AMBIENT AIR PERSISTENT ORGANIC POLLUTANT MONITORING, BACKTRAJECTORY MODELING, AND HEALTH RISK ASSESSMENT

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ABSTRACT

AMBIENT AIR PERSISTENT ORGANIC POLLUTANT MONITORING, BACKTRAJECTORY MODELING, AND HEALTH RISK ASSESSMENT

Turkish Government has officially become a party to the Stockholm Convention as of 2010, therefore, determination of POPs in environmental compartments in Turkey is a critical concern. In this study, 22 organochlorine pesticides (OCPs) and 43 polychlorinated biphenyls (PCBs) were measured in gas and particulate phases of ambient air samples collected in Izmir and Istanbul from May to October 2014 on a weekly basis. Gas chromatography–mass spectrometry was used to quantify the targeted pollutants. Potential source regions were assessed by applying back-trajectory and Potential Source Contribution Function (PSCF). Population carcinogenic risk levels associated with inhalation exposure were estimated by using Monte Carlo simulation, for which sensitivity and uncertainty analyses were also conducted.

The highest mean concentration compounds were heptachlor (61±126 pg/m^3) and *p,p'*-DDE (54±57 pg/m^3) in Izmir and Istanbul, respectively. The mean Σ_{43}PCBs concentration was found as 232±224 pg/m^3 in Izmir, and 104±48 pg/m^3 in Istanbul. Gas phase concentartions of OCPs and PCBs were generally much higher than particle phase. The PSCF results pointed out different potential source regions: Middle East, Eurasia, and Europe. All the estimated carcinogenic risks based on the 95% percentile values for individual OCPs and Σ_{43}PCBs were calculated below the acceptable risk levels (10^{-6}), indicating no significant potential health risk via inhalation route.

ÖZET

DIŞ HAVADAKİ KALICI ORGANİK KİRLETİCİLERİN ÖLÇÜLMESİ, GERİ-İZLEME MODELLEMESİ VE SAĞLIK RİSKİ DEĞERLENDİRMESİ

Türkiye Hükümeti 2010 yılında resmen Stockholm Sözleşmeye taraf olmuştur. Dolayısıyla, KOK seviyelerinin çevresel ortamlarda belirlenmesi Türkiye'de dikkatleri üzerine çeken bir çalışma konusu haline gelmiştir. Bu çalışmada, KOK sınıfına giren organoklorürlü pestisit (OCP) bileşiklerinden 22 tanesinin ve poliklorlu bifenil (PCB) bileşiklerinden 43 tanesinin derişimleri, İzmir'de kırsal olarak nitelendirilebilecek bir alanda, İstanbul'da ise kentsel bir alanda Mayıs-Ekim 2014 zaman aralığında gaz ve partikül fazda toplanan hava örneklerinde ölçülmüştür. Numuneler gaz kromatografisi-kütle spektrometresi kullanılarak analiz edilmiştir. Geri-izleme modellemesi ve PSCF (Potansiyel Kaynak Katkı Fonksiyonu) kullanılarak olası uzun mesafeli taşınım kaynak bölgeleri belirlenmiştir. Hedef kirleticilere teneffüs yoluyla maruz kalma seviyeleri ve bununla ilişkili olarak popülasyon karsinojenik riski düzeyleri, Monte Carlo simülasyonu kullanılarak tahmin edilmiştir.

En yüksek derişim seviyeleri İzmir'de heptaklor (54±57 pg/m^3), İstanbul'da ise *p,p'*-DDE (61±126 pg/m^3) için bulunmuştur. Ortalama Σ_{43}PCBler derişimi, İzmir'de 232±224 pg/m^3, İstanbul'da 104±48 pg/m^3 olarak hesaplanmıştır. Hedeflenen OCP ve PCB kirleticilerinin çoğunun, baskın olarak gaz fazında bulunduğu tespit edilmiştir. PSCF sonuçları, kirleticiler için farklı kıtalarda farklı potansiyel kaynak bölgelerine işaret etmektedir. Baskın muhtemel kaynak bölgeler Orta Doğu, Avrasya ve Avrupa'da yer almaktadır. Hesaplanan tahmini kanserojen risk düzeyi kabul edilen değerin (10^{-6}) altında yer almış, dolayısıyla dikkate değer bir sağlık risk potansiyeli olmadığı saptanmıştır.

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CHAPTER 1

INTRODUCTION

Persistent organic pollutants (POPs) have been known as organic compounds that are resistant to photolytic, biological, and chemical degradation. They are subject to fractionation due to range of their volatility and long range transport. Therefore, they found ubiquitously in the environment even in the places where they have never been used.

POPs are also considerably noticeable with their properties as low water solubility and high lipid solubility leading to bioaccumulation in fatty tissues. Most of the complex synthetic chemicals such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs) are classified as POPs. Therefore many groups are available as POPs and found in the environment as a result of use, transport etc. The distribution of POPs in the atmosphere varies depending on temperature, weather conditions, and other physical/chemical characteristics such as vapor pressure, partition coefficient etc. (Yeo et al. 2003). POPs tend to migrate from warmer to colder regions of the Earth by volatilization process. Thus, OCPs and PCBs have been detected in remote areas where the compounds have never been used or produced (Montone et al. 2003, Baek et al. 2011). Despite the restrictions and prohibitions, these banned compounds have been also detected at high level in ambient air all around the world due to most probably illegal uses or unintentional emissions of production of other chemicals by-products.

Global initiatives on POPs were started due to adverse effects of POPs on human health and the environment. Afterwards, the Stockholm Convention of United Nations Environment Programme (UNEP) about POPs entered into force on 17 May 2004 as a global agreement. Although presence of many thousands of POPs in the versatile natural and anthropogenic forms were known, 12 of them have been accepted as priority compounds because of their higher persistence and bioaccumulative characteristics (Ritter et al. 1995). The 12 POPs consists of OCPs like aldrin, dieldrin, chlordane, dichlorodiphenyl-trichloroethanes (DDTs), endrin, heptachlor (HEPT), mirex, and toxaphene; PCBs, hexachlorobenzene (HCB), and hexabromobiphenyl as industrial products; and polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as unintentional by-products.

OCPs and PCBs are two restricted or banned groups of POPs. OCPs are emitted to environment as a result of extensive use in agriculture, forestry, and in termite, pest, and mosquito control. PCBs were commonly used as dielectric and coolant fluids prior to their ban use (Robertson and Hansen 2001). OCPs and PCBs have many adverse health effects. As a result of chronic exposure, hormone disruption, damage of organ systems, neurodevelopment changes, neurotoxic effects, and cancer can occur (Carpenter 1998, Petrik et al. 2006, Chaturvedi et al. 2013). A significantly outstanding event about adverse effects of POPs, the Yusho incident, occurred in western part of Japan in 1968. Kanemi Company in Kyushu produced PCBs and PCDFs during manufacture of rice bran oil. The accidentially released PCBs led to considerable skin problems such as acne and rashes, and affected health of approximately 14,000 people. Four hundred thousand birds died in the incident (Yoshimura 2003). Another event, the Yu-Cheng incident, occurred in Taiwan in 1979 resulting in similar effects. Both of the incidents caused poor cognitive development on children.

In Turkey, the ambient air concentrations of OCPs and PCBs have been measured in several locations such as Bolu, Bursa, Izmir, and Konya (Kaya et al. 2012, Odabasi and Cetin 2012, Yenisoy-Karakas et al. 2012, Cindoruk and Tasdemir 2014). However, the levels and sources of POPs should be determined regularly due to the Stockholm Convention. Turkey was not a manufacturer of these compounds. Contamination in Turkey could occur from old use of these compounds and long range transport from the countries where these compounds were produced and heavily used. Long range transport from Russia and Europe may be an important contributor for ambient air POP levels in Istanbul and Izmir, respectively. Istanbul and Izmir, two of the most populated provinces in Turkey, are also heavily populated with industrial facilities in and around.

Although independent studies were conducted, no concurrent investigations were made, no exposure-risk assessments were conducted, and potential source regions of long range transport were not studied. The objective of this study was to obtain the concentration profiles of OCPs and PCBs in the ambient air of Istanbul and Izmir by collecting OCPs and PCBs in gas and particle phases from a background site in Izmir and an urban site in Istanbul. In this thesis, spatial differences were explored between Istanbul and Izmir. Back-trajectory modeling was applied along with the use of Potential Source Contribution Function (PSCF) to assess potential source regions. A Monte Carlo simulation was conducted to estimate the population risks by the route of inhalation, for which sensitivity and uncertainty analyses were also conducted.

In the following chapters, information regarding OCPs and PCBs in the literature (Chapter 2), material and methods employed in this study (Chapter 3), and results and discussion (Chapter 4) are presented, followed by the conclusion (Chapter 5).

CHAPTER 2

LITERATURE REVIEW

POPs in ambient air have been widely studied throughout the world. Therefore, there are many studies that report POP levels in air from all around the world. Although it is limited compared to other parts of the world, there are a number of studies conducted in Turkey. The following sections provide a literature review on global initiatives on POPs, chemical structures and properties, sources, transport and fate in environment, health effects, atmospheric concentration and health risk assessment studies, back trajectory analysis and potential source contribution function studies related to OCPs and PCBs.

2.1. Global Initiatives on POPs

The first global initiative on POPs was started with 1996 Intergovernmental Forum due to adverse effects of POPs on human health and the environment. Intergovernmental POPs Review Committee was established in 1997 with a decision of Governing Council of the United Nations Environment Programme (UNEP). Then, 129 countries convened for Stockholm Convention of UNEP on POPs in 2001 which is a global treaty that entered into force on 17 May 2004. Turkey signed the Convention in 2001, became a party in 2009, and the Convention was entered into force in Turkey in 2010. The purpose of this Convention is to protect human health and the environment from the adverse effects of POPs. The assessment on POPs had initially begun with 12 POPs called as “dirty dozen” (listed in Chapter 1) which were selected due to their persistence and bioaccumulative characteristics in biota and in the environment (Ritter et al. 1995). Afterwards, ten new chemicals were added into convention scope in 2009 and 2010 namely chlordecone, HCHs (*α*-, *β*-, and *γ*- isomers), pentachlorobenzene, endosulfan, polybromodiphenylether (tetra-, penta-, hexa-, and hepta-), perflorooctane sulfonic acid (PFOA) and its salts, perfluorooctane sulfonyl fluoride (PFOS), and pentachlorobenzene.

The production, use, import and export, release and disposal; the use of best available techniques and best environmental practices for reduction and/or elimination of unintentionally produced POPs from combustion and chemical processes; and prevention the development of new POPs have to be fulfilled by Turkey and other parties until the year of 2025 as the obligations of Stockholm Convention (UNEP 2005).

2.2. Chemical Structure and Properties of OCPs and PCBs

Aldrin, dieldrin, chlordane, DDTs, endrin, HEPT, mirex, toxaphene, chlordecone, HCHs (*α*-, *β*-, and *γ*-), pentachlorobenzene, endosulfan are the OCPs listed under the Stockholm Convention on POPs and also could be referred as legacy pesticides. The molecular structures of these compounds consist of chlorine-substituted aliphatic or aromatic cyclic rings with five or more chlorine atoms. They have similar physicochemical characteristics such as persistence, toxicity, bioaccumulation, and long-range transport potential due to the chemical structure similarities (Kang et al. 2008). They also show similarity in physical state as being solid such as white crystalline solids (seen in HCB and mirex), colorless solids (seen in aldrin, DDTs and endrin etc.).

The OCPs are highly insoluble in water, have a strong affinity to suspended particles and organic materials. As suspended particles deposit, OCPs can settle down from water to sediment (Yang et al. 2005). They are hydrophobic and lipophilic compounds, therefore they have tendency to bioaccumulate in fatty tissues of living organisms and plants through the food chain. Due to their stability, they are exceptionally persistent in the environment (Yuan et al. 2013). The best studied OCPs are DDTs. They are synthesized with the reaction called as chloral which can occur with chlorobenzene in the presence of sulfuric acid, acting as a catalyst. The technical DDTs, used for insecticidal properties, were originated from two major isomers, *p,p′*-DDT (85%), *o,p′*-DDT (15%) which are white, crystalline, tasteless, and almost odorless solids (Kazantseva et al. 2013). Also, the technical DDTs may contain *o,o′*-DDT in trace amounts or DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(p-chlorophenyl) ethane) as contaminants (ATSDR 2002b). DDE and DDD can be found in the environment as metabolites of DDT due to break down in the structure. This is applicable to some of the other OCPs as well. The important physical and chemical properties of DDT and the other OCPs are tabulated in Table 2.1.

Table 2.1. Chemical and physical properties of some OCPs

Congener Name	**Molecular Formula**	**Molecular Mass (g/mole)**	**Solubility in Water (mg/L)[a]**	**Vapor Pressure (Pa)[a]**	**Henry's Law Constant ($m^3Pa/mole$)**
Aldrin	$C_{12}H_8Cl_6$	364.91	0.180	8.67×10^{-3}	17.23
Dieldrin	$C_{12}H_8Cl_6O$	380.90	0.195	7.20×10^{-4}	1.53
Chlordane	$C_{10}H_6Cl_8$	409.80	0.056	1.33×10^{-3}	4.92
DDT	$C_{14}H_9Cl_5$	354.50	0.025	2.53×10^{-5}	0.82
Endrin	$C_{12}H_8Cl_6O$	380.90	0.250	5.00×10^{-4}	0.76
Endosulfan	$C_9H_6Cl_6O_3S$	406.93	0.33	1.33×10^{-3}	4.65×10^{-4}
HEPT	$C_{10}H_5Cl_7$	373.40	0.180	5.33×10^{-2}	110
α-HCH	$C_6H_6Cl_6$	290.83	69.5	6.00×10^{-3}	0.71
β-HCH	$C_6H_6Cl_6$	290.83	0.2	4.79×10^{-5}	0.07
γ-HCH	$C_6H_6Cl_6$	290.83	7.3	5.59×10^{-3}	0.35
Mirex	$C_{10}Cl_{12}$	545.50	0.085	4.00×10^{-5}	839

[a] estimated at range of temperature between 20°C and 25°C

The other class of POPs, PCBs consist of 209 congeners that were produced by the chlorination of biphenyl in the presence of a suitable catalyst. The general chemical formula for PCBs is $C_{12}H_{10-n}Cl_n$ and the term "n" indicates the number of chlorine atoms within the range of 1-10 (Di Lella et al. 2006). The degree of chlorination changes in the range of 21% to 68% (w/w) in PCBs mixtures. During their production, they are synthesized as a mixture of congeners and were marketed under several trade names such as Aroclor, Clophen, Kanechlor, Fenclor, Apirolio, Ascarele, Delor, Pyralene, Pyronol, etc., depending on their percentage of chlorine content (Hay 1990). The most common ones, Aroclor and Kanechlor were mainly used in America and Japan, (Kim et al. 2004). The 209 PCB congeners were aligned in ascending numerical order by International Union of Pure and Applied Chemistry (IUPAC), as shown in Table 2.2 (WHO 2000).

Table 2.2. IUPAC numbers and chlorine atom positions of all PCB congeners

No.	**Structure**	**No.**	**Structure**	**No.**	**Structure**	**No.**	**Structure**
Mono-CBs		55	2,3,3',4	112	2,3,3',5,6	169*	3,3',4,4',5,5'
1	2	56	2,3,3',4'	113	2,3,3',5',6	***Hepta-CBs***	
2	3	57	2,3,3',5	114[b]	2,3,4,4',5	170[c]	2,2',3,3',4,4',5
3	4	58	2,3,3',5'	115	2,3,4,4',6	171	2,2',3,3',4,4',6
Di-CBs		59	2,3,3',6	116	2,3,4,5,6	172	2,2',3,3',4,5,5'
4	2,2'	60	2,3,4,4'	117	2,3,4',5,6	173	2,2',3,3',4,5,6
5	2,3	61	2,3,4,5	118[b]	2,3',4,4',5	174	2,2',3,3',4,5,6'
6	2,3'	62	2,3,4,6	119	2,3',4,4',6	175	2,2',3,3',4,5',6
7	2,4	63	2,3,4',5	120	2,3',4,5,5'	176	2,2',3,3',4,6,6'
8	2,4'	64	2,3,4',6	121	2,3',4,5',6	177	2,2',3,3',4',5,6
9	2,5	65	2,3,5,6	122	2',3,3',4,5	178	2,2',3,3',5,5',6
10	2,6	66	2,3',4,4'	123[b]	2',3,4,4',5	179	2,2',3,3',5,6,6'
11	3,3'	67	2,3',4,5	124	2',3,4,5,5'	180[c]	2,2',3,4,4',5,5'
12	3,4	68	2,3',4,5'	125	2',3,4,5,6'	181	2,2',3,4,4',5,6
13	3,4'	69	2,3',4,6	126[a]	3,3',4,4',5	182	2,2',3,4,4',5,6'
14	3,5	70	2,3',4',5	127	3,3',4,5,5'	183	2,2',3,4,4',5',6
15	4,4'	71	2,3',4',6	***Hexa-CBs***		184	2,2',3,4,4',6,6'
Tri-CBs		72	2,3',5,5'	128	2,2',3,3',4,4'	185	2,2',3,4,5,5',6
16	2,2',3	73	2,3',5',6	129	2,2',3,3',4,5	186	2,2',3,4,5,6,6'
17	2,2',4	74	2,4,4',5	130	2,2',3,3',4,5'	187	2,2',3,4',5,5',6
18	2,2',5	75	2,4,4',6	131	2,2',3,3',4,6	188	2,2',3,4',5,6,6'
19	2,2',6	76	2',3,4,5	132	2,2',3,3',4,6'	189[b]	2,3,3',4,4',5,5'
20	2,3,3'	77[a]	3,3',4,4'	133	2,2',3,3',5,5'	190	2,3,3',4,4',5,6
21	2,3,4	78	3,3',4,5	134	2,2',3,3',5,6	191	2,3,3',4,4',5',6
22	2,3,4'	79	3,3',4,5'	135	2,2',3,3',5,6'	192	2,3,3',4,5,5',6
23	2,3,5	80	3,3',5,5'	136	2,2',3,3',6,6'	193	2,3,3',4',5,5',6
24	2,3,6	81	3,4,4',5	137	2,2',3,4,4',5	***Octa-CBs***	
25	2,3',4	***Penta-CBs***		138	2,2',3,4,4',5'	194	2,2',3,3',4,4',5,5'
26	2,3',5	82	2,2',3,3',4	139	2,2',3,4,4',6	195	2,2',3,3',4,4',5,6
27	2,3',6	83	2,2',3,3',5	140	2,2',3,4,4',6'	196	2,2',3,3',4,4',5,6'
28	2,4,4'	84	2,2',3,3',6	141	2,2',3,4,5,5'	197	2,2',3,3',4,4',6,6'
29	2,4,5	85	2,2',3,4,4'	142	2,2',3,4,5,6	198	2,2',3,3',4,5,5',6
30	2,4,6	86	2,2',3,4,5	143	2,2',3,4,5,6'	199	2,2',3,3',4,5,6,6'
31	2,4',5	87	2,2',3,4,5'	144	2,2',3,4,5',6	200	2,2',3,3',4,5',6,6'
32	2,4',6	88	2,2',3,4,6	145	2,2',3,4,6,6'	201	2,2',3,3',4',5,5',6
33	2',3,4	89	2,2',3,4,6'	146	2,2',3,4',5,5'	202	2,2',3,3',5,5',6,6'
34	2',3,5	90	2,2',3,4',5	147	2,2',3,4',5,6	203	2,2',3,4,4',5,5',6
35	3,3',4	91	2,2',3,4',6	148	2,2',3,4',5,6'	204	2,2',3,4,4',5,6,6'
36	3,3',5	92	2,2',3,5,5'	149	2,2',3,4',5',6	205	2,3,3',4,4',5,5',6
37	3,4,4'	93	2,2',3,5,6	150	2,2',3,4',6,6'	***Nona-CBs***	
38	3,4,5	94	2,2',3,5,6'	151	2,2',3,5,5',6	206	2,2',3,3',4,4',5,5',6
39	3,4',5	95	2,2',3,5',6	152	2,2',3,5,6,6'	207	2,2',3,3',4,4',5,6,6'
Tetra-CBs		96	2,2',3,6,6'	153	2,2',4,4',5,5'	208	2,2',3,3',4,5,5',6,6'
40	2,2',3,3'	97	2,2',3',4,5	154	2,2',4,4',5,6'	***Deca-CBs***	
41	2,2',3,4	98	2,2',3',4,6	155	2,2',4,4',6,6'	209	2,2',3,3',4,4',5,5',6,6'
42	2,2',3,4'	99	2,2',4,4',5	156[b]	2,3,3',4,4',5		
43	2,2',3,5	100	2,2',4,4',6	157[b]	2,3,3',4,4',5'		
44	2,2',3,5'	101	2,2',4,5,5'	158	2,3,3',4,4',6		
45	2,2',3,6	102	2,2',4,5,6'	159	2,3,3',4,5,5'		
46	2,2',3,6'	103	2,2',4,5',6	160	2,3,3',4,5,6		
47	2,2',4,4'	104	2,2',4,6,6'	161	2,3,3',4,5',6		
48	2,2',4,5	105[b]	2,3,3',4,4'	162	2,3,3',4',5,5'		
49	2,2',4,5'	106	2,3,3',4,5	163	2,3,3',4',5,6		
50	2,2',4,6	107	2,3,3',4',5	164	2,3,3',4',5',6		
51	2,2',4,6'	108	2,3,3',4,5'	165	2,3,3',5,5',6		
52	2,2',5,5'	109	2,3,3',4,6	166	2,3,4,4',5,6		
53	2,2',5,6'	110	2,3,3',4',6	167[b]	2,3',4,4',5,5'		
54	2,2',6,6'	111	2,3,3',5,5'	168	2,3',4,4',5',6		

