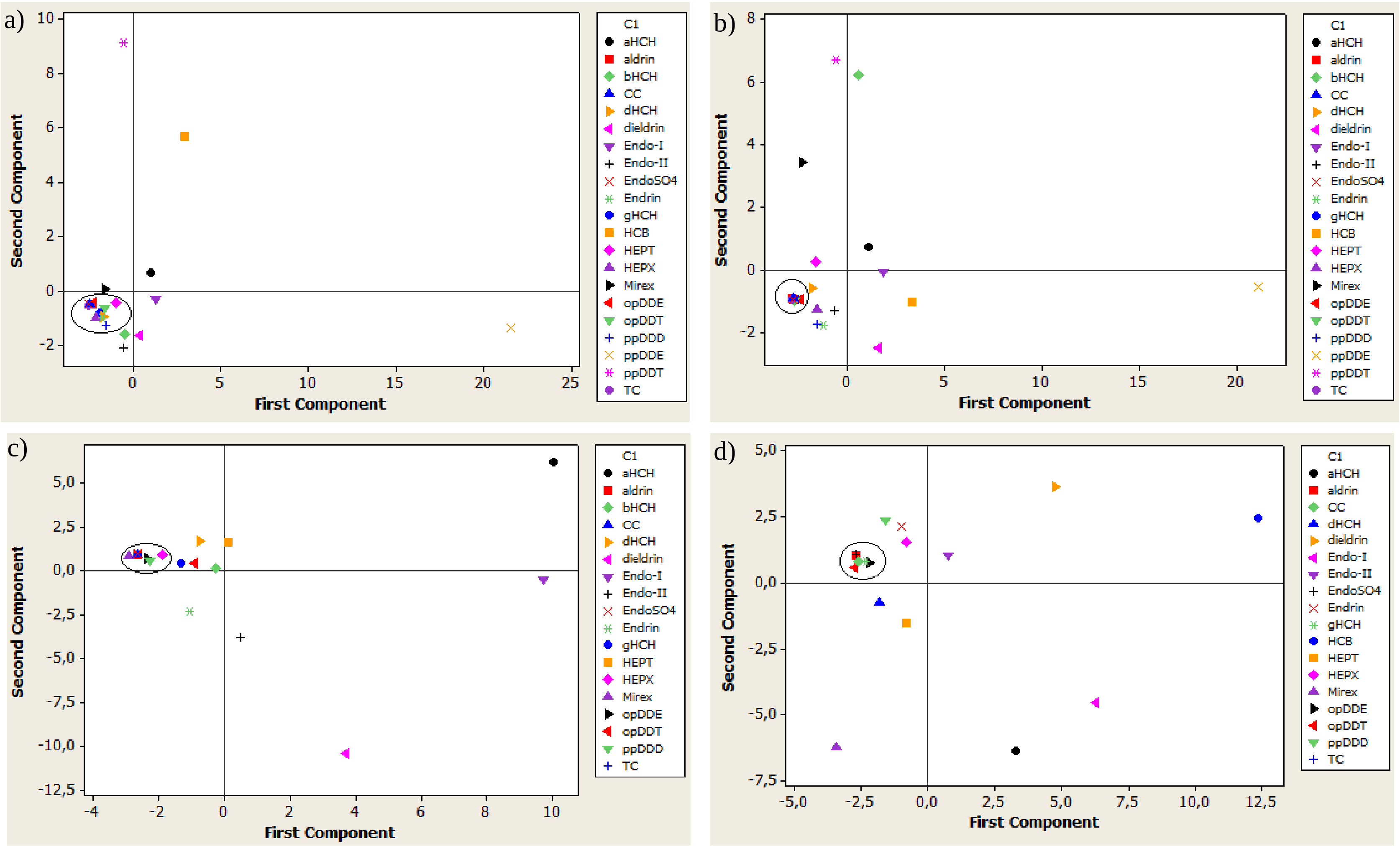


Figure 4.14. Distribution pattern of OCPs at a) urban sites with 4 PC b) rural sites with 4 PC c) urban sites with 6 PC (outliers excluded) d) rural sites with 6 PC (outliers excluded)

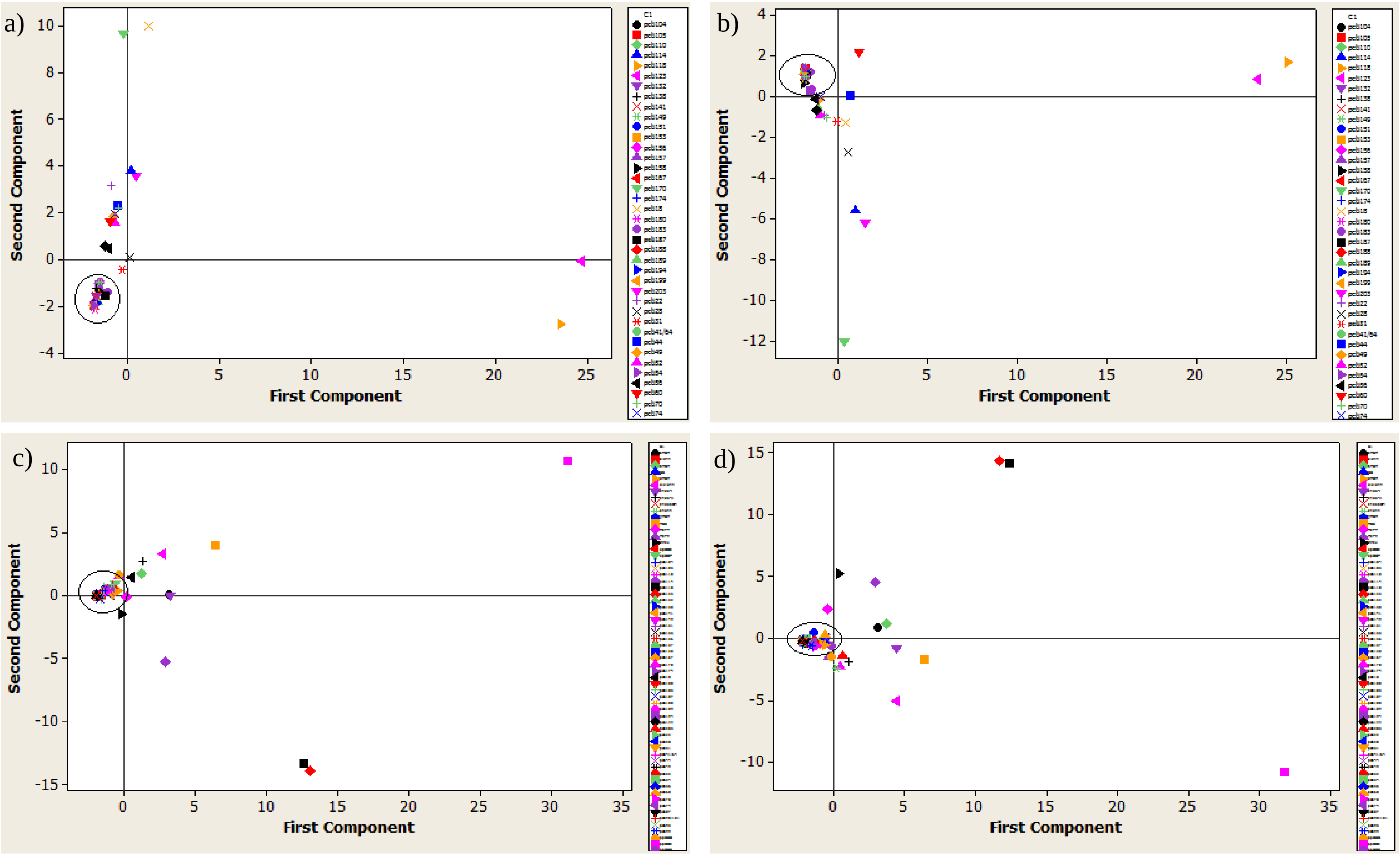


Figure 4.15. Distribution pattern of a) PCBs at urban sites with 4 PC b) PCBs at rural sites with 4 PC c) PCBs and OCP at urban sites with 5 PC d) PCBs and OCPs at urban sites with 5 PC

CHAPTER 5

CONCLUSIONS

The objectives of this study was to measure ambient air levels of 43 PCBs and 22 OCPs in 16 cities at urban and background sites by using polyurethane foam discs (PUF) as passive air samplers (PAS), to investigate spatial variations, and to generate a baseline database which is the first large-scale nationwide database for POP residues in air of Turkey. Air sampling was conducted from May 2014 to April 2015 with three-month sampling periods. Samples were analyzed by gas chromatography - mass spectrometry after extraction, clean-up and volume reduction.

The one-year overall average Σ_{43}PCB concentration was measured as 108±132 pg/m^3. The one-year average of Σ_{43}PCBs ranged from 14.5±14.3 pg/m^3 (Kayseri) to 403±428 pg/m^3 (İzmir) at urban sites with an average of 116±141 pg/m^3, and from 19.0±22.7 pg/m^3 (Aksaray) to 217±353 pg/m^3 (Kastamonu) with an average of 101±122 pg/m^3 at rural sites. PCB 118 had the highest mean concentration among the 43 PCB congeners with the value of 26.3±44.6 pg/m^3. Penta-CBs had the highest contribution to the total concentration with 54.3%, whereas hexa-CBs were the homologue group with the lowest contribution (3.2%). It was concluded that contribution of homologue groups with higher molecular weight was lower because of increasing number of chlorine atom and decreasing vapor pressure.

Overall one-year average Σ_{22}OCP concentration was found to be 341±870 pg/m^3 with a range of 55.3±36.5 pg/m^3 (Çankırı) to 1294±2153 pg/m^3 (Kırklareli). Among the OCP groups, ΣDDT had the highest overall average level with 134±296 pg/m^3. The highest concentration five OCP compounds were *p'p*-DDE (97.6±236 pg/m^3), HCB (45.3±197 pg/m^3), *α*-HCH (22.0±92.8 pg/m^3), *β*-HCH (21.8±96.1 pg/m^3), and *p'p*-DDT (21.3±77.4 pg/m^3). The mean concentrations of remaining OCPs were <20 pg/m^3.

Principle Components Analysis showed that, in addition to the OCP with the highest concentration (*p'p*-DDE), parent OCP compounds such as *α*-endosulfan, *α*-HCH, HCB, and *p'p*-DDT differed from the others, and some of the remaining decay products of OCPs were grouped together indicating similar behavior. In general, highly chlorinated PCB congeners were clustered together. Mann-Whitney U test indicated that the difference in the median concentrations of urban and rural sites was not significant. It was also used to test the significance of temperature effect on the median concentrations measured at a high and a low temperature range. The medians were significantly different for HCB, dieldrin, *p'p*-DDT, and *β*-endosulfan at urban sites but not significant for the remaining OCPs and ΣPCBs. The difference in the medians was significant for HCB, heptachlor, dieldrin, endrin, *p'p*-DDE, Mirex, and Σ_{43}PCBs at rural sites.

The use of these pollutants has been banned in Turkey in different times during 1979-2001. Therefore, the reason for detection of varying concentrations that reach levels which can be considered as high when compared to the literature reported values around the globe may be local volatilization and long range atmospheric transport from the sites of past use. Regular measurement of POP levels in Turkey's atmosphere should be conducted as the continuation of this work to be able to elaborate on this conclusion of this study.

REFERENCES

Abdi, H., and L. J. Williams. 2010. "Principal component analysis." Wiley Interdisciplinary Reviews: Computational Statistics 2 (4):433-459.

Ahioğlu, S. S. 2008. "Tarım sektöründe iş sağlığı ve güvenliği ve risk değerlendirmesi." İş Sağlığı ve Güvenliği Uzmanlık Tezi.

Aigner, E. J., A. D. Leone, and R. L. Falconer. 1998. "Concentrations and Enantiomeric Ratios of Organochlorine Pesticides in Soils from the U.S. Corn Belt." Environmental Science & Technology 32 (9):1162-1168.

Aliyeva, G., R. Kurkova, I. Hovorkova, J. Klanova, and C. Halsall. 2012. "Organochlorine pesticides and polychlorinated biphenyls in air and soil across Azerbaijan." Environmental Science and Pollution Research 19 (6):1953-1962.

Atlas, E, and C. S. Giam. 1988. "Ambient concentration and precipitation scavenging of atmospheric organic pollutants." Water, Air, and Soil Pollution 38 (1-2):19-36.

ATSDR. 1995. "Toxicological profile for mirex and chlordecone" U.S.Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR. 2002. "Toxicological profile for DDT, DDE, and DDD." U.S.Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR. 2005. "Toxicological profile for alpha-, beta-, gamma-, and delta-hexachlorocyclohexane." U.S.Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR. 2007. "Toxicological profile for heptachlor and heptachlor epoxide." U.S.Department of Health and Human Services, Public Health Service Agencyfor Toxic Substances and DiseaseRegistry.

ATSDR. 2013. "Draft toxicological profile for endoulfan." U.S.Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR. 2014. "Case Studies in Environmental Medicine Polychlorinated Piphenyls (PCBs) Toxicity." U.S.Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.

Aydın, M. E., S. Sarı, S. Özcan. 2004. "Konya katı atık depo sahasındaki poliklorlu bifenil bileşiklerinin (PCBs belirlenmesi)." V. Ulusal Çevre Mühendisliği Kongresi.

Baek, S. Y., S. D. Choi, and Y. S. Chang. 2011. "Three-Year Atmospheric Monitoring of Organochlorine Pesticides and Polychlorinated Biphenyls in Polar Regions and the South Pacific." Environmental Science & Technology 45 (10):4475-4482.