[a] non-*ortho* congener
[b] mono-*ortho* congener
[c] di-*ortho* congener

The chemical and physical properties of these compounds depend primarily on the number and position of chlorine atoms. PCBs with different number of chlorine atoms show variation in physical state from light to dark- yellow oily liquids to white crystalline-solids and hard non-crystalline resins (NTP 1980). Relative molecular mass of PCBs ranges between 188 g/mole for monochlorobiphenyl and 494 g/mole for completely chlorinated biphenyl (Table 2.3). PCBs are typically characterized as having low water solubility and high lipid solubility. However, these properties can also vary depending on chlorine content. Whilst fewer number of chlorine atoms cause to be more soluble in water, more volatile, and easier to metabolize; larger chlorine atoms increase the resistance to biodegradation, thus increase bioaccumulation in the environment (NTP 1980). Their persistency in air, water, and soil depends on water solubility and vapor pressure. PCBs with fewer numbers of chlorine atoms (PCB 18, 27, 28, 49, 52, 60, 66 etc) have high vapor pressure and high water solubility, and exist mainly as gases in the atmosphere. Whereas, PCBs with larger number of chlorine atoms (PCB 87, 118, 126, 170, 183, 187, 209 etc) have low vapor pressure and low water solubility. Thus, they can settle more easily to plants, soil etc., and evaporate less to the atmosphere due to having lower vapor pressure than PCBs with fewer numbers of chlorine atoms (Yeo et al. 2003). PCBs are very resistant to biological, photochemical or chemical degradation, and have a tendency to bioaccumulate in animals (McConnell et al. 1998, Fillmann et al. 2002). When released to the environment, they are absorbed strongly onto the organic matter. Due to their hydrophobicity and lipophilicity, they can accumulate on the fatty tissues and enter the food chain.

Table 2.3. Chemical and physical properties of some PCBs

Congener Name	**Chlorine Place in the Structure**	**Molecular Mass (g/mole)**	**Solubility in Water (mg/L)[a]**	**Vapor Pressure (Pa)[a]**	**Henry's Law Constant (m^3Pa/mole)**
PCB 3	4	188.65	3.226	0.469	36.31
PCB 15	4,4′	223.10	1.116	0.059	14.13
PCB 28	2,4,4′	257.54	0.260	0.024	33.11
PCB 61	2,3,4,5	291.99	0.106	$7.24x10^{-3}$	20.42
PCB 101	2,4,5,2′,5′	326.45	0.031	$2.40x10^{-3}$	31.62

(Cont. on next page)

Table 2.3. (Cont.)

Congener Name	Chlorine Place in the Structure	Molecular Mass (g/mole)	Solubility in Water (mg/L)[a]	Vapor Pressure (Pa)[a]	Henry's Law Constant (m^3Pa/mole)
PCB 138	2,3,4,2′,4′,5′	360.88	$7.51x10^{-3}$	$5.37x10^{-4}$	39.81
PCB 180	2,3,4,5,2′,4′,5′	395.32	$3.17x10^{-3}$	$1.32x10^{-4}$	5.88
PCB 194	2,3,4,5,2′,3′,4′,5′	429.77	$3.79x10^{-3}$	$2.04x10^{-5}$	6.76
PCB 206	2,2′,3,3′,4,4′,5,5′,6	464.26	$1.10x10^{-4}$	$1.20x10^{-5}$	82.20
PCB 209	2,2′,3,3′,4,4′,5,5′,6,6′	498.71	$1.00x10^{-6}$	$3.00x10^{-5}$	20.84

[a] estimated subcooled liquid at 25°C

2.3. Sources of OCP and PCB Emissions

The sources of POP emissions vary depending on the type of POP compounds. The sources may be results of intentional emissions of OCPs at their point of application, unintentional emissions from industrial products (PCBs) by volatilization, leakage or leaching throughout a product's service life or following eventual disposal, and they may be unintentionally formed by industrial or combustion processes emitted from stationary and mobile sources (Vallack et al. 1998).

The OCPs were extensively used for termite, pest, mosquito controls in residential and agricultural uses. During the Second World War, these compounds usually used to protect soldiers and civilians against malaria, typhus and other diseases spread by insects (UNEP 2005). Then, restrictions and bans on the use of many OCPs came into force in the 1970s and 1980s because of their toxic and carcinogenic human health effects on the environment, as well as high accumulation affinity of DDTs in fatty tissues (UNEP 2005). Although banned in many countries, OCPs (especially DDTs and HCHs) are still in-used in some developing countries for agricultural and sanitary purposes due to their low price and effectiveness in controlling insects (Wong et al. 2005, Zhou et al. 2013). Agricultural activities and use of pesticides are intensive especially in the United States and EU countries. Lower levels of pesticides use are observed in Turkey relative to developed countries. It is known that OCPs are deliberately released at their point of application (Vallack et al. 1998) and then, they disperse to different environmental media via volatilization, diffusion, and atmospheric transport (Ouyang et al. 2012, Zhou et al. 2013).

PCBs were widely used as electrical insulation, heat exchange fluid, plasticizers in paints, and ink solvent/carriers in carbonless copy paper, adhesives, sealants, flame retardants, and plastics due to their thermal stability, acid-, alkali-, and hydrolysis- resistance (Kim et al. 2004, Pomerantz et al. 1978). The commercial production of PCBs started in the 1930s and reached a maximum level in 1970s with an amount of 33000 tons. Then, the total production of PCBs was more than 1 million tons at the end of 1980s (IPCS 1992). PCBs were demanded in many industrial processes due to their technological properties. However, they have been restricted since 1996 due to their toxic effects on human body, bio-accumulation in the food chain, and their persistence which leads to long-range atmospheric transport (Manodori et al. 2006, UNEP 2005). Now, PCBs may still be produced as an industrial by-product of thermal processes such as waste incineration, uncontrolled waste incineration, metal smelting and refining processes, thermal power generation, cement kilns, the burning of wood and other biomass fuels used in transport vehicles with combustion or industrial processes such as paper manufacturing processes and chlorine bleaching of pulp and paper (Covaci et al. 2001, Acara 2006). In a study conducted in Turkey, it was stated that total number of transformers containing PCBs are about 250000 but only 50000 of them are examined and it was found that 4000 tons of PCBs are available at the summation of public and private sector but this amount may be higher (Acara 2006).

2.4. Transport and Fate of OCPs and PCBs in the Environment

Atmosphere is the main pathway for the transport of POPs from the point of releases in the atmosphere without deposition thanks to their semi-volatile characteristics. Cool temperature at high latitudes cause their deposition from the atmosphere onto soil and water rather than evaporation processes. POPs in Polar Regions become more persistent due to higher ability of adsorption onto atmospheric particulate matter and slower natural decomposition. On the other hand, evaporation from Earth’s surface is more dominant process at low latitudes such as tropical and temperature regions due to warm temperature (Wania and Mackay 1996). So, POPs tend to migrate from warmer to colder regions of the Earth by volatilization process.

The tendency is called as global distillation (grasshopper effect). POPs migration could occur with fractionation based on volatility, hopping migration, deposition, and then migration again with seasonal temperature changes at mid-latitudes. The migration of POPs is schematized in Figure 2.1.

Characteristics of POPs such as their vapor pressure, solubility, octanol-air partition coefficient (K_{OA}) are determinants of the migration process. When number of chlorine atoms increases, log K_{OA} increases, vapor pressure and solubility in water decreases for PCBs. The PCB congeners with 8-10 chlorines rapidly deposit, and retain close to point of source (low mobility). The congeners with 4-8 chlorines tend to deposit and accumulate in mid-latitudes (relatively low mobility), but PCBs with 1-4 chlorines are those that can be found even in Polar Regions (relatively high mobility). The congeners with one chlorine atom are the highest mobility compounds, they do not prefer to deposit. Briefly, lower volatile PCB congeners with larger number of chlorine atoms tend to partition water, soil etc., and their levels are higher in tropical areas. However, levels of higher volatile PCB congeners are higher in temperate and Polar Regions. They tend to remain airborne and migrate faster. The OCPs are also ranged from low mobility (mirex) to relatively low mobility (polychlorinated camphenes, DDTs, chlordanes), and then to relatively high mobility (HCB, HCHs, dieldrin).

Figure 2.1. POPs migration process
(Source: adapted from Wania and Mackay, 1996)

2.5. Health Effects of OCPs and PCBs

OCPs are biologically active or toxic to kill or repel insects, fungi, vegetation etc. So, they are also potentially hazardous to humans, animals, other organisms, and the environment. The World Health Organization states that 3 million people get pesticide poisoned each year, essentially in developing countries. Dermal contact is the primary route of exposure to pesticides, predominantly while spraying (Sanborn et al. 2004). Dermatological effects of pesticides are illustrated as irritant and allergic contact dermatitis, skin infections, injuries etc. Besides, pesticide exposure also occurs by the route of inhalation. Pesticides enter the human lungs, move into the bloodstream and reach other organs, thus cause damages. Asthma is a disease which is usually encountered in farmers due to inhalation of pesticides (National Research Council 1993). Most of pesticides are neurotoxic. Short-term effects are headache, dizziness, nausea, vomiting etc. Long term exposure can result in reduced IQ and learning disability, associated with permanent brain damage (Kamel and Hoppin 2004, Chaturvedi et al. 2013). A commonly used pesticide, chlorpyrifos causes birth defects in children. Hormone disruption (Figure 2.2) is another adverse effect on human beings. In general, a hormone receptor bind to a specific hormone, then produce a biological response. However, when pesticides come together with receptors and bind the hormones, response can be inhibited or produced at the wrong time. The cancer risk raises with long-term exposure to the pesticide over a certain level (Chaturvedi et al. 2013). International Agency for Research on Cancer (IARC) classified most of OCPs as possibly human carcinogens (Group 2B) based on animal studies, such as DDTs, chlordane, chlordecane, heptachlor, HCHs, and mirex.

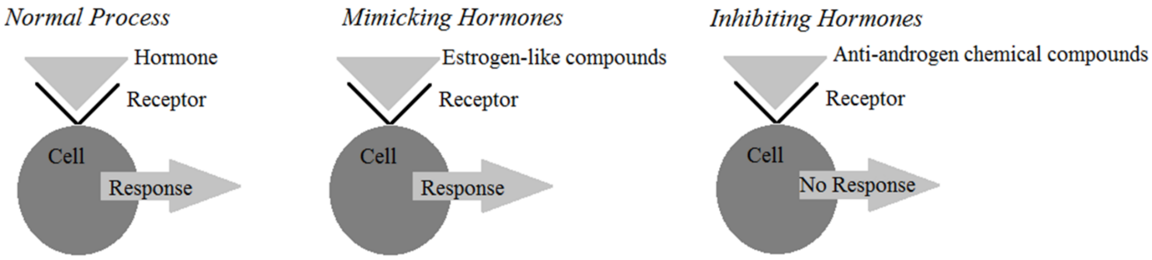

Figure 2.2. Hormone disruption mechanism
(Source: adapted from Colborn et al., 1997)

PCBs can enter the human body through the skin, eyes, lungs and mouth. Exposure to high levels of PCBs may result in irritation of the nose and lungs, skin irritations such as severe acne (chloracne) and rashes, and eye problems (Johnson et al. 1999). Hormone disruption also occurs due to PCB exposure. The hormone disruption mechanism is the same as pesticides. Immune system is affected by exposure to PCBs. The immune system elements like lymphocytes and T cells can be disturbed by PCBs binding to receptors that control immune system functions (Carpenter 1998). PCBs may also cause adverse developmental effects such as neurodevelopmental changes, reduced birth weight, poor short-term memory, and reduced IQ. PCBs have also been investigated for cancer risk factors due to their potential to act as direct and indirect carcinogens, their estrogenic and anti-estrogenic properties (Petrik et al. 2006). Melanomas, liver cancer, gall bladder cancer, biliary tract cancer, gastrointestinal tract cancer, and brain cancer are linked with PCBs (ATSDR 2000). IARC classified them into Group 2A (probably carcinogenic to human) based on various levels of carcinogens derived from animal and human studies. PCB toxicity depends on type and quantity of individual congeners. The number of chlorine atoms and the specific position of each chlorine on biphenyl rings are significant factors to determine degree of toxicity. It is generally stated that higher number of chlorine atoms causes to higher toxicity levels.

2.6. Ambient Concentrations of OCPs and PCBs around the World

Atmospheric POPs concentrations have been measured all around the globe. Concentrations of POPs vary widely on the basis of measurement locations and seasonal differences. An overview of concentrations of POPs in ambient air on a global scale is provided in this section by continents.

Remote areas such as Arctic and Antarctic can be directly affected by POP emissions from worldwide sources due to long range atmospheric transport. By this reason, Baek et al. (2011) made a 3-year air sampling investigation to estimate the trend in the levels of OCPs, PCBs in Polar Regions and the South Pacific. The air samples were collected from 3 sites in Ny-Alesund on the high Arctic island of Norway, 3 sites in King George Island, Antarctic and 3 sites in Chuuk Island, South Pacific during 3 sampling periods. Meteorological conditions at Ny-Alesund and King George Island showed similar behaviors at each station during every sampling period. The highest range of ΣOCPs level was detected as from 68.8 to 176 pg/m^3 during third sampling period in Ny-Alesund. In King George Island, average ΣOCPs concentration (provided from first and second sampling period results) was 20 pg/m^3. The results of air samples collected from the 3 sites at Chuuk Island showed that while two of these results were similar to King George Island results, other one was comparable with OCP concentrations in Ny-Alesund, ranging from 100 to 313 pg/m^3 as a result of local emissions. The highest average Σ_{206}PCBs concentration was measured as 308 pg/m^3 at a site of Chuuk Island where the OCP levels were higher than the other two sites. Higher average Σ_{206}PCBs concentrations were also found as 150 and 80.1 pg/m^3 at a site of Ny-Alesund during second and third sampling periods. In King George Island, the average concentration of PCB 11 (60.3 pg/m^3) was 71% of average Σ_{206}PCB concentration. Whilst the PCB 11 level at Chuuk Island (58.4 pg/m^3) was similar to that of King George Island, Ny-Alesund had concentration of PCB 11 (5.44 pg/m^3) not comparable to those in King George Island. It means that important sources of PCB 11 may be located in the tropics and Southern Hemisphere. Arctic region was predominantly influenced by pollutant emissions from Russia, Canada, and European countries. Thus, Arctic region had higher OCP and PCB levels than those of Antarctic region thanks to location of these regions.

Another study was conducted by Melymuk et al. (2012) in Canada. The air sampling of POPs were carried out for a year at 19 sites including high density commercial/residential land use, low density suburban residential areas, and rural/ agricultural land. ΣPCBs in bulk air was measured in the range of 72 to 3800 pg/m^3 by using high volume samplers. On the other hand, the concentrations of ΣPCBs ranged from 6 to 1300 pg/m^3 by applying passive sampling method. Urban levels of ΣPCBs were 39 times higher than those of rural sites, respectively. The seasonal variation showed that ΣPCBs was at the highest level in summer compared to the other seasons due to strong relationship between temperature and partial pressure of the gas phase PCBs. It was stated that the emissions originated from temperature related processes such as volatilization from local sources at warm temperatures, condensations and deposition of emissions at cold temperatures, and ventilation of indoor air with elevated concentrations had a significant impact on PCB level, higher than winter emissions from domestic heating.

A recent study in United States of America investigated atmospheric concentrations and potential sources of PCBs, PBDEs, and pesticides: Sofuoglu et al. (2013) collected air samples from McFarland Hill class I air station at Acadia National Park (ANP) near Bar Harbor, ME between 2007 and 2010. The mean and median concentrations of Σ_{30}PCBs were found as 169 and 153 pg/m^3. OCPs except for Endo-I (21 pg/m^3) were detected at concentrations ranging from 0.3 to 2.2 pg/m^3. While the higher level of PCBs was found in urban/industrial areas where they have or had been manufactured or utilized in large quantities as chemical flame retardants, the lower levels were at similar in rural/remote sites. The analysis about OCPs showed that the sources of OCP congeners included current and past agricultural areas, and termite control areas. Besides, measured concentrations in summer period were the highest, followed by spring, fall, and winter due to the relationship between temperature and vapor pressure.