Baek, S. Y., S. D. Choi, S. J. Lee, and Y. S. Chang. 2008. "Assessment of the spatial distribution of coplanar PCBs, PCNs, and PBDEs in a multi-industry region of South Korea using passive air samplers." Environmental science & technology 42 (19):7336-7340.

Baek, S. Y., S. D. Choi, H. Park, J. H. Kang, and Y. S. Chang. 2010. "Spatial and seasonal distribution of polychlorinated biphenyls (PCBs) in the vicinity of an iron and steel making plant." Environmental science & technology 44 (8):3035-3040.

Bogdal, C., E. Abad, M. Abalos, B. van Bavel, J. Hagberg, M. Scheringer, and H. Fiedler. 2013. "Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents." Trac-Trends in Analytical Chemistry 46:150-161.

Bowes, G. W., and C. J. Jonkel. 1975. "Presence and distribution of polychlorinated biphenyls (PCB) in arctic and subarctic marine food chains." Journal of the Fisheries Board of Canada 32 (11):2111-2123.

Brubaker, W. W., and R. A. Hites. 1998. "OH Reaction Kinetics of Gas-Phase α- and γ-Hexachlorocyclohexane and Hexachlorobenzene." Environmental Science & Technology 32 (6):766-769.

Castro-Jiménez, J., G. Deviller, M. Ghiani, R. Loos, G. Mariani, H. Skejo, G. Umlauf, J. Wollgast, T. Laugier, K. Héas-Moisan, F. Léauté, C. Munschy, C. Tixier, and J. Tronczyński. 2008. "PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France)." Environmental Pollution 156 (1):123-135.

Chaemfa, C., J. L. Barber, K. S. Kim, T. Harner, and K. C. Jones. 2009. "Further studies on the uptake of persistent organic pollutants (POPs) by polyurethane foam disk passive air samplers." Atmospheric Environment 43 (25):3843-3849.

Chaemfa, C., J. L. Barber, T. Gocht, T. Harner, I. Holoubek, J. Klanova, and K. C. Jones. 2008. "Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides." Environmental Pollution 156 (3):1290-1297.

Choi, S. D., S. Y. Baek, Y. S. Chang, F. Wania, M. G. Ikonomou, Y. J. Yoon, B. K. Park, and S. Hong. 2008. "Passive air sampling of polychlorinated biphenyls and organochlorine pesticides at the Korean Arctic and Antarctic research stations: Implications for long-range transport and local pollution." Environmental Science & Technology 42 (19):7125-7131.

Cleverly, D., J. Ferrario, C. Byrne, K. Riggs, D. Joseph, and P. Hartford. 2007. "A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States." Environmental science & technology 41 (5):1537-1544.

Devi, N. L., Q. Shihua, C. Paromita, G. Zhang, and I. C. Yadav. 2011. "Passive air sampling of organochlorine pesticides in a northeastern state of India, Manipur." Journal of Environmental Sciences 23 (5):808-815.

Ding, L., Y. M. Li, P. Wang, X. M. Li, Z. S. Zhao, T. Ruan, and Q. H. Zhang. 2013. "Spatial concentration, congener profiles and inhalation risk assessment of PCDD/Fs and PCBs in the atmosphere of Tianjin, China." Chinese Science Bulletin 58 (9):971-978.

Drum, C. 1980. "Soil chemistry of pesticides, PPG Industries." Inc. USA.

Du, S., S. J. Wall, D. Cacia, and L. A. Rodenburg. 2009. "Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia Metropolitan Area." Environmental Science & Technology 43 (5):1287-1292.

EEA. 2005. "Sources of hexachlorobenzene emissions" EMEP/CORINAIR Guidebook, European Environmental Agency, Copenhagen, Denmark.

Érseková, A., K. Hilscherová, J. Klánová, J. P. Giesy, and J. Novák. 2014. "Effect-based assessment of passive air samples from four countries in Eastern Europe." Environmental Monitoring and Assessment:1-12.

Esen, F. 2013. "Development of a Passive Sampling Device Using Polyurethane Foam (PUF) to Measure Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs) near Landfills." Environmental Forensics 14 (1):1-8.

Estellano, V. H., K. Pozo, T. Harner, S. Corsolini, and S. Focardi. 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 (1):88-94.

Estellano, V. H., K. Pozo, C. Silibello, M. D. Mulder, C. Efstathiou, M. P. Tomasino, F. Funaro, I. Donadio, and S. Focardi. 2014. "Characterization of urban pollution in two cities of the Puglia region in Southern Italy using field measurements and air quality (AQ) model approach." Atmospheric Pollution Research 5 (1):34-41.

Farrar, N. J., T. Harner, M. Shoeib, A. Sweetman, and K. C. Jones. 2004. "Field Deployment of Thin Film Passive Air Samplers for Persistent Organic Pollutants: A Study in the Urban Atmospheric Boundary Layer." Environmental Science & Technology 39 (1):42-48.

Gouin, T., T. Harner, P. Blanchard, and D. Mackay. 2005. "Passive and Active Air Samplers as Complementary Methods for Investigating Persistent Organic Pollutants in the Great Lakes Basin." Environmental Science & Technology 39 (23):9115-9122.

Halse, A. K., M. Schlabach, A. Sweetman, K. C. Jones, and K. Breivik. 2012. "Using passive air samplers to assess local sources versus long range atmospheric transport of POPs." Journal of Environmental Monitoring 14 (10):2580-2590.

Harner, T., and T. F. Bidleman. 1996. "Measurements of octanol-air partition coefficients for polychlorinated biphenyls." Journal of Chemical and Engineering Data 41 (4):895-899.

Harner, T., M. Shoeib, M. Diamond, G. Stern, and B. Rosenberg. 2004. "Using Passive Air Samplers To Assess Urban−Rural Trends for Persistent Organic Pollutants. 1. Polychlorinated Biphenyls and Organochlorine Pesticides." Environmental Science & Technology 38 (17):4474-4483.

Gevao, B., H. Alegria, F. M. Jaward, U. B. Beg. 2010. "Persistent Organic Pollutants in the Developing World." in persistent organic pollutants, edited by S. Harrad, 137-170. Wiley United Kingdom.

Hayward, S. J., T. Gouin, and F. Wania. 2010. "Comparison of Four Active and Passive Sampling Techniques for Pesticides in Air." Environmental Science & Technology 44 (9):3410-3416.

Ishikawa, Y, Y. Noma, Y. Mori, and S. Sakai. 2007. "Congener profiles of PCB and a proposed new set of indicator congeners." Chemosphere 67 (9):1838-1851.

Jaward, F. M., N. J. Farrar, T. Harner, A. J. Sweetman, and K. C. Jones. 2004. "Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe." Environmental Science & Technology 38 (1):34-41.

Jones, K. C., and P. de Voogt. 1999. "Persistent organic pollutants (POPs): state of the science." Environmental Pollution 100 (1–3):209-221.