Klanova et al. (2009) conducted a study about monitoring of POPs in Africa at 26 different sites including continental, rural and urban backgrounds, agricultural and industrial sites in 15 participating countries (Tunisia, Egypt, Sudan, Mali, Senegal, Nigeria, Togo, Ghana, Ethiopia, Kenya, Congo, DR Congo, Zambia, Mauritius, and South Africa). The highest median concentration of $\sum_7$PCBs was detected as 500 pg/m^3 in Dakar, Senegal. The level of PCBs was ranked as industrial sites (e.g. Kenya and Kinshasa), urban sites (e.g. Congo, Ghana, Tunisia), rural and background sites (e.g. Ethiopia, Mali, Mauritius), in a descending order. The concentrations of OCPs showed a significant variation between the different sampling sites. For instance in Kitengela, the highest concentrations of DDT and HCHs were measured as 3980 and 4520 ng/sample, where 100-200 m^3 air was collected by sampler deployed for 28 days, respectively. However, the concentrations of DDT and HCHs in Mali Tombouctou or South Africa Molopo Reserve have at least three orders of magnitude lower than the levels in Kitengela. It means that levels of these pesticides ranged between 10 and 100 pg/m^3 in the most of participating countries, though several numbers of these compounds were above 1 ng/m^3.

In Korea, the nationwide monitoring program was established in 2008 to observe POPs. Under this program, ambient air samples were collected from 7 industrial, 22 residential, and 8 rural sites in South Korea to estimate the levels of OCPs, dioxin-like PCBs, and PCDD/Fs (Park et al. 2011). The average atmospheric concentrations of aldrin, endrin, dieldrin, HCB, ΣDDTs, Σchlordane, and Σheptachlor were measured as 0.10, 0.03, 0.53, 148.2, 5.24, 5.76, and 1.28 pg/m^3, respectively. Regional averages of HCB concentration, with the highest levels among these OCPs, varied slightly with a ratio of highest/lowest concentration of approximately 4. The levels of dioxin-like PCBs were reported in the form of toxic equivalent concentration (TEQ), using toxic equivalency factors (TEFs) recommended by WHO. The average concentrations of dioxin-like PCBs were found as 0.008 pg WHO-TEQ/m^3. The results showed that PCB levels were slightly affected from seasonal differences. North-west area of South Korea was identified as having the highest levels of dioxin-like PCBs because of being close to Seoul, the biggest city of South Korea with high potential contributions and effects of anthropogenic sources. The comparison of dioxin-like PCB levels between 1998 and 2008 demonstrated the decline of dioxin-like PCBs in air in South Korea due to restrictions and applications for reducing emissions (Shin et al. 2011).

Supported by the Global Monitoring Plan under the Stockholm Convention on POPs, the ambient air monitoring network was established in 22 countries of Central and Eastern Europe (Armenia, Belarus, Bosnia and Herzegovina, Bulgaria, Estonia, Hungary, Croatia, Czech Republic, Kazakhstan, Kyrgyzstan, Latvia, Lithuania, Macedonia, Moldova, Montenegro, Poland, Romania, Russian Federation, Serbia, Slovakia, Slovenia, Ukraine). Pribylova et al. (2012) collected air samples at remote, rural, suburban, and urban sites between 2006 and 2008. The PCB levels measured at European Monitoring and Evaluation Program (EMEP) stations ranged from 10 to 293 pg/m^3. The highest PCB level was found at industrial complex of capacitor plants in Ust-Kamenogorsk, Kazakhstan, followed by an urbanized/industrialized site in Romania. The concentrations of HCH measured at EMEP stations varied between 42 and 503 pg/m^3, reaching the maximum level at the industrialized site in Romania. Like HCH level, the industrialized site in Romania had the highest DDT concentrations measured among EMEP stations, with a value of 554 pg/m^3. HCB had lower levels than the other pesticides, ranging between 1 and 557 pg/m^3, reaching the highest concentration in Russian Federation. The study showed that rural sites have higher concentrations of PCBs, HCHs, DDTs, HCBs relative to urban sites, and OCPs are still a critical problem around Central and Eastern Europe.

In Italy, air concentration distributions of PCBs, PBDEs, and OCPs were studied in the Tuscany Region at 9 urban, 7 rural and 3 agricultural sites (Estellano et al. 2012).

Σ_6PCBs level (the sum of PCB 28, 31, 52, 99,105, 118) varies between BDL and 300 pg/m^3. The Σ_6PCBs levels at the agricultural sites were BDL and the level at rural sites (18±19 pg/m^3) were lower than that at urban sites (80±120 pg/m^3). The Σ_6PCBs concentration peaked in Piombino (310 pg/m^3) and Prato (270 pg/m^3). The urban sites in the Tuscany Region had lower Σ_6PCBs concentration than other countries as a result of lower industrial activity and few emission sources. Five OCP congeners (α-HCH, β-HCH, HCB, Endo-I and *p,p′*-DDT) were analyzed in the study. The α-HCH level ranging from BDL to 610 pg/m^3 and β-HCH levels ranging from BDL to 1100 pg/m^3 were argued to be highly caused by possible continued and illegal use. HCH congeners had high levels at urban sites, and low levels in rural sites. The other OCP congeners, HCB, Endo-I, and *p,p′*-DDT varied between BDL and 170 pg/m^3, BDL and 2200 pg/m^3, and BDL and 730 pg/m^3 with various spatial distributions: rural > agricultural > urban for HCB, agricultural > urban > rural for Endo-I, and agricultural > rural > urban for *p,p′*-DDT.

Considering the above-mentioned studies as examples of the pertinent literature, it can be concluded that long range atmospheric transport may result in high OCP levels (maximum concentration of 313 pg/m^3) in remote areas where the compounds have never been used or produced (Baek et al. 2011). HCHs and DDTs were abundantly detected in different countries. The level of β-HCH reached maximum level of 1100 pg/m^3 in Italy, most probably due to continued and illegal use (Estellano et al. 2012). The highest concentration of DDTs was also measured in Italy as 730 pg/m^3, followed by the value of 554 pg/m^3 in Romania (Estellano et al. 2012, Pribylova et al. 2012). The detected DDTs and HCHs in USA and African countries were found at lower levels ranging between BDL to 100 pg/m^3 (Sofuoglu et al. 2013, Klanova et al. 2009). In Italy, the concentration of Endo-I was also high at 2200 pg/m^3. HCB had noticeable levels in Russian Federation and Korea with maximum concentrations of 557 and 344 pg/m^3, respectively (Pribylova et al. 2012, Park et al. 2011). In addition to OCPs, PCBs move long distances in the atmosphere, and deposit in remote areas, Arctic and Antarctic. The highest level of PCBs was found in Toronto, Canada as 3800 pg/m^3, followed by 308 pg/m^3 in Chuuk Island (Melymuk et al. 2012, Baek et al. 2011). The literature agree on spatial and seasonal variations. The spatial variation of the compounds revealed that the highest concentrations were generally found in urbanized/industrialized sites, followed by suburban, rural sites. The seasonal variation showed that the levels measured in warmer temperatures were higher, relative to cooler temperatures. The OCP and PCB concentrations measured by active sampling method in many countries from 2012 to 2014 are given in Table 2.4 and Table 2.5.

Table 2.4. Air concentrations of OCPs collected by active sampling method at different locations over the World from 2012 to 2014

Reference	**Sampling Period**	**Sampling Site**		**OCP**	**Mean concentration[a] (pg/m^3)**			
					Gosan	**Goisan**	**Taean**	
Jin et al. (2013)	June 2008-Dec 2009	Gosan, Goisan, Taean, Korea	Rural sites	α-HCH	113±116	166±189	69±55	
				β-HCH	2.13±1.90	1.50±2.15	2.09±1.44	
				γ-HCH	22.80±25	33.60±40	15.14±13	
				Dieldrin	0.70±0.60	0.62±0.76	0.45±0.47	
				Endrin	0.28±0.48	0.38±0.64	0.25±0.33	
				TC	0.60±0.60	0.38±0.34	0.54±0.63	
				CC	0.94±0.92	0.39±0.39	0.57±0.77	
				HEPT	0.21±0.30	0.14±0.14	0.12±0.10	
				t-HEPX	0.01±0.02	0.02±0.05	0.01±0.02	
				c-HEPX	0.70±0.60	0.54±0.64	0.38±0.29	
				o,p′-DDT	1.84±3.29	0.50±0.60	1.31±2.15	
				p,p′-DDT	1.52±1.65	0.48±0.52	1.22±1.98	
				o,p′-DDD	0.30±0.32	0.06±0.05	0.27±0.29	
				p,p′-DDD	0.28±0.24	0.05±0.07	0.16±0.15	
				o,p′-DDE	0.82±1.97	0.24±0.23	0.34±0.26	
				p,p′-DDE	3.36±5.12	0.81±0.73	1.84±0.79	
					Summer	**Spring**	**Autumn**	**Winter**
Sofuoglu et al. (2013)	June 2007 -Aug 2010 (n=110)	Acadia National Park, Maine/ USA	Rural site	Endo-I	-	9	4	2
				Endo-II	-	1.80	1.30	0.75
				CC	3.5	0.20	0.95	0.60
				TC	2.80	1.20	0.70	0.20
				Dieldrin	5	2.30	0.98	0.07
				Endrin	1	0.85	0.40	0.30
				p,p′-DDE	2.30	1.15	0.75	0.30
				p,p′-DDT	1	1.95	0.10	0.50

[a] gas+particle concentration

Table 2.5. Air concentrations of ΣPCBs collected by active sampling method at different locations over the World from 2012 to 2014

Reference	**Sampling Period**	**Sampling Site**		**Mean concentration (pg/m^3)**
Arruti et al. (2012)	2008-2009	Cantabria Region/ Spain	Urban site	PP[a] Σ_{11}PCBs = 0.79
			Rural site	PP Σ_{11}PCBs = 2.72
Castro-Jiménez et al. (2012)	Apr 2005-2006 (n=108)	JRC Ispra/ Italy	Suburban site	GP[b] Σ_{12}PCBs = 6.11 PP Σ_{12}PCBs = 1.30

(Cont. on next page)

Table 2.5. (Cont.)

Reference	Sampling Period	Sampling Site	Mean concentration (pg/m^3)	
Melymuk et al. (2012)	Oct 2007-2008 (n=106) (passive+active sampling)	Toronto/ Canada	Urban site	spring, GP Σ_{86}PCBs = 188 summer, GP Σ_{86}PCBs = 160 autumn, GP Σ_{86}PCBs = 226 winter, GP Σ_{86}PCBs = 112
			Suburban site	spring, GP Σ_{86}PCBs = 231 summer, GP Σ_{86}PCBs = 189 autumn, GP Σ_{86}PCBs = 76 winter, GP Σ_{86}PCBs = 111
			Rural site	spring, GP Σ_{86}PCBs = 43 summer, GP Σ_{86}PCBs = 28 autumn, GP Σ_{86}PCBs = 49 winter, GP Σ_{86}PCBs = 106
Bogdal et al. (2013)	Aug 2010, Jan-Feb 2011 (n=31)	Zurich/ Switzerland	Urban site	2010 summer, GP Σ_{18}PCBs = 205 2011 winter, GP Σ_{18}PCBs = 45
Colombo et al. (2013)	(n=56)	Brecia/ Italy	Industrial site	TP[c] Σ_{18}PCBs = 1073
Sofuoglu et al. (2013)	June 2007- Aug 2010 (n=110)	Acadia National Park, Maine/ USA	Rural site	spring, TP Σ_{30}PCBs = 147[d] summer, TP Σ_{30}PCBs = 245[d] autumn, TP Σ_{30}PCBs = 91[d] winter, TP Σ_{30}PCBs = 59[d]
Xu, Zhu, et al. (2013)	Nov 2009- Oct 2010 (passive+active sampling)	Dalian/ China	Dalian Jiaotong University (DJU)	spring, TP Σ_{18}PCBs = 27 summer, TP Σ_{18}PCBs = 53 autumn, TP Σ_{18}PCBs = 35 winter, TP Σ_{18}PCBs = 51
			Dalian Observatory (DMO)	spring, TP Σ_{18}PCBs = 82 summer, TP Σ_{18}PCBs = 61 autumn, TP Σ_{18}PCBs = 30 winter, TP Σ_{18}PCBs = 53
Chen et al. (2014)	July 2007- June 2008 (n=60)	Qingyuan/ China	E-waste site	TP Σ_{171}PCBs = 25612
			Rural site	TP Σ_{171}PCBs = 2210

[a] GP: gas phase
[b] PP: particle phase
[c] TP: total (gas+particle) phase
[d] median concentration

2.7. Ambient Concentrations of OCPs and PCBs in Turkey

A number of studies regarding the atmospheric OCPs and PCBs levels in Turkey could be found in the literature. Ambient air concentrations of OCPs and PCBs have been measured in several locations such as Bolu, Bursa, Izmir, Konya (Kaya et al. 2012, Odabasi and Cetin 2012, Yenisoy-Karakas et al. 2012, Cindoruk and Tasdemir 2014).

Seasonal variation in OCP levels was considered in a limited number of studies. Bozlaker et al. (2009) analyzed atmospheric samples which were collected between August, 2004 and March-April, 2005 at an industrial site, Aliaga, Izmir. The measured average seasonal concentrations ranged from 0.2 (*cis*-nonachlor) to 2152 pg/m^3 (Endo-I) in summer, and from BDL (*δ*-HCH, *cis*-nonachlor) to 121 pg/m^3 (chlorpyrifos) in winter. The summer/winter ratio of overall OCP levels was found as ~12. Odabasi et al. (2008) studied atmospheric OCP concentrations in Guzelyali, Izmir. Average total OCP concentrations in summer and winter were found as 6628±2012 and 1524±527 pg/m^3, respectively. Hence, summer/winter ratio was about 4. The most abundant OCP compound was chlorpyrifos, with an average concentration of 122 and 65 pg/m^3 in summer and winter, respectively. Higher levels were also detected for HCHs and endosulfan in both of these seasons. Spatial variation in ΣOCPs levels revealed that the highest ΣOCPs concentrations were generally found in urbanized/industrialized sites, followed by suburban, and rural sites. Cindoruk (2011) conducted a study for estimate OCP levels in a metropolitan city, Bursa. The OCP levels were ranked as 1031±454 pg/m^3 in urban/traffic site, 723±352 pg/m^3 at the urban/residential site, 551±278 pg/m^3 at the coastal site, and 520±278 pg/m^3 at the semi-rural site. *β*-HCH was the most dominant compound with the maximum concentration of 707 pg/m^3. Besides, the OCP concentrations measured by active sampling method in Turkey from 2012 to 2014 are also tabulated in Table 2.6.

Table 2.6. Air concentrations of OCPs collected by active sampling method in Turkey from 2012 to 2014

Reference	**Sampling Site/ Period**	**OCP**	**Mean concentration (pg/m^3)**			
			Gas Phase		**Particle Phase**	
			Winter	**Summer**	**Winter**	**Summer**
Odabasi and Cetin (2012)	• Izmir (industrial site) • Mar-Dec 2005 (n=6) • June 2005 (n=7)	*α*-HCH	17.10±10.7	71.90±9.80	0.16±0.04	0.61±0.52
		γ-HCH	5.40 ± 4.50	29.80±14.6	0.28±0.07	0.65±0.40
		HEPX	1.50 ± 1.90	4.50±3.80	0.51±0.38	0.26±0.13
		TC	0.62±0.52	0.73±0.30	0.05±0.02	0.14±0.05
		Endo-I	14.20±8.70	168±118	1.10±0.70	2.10±1.20
		Endo-II	2.30±3.10	24.80±16.9	1.90±1.30	3.40±1.30
		CC	0.46±0.25	0.79±0.15	0.07±0.05	0.14±0.03
		p,p′-DDD	0.90±0.37	0.95±0.42	1.2±0.6	0.44±0.21
		EndoSO_4	0.28±0.27	3.10±2.70	0.71±0.18	2.40±0.80
		p,p′-DDT	3.40±2.0	3.90±1.60	1.90±0.8	1.20±0.50

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Table 2.6. (Cont.)

Reference	**Sampling Site/ Period**	**OCP**	**Mean concentration (pg/m^3)**			
			Gas Phase		**Particle Phase**	
			Winter	**Summer**	**Winter**	**Summer**
Yenisoy-Karakas et al. (2012)	• Bolu (suburban site) • June-Aug 2007 (n=120) • Dec-Feb 2008 (n=120)	HEPX	0.02	-	0.01	-
		Endo-I	0.01	0.055	0.02	0.03
		p,p′-DDE	0.005	0.005	0.003	0.003
		Endrin	0.065	0.045	0.14	0.045
		p,p′-DDD	0.01	0.01	0.005	0.02
Esen (2013)	• Bursa (urban site) • June 2008-2009 (n=13)	α-HCH	31			
		β-HCH	184			
		γ-HCH	46			
		HEPT	114			
		Aldrin	16			
		Endo-I	112			
		Endo-II	76			

Odabasi et al. (2008) studied atmospheric PCB concentrations in Guzelyali, Izmir. The average concentration of Σ_{29}PCBs was measured as 2119 and 1716 pg/m^3 in summer and winter, respectively. In the study, it was stated that 3- and 4-CBs had higher gas-phase concentrations than other CBs due to higher vapor pressures. Bozlaker et al. (2008) also analyzed the ambient air samples collected from an industrial site, Aliaga, Izmir between 2004 and 2005. The Σ_{41}PCBs level was higher in summer (3370 pg/m^3) than in winter (1164 pg/m^3). PCBs with lower number of chlorine atoms were more dominant, similar to the study conducted by Odabasi et al. (2008). Air samples were also collected between 2009 and 2010 from Aliaga, Izmir by Kaya et al. (2012). A great increase of the Σ_{41}PCBs levels was detected in both summer and winter, with the maximum levels of 231 and 22 ng/m^3. Tasdemir et al. (2012) explored the effects of location and seasonal differences in Bursa. The average concentrations of Σ_{83}PCBs in Yavuz Selim (urban site) were found as 335 pg/m^3 in summer and 308 pg/m^3 in winter, whilst these statistics at Uludag University (25 km away from the city center) were 344 and 235 pg/m^3, respectively. There was no significant difference between the sampling sites. Yolsal et al. (2014) collected air samples from BUTAL (dense traffic) and Mudanya (coastal site). The mean concentrations measured in summer and winter were 430 and 335 pg/m^3 in BUTAL, 780 and 150 pg/m^3 in Mudanya. PCBs in Mudanya was approximately 2 times higher than the BUTAL region in summer. Possible explanation could be the PCBs evaporating from the polluted Marmara Sea and being carried from the industrial areas around Mudanya. The ΣPCBs levels measured by active sampling method in Turkey from 2012 to 2014 are also tabulated in Table 2.7.

The studies generally show that chlorpyrifos, endosulfans, HCHs and PCBs with lower number of chlorine atoms were found abundantly in ambient air of Turkey. Spatial and seasonal variations in OCPs and PCBs were similar to the other studies conducted in different countries. Their levels could be ranked as urbanized/ industrialized, suburban, and rural sites, in descending order. The concentrations of these compounds in non-heating period were also detected at higher levels, relative to heating period.

Table 2.7. Air concentration of ΣPCBs collected by active sampling method in Turkey from 2012 to 2014

Reference	**Sampling Period**	**Sampling Site**		**Mean concentration (pg/m^3)**
Birgul and Tasdemir (2012)	June 2008-2009 (n=34)	Bursa	Urban site	GP[a] Σ_{83}PCBs = 320±110 PP[b] Σ_{83}PCBs = 40±30
Tasdemir et al. (2012)	July 2008- June 2009 (n=60)	Bursa	Uludag University	spring, TP[c] Σ_{83}PCBs = 200 summer, TP Σ_{83}PCBs = 344 autumn, TP Σ_{83}PCBs = 307 winter, TP Σ_{83}PCBs = 235
			Urban site: Yavuzselim	spring, TP Σ_{83}PCBs = 337 summer, TP Σ_{83}PCBs = 335 autumn, TP Σ_{83}PCBs = 278 winter, TP Σ_{83}PCBs = 308
Yenisoy-Karakas et al. (2012)	June-Aug 2007 (n=120) Dec 2007-Feb 2008 (n=120)	Bolu	Suburban site	summer, GP Σ_{14}PCBs = 91 summer, PP Σ_{14}PCBs = 33 winter, GP Σ_{14}PCBs = 179 winter, PP Σ_{14}PCBs = 93
Kuzu et al. (2014)	May-Oct 2012 (n=20)	Istanbul	Urban site	GP Σ_{92}PCBs = 372±134 PP Σ_{92}PCBs = 49±17
Yolsal et al. (2014)	July 2008-June 2009 (n=50)	Bursa	Urban site	spring, Σ_{82}PCBs = 250±135 summer, Σ_{82}PCBs = 430±210 autumn, Σ_{82}PCBs = 480±270 winter, Σ_{82}PCBs = 335±195
			Coastal site	spring, Σ_{82}PCBs = 355±160 summer, Σ_{82}PCBs = 780±200 autumn, Σ_{82}PCBs = 445±290 winter, Σ_{82}PCBs = 150±75

[a] GP: gas phase
[b] PP: particle phase
[c] TP: total (gas+particle) phase

2.8. Back Trajectory Analysis and Potential Source Contribution Function of OCPs and PCBs in Turkey

The long-range transport of pollutants from a location to another one is especially related to atmospheric conditions which affect both of the vertical and lateral transports. The relation between atmospheric transport and meteorology complicates matter further. Some trajectory modelling techniques were developed to identify air transport. One of the trajectory modelling techniques, back trajectory modelling, is used to provide an air parcel's path back in time and specify where the air parcel was before it reaches a site where it is analyzed (McNeal and Carroll 2008). Potential source contribution function (PSCF) is improved version of back trajectory modelling. A specific air mass with a known pollutant concentrations passes through a specific geographical cell and then reaches to a receptor site. PSCF is a probability function that follows this behavior to identify possible source locations by using back trajectories. A limited number of studies regarding the back trajectory analysis and PSCF of OCPs and PCBs in Turkey could be found in the literature. Two of them were conducted at an industrial and a suburban site, Bursa, other one was conducted at an urban site, Istanbul (Cindoruk et al. 2007, Cindoruk and Tasdemir 2008, Kuzu et al. 2014).

Cindoruk et al. (2007) investigated PCB levels in gas and particle samples collected from an industrial site in Bursa between July 2004 and May 2005. It was stated that flue gas of waste incinerators and volatilization of PCBs from their stored or spilled sites are possible sources for emissions of lower molecular weight PCBs. There was a landfill located to the ENE-NE of the sampling site and a waste incineration plant located to the WSW of the sampling site. To investigate their effects, back trajectory analysis was conducted for the sampling dates at which the highest PCB levels were measured. The starting heights were chosen as 10 and 500 m-AGL, and back-trajectory was calculated for 24 hr. It was shown that there was an air motion from westerly directions (SW-NW), causing an increase in PCB concentrations at the sampling site. Cindoruk and Tasdemir (2008) also conducted a similar study in a suburban site, Bursa in the same sampling period. Back trajectory analysis showed that N-NE, E-NE directions are more dominant compared to E-SE wind directions. The dominant wind directions brought polluted air from industries, city landfill area, and leachate treatment plant. These sources were assumed as the major sources of PCBs in the sampling site, addition to evaporation process.

Kuzu et al. (2014) investigated the effects of meteorological conditions on PCB concentrations in samples collected from the metropolitan city of Istanbul in summer and autumn, 2012. Back trajectories were calculated for 12 hr. The short time period was explained with the aim of the study focusing on short range sources. Then, PSCF analysis was conducted and showed that northerly and southerly winds affected the PCB levels at the sampling site. The northerly winds caused an increase on di-CB concentrations due to medical waste incineration plant, and southerly winds brought contaminants occurred by volatilization from Marmara sea and industrial discharges along coastline.

2.9. Exposure and Health Risk Levels Due to OCPs and PCBs

The estimations of PCBs and OCPs exposure and health risk have been reported in a limited number of studies all around the World (Ding et al. 2013, Vilavert et al. 2014, Wang et al. 2013, Xu, Tian, et al. 2013, Tue et al. 2013, Zhang et al. 2013).

Concentrations of OCPs and PCBs in air were studied by Zhang et al. (2013) in the Yangtze River Delta (YRD) that is an industrialized and urbanized area in eastern China. Air sampling of the pollutants were carried out for a year at 31 sites. The mean annual Σ_6PCBs, HCB, ΣDDTs, ΣHCHs, Σchlordane, and mirex levels were measured as 35, 151, 168, 18.8, 110, and 17.9 pg/m^3, respectively. Lifetime cancer risks due to OCPs and PCBs exposure were calculated as 0.77×10^{-6}, 0.83×10^{-6}, and 0.54×10^{-6} for urban, urban-rural transition, and rural dwellers, respectively. All of the estimated inhalation risks were found below the acceptable risk level (10^{-6}), indicating not serious adverse health effects. The highest cancer risk was found for HCB (more than 53% of the total (OCPs + PCBs) cancer risk), followed by PCBs, DDTs, CDs, HCHs, and mirex, in descending order. The seasonal differences were also explored for OCPs, seen in the order of winter>autumn >spring>summer.

Vilavert et al. (2014) collected air samples from Tarragona (Catalonia, Spain) during 2010-2011 for the determination of PCBs levels. The highest concentrations of Σ_7PCBs were found in spring of 2011, with a mean value of 27.7 pg/m^3. It was noted a significant seasonal difference between spring and autumn in the same year for PCB concentrations. The cancer risk was estimated for the routes of inhalation, dermal contact, and ingestion. Air inhalation was the main exposure route for Σ_7PCBs, with the maximum level of 7.59 pg/kg/day. Inhalation exposure levels were 1.83-4.20 times higher than that of the dermal route. The results indicated that none of the non-carcinogenic and carcinogenic risks for PCB congeners exceeded the respective threshold levels, 10^{-5} for carcinogenic risk that is legislatively established in Spain.

Wang et al. (2013) conducted a study to assess risk levels of OCP exposure via indoor and outdoor dust in Guangzhou and Hong Kong from August to October 2010 through 3 pathways: ingestion, dermal absorption, and inhalation. Considering the moderate exposure of OCP compounds, dermal contact contributed 82% of the overall exposure, whereas this percentage was 1.57% for inhalation route. The cancer risk estimates for DDT, HCH, HCB, CHL and heptachlor ranged between 1×10^{-6} - 1×10^{-4}, indicating not very potent health effects.

The limited number of studies reported acceptable levels for health risk due to PCBs and OCPs exposure. Despite the known adverse health effects of OCPs and PCBs, there is no available study about exposure and risk assessment of OCPs and PCBs in ambient air of Turkey.

CHAPTER 3

MATERIALS AND METHODS

This chapter presents the sampling techniques and experimental procedures, quality assurance and control measures, back trajectory and PSCF computational methods, and exposure and health risk assessments.

3.1. Sampling Sites

A part of samples were collected from a background site at the Izmir Institute of Technology (IZTECH, 38°19'4.31"N, 26°38'17.71"E), located in Urla near Gulbahce village, 60 km away from Izmir city center. Izmir is the third most populated province in Turkey, with a population of 4,061,074 (TUIK 2013). The city’s climate is Mediterranean. The average temperature during sampling period was 24.07°C (TSMS 2014). The sampling site is surrounded with agricultural areas and it could be under the effect of huge industrial enterprizes in Aliaga which is located in 60 km north of the site.

Figure 3.1. Locations of sampling sites

Remaining part of samples were also collected from an urban site in Besiktas, Istanbul (41°2'46.31"N, 29°0'29.13"E). Istanbul is the largest metropolis in Turkey, with a population of 14,160,467 (TUIK 2013). The average temperature during sampling period was 19.53°C (TSMS 2014). Istanbul has a diverse industrial economy, producing commodities such as olive oil, tobacco, transport vehicles, and electronics.

Electricity and suitable places regarding in an aim of this study were required during the sample collection, and it was supplied in the selected sampling sites: one of them is located in a background site of Izmir and other is located in an urban site of Istanbul regarding in an aim of this study.

3.2. Sample Collection

Samples were collected on weekdays for a 24-hour period between May and October 2014 in both of the sampling sites. In Izmir, samples were collected twice a week while it was collected once in a week in Istanbul. Meteorological data was obtained from Turkish State Meteorological Service. Meteorological data of the sampling dates for Izmir and Istanbul are tabulated in Table 3.1 and Table 3.2.

Table 3.1. Sampling information for Izmir

Date	Sample Number	T (°C)	Relative Humidity (%)	Wind Speed (km/h)	Precipitation (mm)
01.05.2014	1	18.00	72	10	0
08.05.2014	2	18.00	60	24	0
12.05.2014	3	18.50	65	6	0
15.05.2014	4	19.50	51	19	0
20.05.2014	5	21.50	55	10	0
22.05.2014	6	22.00	48	21	0
28.05.2014	7	23.50	53	6	0
29.05.2014	8	23.00	53	11	0
05.06.2014	9	21.00	74	16	0
06.06.2014	10	19.50	70	16	0
09.06.2014	11	23.50	65	14	34.04
12.06.2014	12	26.00	38	27	0

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Table 3.1. (Cont.)

Date	Sample Number	T (°C)	Relative Humidity (%)	Wind Speed (km/h)	Precipitation (mm)
19.06.2014	13	25.50	46	19	0
25.06.2014	14	27.50	31	14	0
26.06.2014	15	28.00	39	8	0
01.07.2014	16	25.50	54	11	0
03.07.2014	17	27.00	39	29	0
04.07.2014	18	26.00	34	39	0
12.07.2014	19	25.50	57	11	0
31.07.2014	20	28.00	42	10	0
03.08.2014	21	27.00	64	16	0
07.08.2014	22	27.00	71	11	3.05
10.08.2014	23	29.50	44	31	0
11.08.2014	24	31.00	41	21	0
14.08.2014	25	29.50	47	11	0
19.08.2014	26	27.50	49	27	0
21.08.2014	27	27.00	48	11	0
28.08.2014	28	28.50	47	13	0
04.09.2014	29	26.00	65	27	1.02
11.09.2014	30	25.00	50	8	0
18.09.2014	31	22.00	55	24	0
25.09.2014	32	19.00	48	11	0
02.10.2014	33	22.50	46	21	0
09.10.2014	34	22.00	55	27	0
16.10.2014	35	22.00	61	8	0
23.10.2014	36	19.50	73	24	2.03
30.10.2014	37	14.50	80	19	0

Table 3.2. Sampling information for Istanbul

Date	Sample Number	T (°C)	Relative Humidity (%)	Wind Speed (km/h)	Precipitation (mm)
07.05.2014	1	14.50	67	19	0
16.05.2014	2	19.50	52	6	0
23.05.2014	3	20.50	74	13	0

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Table 3.2. (Cont.)

Date	Sample Number	T (°C)	Relative Humidity (%)	Wind Speed (m/s)	Precipitation (mm)
30.05.2014	4	21.50	70	19	13.97
06.06.2014	5	19.00	87	14	4.06
20.06.2014	6	21.50	65	13	0
26.06.2014	7	28.00	51	11	0
03.07.2014	8	24.00	61	16	0
11.07.2014	9	28.00	51	8	0
18.07.2014	10	25.00	60	8	0
24.07.2014	11	25.50	72	13	0
31.07.2014	12	24.00	58	14	0
07.08.2014	13	32.00	70	16	34.04
14.08.2014	14	28.50	66	14	0
21.08.2014	15	26.00	66	10	0
28.08.2014	16	23.00	66	16	0
04.09.2014	17	25.00	72	19	0
11.09.2014	18	24.00	61	13	0
18.09.2014	19	18.50	82	16	8.89
25.09.2014	20	17.00	57	10	0
01.10.2014	21	18.00	67	10	0
09.10.2014	22	19.00	70	21	0
16.10.2014	23	21.50	73	14	0
23.10.2014	24	19.00	57	16	0.51
30.10.2014	25	12.50	86	24	5.08

3.3. Sampling Method

Modified GPS-11 (Thermo-Andersen Inc.) and TE-HVPLUS-BL (Tisch Environmental Inc) high volume samplers were used for the collection of gaseous and particulate samples in Izmir and Istanbul, respectively. The compact unit of samplers (Figure 3.2) contains an electric motor driven, a high speed-high volume blower, a filter holder capable of supporting a filter, and a protective housing.

The samplers collected 200-240 m^3 of air per sample in both Izmir and Istanbul. Particle and gas phase samples were collected on quartz filters and polyurethane foam

(PUF), respectively. The diameter of quartz filter was 102 mm. The PUF was 5 cm thick sheet stock polyurethane type (density 0.222 g/cm^3), fully fitted in the PUF cartridge. Two PUFs were placed in series to eliminate breakthrough.

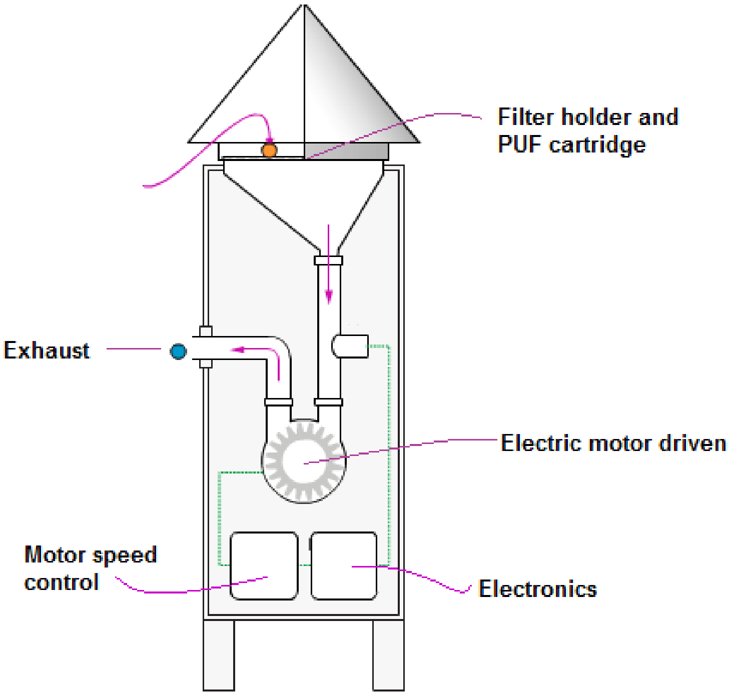


Figure 3.2. Schematic of high-vol sampler

3.4. Sample Preparation and Handling

Laboratory equipment used in the processes of sampling and analysis was cleaned on the basis of the method “Chapter Four: Organic Analytes” recommended by USEPA (USEPA 2007a). It was aimed to minimize error formed due to the lab equipment by purifying from contaminants, prior to each experiment. Equipment was rinsed with technical alcohol, then left in the mixture of hot water and Alconox detergent until the water got cooled. After brushing the equipment with the mixture, they were rinsed with tap water. Glassware was rinsed with chromic acid, tap water, and then distilled water. The openings of them were covered with aluminum foil and dried in an oven at 300°C. The others such as Teflon taps, lids etc. were directly rinsed with pure water, and allowed to dry in an oven.

The sampler parts, where the PUF glass cartridges are placed, were cleaned with acetone before use. The PUF glass cartridges were cleaned using the above procedure.

Then, the cartridges were kept in oven 450°C for 4 hours, cooled, and rinsed with hexane and then with acetone. The PUFs were kept in warm tap water for 4 hours, and in pure water for 2 hours, respectively. Then they were cleaned by Soxhlet extraction in 3 steps: Using acetone for 12 hours, acetone:hexane (1:1) for 12 hours, and then hexane for 12 hours. Then, PUFs were dried in a desiccator at 70°C for minimum of 4 hours. The cleaned PUFs were placed into the cleaned cartridges and kept in a Teflon lined jar in a freezer till use. Quartz filters were wrapped loosely with aluminum foil and baked in a muffle furnace at 450°C for 12 hours to remove any organic residues. Then, they were allowed to cool to room temperature in desiccator for 2 hours. Finally, their weights were recorded, wrapped in aluminum foil, placed in zipped bags, and stored at -20°C until sampling.

Cleaned and prepared PUFs, cartridges, and quartz filters were transported to the sampling fields from the labs in air-tight containers to prevent any exposure to air before sampling. After sampling, the PUF cartridges were wrapped with aluminum foil, placed into the glass jars, thus minimized the interaction with air. Quartz filters were also transferred to the labs in a box, kept in a desiccator for 2 hours. Then, their weights were recorded again, wrapped with aluminum foil. Finally, the cartridges and quartz filters were stored at -20°C until extraction.

3.5. Sample Extraction and Clean-up

Prior to extraction, all samples were spiked with a mixture of surrogate standards (given in Table 3.3, 10 ng each) to monitor the analytical recovery efficiencies. The samples were extracted by Soxhlet extraction with a mixture of hexane:acetone (1:1) for 18 hours.

Table 3.3. Surrogate standards

Surrogate Standard	
$^{13}C_{12}$-PCB 28	$^{13}C_{12}$-PCB 153
$^{13}C_{12}$-PCB 52	$^{13}C_{12}$-PCB 180
$^{13}C_{12}$-PCB 101	$^{13}C_{12}$-PCB 209
$^{13}C_{12}$-PCB 138	

All sample extracts were concentrated using a rotary evaporator (BUCHI-Rotavapor-R210). They were evaporated approximately to 3 mL. Water bath temperature of the evaporator was maintained at 36°C during sample concentration. The 3 mL sample was transferred to a 40 mL vial, and isooctane was added. The total volume was concentrated down to 0.5 mL by gently blowing a high purity stream of N_2 on the surface at a flow rate of 150-200 mL/min. In accordance with EPA Method 3610B, neutral alumina (Al_2O_3, particle size of 0.063–0.30 mm) was used to obtain fraction of OCPs and PCBs and also to get rid of any other organic contamination. Before the use, the alumina was dried at 400°C for minimum 12 hours, and then cooled in desiccator. The alumina was deactivated by adding deionized water with a mass percentage of 6%. Then it was stored in amber bottle until use. Sodium sulfate (Na_2SO_4) was also used in the clean-up and fractionation process. It was baked in a muffle furnace at 450°C, then cooled in a desiccator. The fractionation column (10 mm inner diameter × 200 mm height) was prepared by placing 3 gr deactivated alumina, and adding 1 cm Na_2SO_4, shown in Figure 3.3.