Kaya, E., Y. Dumanoglu, M. Kara, H. Altiok, A. Bayram, T. Elbir, and M. Odabasi. 2012. "Spatial and temporal variation and air-soil exchange of atmospheric PAHs and PCBs in an industrial region." Atmospheric Pollution Research 3 (4):435-449.

Kim, J. H., and A. Smith. 2001. "Distribution of organochlorine pesticides in soils from South Korea." Chemosphere 43 (2):137-140.

Klanova, J., P. Cupr, I. Holoubek, J. Boruvkova, P. Pribylova, R. Kares, T. Tomsej, and T. Ocelka. 2009. "Monitoring of persistent organic pollutants in Africa. Part 1: Passive air sampling across the continent in 2008." Journal of Environmental Monitoring 11 (11):1952-1963.

Klánová, J., J. Kohoutek, L. Hamplová, P. Urbanová, and I. Holoubek. 2006. "Passive air sampler as a tool for long-term air pollution monitoring: Part 1. Performance assessment for seasonal and spatial variations." Environmental Pollution 144 (2):393-405.

Lammel, G., O. Audy, A. Besis, C. Efstathiou, K. Eleftheriadis, J. Kohoutek, P. Kukučka, M. D. Mulder, P. Přibylová, R. Prokeš, T. P. Rusina, C. Samara, A. Sofuoglu, S. C. Sofuoglu, Y. Taşdemir, V. Vassilatou, D. Voutsa, and B. Vrana. 2015. "Air and seawater pollution and air–sea gas exchange of persistent toxic substances in the Aegean Sea: spatial trends of PAHs, PCBs, OCPs and PBDEs." Environmental Science and Pollution Research 22 (15):11301-11313.

Li, Y. M., D. W. Geng, Y. B. Hu, P. Wang, Q. H. Zhang, and G. B. Jiang. 2012. "Levels and distribution of polychlorinated biphenyls in the atmosphere close to Chinese Great Wall Station, Antarctica: Results from XAD-resin passive air sampling." Chinese Science Bulletin 57 (13):1499-1503.

Li, Y. M., D. W. Geng, F. B. Liu, T. Wang, P. Wang, Q. H. Zhang, and G. B. Jiang. 2012. "Study of PCBs and PBDEs in King George Island, Antarctica, using PUF passive air sampling." Atmospheric Environment 51:140-145.

Mahmood, A., J. H. Syed, R. N. Malik, Q. Zheng, Z. N. Cheng, J. Li, and G. Zhang. 2014. "Polychlorinated biphenyls (PCBs) in air, soil, and cereal crops along the two tributaries of River Chenab, Pakistan: Concentrations, distribution, and screening level risk assessment." Science of the Total Environment 481:596-604.

Meire, R. O., S. C. Lee, A. C. Targino, J. P. M. Torres, and T. Harner. 2012. "Air concentrations and transport of persistent organic pollutants (POPs) in mountains of southeast and southern Brazil." Atmospheric Pollution Research 3 (4):417-425.

Nasir, J., X. Wang, B. Xu, C. Wang, D. R. Joswiak, S. Rehman, A. Lodhi, S. Shafiq, and R. Jilani. 2014. "Selected Organochlorine Pesticides and Polychlorinated Biphenyls in Urban Atmosphere of Pakistan: Concentration, Spatial Variation and Sources." Environmental Science & Technology 48 (5):2610-2618.

Odabasi, M., A. Bayram, T. Elbir, R. Seyfioglu, Y. Dumanoglu, A. Bozlaker, H. Demircioglu, H. Altiok, S. Yatkin, and B. Cetin. 2009. "Electric Arc Furnaces for Steel-Making: Hot Spots for Persistent Organic Pollutants." Environmental Science & Technology 43 (14):5205-5211.

Ogura, I., S. Masunaga, and J. Nakanishi. 2004. "Quantitative source identification of dioxin-like PCBs in Yokohama, Japan, by temperature dependence of their atmospheric concentrations." Environmental science & technology 38 (12):3279-3285.

Pozo, K., T. Harner, S. C. Lee, R. K. Sinha, B. Sengupta, M. Loewen, V. Geethalakshmi, K. Kannan, and V. Volpi. 2011. "Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers." Environmental Pollution 159 (2):646-653.

Pozo, K., T. Harner, A. Rudolph, G. Oyola, V. H. Estellano, R. Ahumada-Rudolph, M. Garrido, K. Pozo, R. Mabilia, and S. Focardi. 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 (4):426-434.

Pozo, K., T. Harner, M. Shoeib, R. Urrutia, R. Barra, O. Parra, and S. Focardi. 2004. "Passive-Sampler Derived Air Concentrations of Persistent Organic Pollutants on a North−South Transect in Chile." Environmental Science & Technology 38 (24):6529-6537.

Pozo, K., T. Harner, F. Wania, D. C. G. Muir, K. C. Jones, and Leonard A. Barrie. 2006. "Toward a Global Network for Persistent Organic Pollutants in Air: Results from the GAPS Study." Environmental Science & Technology 40 (16):4867-4873.

Qing Q. L., A. Loganath, Y. S. Chong, J. Tan, and J. P. Obbard. 2006. "Persistent Organic Pollutants and Adverse Health Effects in Humans." Journal of Toxicology and Environmental Health, Part A 69 (21):1987-2005.

RůŽičková, P., J. Klánová, P. Čupr, G. Lammel, and I. Holoubek. 2007. "An Assessment of Air−Soil Exchange of Polychlorinated Biphenyls and Organochlorine Pesticides Across Central and Southern Europe." Environmental Science & Technology 42 (1):179-185.

Santiago, E. C., and M. G. Cayetano. 2011. "Organochlorine Pesticides in Ambient Air in Selected Urban and Rural Residential Areas in the Philippines Derived from Passive Samplers with Polyurethane Disks." Bulletin of Environmental Contamination and Toxicology 86 (1):50-55.

Shoeib, M., and T. Harner. 2002a. "Characterization and comparison of three passive air samplers for persistent organic pollutants." Environmental Science & Technology 36 (19):4142-4151.

Shoeib, M., and T. Harner. 2002b. "Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides." Environmental Toxicology and Chemistry 21 (5):984-990.

Shunthirasingham, C., C. E. Oyiliagu, X. Cao, T. Gouin, Fr.Wania, S. C. Lee, K. Pozo, T. Harner, and D. C. G. Muir. 2010. "Spatial and temporal pattern of pesticides in the global atmosphere." Journal of Environmental Monitoring 12 (9):1650-1657.

Simcik, M. F., H. X. Zhang, S. J. Eisenreich, and T. P. Franz. 1997. "Urban contamination of the Chicago coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLOS." Environmental Science & Technology 31 (7):2141-2147.

Su, Y., H. Hung, P. Blanchard, G. W. Patton, R. Kallenborn, A. Konoplev, P. Fellin, H. Li, C. Geen, G. Stern, B. Rosenberg, and L. A. Barrie. 2006. "Spatial and Seasonal Variations of Hexachlorocyclohexanes (HCHs) and Hexachlorobenzene (HCB) in the Arctic Atmosphere." Environmental Science & Technology 40 (21):6601-6607.