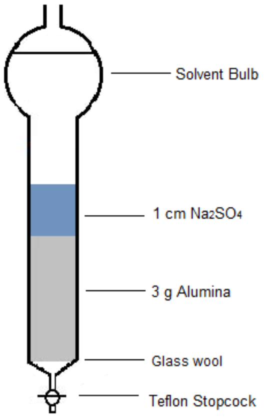


Figure 3.3. Clean-up and fractionation column

The column was prewashed with 10 mL elution solution of dichloromethane: hexane (1:4). The concentrated sample was added into the column with a total 1 mL rinse of the eluted solution at two steps and eluent was collected in a vial. After collecting the sample in the vial, 35 mL elution solution was added and collected in the same vial. Both of OCP and PCB compounds are collected in the same fraction. Solvent exchange into isooctane and volume reduction was applied by rotary evaporator and blowing under purity stream of N_2. Fifty ng of $^{13}C_{12}$PCB 105 (10 µL) was added as internal standard to the 1 mL samples as the last step before gas chromatography.

3.6. GC/MS Analysis

PCB and OCP analyses was carried out by using gas chromatography (GC)-mass spectrometry (MS) (Agilent 7890B GC and S977 MSD) with a detector of electron ionization (EI) and chemical ionization (CI)

Selective ion monitoring mode (SIM) was used for both PCB and OCP analyses, while ionization was electron ionization (EI) for PCBs and negative chemical ionization (NCI) was applied for OCPs analysis. Methane was used as reagent gas in NCI mode. In both of PCBs and OCPs analyses, after injection of 2 µL extracted in the splitless mode, samples went in the capillary column with helium (carrier gas). GC/MS operating conditions are given in Table 3.4.

Table 3.4. GC/MS operating conditions

Operating Condition	**PCB Analysis**	**OCP Analysis**
Column	DB-5, 30 m, 0.25 mm ID, 0.25 µm film thickness	DB-5, 15 m, 0.25 mm ID, 0.1 µm film thickness
Ionization mode	Electron ionization	Negative Chemical Ionization
Reagent gas	-	Methane
Carrier gas	Helium	Helium
Carrier gas flow rate	1.1 mL/min	1.1 mL/min
Injection mode	Splitless	Splitless
Injection temperature	200°C	200°C
Injection volume	2 µL	2 µL
Ion source (70eV) temperature	230°C	150°C
Quadrupole temperature	150°C	150°C
Auxiliary temperature	310°C	310°C
Temperature program	• Initial oven temperature: 90ºC for 1 min, • Raised to: 160ºC at 15ºC/min, 210ºC at 3ºC/min, 310ºC at 10ºC/min (waiting 10 min), respectively	• Initial oven temperature: 80ºC for 2 min, • Raised to: 285ºC at 10ºC/min, (waiting 5 min) 315ºC at 25ºC/min, (waiting 5 min), respectively

Concentrations of 22 OCP compounds and 43 PCB congeners were determined during GC/MS analysis (Table 3.5).

Table 3.5. Target analytes

OCPs	
aldrin	aldrin
α-HCH	α-hexachlorocyclohexane
β-HCH	β- hexachlorocyclohexane
γ-HCH	γ-hexachlorocyclohexane (Lindane)
δ-HCH	β-hexachlorocyclohexane
o,p′-DDT	ortho-para dichloro diphenyl trichloroethane
p,p′-DDT	para-para dichloro diphenyl trichloroethane
o,p′-DDD	ortho-para dichloro diphenyl dichloroethane
p,p′-DDD	para-para dichloro diphenyl dichloroethane
o,p′-DDE	ortho-para dichloro diphenyl dichloroethylene
p,p′-DDE	para-para dichloro diphenyl dichloroethylene
dieldrin	dieldrin
HEPT	heptachlor
HEPX	heptachlorepoksit
TC	trans (alfa) chlordane
CC	cis (gamma) chlordane
Endo-I	α-endosulfan
Endo-II	β-endosulfan
EndoSO$_4$	endosulfan sulfate
endrin	endrin
Mirex	mirex
HCB	hexachlorobenzene

PCBs	
PCB 18	PCB 123
PCB 22	PCB 132
PCB 28	PCB 138
PCB 31	PCB 141
PCB 41/64	PCB 149
PCB 44	PCB 151
PCB 49	PCB 153
PCB 52	PCB 156
PCB 54	PCB 157
PCB 56	PCB 158
PCB 60	PCB 167
PCB 70	PCB 170
PCB 74	PCB 174
PCB 87	PCB 180
PCB 90/101	PCB 183
PCB 95	PCB 187
PCB 99	PCB 188
PCB 104	PCB 189
PCB 105	PCB 194
PCB 110	PCB 199
PCB 114	PCB 203
PCB 118	

3.7. Quality Assurance / Quality Control

All kinds of equipment such as samples, chemical etc. used in various stages of analytical methods audited with strict quality control measures during the performance of experiments. The glass, metal, aluminum or Teflon materials were preferred as possible as at each stage of the experiments.

3.7.1. Laboratory Control Samples

PUF plugs were stored in clean aluminum foil + metal box + ziplock plastic bag in the freezer. Quartz filters were baked and weighed, then stored in aluminum foil + lock plastic bag in the freezer. For every group of 5 samples (when 6 units Soxhlet apparatus was used) or group of 10 samples (when 12 units Soxhlet apparatus was used), 1 control sample was also included as laboratory blank. The number of control samples are 8 and 10 for PUF plugs and filters, respectively. Average Σ_{43}PCBs concentrations of the control samples were calculated as 0.086 and 0.089 pg/μL in PUF and filter, respectively. The OCPs were usually not detected, except endrin (2.44 pg/μL), γ-HCH (0.69 pg/μL), and HCB (0.34 pg/μL) in PUF, α-HCH (3.23 pg/μL) and HCB (0.29 pg/μL) in filter. The concentrations of OCPs and PCBs in the laboratory control samples are given in the Appendix, Table A.1.

3.7.2. Calibration Standards

The calibration standard solution contained 43 PCBs and 22 OCPs. The third level calibration standard (usually 50-60 pg/μL) was selected as quality control standard in order to control calibration during GC/MS analysis. The quality control standard was analyzed for every 25 samples as a regular sample to check validity of calibration graph. The linear fit was found satisfactory (R^2>0.99) for all congeners/compounds (Table A.2 in the Appendix).

3.7.3. Procedural Recovery

Each sample was spiked with surrogate standards, 10 ng $^{13}C_{12}$PCBs, prior to extraction to determine the recovery efficiencies of the standards. The procedural recovery efficiency was calculated as,

$$Recovery\ Efficiency\ (\%) = 100 \times (C_f / C_i) \tag{3.1}$$

where C_f is the concentration of the spiked sample processed as a real sample and C_i is the initial concentration in the spike solution. The efficiencies are summarized in Table 3.6.

Table 3.6. Recovery efficiencies (%) of surrogate standards

Surrogate Standard	**Min**	**Max**	**Mean**	**SD[a]**
$^{13}C_{12}$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
$^{13}C_{12}$PCB138	57.6	137	90.3	14.6
$^{13}C_{12}$PCB153	60.2	134	85.8	14.1
$^{13}C_{12}$PCB180	59.4	140	87.2	16.0
$^{13}C_{12}$PCB209	58.8	139	79.4	15.4

[a] SD: Standard Deviation

A known quantity of a target analyte was injected to the mixture of acetone-hexane prior to extraction. After extraction and clean-up stages, the loss rate of target analyte was detected with GC/MS analysis. The average procedural recoveries of PCBs (n=6) and OCPs (n=6) ranged from 65% (PCB 153) to 100% (PCB 138) and from 64% (*p,p′*-DDD) to 103% (Endrin). The recovery efficiencies of target analytes are given in the Appendix, Table A.3.

3.7.4. Detection Limits

The instrumental detection limits (IDLs) were calculated for the concentrations detected by internal standard calibration method. The IDLs were calculated from the instrument response to the lowest standard and extrapolating downward to the corresponding amount of analyte that would generate a signal to noise ratio of 3:1. The method detection limit (MDL) was calculated as the mean of the field blank plus three standard deviations (mean+3σ). When compounds were not detected in blanks, 2/3 of the instrumental detection limits (IDLs) were used for calculating the MDL. The MDL was assumed to equal to IDL for the non-detected analyte in field blanks (Hassan and Shoeib 2015). The MDLs for PCBs and OCPs for both of PUFs and filters are given in Table 3.7.

Table 3.7. Method detection limits for target analytes

Analyte	**Gas (pg/m^3)**	**Particle (pg/m^3)**
PCB 18	1.52	5.27
PCB 22	2.95	1.53
PCB 28	1.90	1.42
PCB 31	3.27	1.40
PCB 41/64	1.79	7.72
PCB 44	5.60	8.29
PCB 49	1.86	1.43
PCB 52	1.12	3.15
PCB 54	2.14	5.27
PCB 56	1.64	3.45
PCB 60	1.59	5.21
PCB 70	2.89	2.35
PCB 74	3.02	2.58
PCB 87	2.10	4.72
PCB 90/101	1.88	1.59
PCB 95	4.51	1.23
PCB 99	2.88	1.91
PCB 104	1.48	1.38
PCB 105	1.59	1.95
PCB 110	1.68	1.09
PCB 114	1.22	1.80
PCB 118	2.44	1.06
PCB 123	1,82	1,55
PCB 132	2.47	3.54
PCB 138	1.95	3.02
PCB 141	2.34	1.36
PCB 149	2.46	0.64
PCB 151	1,98	1,46
PCB 153	1.10	3.50
PCB 156	1.41	2.52
PCB 157	3.35	1.85
PCB 158	1.96	8.68
PCB 167	1.57	2.15
PCB 170	1.55	2.25
PCB 174	3.80	2.77
PCB 180	1.64	2.13
PCB 183	1.27	1.32
PCB 187	2.53	1.47
PCB 188	2.71	1.14
PCB 189	1.81	4.62
PCB 194	2.83	6.85
PCB 199	4.37	4.37
PCB 203	4.16	6.85
HCB	5.46	4.02
α-HCH	4.44	8.67
β-HCH	4.44	4.44
γ-HCH	4.44	4.44
δ-HCH	4.44	4.44
HEPT	4.44	4.44
HEPX	4.44	4.44
Aldrin	4.44	4.44
Dieldrin	4.44	4.44
Endrin	4.44	4.44
Endo-I	4.44	6.18
Endo-II	4.44	4.44
EndoSO_4	4.44	4.44
CC	4.44	3.30
TC	4.44	4.44
o,p′-DDD	4.44	4.44
p,p′-DDD	7.61	6.68
o,p′-DDE	4.44	4.44
p,p′-DDE	4.44	4.44
o,p′-DDT	4.44	4.44
p,p′-DDT	4.44	4.44
Mirex	4.44	4.18

[a] SD: standard deviation

3.8. Back Trajectory Analysis

Hybrid-Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model is a commonly used trajectory model related atmospheric transport and dispersion. This model was developed by the National Oceanic and Atmospheric Administration’s (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess 2005).

3.8.1. Trajectory Computational Method

A trajectory is computed from the time (*t*) integration of the three-dimensional position vector (*P*) which obtains a velocity vector (*V*). Only the parameters, particle position and time, are considered in trajectory computation, due to the assumption of particles passively following the wind. Equation 2 can be solved numerically by the modified Euler method.

$$\frac{dP}{dt} = V\,(x,y,z,t) = V(P,t) \tag{3.2}$$

The first guess position is calculated by using Simple Euler Method,

$$P'(t+\Delta t) = P(t) + V(P,\ t)\Delta t \tag{3.3}$$

then the final position is calculated by using Modified Euler Method which is more accurate than Simple Euler Method,

$$P(t+\Delta t) = P(t) + 0.5\ [V(P,\ t)\Delta t + V(P',\ t+\Delta t)\Delta t] \tag{3.4}$$

The integration time steps (Δt) can vary during the simulation and can be determined by using stability ratio which refers to the grid cell fraction allowing the trajectory pass within one time step. Time steps can vary from 1 minute to 1 hour and are calculated as;

$$U_{max}\,(grid\text{-}units/min)\ \Delta t\ (min) < Stability\ ratio\ (grid\text{-}units) \tag{3.5}$$

where U_{max} is the maximum particle transport speed during previous hour. Higher order integration methods are not used to calculate final position because the wind vectors are linearly interpolated from grid to the integration point, thus they are not yield higher precision (Draxler and Hess 1998).

3.9. Potential Source Contribution Function

The possible source regions subdivided into grid cells. The numbers of trajectory endpoints placed in all grid cells were calculated, individually. Then, the number of endpoints which are higher than the specified threshold level were detected in each grid cell. The threshold levels are commonly accepted as arithmetic mean concentrations of each pollutant (Choi et al. 2008). PSCF is the ratio between the number of high concentration endpoints to total number of endpoints in a specified grid cell,

$$PSCF_{ij} = m_{ij} / n_{ij} \tag{3.6}$$

where n_{ij} is the total number of endpoints falling within the ij-th cell and m_{ij} is the number of high endpoints falling within the ij-th cell while the possible source region is subdivided into a gridded *i* by *j* array. The grid cells were selected as 1° latitude by 1° longitude. Chemical transformations are not considered in PSCF and it was assumed that all pollutants are conservative compounds (Sofuoglu et al. 2013).

Small number of endpoints placed in a grid cell (< three times the average number of end points for all cells) cause high uncertainties in PSCF calculations (Zeng and Hopke 1989). Small values are often shown at more distant sources from the sampling location and results thanks to sparse trajectory distributions. PSCF values are multiplied by an arbitrary weighting function (W_{ij}) to reduce the uncertainty in a grid cell. The function used was

$$W_{ij} = \left\{ \begin{array}{ll} 1.00 & n_{ij} > 2\times ave \\ 0.75 & ave < n_{ij} < 2\times ave \\ 0.50 & 0.5\times ave < n_{ij} < ave \\ 0.15 & 0 < n_{ij} < 0.5\times ave \end{array} \right\} \tag{3.7}$$

where *ave* is the average number of the end points in each cell.

3.10. Exposure Assessment

Chronic daily intake (*CDI*) was calculated (USEPA 1997) as an estimate of inhalation exposure for each compound (*i*):

$$\sum_{i}^{I} CDI = \frac{C_i \times IR \times ED \times EF}{BW \times AT} \tag{3.8}$$

where *C* is the contaminant concentration (pg/m^3), *IR* is inhalation rate (m^3/day), *ED* is exposure duration (yr), *EF* is exposure frequency (days/yr), *BW* is body weight (kg), *AT* is averaging time which was assumed as lifetime and calculated as *ED*×365 days/yr, *CDI* is inhalation chronic daily intake (pg/kg/day). Lifetime exposure was assumed for the assessment (*ED* = 70 years). Samples were collected 6 months, thus *EF* was taken as 180 days/yr. Distribution of *BW* (lognormal distribution; mean=65.56 kg, standard deviation=13.02 kg) was taken from Kavcar et al. (2006) who constructed it to represent the Izmir population. Distribution of *IR* (uniform distribution; minimum=0.21 m^3/h, maximum=0.74 m^3/h) was also taken from the literature (Gephart et al. 1994).

Exposure was estimated for individual OCPs, which were detected in gas phase with a sample number exceeding 50% of total number of sample. Missing data were randomly generated using the fitted distribution to the measured concentrations. Then, a probability distribution was re-fitted with whole data set to perform exposure and risk assessment. Besides, exposure was estimated for total PCBs (nondioxin-like PCBs+dioxin-like PCBs) which had a sample number exceeding 50% of total number of sample. The concentrations of the targeted dioxin-like PCBs (PCB 105, 114, 118, 123, 167, and 189) were converted to dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin) toxic equivalent by multiplying with a TEF value of 0.00003 (USEPA 2010).

3.11. Risk Assessment

Cancer risk associated with inhalation exposure is calculated for OCPs and PCBs using the following equations (USEPA 2005, 1996)

$$R = R\left(dioxin\text{-}like\right) + R\ (nondioxin\text{-}like,\ \textstyle\sum_{37} PCBs) \tag{3.9}$$

$$R = CDI \times SF \tag{3.10}$$

where R is excess cancer risk, SF is slope factor of the chemical (pg/kg/day)$^{-1}$, CDI is the chronic daily intake (pg/kg/day). All SF values were taken from USEPA (2007b), tabulated in Table 3.8.

Table 3.8. Values of slope factor for targeted pollutants

Pollutant	**SF (pg/kg/day)$^{-1}$**
α-HCH	6.3×10^{-9}
γ-HCH	1.3×10^{-9}
HEPT	$4.5\text{x}10^{-9}$
HEPX	$9.1\text{x}10^{-9}$
Dieldrin	$1.6\text{x}10^{-8}$
DDE	$3.4\text{x}10^{-10}$
CC	$3.5\text{x}10^{-10}$
TC	$3.5\text{x}10^{-10}$
PCBs	$2.0\text{x}10^{-9}$
Dioxin	$1.5\text{x}10^{-4}$

Monte Carlo simulation was carried out to estimate population risk by using Crystal Ball software (v 4.0e). Statistical sampling techniques are applied in this simulation, which is a computer-based method of analysis, in order to obtain a probabilistic approximation to the output of a mathematical equation or a model. A probability distribution was used to represent the possible values for each variable in the exposure-risk model. The fit of probability distribution to the measured data was determined by applying Kolmogorov-Smirnov (KS), and Anderson-Darling (AD) tests. Beta, exponential, gamma, normal, lognormal, logistic, pareto, and Weibull distributions were tried, and then the best fitting distribution was chosen. The simulation was run for 10,000 trials constructing 10,000 forecasts (or possible outcomes) which were used to obtain distributions that describe population exposure and risk. Crystal Ball software was also used to apply sensitivity analysis. The rank correlation coefficients between each input and output were calculated to range the input parameters on the basis of their effect on the output variables. Uncertainty analysis was also conducted in this study. The bootstrap method was applied, and 200 simulations were applied with 1000 trials each.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Ambient Air Concentrations of POPs

4.1.1. Ambient OCP concentrations

Concentrations of 22 OCP species were measured during a sampling period between May to October 2014 at a background site of Izmir and an urban site in Istanbul. The detected OCPs with a sample number exceeding 25% percentage of total number of samples were considered in this study.

The total concentration of OCP compounds was measured as 316 and 216 pg/m^3 in Izmir and Istanbul stations, respectively. Higher levels for most of the OCP compounds, especially γ-HCH, HCB, HEPT, Endo-I, -II, EndoSO$_4$, CC, TC, and mirex were measured in Izmir station in comparison with Istanbul station. The potential source of OCP compounds is primarily treated agricultural soils. Izmir station is located in a background site, where agricultural practices were applied more than in an urban site of Istanbul. Average air temperature is also higher in Izmir, thus volatilization from the soil into the air in Izmir would be higher than Istanbul. A significant rise in the levels of OCP compounds (γ-HCH, HEPT, Dieldrin, Endrin, Endo-I, -II, and Mirex) was observed during a specific date range from 19/08/2014 to 02/10/2014 in Izmir station. Most of the targeted OCP compounds have been banned for many years, thus theoretically there is no fresh potential input near the sampling sites. However, OCPs have long range transport potential due to their chemical properties. Therefore, the possibility of the targeted compound detection in gas phase would be much higher than in particle phase. A similar trend was observed in this study.

HCH is available in two different formulations namely lindane and technical HCH. Technical HCH mixture consists of 70% α-HCH, 5-12% β-HCH, 10-15% γ-HCH, 6-10% δ-HCH, and other isomers (ATSDR 2005). Ninety percent of lindane is produced from γ-HCH. HCH production was banned in 2009 by Stockholm Convention, while lindane had been already banned in Turkey since 1985. α-, β-, γ-, and δ-HCH were chosen as targeted HCH isomers in this study. *α*- and *γ*-HCH were widely detected isomers in both of the sampling sites (Figure 4.1). The total (gas+particle) *α*- and *γ*-HCH concentrations ranged from 1.24 to 46.93 pg/m^3 (mean of 11.80±12.86 pg/m^3) and 1.64 to 686 pg/m^3 (mean of 60.38±133 pg/m^3) in Izmir station, respectively. The range for Istanbul were 1.75 to 64.40 pg/m^3 (15.40±13.63 pg/m^3) and 4.29 to 55.69 pg/m^3 (21.97±17.59 pg/m^3), respectively. The measured total levels of α-HCH in warmer period ranged from 62.8±19 to 111±125 pg/m^3 in the previous studies conducted by Sofuoglu et al. (2004), Odabasi et al. (2008), Bozlaker et al. (2009), and Odabasi and Cetin (2012). Therefore, it can be seen that the levels of *α*-HCH were considerably lower in this study. However, the levels of *γ*-HCH were measured in the range of 30±8.10 to 117±157 pg/m^3 in those studies, thus the difference in the *γ*-HCH levels between the literature and this study is not as apparent, as well as *α*-HCH level. In this study, the higher *γ*-HCH levels in every station were detected with the increase of temperature. This can be primarily based on volatilization from agricultural soil to the atmosphere. *γ*-HCH has relatively high water solubility, thus it is tend to be attach to water. The increase of temperature in warmer sampling dates also caused volatilization of it from water to the atmosphere (Mackay and Wolkoff 1973). The particle phase α- and *γ*-HCH were detected in few samples in the stations. The sample collected in 07/08/2014 in Izmir station comprised the highest particle phase levels of both *α*- and *γ*-HCH (26 and 671 pg/m^3, respectively) by implying of an unexplained episodic situation. The particle phase levels, especially *γ*-HCH level, were much high for the sites where usage of HCH have been banned.

HCB is formed as by-product in the production process of atrazine, propazine, simanize, mirex, and HCB-contaminated pesticides; several chlorinated solvents (tetrachloroethylene, trichloroethylene etc.). Incineration of municipal and hazardous wastes, base metal smelting, and combustion of fossil fuel are other probable sources of HCB emission (EEA 2005). Therefore, the release of HCB to the atmosphere as by-product might most probably lead to detect high gas level of HCB in this study, even though the ban on use and production of this compound have been effective since 1982 in Turkey. The total concentration of HCB ranged from 7.57 to 110 pg/m^3 (47.76±24.19 pg/m^3) in Izmir station, and 8.63-75 pg/m^3 (41.27±18.38 pg/m^3) in Istanbul station (Figure 4.2). While gas phase HCB was detected in all sampling dates in both of two stations, it was rarely detected in particle phase for Izmir station (n=6), for Istanbul station (n=1). The HCB level was not measured in the studies conducted in Turkey. There was not a specific trend for HCB level was observed with the change of temperature in both of sites.

HEPT does not have any natural source (ATSDR 2007). This compound was commonly used in the past as an insecticide, especially applied in soil treatment, as a seed treatment (maize, small grains and sorghum) or directly to foliage (WHO 2004). It was banned in Turkey in 1979. HEPT was also listed as a dirty dozen in Stockholm Convention to eliminate the production and use of it. The total concentration of HEPT was measured in the range from 3.49 to 683 pg/m^3 (mean: 61±126 pg/m^3) and 10 to 38 pg/m^3 (mean: 11±14 pg/m^3) in Izmir and Istanbul respectively (Figure 4.3). HEPT level was rarely measured in the studies conducted in Turkey. A high level was found as 114 pg/m^3 in Hamitler, Bursa by using passive air sampler in the study conducted by Esen (2013). Besides, the total level of HEPT and HEPX (an oxidation product of HEPT) was measured as 41±35.51 pg/m^3 in Izmir from 14-23 May 2003 (Sofuoglu et al. 2004).

Aldrin and dieldrin, which have been forbidden in Turkey since 1970s, were other two target OCP compounds in this study. They were typically used on crops and their foliage and also used for treating seed and soil, termite proofing (Zitko 2003). Aldrin does not act a stable behavior in environment and rapidly converts to dieldrin (ATSDR 2002a). As expected, aldrin was not detected in Izmir station, and nearly not detected in Istanbul station (n=2). The total concentration of dieldrin reached to 131 and 91 pg/m^3, having the mean level of 17.43±32.39 and 20.52±25.20 pg/m^3 in Izmir and Istanbul stations, respectively (Figure 4.4). Dieldrin in particle phase was not detected in Izmir station, and also detected in only one sample collected from Istanbul station, implying no nearby potential source. Despite the prohibition of the use of dieldrin for many years, the dieldrin level just dropped to half of the level measured by Sofuoglu et al. (2004) as 35±39 pg/m^3 measured in May 2003 in Izmir, due to highly persistency. Endrin, another target OCP compound, was used for the similar applications of aldrin and dieldrin, except termite proofing. However, it was found at higher levels ranged from 3.70 to 88.86 pg/m^3 (9.96±19.28 pg/m^3) in Izmir station and from 1.19 to 144 pg/m^3 (37.70±43.10 pg/m^3) in Istanbul station. There was no a specific trend for endrin level between sampling periods. This might be explained with its low vapor pressure, thus slowly evaporate from soil to air.

Figure 4.1. Daily air concentrations of α- and γ-HCH measured in a) Izmir and b) Istanbul

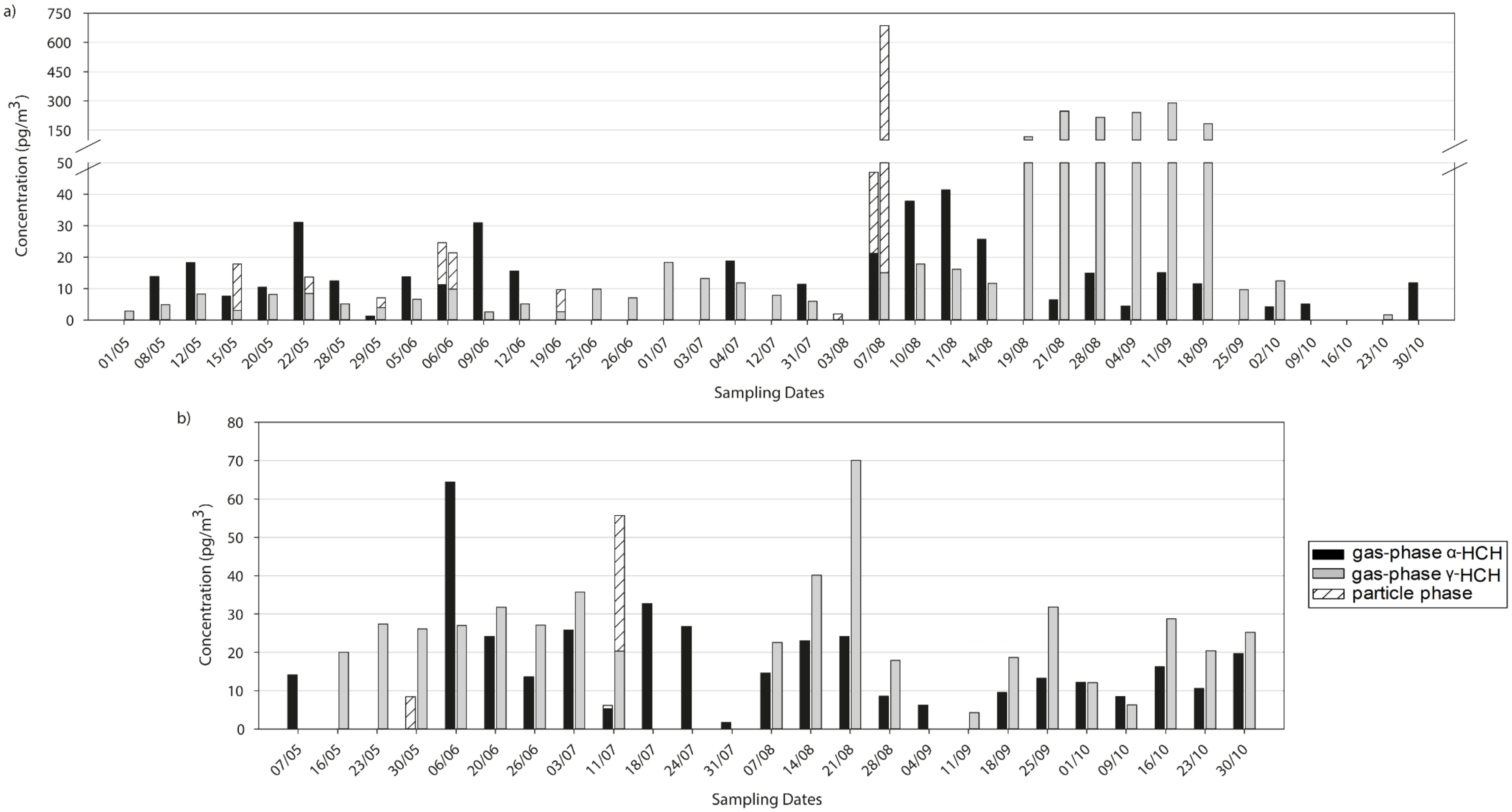


Figure 4.2. Daily air concentrations of HCB measured in a) Izmir and b) Istanbul

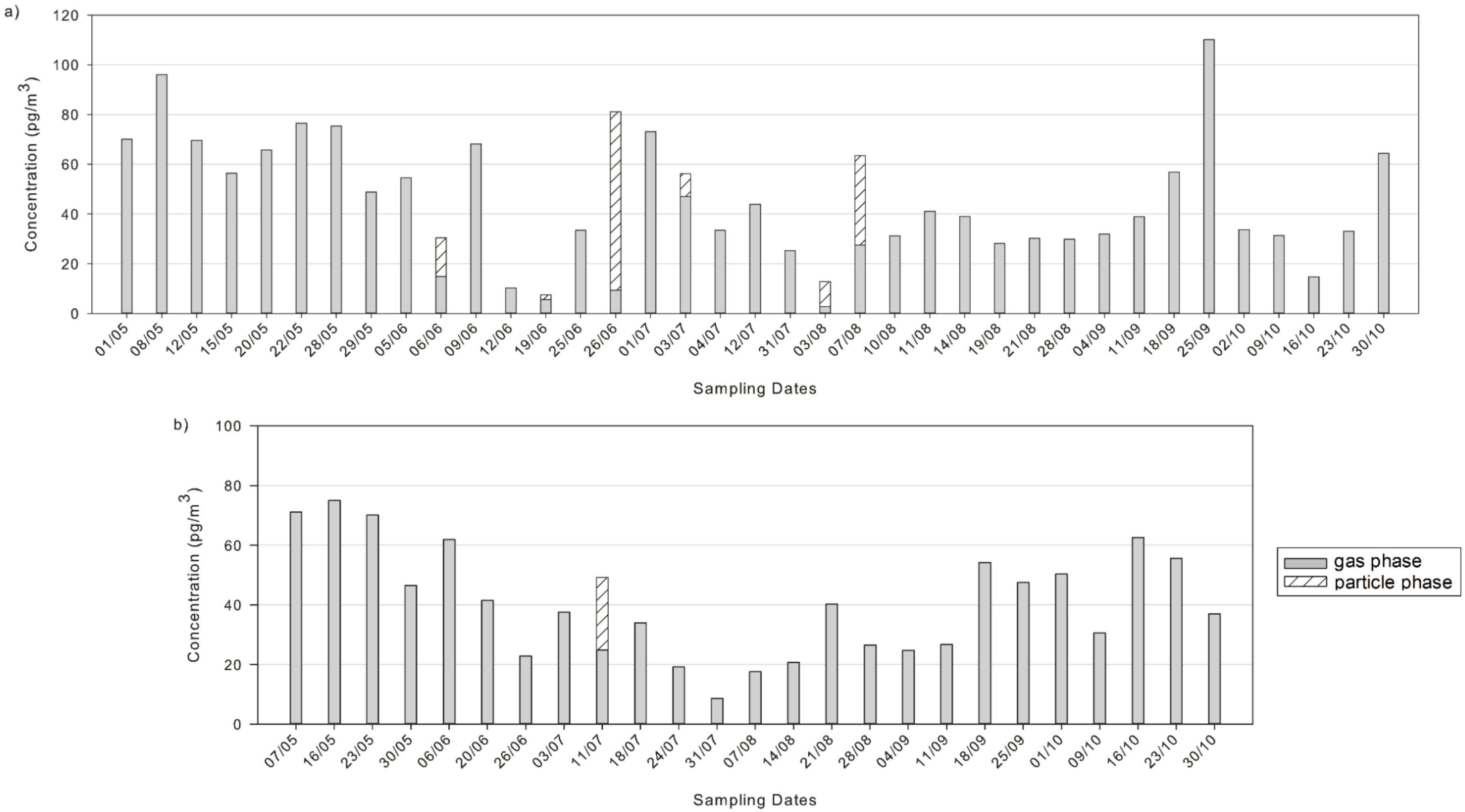


Figure 4.3. Daily air concentrations of HEPT measured in a) Izmir and b) Istanbul

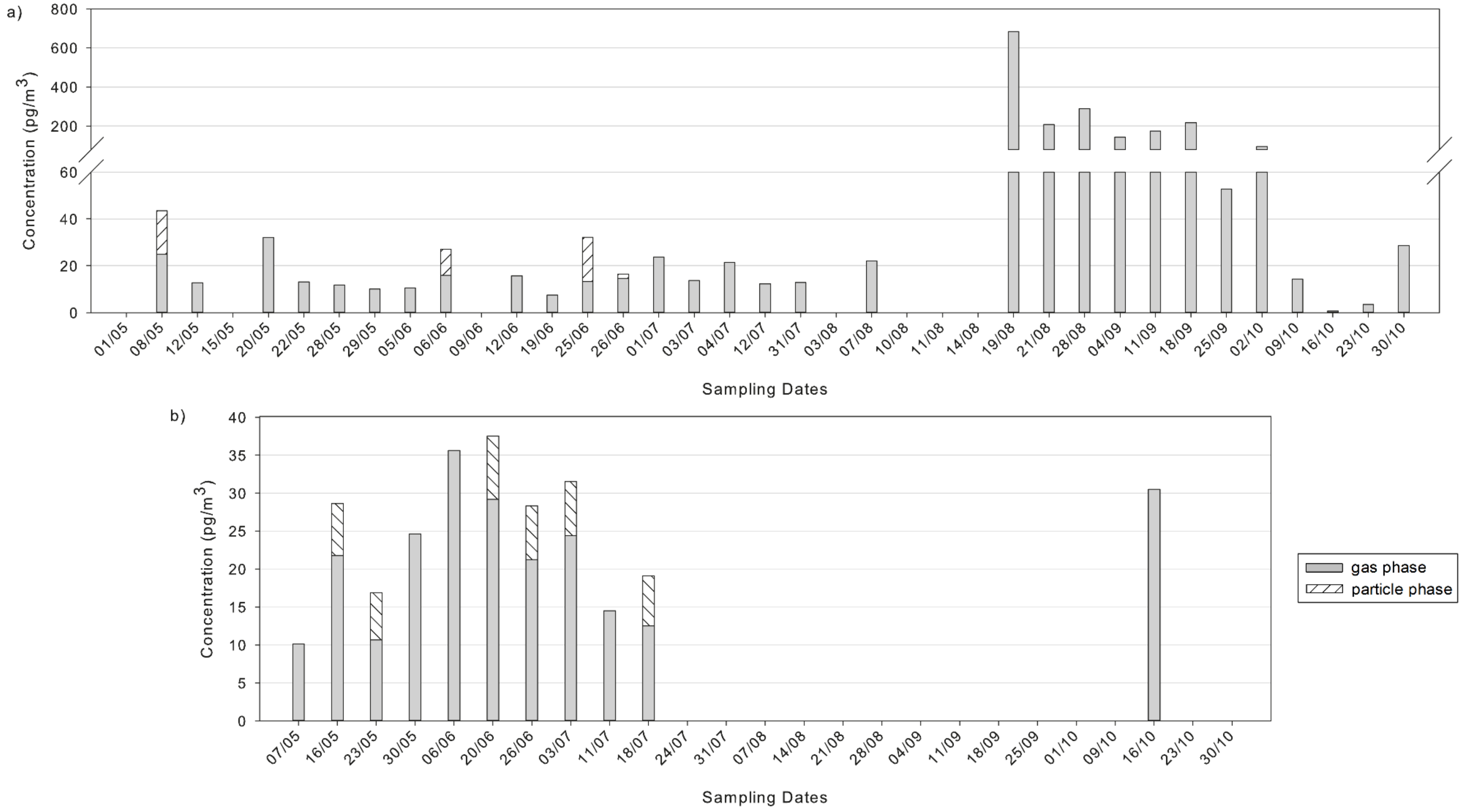
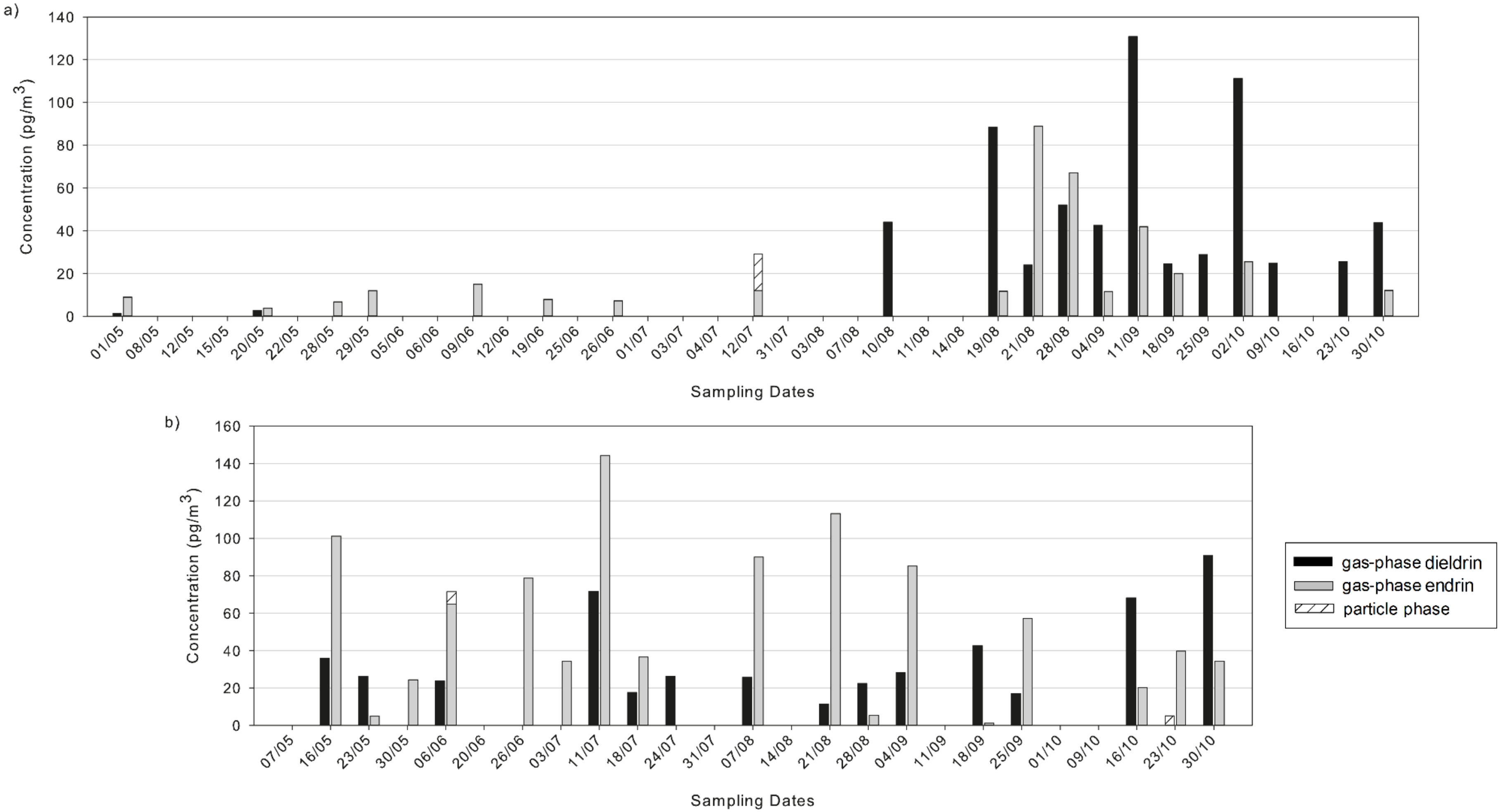