Syed, J. H., R. N. Malik, J. Li, G. Zhang, and K. C. Jones. 2013. "Levels, distribution and air-soil exchange fluxes of polychlorinated biphenyls (PCBs) in the environment of Punjab Province, Pakistan." Ecotoxicology and Environmental Safety 97:189-195.

Tombesi, N., K. Pozo, and T. Harner. 2014. "Persistent Organic Pollutants (POPs) in the atmosphere of agricultural and urban areas in the Province of Buenos Aires in Argentina using PUF disk passive air samplers." Atmospheric Pollution Research 5 (2):170-178.

UNEP. 1995. "Substance profiles for the POPs" http://www.chem.unep.ch/pops/indxhtms/asses6.html#ENDR. Accessed on October 2015.

UNEP. 2007. “Guidance on the Global Monitoring Plan for Persistant Organic Contaminants.” Chatelaine, Geneva, Switzerland. P. 147.

USEPA. 2007. "Chapter Four: Organic Analytes" http://www.epa.gov/solidwaste/hazard/testmethods/sw846/pdfs/chap4.pdf. Accessed on October 2015.

USEPA. 2010. "PCBs and Human Health" http://www3.epa.gov/region02/superfund/hudson/humanhealth.htm. Accessed on September 2015.

USEPA. 2015. "Groups of Pesticides in Registiration Review" http://www.epa.gov/pesticide-reevaluation/groups-pesticides-registration-review#imadazol. Accessed on December 2015.

Vardar, A., Eker, B. 2003. "Trakya yöresi kırsal kesiminde kurulabilecek rüzgar türbinleri için öneriler." II. Yenilenebilir Enerji Kaynakları Sempozyumu, İzmir.

Vijgen, J., L. F. Yi, M. Forter, R. Lal, and R. Weber. 2006. "The legacy of lindane and technical HCH production." Organohalogen Compounds 68:899-904.

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

Wang, X. Ping, P. Gong, T. D. Yao, and K. C. Jones. 2010. "Passive Air Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers Across the Tibetan Plateau." Environmental Science & Technology 44 (8):2988-2993.

Wania, F., L. Shen, Y. D. Lei, C. Teixeira, and D. C. G. Muir. 2003. "Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere." Environmental Science & Technology 37 (7):1352-1359.

Weber, L. W. D., and H. Greim. 1997. "The toxicity of brominated and mixed-halogenated dibenzo-p-dioxins and dibenzofurans: An overview." Journal of Toxicology and Environmental Health 50 (3):195-215.

Wick, A.F., N.W. Haus, B.F. Sukkariyah, K.C. Haering, and W.L. Daniels. 2011. "Remediation of PAH-contaminated soils and sediments: A literature review." CSES Department, Internal Research Document:102.

Yeo, H. G., M. Choi, M. Y. Chun, and Y. Sunwoo. 2003. "Concentration distribution of polychlorinated biphenyls and organochlorine pesticides and their relationship with temperature in rural air of Korea." Atmospheric Environment 37 (27):3831-3839.

Zhang, G., P. C., Jun Li, P. Sampathkumar, T. Balasubramanian, K. Kathiresan, S. Takahashi, A. Subramanian, S. Tanabe, and K. C. Jones. 2008. "Passive Atmospheric Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban, Rural, and Wetland Sites along the Coastal Length of India." Environmental Science & Technology 42 (22):8218-8223.

Zhang, L. F., L. Dong, W. L. Yang, L. Zhou, S. X. Shi, X. L. Zhang, S. Niu, L. L. Li, Z. X. Wu, and Y. R. Huang. 2013. "Passive air sampling of organochlorine pesticides and polychlorinated biphenyls in the Yangtze River Delta, China: Concentrations, distributions, and cancer risk assessment." Environmental Pollution 181:159-166.

APPENDIX A

DETAILED INFORMATION ABOUT GC-MS ANALYSIS AND QUALITY ASSURANCE / QUALITY CONTROL

Table A.1. Detailed information about GC/MS analysis

Congener	**Retention time (RT)**	**Target ion**	**Qualifier Ion 1, Q1**	**Calibration graph r^2 values**	**Minimum concentration at the calibration range (pg/uL)**	**Ionization type**
PCBs						
30	12.047	56	258	0.998498	0.2	EI
18	12.609	256	258	0.996501	0.2	EI
31	14.549	256	258	0.998196	0.2	EI
28	14.606	256	258	0.998633	0.2	EI
22	15.373	256	258	0.999574	0.2	EI
54	13.931	290	292	0.997652	0.2	EI
52	16.177	290	292	0.998515	0.2	EI
49	16.383	290	292	0.999104	0.2	EI
44	17.165	290	292	0.999354	0.2	EI
41/64	17.762	290	292	0.999556	0.2	EI
74	18.949	290	292	0.998870	0.2	EI
70	19.141	290	292	0.998340	0.2	EI
60	20.015	290	292	0.999254	0.2	EI
56	20.172	290	292	0.999048	0.2	EI
104	19.652	324	326	0.998593	0.2	EI
95	19.355	324	326	0.998157	0.2	EI
90/101	20.570	324	326	0.997539	0.2	EI
99	20.841	324	326	0.997961	0.2	EI
87	21.942	324	326	0.998750	0.2	EI
110	22.479	324	326	0.998646	0.2	EI
123	23.747	324	326	0.999531	0.2	EI
118	23.888	324	326	0.997480	0.2	EI
114	24.454	324	326	0.998668	0.2	EI

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Table A.1. (Cont.)

Congener	**Retention time (RT)**	**Target ion**	**Qualifier Ion 1, Q1**	**Calibration graph r^2 values**	**Minimum concentration at the calibration range (pg/uL)**	**Ionization type**
PCBs						
105	25.281	324	326	0.994432	0.2	EI
155	20.051	360	362	0.999888	0.2	EI
151	23.120	360	362	0.998454	0.2	EI
149	23.761	360	362	0.988911	0.2	EI
153	25.106	360	362	0.996875	0.2	EI
132	25.178	360	362	0.996760	0.2	EI
$^{13}C_{12}$PCB105	25.288	338	-	-	-	EI
141	25.774	360	362	0.998459	0.2	EI
138	26.505	360	362	0.997271	0.2	EI
158	26.609	360	362	0.998997	0.2	EI
167	27.691	360	362	0.998316	0.2	EI
156	28.472	360	362	0.994854	0.2	EI
157	28.659	360	362	0.999221	0.2	EI
188	24.692	394	396	0.997869	0.2	EI
187	27.333	394	396	0.997885	0.2	EI
183	27.431	394	396	0.996033	0.2	EI
174	28.087	394	396	0.996858	0.2	EI
180	29.013	394	396	0.997005	0.2	EI
170	29.859	394	396	0.991004	0.2	EI
189	30.620	394	396	0.997722	0.2	EI
199	29.340	426	428	0.997672	0.2	EI
203	30.229	426	428	0.993854	0.2	EI
194	31.459	426	428	0.996177	0.2	EI
Depuration Chemicals						
$^{13}C_{12}$PCB9	10.432	234	236	0.999721	0.8	EI
$^{13}C_{12}$PCB15	12.790	234	236	0.998582	0.8	EI
$^{13}C_{12}$PCB32	13.424	268	270	0.998661	0.8	EI
PCB 107	23.635	326	324	0.999725	0.8	EI
PCB198	29.995	428	426	0.999656	0.8	EI
$^{13}C_{12}\gamma$HCH	9.530	261	263	0.999452	1.6	NCI

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Table A.1. (Cont.)