Figure 4.4. Daily air concentrations of Dieldrin and Endrin measured in a) Izmir and b) Istanbul



DDT is a mixture of *o,p′*-DDT (15%), *p,p′*-DDT (85%), and *o,o′*-DDT at a trace amount, also the mixture might involve DDE, and DDD (ATSDR 2002b). DDT has been banned in Turkey in 1985 and also listed as a dirty dozen in Stockholm Convention. However, it is still being used by developing countries for agricultural and sanitary purposes due to their low price and effectiveness in controlling (Zhou et al. 2013). The species of DDT, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, and p,p′-DDT were chosen as targeted compounds. *o,p′*-DDE and *p,p′*-DDE were widely detected isomers of DDT in Izmir station, while *p,p′*-DDE was detected frequently in Istanbul station. The total level of *o,p′*-DDE and *p,p′*-DDE were found in the range from 0.7 to 48.41 pg/m^3 (4.17±9.30 pg/m^3) and from 1.42 to 322 pg/m^3 (47±75 pg/m^3) in Izmir station, respectively (Figure 4.5). The *p,p′*-DDE level was also reached to 272 pg/m^3 in Istanbul station, having a mean level of 54±57 pg/m^3. In previous studies conducted in Turkey, the dominant DDT species was determined as *p,p′*-DDT in the range from 5.10±1.68 pg/m^3 (measured in 2005 summer in an industrial site of Izmir by Odabasi and Cetin (2012)) to 58±16 pg/m^3 (measured in 2005 summer in another industrial site of Izmir by Bozlaker et al. (2009). The numbers of detected *p,p′*-DDT level in this study were between 1-3. Thus, it was understood that DDT broke down in the structure and mostly converted DDE with time. Besides, these high levels of DDEs in this study were already expected due to the relationship between mobility properties of DDTs and location of Turkey lied between latitudes 35°N and 45°N. Because, compounds which have a property of relatively low mobility generally deposit and accumulate in mid-latitudes.

Endosulfan was added to the list of Stockholm Convention in 2011 in order to eliminate production and use of it. It was used for particularly effective against aphids, fruit worms, beetles, leafhoppers, moth larvae, and white flies on a wide variety of crops for many years before it was banned (ATSDR 2013). They were generally found as dominant OCP compound in the studies conducted when these compounds were in-use in Turkey (Bozlaker et al. 2009, Sofuoglu et al. 2004, Odabasi et al. 2008). Endo-I, -II were typically detected in Izmir and Istanbul stations (Figure 4.6). The detected total level of Endo-I, -II ranged from 8.23 to 63 pg/m^3 (25.16±13.54 pg/m^3) and from 2.90 to 112 pg/m^3 (16.24±27 pg/m^3) in Izmir station, respectively. The detected total concentrations of Endo-I was also measured in the range from 1.92 to 25 pg/m^3

(8.34±6.67 pg/m^3) and Endo-II reached to 77 pg/m^3 with a mean level of 3.60±15.50 pg/m^3 in Istanbul station. The particle phase endosulfans was detected in few samples in both of the two stations, due to the ban of use of them, thus no fresh input. In addition to mother compound of Endosulfane, EndoSO$_4$ was another widely detected endosulfan specie in Izmir station, though it was detected in only 3 samples in Istanbul station. The total concentration of EndoSO$_4$ was found in the range from 3.21 to 7.63 pg/m^3 (1.31±1.94 pg/m^3) in Izmir station. It was seen that seasonal change did not affect significantly the level of EndoSO$_4$. This can be explain with high resistance of EndoSO$_4$ in water and soil, difficultly breaking down from them to the atmosphere.

Chlordane has been banned in Turkey since 1970s. Before that time, chlordane was used as a pesticide on agricultural crops, lawns, and gardens (ATSDR 1994). Chlordane consisting of CC and TC was also measured in this study. Both of CC and TC were usually detected in Izmir station, though only TC was detected frequently in Istanbul station. The total concentrations of CC and TC reached to the value of 10.29 and 20 pg/m^3 in Izmir station, with mean levels of 1.63±3.87 and 4.22±4.96 pg/m^3, respectively (Figure 4.7). The total level of TC in detected samples was also measured in the range between 1.54 and 21.37 pg/m^3 (2.08±4.35 pg/m^3) in Istanbul station. CC and TC levels in particle phase were detected in few samples in Izmir station. However, TC in particle phase was not detected in any sample in Istanbul station. The concentration values of CC measured in warmer periods were reported in the range between 0.93±0.15 (Odabasi et al. 2008) and 3.0±1.4 pg/m^3 (Bozlaker et al. 2009). The detected CC level in this study was in this literature range. The TC level in literature studies conducted in Turkey reached to the maximum level of 158±262 pg/m^3 in the study conducted by (Sofuoglu et al. 2004), which are much larger than the detected mean level of TC in Izmir and Istanbul station.

Mirex was used as flame retardant and a stomach insecticide in Turkey until forbidden in 2001 by Stockholm Convention. Mirex had not been measured in Turkey, before this study. The gas phase mirex was detected in 18 samples in Izmir station, but in only 4 samples in Istanbul station. Its total level ranged between 1.06 and 61 pg/m^3 in Izmir station, with a mean level of 8.12±12.92 pg/m^3 (Figure 4.8). It was shown that there is no specific seasonal trend due to most probably significant attachment of mirex onto the soil and water (ATSDR 1995).

Figure 4.5. Daily air concentrations of *o,p′*-DDE and *p,p′*-DDE measured in a) Izmir and b) Istanbul

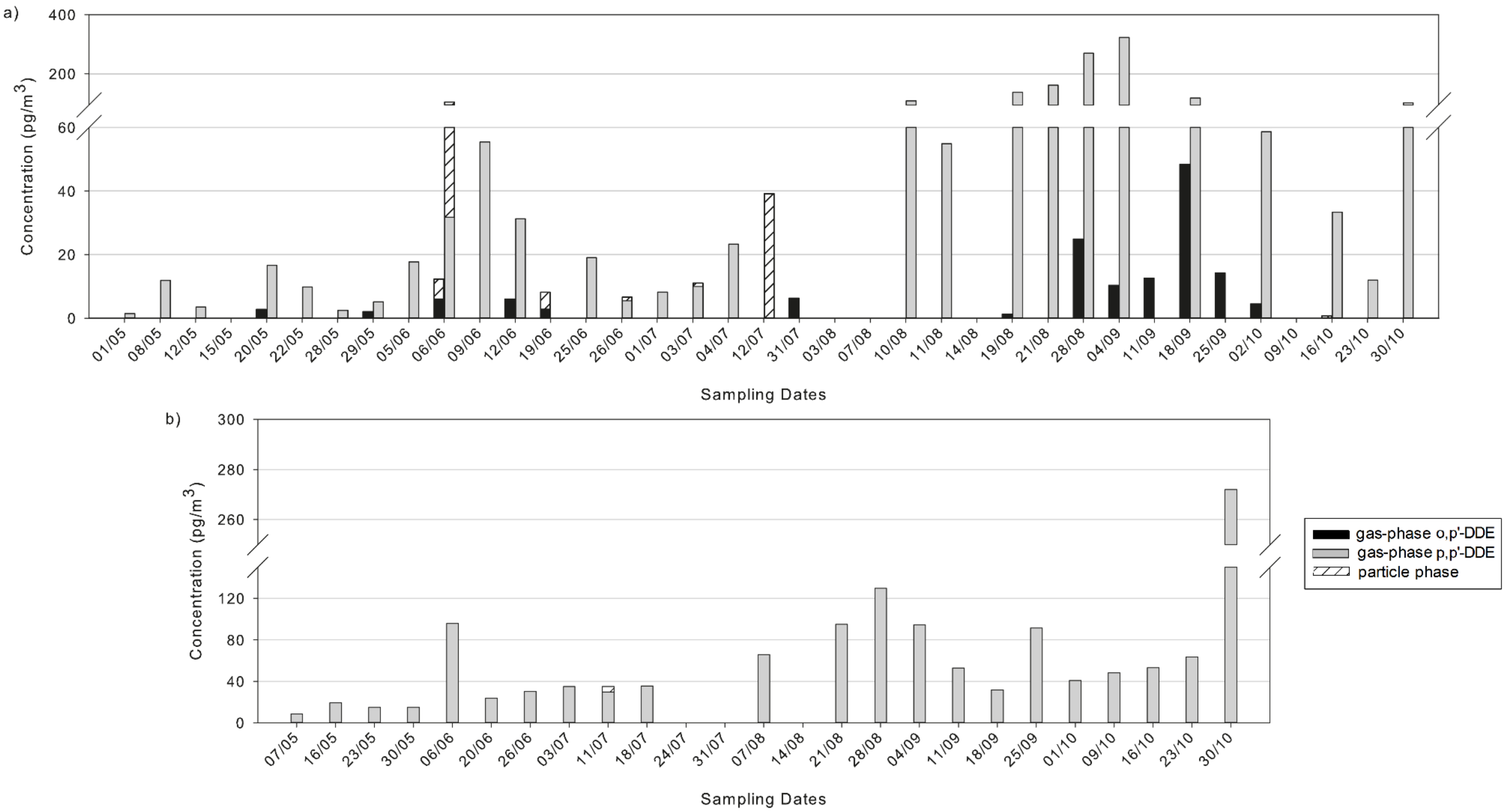


Figure 4.6. Daily air concentrations of Endo-I and Endo-II measured in a) Izmir and b) Istanbul

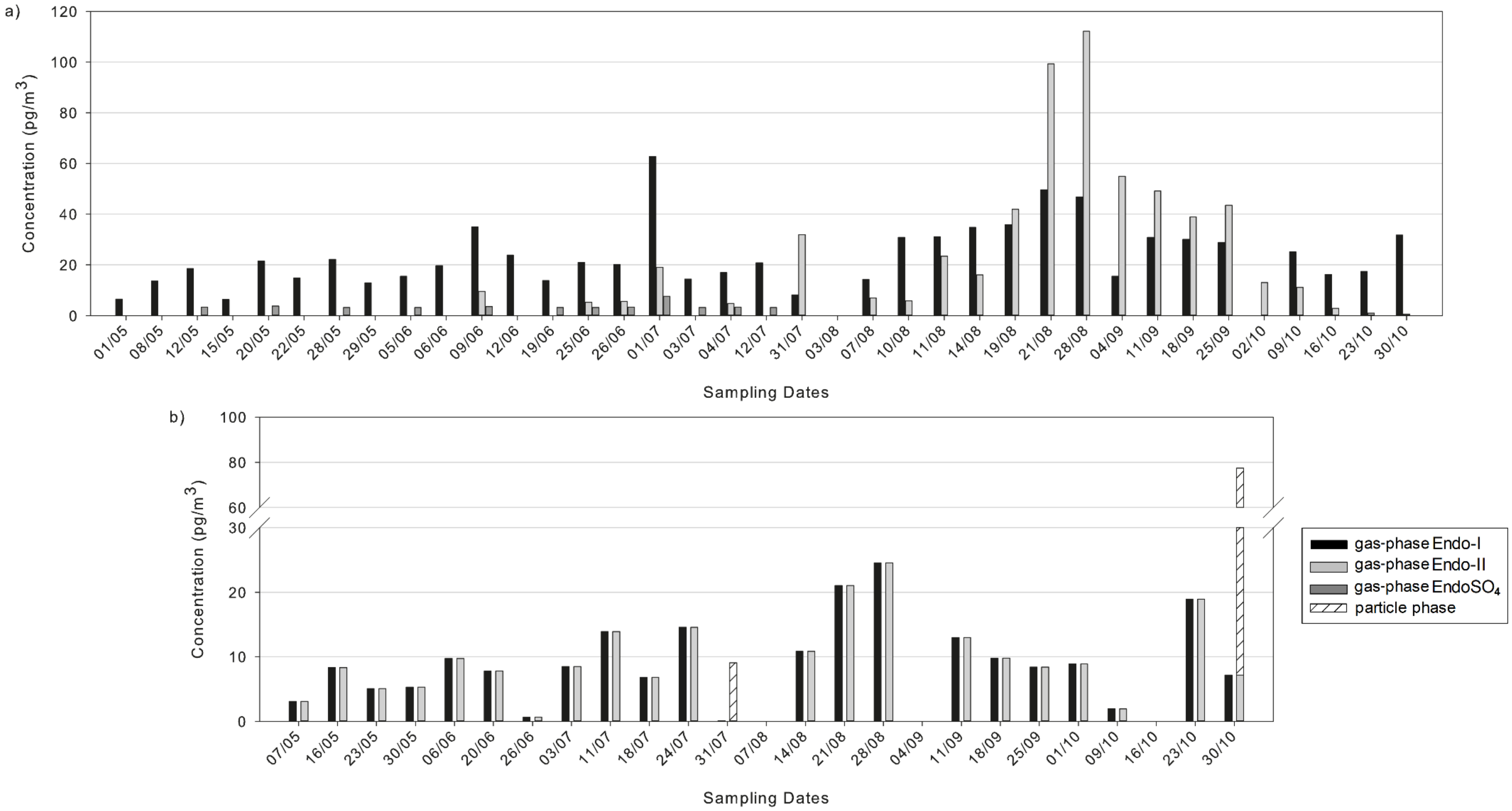
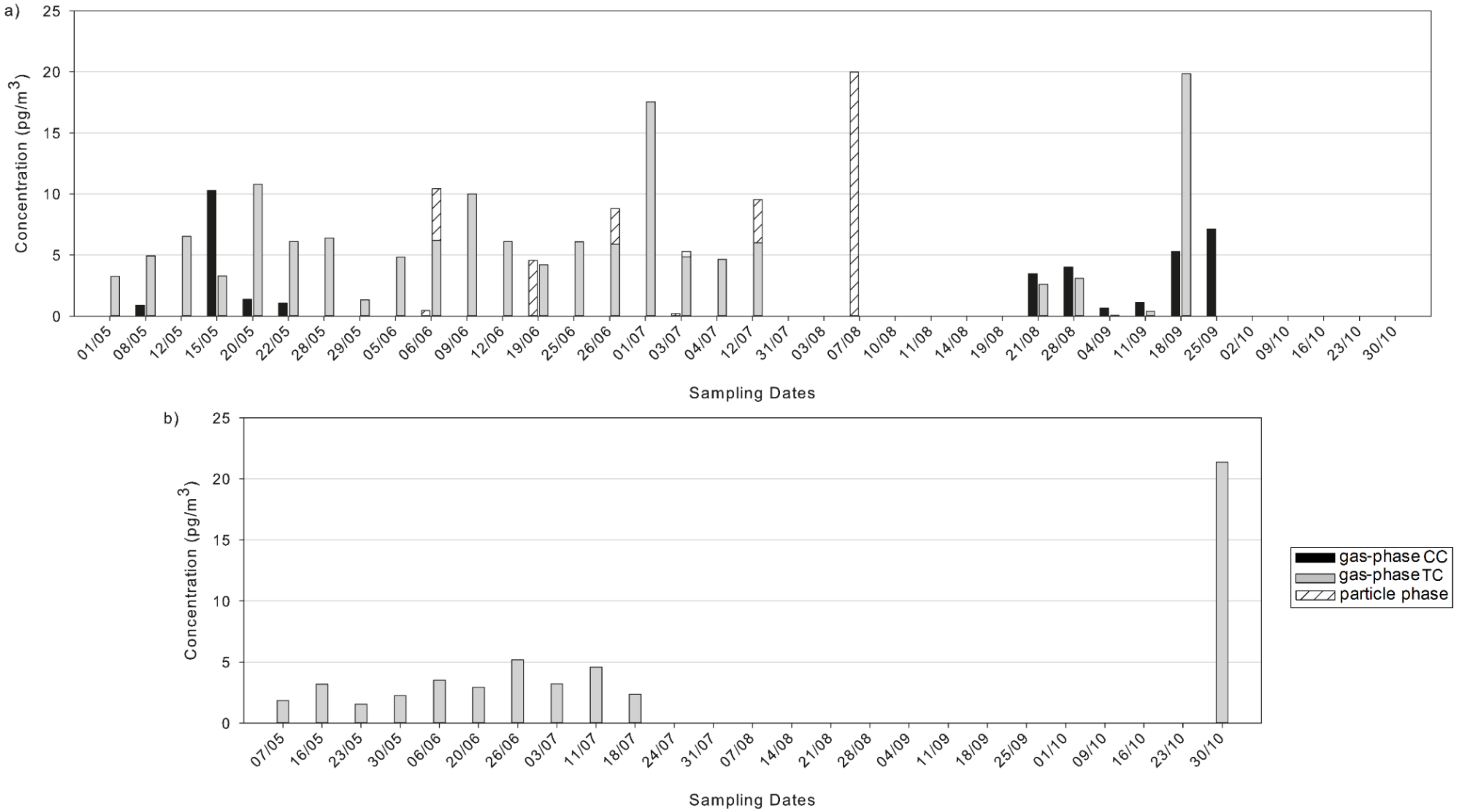


Figure 4.7. Daily air concentrations of CC and TC measured in a) Izmir and b) Istanbul



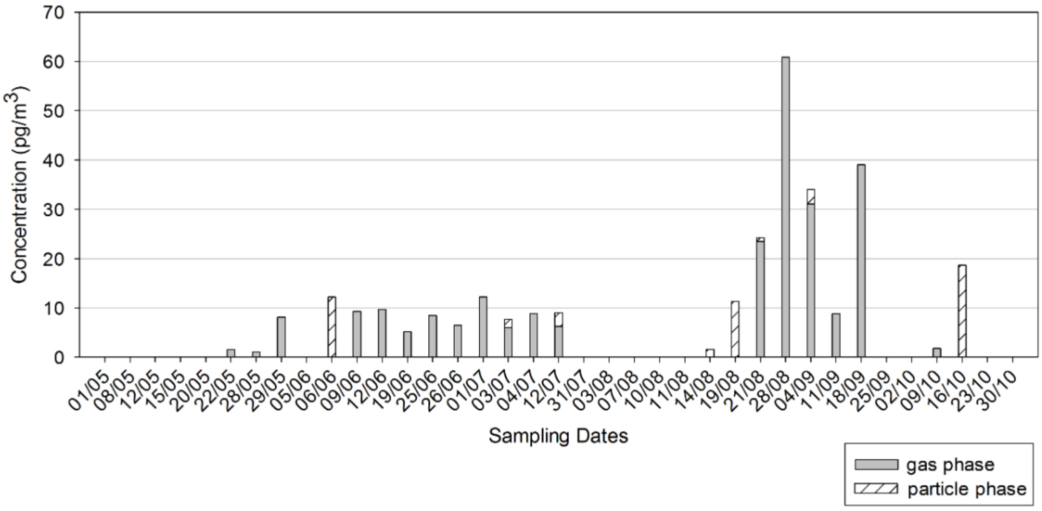


Figure 4.8. Daily air concentrations of Mirex measured in Izmir

4.1.2. Ambient PCB concentrations

The results of ambient concentrations of 43 PCB congeners for homolog groups (tri-, tetra-, penta-, hexa-, hepta-, octa-CBs) were given in this part.