Congener	**Retention time (RT)**	**Target ion**	**Qualifier Ion 1, Q1**	**Calibration graph r^2 values**	**Minimum concentration at the calibration range (pg/uL)**	**Ionization type**
Surrogate Chemicals for Recovery Performance						
$^{13}C_{12}$PCB28	14.663	268	270	0.999967	0.2	EI
$^{13}C_{12}$PCB52	16.219	302	304	0.999911	0.2	EI
$^{13}C_{12}$PCB101	20.584	336	338	0.999974	0.2	EI
$^{13}C_{12}$PCB153	25.105	374	372	0.999833	0.2	EI
$^{13}C_{12}$PCB138	26.494	374	372	0.999741	0.2	EI
$^{13}C_{12}$PCB180	29.382	406	408	0.999504	0.2	EI
$^{13}C_{12}$PCB209	32.891	508	510	0.999345	0.2	EI
OCPs						
HCB	8.832	284	286	0.999761	1	NCI
α-HCH	8.837	255	253	0.993100	1	NCI
β-HCH	9.391	253	255	0.990847	1	NCI
γ-HCH	9.524	255	253	0.999704	1	NCI
δ-HCH	10.207	255	253	0.997076	1	NCI
HEPT	10.907	266	268	0.997586	1	NCI
ALD	11.538	237	235	0.999855	1	NCI
CC	12.774	410	412	0.999681	1	NCI
o,p'-DDE	12.939	246	248	0.999498	1	NCI
ENDO-I	12.966	406	408	0.999327	1	NCI
TC	13.000	410	412	0.998765	1	NCI
DIELD	13.461	237	235	0.998784	1	NCI
o.p'-DDD	13.661	248	246	0.999424	1	NCI
p.p'-DDE	13.573	318	316	0.999943	1	NCI
END	13.805	380	382	0.997534	1	NCI
ENDO-II	14.047	406	408	0.996295	1	NCI
o.p'-DDT	14.310	248	246	0.996839	1	NCI
p.p'-DDD	14.338	248	250	0.998791	1	NCI
ENDOSULP	14.767	386	388	0.998809	1	NCI
p.p'-DDT	14.979	248	250	0.997181	2	NCI
Mirex	16.544	368	370	0.999452	1	NCI

Table A.2. Laboratory control samples

(pg/µL) (n=8)						**(pg/µL) (n=8)**		
PCBs	**Avg**	**SD**	**PCBs**	**Avg**	**SD**	**OCPs**	**Avg**	**SD**
PCB30	0.05	0.02	PCB114	0.12	0.03	HCB	0.34	0.11
PCB18	0.09	0.04	PCB105	0.11	0.04	*α*-HCH	N.D.	
PCB31	0.06	0.02	PCB155	0.03	0.01	*β*-HCH	N.D.	
PCB28	0.04	0.02	PCB151	0.04	0.02	*γ*-HCH	0.69	0.04
PCB22	0.06	0.02	PCB149	0.05	0.03	*δ*-HCH	N.D.	
PCB54	0.05	0.03	PCB153	0.08	0.02	HEPT	N.D.	
PCB52	0.07	0.03	PCB132	0.07	0.02	ALD	N.D.	
PCB49	0.09	0.03	PCB141	0.10	0.03	HEPX	N.D.	
PCB44	0.08	0.03	PCB138	0.10	0.03	CC	N.D.	
PCB41/60	0.03	0.01	PCB158	0.06	0.02	TC	N.D.	
PCB74	0.06	0.02	PCB167	0.11	0.04	*o,p'*-DDE	N.D.	
PCB70	0.05	0.02	PCB156	0.10	0.04	TC	N.D.	
PCB60	0.13	0.05	PCB157	0.12	0.06	DIELD	N.D.	
PCB56	0.02	0.01	PCB188	0.08	0.08	*o.p'*-DDD	N.D.	
PCB104	0.09	0.03	PCB187	0.11	0.07	*p.p'*-DDE	N.D.	
PCB95	0.08	0.03	PCB183	0.09	0.04	END	2.44	0.40
PCB90/101	0.06	0.03	PCB174	0.14	0.08	ENDO-II	N.D.	
PCB99	0.07	0.03	PCB180	0.13	0.06	*o.p'*-DDT	N.D.	
PCB87	0.10	0.05	PCB170	0.13	0.02	*p.p'*-DDD	N.D.	
PCB110	0.09	0.03	PCB189	0.10	0.04	ENDOSULP	N.D.	
PCB123	0.08	0.02	PCB199	0.15	0.03	*p.p'*-DDT	N.D.	
PCB118	0.07	0.05	PCB203	0.23	0.12	Mirex		

Table A.3. Calibration Control Standards

Analyte	**Avg RSD**	**Std**	**Min RSD**	**Max RSD**	**Analyte**	**Avg RSD**	**std**	**Min RSD**	**Max RSD**
PCBS									
PCB30	9.38	5.14	0.80	14.93	PCB114	5.83	2.67	0.67	8.93
PCB18	14.10	4.82	5.57	18.80	PCB105	5.06	4.29	0.50	10.77
PCB31	9.57	4.68	0.40	14.60	PCB155	9.90	4.65	2.00	15.93
PCB28	5.73	5.46	0.20	14.87	PCB151	7.27	2.62	2.27	9.97
PCB22	12.98	5.40	0.83	16.23	PCB149	8.02	2.21	5.03	10.43
PCB54	12.38	6.15	0.97	19.53	PCB153	13.39	6.63	0.60	19.87
PCB52	10.68	5.11	0.10	15.87	PCB132	12.38	1.90	10.37	14.67
PCB49	11.79	5.18	1.07	15.73	PCB141	5.66	2.74	0.67	8.33
PCB44	11.36	4.20	2.97	16.23	PCB138	2.31	2.04	0.47	6.37
PCB41/60	13.17	5.52	1.00	16.50	PCB158	8.17	3.71	0.90	11.47
PCB74	6.45	2.60	1.03	9.00	PCB167	2.15	1.89	0.17	5.40
PCB70	8.81	3.08	4.67	12.57	PCB156	2.72	2.23	0.17	5.50
PCB60	5.52	2.52	2.10	9.03	PCB157	6.47	3.56	0.73	10.70
PCB56	11.27	4.49	1.37	14.10	PCB188	8.10	2.82	3.27	11.17
PCB104	13.35	4.71	4.17	17.77	PCB187	4.69	1.97	2.27	8.17
PCB95	11.07	2.53	7.27	14.60	PCB183	4.38	2.24	1.63	8.50
PCB90/101	10.03	3.79	1.60	12.33	PCB174	3.70	2.48	0.60	6.37
PCB99	9.80	2.45	6.50	12.63	PCB180	4.69	2.74	0.57	7.77
PCB87	9.90	4.49	0.73	14.90	PCB170	3.59	2.72	0.30	8.87
PCB110	5.62	3.59	0.67	9.37	PCB189	4.06	4.15	0.73	12.50
PCB123	3.27	1.60	1.20	5.40	PCB199	4.76	4.71	0.27	13.17
PCB118	10.98	2.43	8.33	15.33	PCB203	6.96	4.54	1.47	12.77
OCPs									
HCB	1.67	1.06	0.05	3.38	ENDO-I	8.98	5.36	1.85	19.85
α-HCH	6.56	5.01	0.30	13.43	DIELD	4.76	3.05	1.63	12.65
β-HCH	6.04	4.00	0.78	1.83	*o,p'*-DDD	6.62	5.87	1.20	18.88
γ-HCH	8.58	6.07	0.33	9.50	*p,p'*-DDE	4.34	3.26	0.72	10.25
δ-HCH	6.36	6.46	0.78	7.80	ENDR	4.62	3.68	1.35	13.85
HEPT	8.71	5.23	0.75	7.50	ENDO-II	4.36	3.14	1.20	11.15
ALD	7.38	5.06	1.88	17.00	*o,p'*-DDT	3.73	2.54	0.90	9.40
HEPX	9.08	4.05	3.20	15.10	*p,p'*-DDD	6.75	4.00	2.17	13.15
CC	4.84	4.12	0.53	12.05	ENDOSULP	6.74	4.38	0.37	14.38
TC	7.45	3.22	3.13	13.48	*p,p'*-DDT	7.36	3.72	2.17	11.70
o,p'-DDE	4.73	2.19	1.37	7.13	Mirex	5.64	4.47	0.98	13.85

APPENDIX B

C/C_o RATIOS FOR SAMPLING PERIODS

C/C_o ratios of depuration compounds required to calculate air uptake rate through PUF discs are shown in Table B1 and Table B2 for all sampling locations.

Table B.1. C/Co values for 1st and 2nd sampling periods

	C/C_0													
	Phase-I							**Phase-II**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d_6-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d_6-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Aksaray (U)	0.156	0.150	0.018	0.034	0.033	0.890	0.950	0.304	0.026	0.010	0.015	0.029	0.780	0.870
Aksaray (R)	0.027	0.120	0.033	0.009	0.005	0.850	0.920	0.241	0.160	0.032	0.036	0.040	0.800	0.900
Antalya (U)	0.115	0.200	0.009	0.034	0.027	1.000	1.000	0.180	0.010	0.007	0.036	0.023	0.780	0.830
Antalya (R)	0.145	0.180	0.042	0.001	0.018	0.850	0.950	0.293	0.110	0.028	0.040	0.004	0.780	0.870
Çankırı (U)	0.398	0.030	0.015	0.034	0.021	0.940	0.900	0.335	0.034	0.007	0.050	0.040	0.850	0.920
Çankırı (R)	0.251	0.032	0.049	0.038	0.004	0.780	0.880	0.174	0.045	0.040	0.028	0.009	0.710	0.860
Elazığ (U)	0.290	0.025	0.020	0.026	0.039	0.750	0.850	0.299	0.015	0.024	0.031	0.360	0.760	0.870
Elazığ (R)	0.066	0.018	0.007	0.031	0.027	0.800	0.880	0.370	0.160	0.200	0.032	0.010	0.810	0.890
İstanbul (U)	0.376	0.024	0.029	0.020	0.035	0.750	0.870	0.242	0.170	0.035	0.033	0.020	0.710	0.860
İstanbul (R)	0.356	0.019	0.048	0.049	0.008	0.700	0.780	0.120	0.022	0.037	0.014	0.014	0.730	0.890
İzmir (U)	0.318	0.280	0.039	0.000	0.048	0.850	0.910	0.111	0.033	0.028	0.046	0.019	0.740	0.910
İzmir (R)	0.230	0.100	0.007	0.006	0.010	0.760	0.870	0.072	0.023	0.001	0.007	0.018	0.750	0.920
Kars (U)	0.261	0.012	0.049	0.019	0.012	0.850	0.870	0.010	0.033	0.019	0.300	0.600	0.710	0.850
Kars (R)	0.161	0.150	0.035	0.002	0.045	0.780	0.870	0.192	0.041	0.043	0.028	0.039	0.840	0.920

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Table B.1 (Cont.)

	C/C_0													
	Phase-I							**Phase-II**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d_6-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d_6-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Kastamonu (U)	0.432	0.350	0.034	0.022	0.000	0.820	0.880	0.284	0.031	0.031	0.024	0.027	0.860	0.910
Kastamonu (R)	0.159	0.006	0.120	0.350	0.021	0.720	0.870	0.409	0.017	0.033	0.021	0.019	0.790	0.890
Kayseri (U)	0.132	0.150	0.250	0.032	0.049	0.750	0.800	0.200	0.043	0.026	0.017	0.022	0.750	0.870
Kayseri (R)	0.202	0.032	0.039	0.019	0.040	0.730	0.820	0.225	0.046	0.023	0.100	0.039	0.710	0.860
Kırıkkale (U)	0.202	0.032	0.039	0.019	0.040	0.800	0.850	0.340	0.009	0.020	0.023	0.027	0.860	0.910
Kırıkkale (R)	0.318	0.011	0.033	0.005	0.042	0.750	0.830	0.407	0.012	0.033	0.035	0.013	0.810	0.850
Kırklareli (U)	0.332	0.025	0.025	0.015	0.010	0.870	0.890	0.285	0.015	0.027	0.028	0.027	0.810	0.920
Kırklareli (R)	Sampler was lost							0.366	0.366	0.010	0.018	0.031	0.036	0.750
Konya (U)	0.191	0.150	0.012	0.007	0.005	0.730	0.850	0.171	0.015	0.028	0.047	0.003	0.770	0.860
Konya (R)	0.093	0.170	0.013	0.035	0.017	0.870	0.860	0.160	0.038	0.020	0.023	0.270	0.810	0.860
Malatya (U)	0.338	0.210	0.015	0.030	0.006	0.720	0.850	0.266	0.048	0.026	0.042	0.010	0.730	0.860
Malatya (R)	0.181	0.120	0.018	0.038	0.039	0.670	0.750	0.297	0.024	0.044	0.038	0.024	0.840	0.930
Mersin (U)	0.128	0.100	0.023	0.047	0.021	0.730	0.810	0.181	0.014	0.027	0.024	0.038	0.700	0.850
Mersin (R)	0.318	0.014	0.020	0.013	0.032	0.670	0.870	0.158	0.033	0.032	0.030	0.042	0.740	0.870

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Table B.1. (Cont.)

	C/C_0													
	Phase-I							**Phase-II**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d_6-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d_6-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Uşak (U)	0.155	0.135	0.013	0.040	0.024	0.750	0.820	0.322	0.031	0.044	0.030	0.039	0.840	0.910
Uşak (R)	0.186	0.001	0.024	0.010	0.001	0.720	0.800	0.251	0.018	0.038	0.039	0.038	0.760	0.870
Van (U)	0.537	0.090	0.049	0.032	0.004	0.710	0.890	0.287	0.021	0.022	0.035	0.025	0.790	0.870
Van (R)	0.331	0.020	0.041	0.014	0.034	0.750	0.850	0.248	0.019	0.150	0.037	0.039	0.810	0.880

Table B.2. C/Co values for 3rd and 4th sampling periods

	C/C$_0$													
	Phase-III							**Phase-IV**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d$_6$-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d$_6$-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Aksaray (U)	0.656	0.248	0.511	0.500	0.363	0.846	0.943	0.472	0.295	0.522	0.511	0.385	0.798	0.846
Aksaray (R)	0.493	0.080	0.385	0.338	0.151	0.824	0.912	0.509	0.088	0.434	0.416	0.180	0.807	0.944
Antalya (U)	0.774	0.550	0.543	0.563	0.515	0.865	0.978	0.412	0.187	0.440	0.419	0.246	0.829	0.924
Antalya (R)	0.629	0.433	0.630	0.572	0.531	0.852	0.834	0.605	0.293	0.573	0.520	0.423	0.941	0.936
Çankırı (U)	0.450	0.113	0.346	0.343	0.164	0.681	0.778	0.496	0.181	0.515	0.492	0.288	0.823	0.842
Çankırı (R)	0.135	0.124	0.130	0.133	0.127	0.157	0.187	0.448	0.148	0.472	0.402	0.257	0.836	0.719
Elazığ (U)	0.396	0.333	0.364	0.358	0.347	0.452	0.531	0.520	0.327	0.539	0.496	0.398	0.795	0.904
Elazığ (R)	0.123	0.068	0.134	0.122	0.094	0.219	0.233	0.578	0.200	0.506	0.474	0.315	0.831	0.940
İstanbul (U)	0.364	0.171	0.273	0.261	0.209	0.468	0.527	0.403	0.071	0.340	0.388	0.123	0.753	0.895
İstanbul (R)	0.193	0.127	0.208	0.191	0.166	0.307	0.292	0.491	0.290	0.574	0.568	0.395	0.818	0.965
İzmir (U)	0.477	0.284	0.377	0.357	0.309	0.573	0.624	0.447	0.226	0.488	0.453	0.326	0.785	0.919
İzmir (R)	0.418	0.078	0.440	0.398	0.152	0.887	0.858	0.384	0.044	0.379	0.674	0.095	0.845	0.964
Kars (U)	0.587	0.427	0.506	0.503	0.472	0.716	0.809	0.402	0.114	0.383	0.375	0.188	0.737	0.890
Kars (R)	0.501	0.266	0.535	0.497	0.383	0.817	0.834	0.319	0.025	0.281	0.297	0.059	0.722	0.887

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Table B.2. (Cont.)

	C/C_0													
	Phase-III							**Phase-IV**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d_6-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d_6-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Kastamonu (U)	0.650	0.355	0.390	0.471	0.305	0.865	1.000	0.563	0.322	0.543	0.885	0.377	0.836	0.974
Kastamonu (R)	0.488	0.427	0.603	0.551	0.527	0.820	0.762	0.473	0.135	0.472	0.778	0.267	0.770	0.925
Kayseri (U)	0.787	0.505	0.486	0.551	0.479	0.822	0.946	0.537	0.251	0.485	0.441	0.340	0.778	0.929
Kayseri (R)	0.752	0.479	0.451	0.501	0.484	0.803	0.929	0.426	0.153	0.448	0.392	0.253	0.762	0.878
Kırıkkale (U)	0.553	0.281	0.526	0.501	0.362	0.798	0.822	0.421	0.326	0.429	0.576	0.328	0.766	0.919
Kırıkkale (R)	0.448	0.087	0.477	0.421	0.174	1.029	0.819	0.371	0.110	0.396	0.363	0.202	0.684	0.828
Kırklareli (U)	0.699	0.279	0.355	0.419	0.318	0.737	0.831	0.411	0.063	0.345	0.416	0.104	0.867	0.961
Kırklareli (R)	0.657	0.387	0.554	0.527	0.454	0.856	0.956	0.490	0.073	0.412	0.443	0.151	0.834	0.971
Konya (U)	0.682	0.486	0.525	0.567	0.511	0.834	0.915	0.377	0.091	0.404	0.421	0.219	0.750	0.884
Konya (R)	0.604	0.381	0.613	0.546	0.471	0.837	0.789	0.246	0.019	0.244	0.253	0.049	0.692	0.852
Malatya (U)	0.695	0.409	0.424	0.458	0.442	0.629	0.667	0.617	0.348	0.552	0.561	0.375	0.896	1.000
Malatya (R)	0.437	0.436	0.578	0.533	0.520	0.770	0.715	0.617	0.387	0.627	0.613	0.498	0.959	0.977
Mersin (U)	0.667	0.438	0.666	0.602	0.526	0.916	0.903	0.574	0.171	0.447	0.455	0.252	0.839	0.969
Mersin (R)	0.422	0.042	0.376	0.323	0.080	0.885	0.984	0.617	0.055	0.380	0.369	0.120	0.808	0.996

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Table B.2. (Cont.)

	C/C_0													
	Phase-III							**Phase-IV**						
		$^{13}C_{12}$PCB-			**PCB-**				**$^{13}C_{12}$PCB-**			**PCB-**		
	d_6-γHCH	**9**	**15**	**32**	**30**	**107**	**198**	**d_6-γHCH**	**9**	**15**	**32**	**30**	**107**	**198**
Uşak (U)	0.654	0.395	0.599	0.543	0.410	0.886	0.818	0.768	0.322	0.558	0.569	0.415	0.903	0.973
Uşak (R)	0.377	0.061	0.369	0.333	0.124	0.813	0.820	0.535	0.087	0.423	0.391	0.171	0.738	0.874
Van (U)	0.695	0.470	0.542	0.521	0.443	0.832	0.958	0.503	0.264	0.562	0.549	0.349	0.833	0.970
Van (R)	0.669	0.748	0.822	0.719	0.803	0.901	0.896	0.424	0.058	0.404	0.379	0.113	0.801	0.953