The mean total concentrations of Σ_{43}PCB were calculated as 232±224 and 104±48 pg/m^3 in Izmir and Istanbul stations, respectively. The PCB congeners contribution was widely from gas phase compared to particle phase. Ninety five percentage and 88% of gas+particle concentration of Σ_{43}PCB resided in gas phase in Izmir and Istanbul stations, respectively. Kuzu et al. (2014) investigated the ambient PCB concentrations in samples collected from an urban site in Istanbul between May-Nov 2012. The total Σ_{92}PCB concentrations were measured as 420 pg/m^3. The contribution to total concentration was 88% from gas phase. Air samples were also collected between 2009 and 2010 during four seasons by Kaya et al. (2012) from an industrial site, Aliaga. The Σ_{41}PCBs levels were detected in both summer and winter, with the maximum levels of 231 and 22 ng/m^3. It was stated that iron-steel plants and ship dismantling facilities were the major PCB emitters in that region.

The PCB congeners included in tri-chlorinated PCB homologs had the highest concentrations compared to other targeted PCB congeners in Izmir station (Figure 4.10). The mean gas+particle concentrations of the most dominant congeners, PCB 28 and 18, were measured as 22.26±18.79 and 19.30±13.63 pg/m^3, respectively. High levels were also found for PCB 31 and PCB 22 as 18.37±15.94 and 16.18±12.86 pg/m^3, respectively. In Istanbul station, PCB 18 had the highest average total concentration

(15.82±10.44 pg/m^3), followed by PCB 44, 60, and 28 (9.52±11.13, 9.06±12.52, and 8.94±12.19 pg/m^3, respectively), which are mainly tri and tetra-chlorinated PCB homologs.

The contribution of homolog groups on the Σ_{43}PCB concentrations for each station is shown in Figure 4.9. The contribution of tri- and tetra-CBs were found as the highest ones for both of the stations. It is known that tri- and tetra-chlorinated PCB homologs are more soluble in water, more volatile, and more easily metabolized. They are classified as in higher mobility compounds in comparison with the homologs having larger number of chlorine atoms. Therefore, PCBs among tri- and tetra-chlorinated PCB homologs were already expected to be the dominant PCB congeners. Similar results were also shown in many studies conducted by Odabasi et al. (2008), Zhang et al. (2013), Kuzu et al. (2014), and Vilavert et al. (2014) etc. The contribution on total amount of PCBs in gas phase decreased with an increase in number of chlorine atoms. In contrast with PCBs having fewer number of chlorine atoms, PCBs with larger chlorine atoms increase the resistance to biodegradation, thus increase bioaccumulation in the environment. They prefer to deposit and retain close to point of source. No production was available in Turkey and the use of PCBs has been banned in Turkey since 1996, However, it may still be produced unintentionally as an industrial by-product of thermal processes such as uncontrolled waste incineration, metal smelting and refining processes, thermal power generation, cement kilns, the burning of wood and other biomass fuels used in transport vehicles with combustion or industrial processes such as paper manufacturing processes and chlorine bleaching of pulp and paper (Covaci et al. 2001, Acara 2006). Therefore, the detected PCBs having larger number of chlorine atoms such as PCB 138, 149, 157, 170, 199 might be released from the close sources to the stations, then mostly settled to water and soil, and evaporated less to the atmosphere.

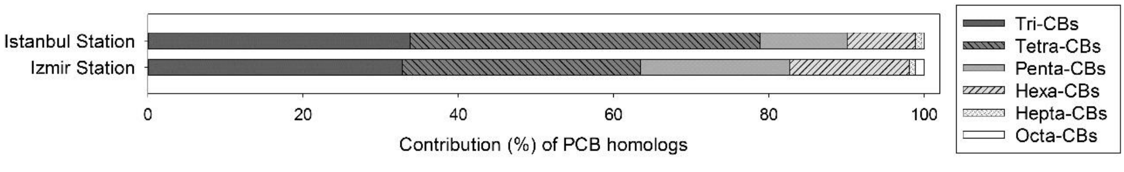


Figure 4.9. Contribution of homolog groups on Σ_{43}PCB concentrations for each station

Figure 4.10. Mean gas+particle phase concentrations of each target PCB congeners measured in a) Izmir and b) Istanbul

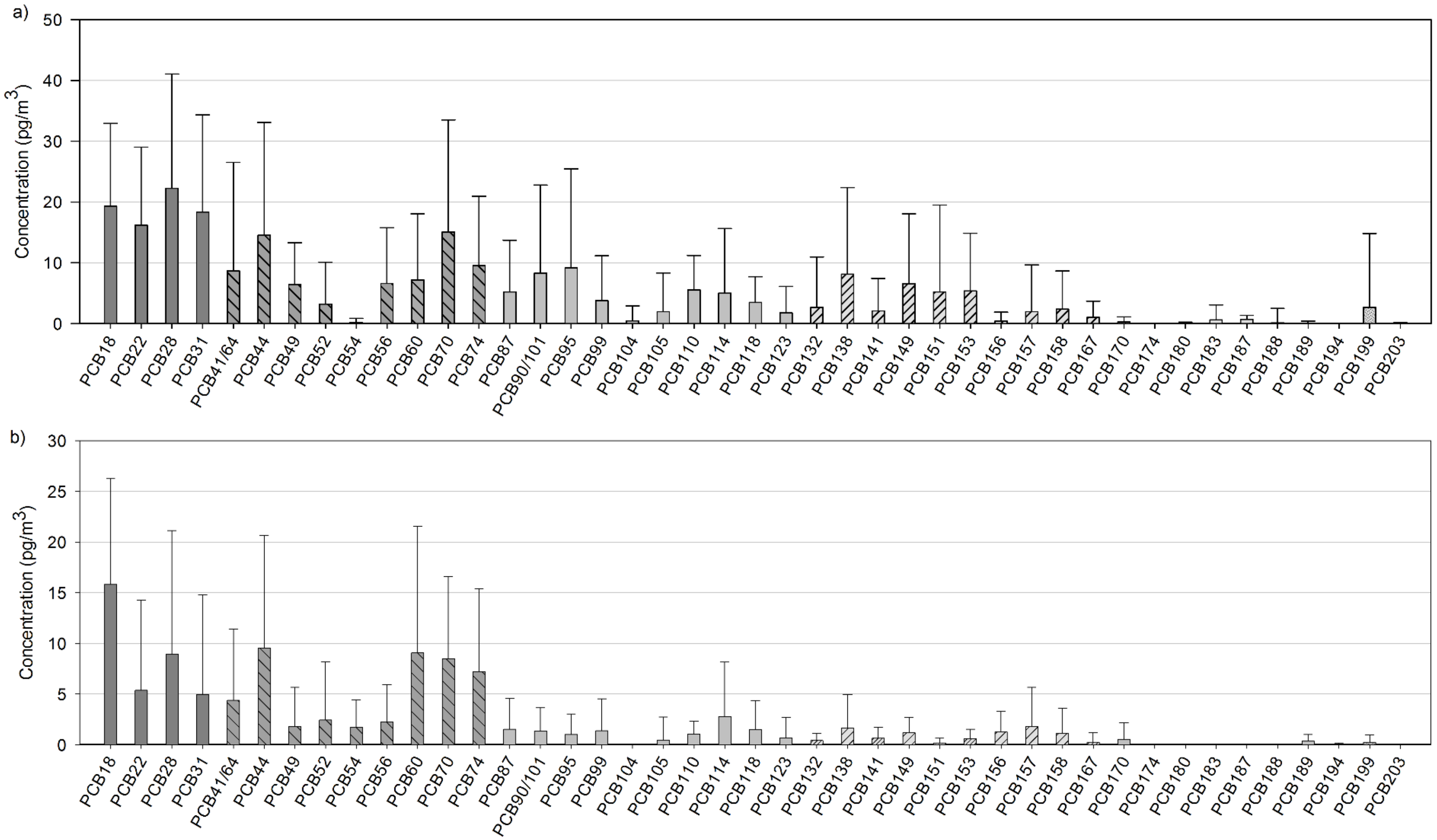
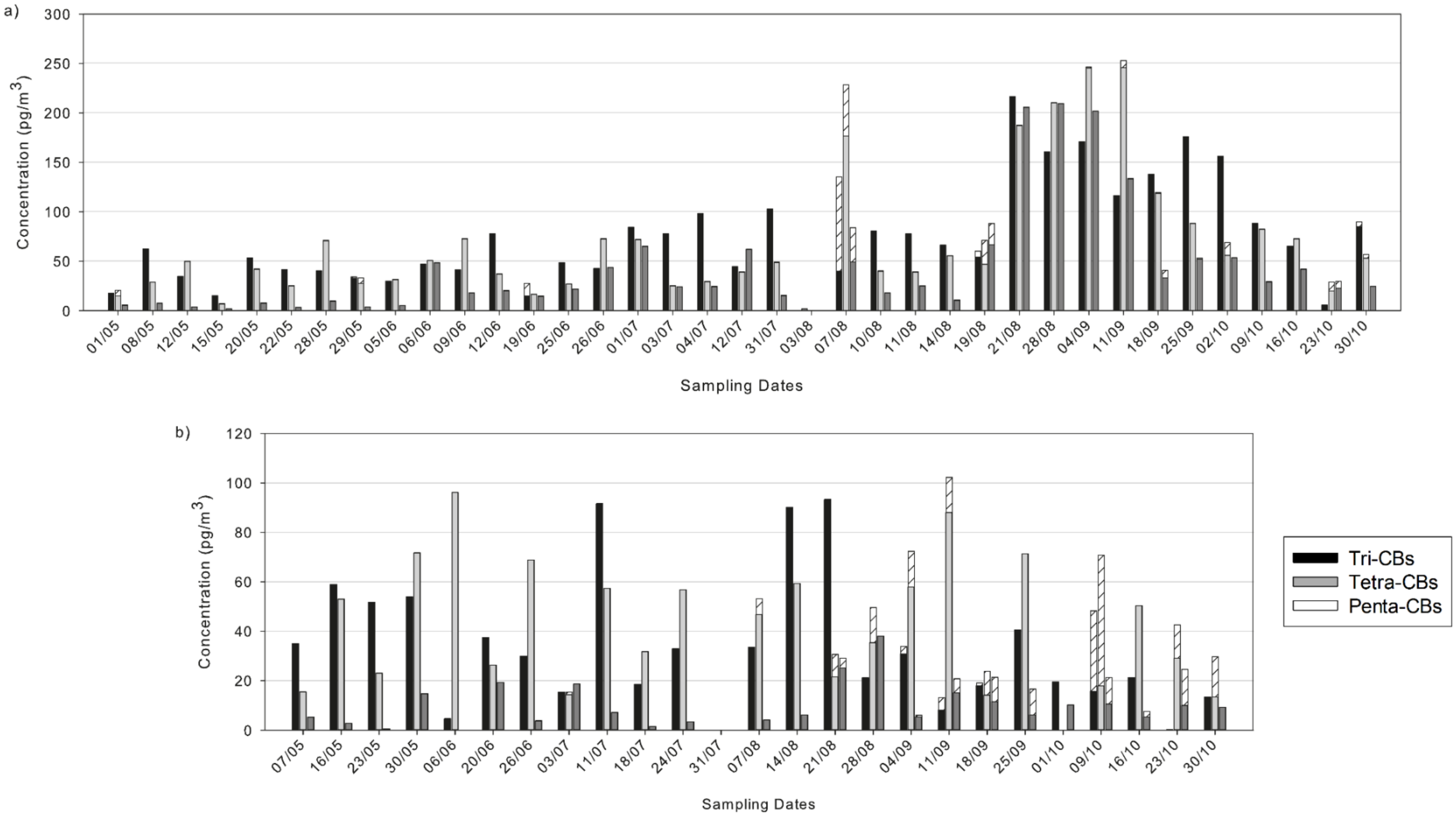


Figure 4.11. Daily air concentrations of dominant PCB homologs measured in a) Izmir and b) Istanbul



The effect of temperature on PCB homolog groups was also investigated in this study. There is a strong relationship between ambient temperature and air concentrations of POPs. An increase of temperature increases the volatilization process from contaminated terrestrial surfaces to the atmosphere (Sofuoglu et al. 2001). The daily gas- and particle-phase concentrations of the most dominant three homolog groups, tri-, tetra- and penta-CBs, were shown in Figure 4.11. The higher tri-, tetra-, and penta-CB levels in Izmir station were detected clearly with the increase of temperature, thus more volatilization from soil and water to atmosphere. Like most of OCP compounds, a sharp rise in the levels of PCB homolog groups was observed with an implication of episodic situation.

4.2. Back Trajectory and PSCF Modelling for OCPs and PCBs

4.2.1. Back Trajectory Analysis

In order to begin the back trajectory analysis, some input parameters must be defined to the HYSPLIT model program. These are receptor coordinates, sampling dates, input meteorological data, maximum endpoint height, starting height, and trajectory length. Simple trajectory analysis with a specific input combination never reaches a best result. Use of multiple trajectories is the key point to increase sensitivity of the analysis. Therefore, the best input parameters for the trajectory analysis were chosen by iteratively combining input variables.

4.2.1.1. Selection of Input Parameters

4.2.1.1.1. Input Meteorological Data

National Oceanic and Atmospheric Administration’s (NOAA) Air Resources Laboratory (ARL) HYSPLIT model provides meteorological datasets which are supplied from ETA data assimilation system (EDAS), North American mesoscale forecast system (NAM), nested grid model (NGM), and global data assimilation system (GDAS). All of them give information about meteorological properties such as temperature, pressure, wind speed and direction, relative humidity in a specific range of latitude and longitude and a specific time period. The domain of analysis by using GDAS dataset includes all of the world, thus Turkey. Other datasets are suitable for continent of America. Hence, dataset supplied from GDAS was chosen as input meteorological data in this study.

4.2.1.1.2. Maximum Endpoint Height

The input parameter, maximum endpoint height, is specified within troposphere, the lowest layer of Earth's atmosphere, which contains %75-80 mass of the atmosphere, and where nearly all of weather events occur. The sublayer of troposphere next to the surface of Earth is known as planetary boundary layer. While the range of troposphere from Polar Regions to tropics is between 7 and 20 km, boundary layer is generally from few hundreds of meter to 2 km. In this sublayer, surface features like mountains, forests, and buildings influence air flow. Thus, the trajectory analysis applied in boundary layer typically represents complex wind directions. Boundary layer depths in sampling period were obtained from HYSPLIT model program, and was found in the range from 300 m to 850 m, considering all of sampling stations (Figure 4.12). A height below maximum boundary layer (800 m) was chosen to investigate this case. Besides, 3000 m and 10000 m were chosen as the other maximum endpoints heights above boundary layer.

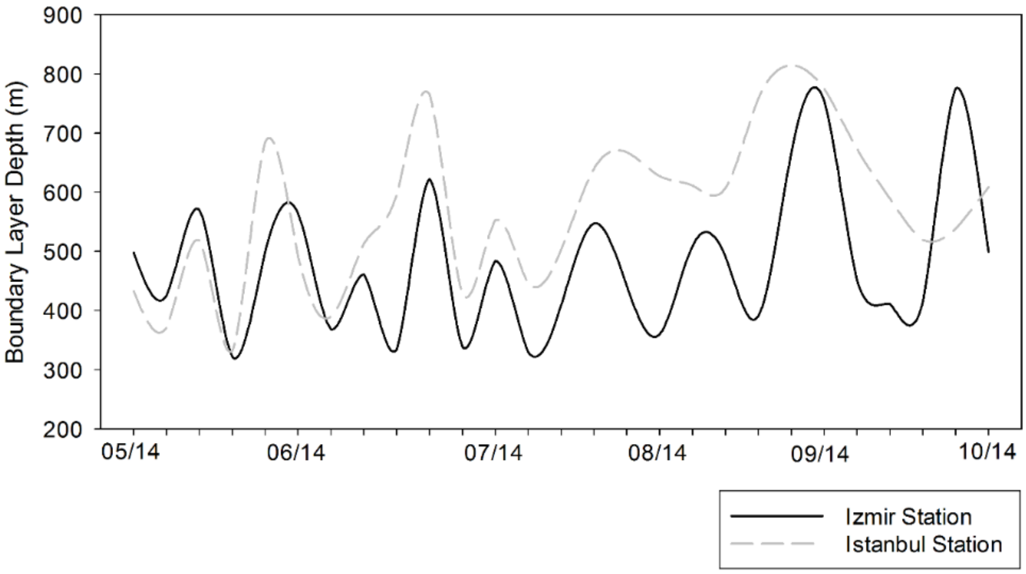


Figure 4.12. Boundary layer depth in sampling period for sampling sites

4.2.1.1.3. Trajectory Starting Height

Trajectory starting height is an input parameter to be chosen carefully. It should be within the boundary layer depth, but also high enough to prevent effects of surface features such as terrains and buildings. Terrain height for sampling sites can be calculated, and then a level above the calculated terrain height can be selected as starting height to minimize surface effects. The surface pressure (SPRS) and the mean sea level pressure (MSLP) at the starting location are used in the terrain height calculation (Coutant et al. 2003). In this study, the terrain height calculation was conducted for every station, and the height was found as 200 m and 250 m. A sample calculation is given below.

Izmir station has 1020 mb MSLP and 990 mb SPRS. The pressure difference between them is 30 mb. On the basis of an assumption of hydrostatic pressure, height is directly proportional with the pressure as about 10 meters/ 1 mb. This gives surface level (MASL) of 300 m. The real height of this site is 46 m. Thus, the starting height should be ~250 m above the real height.

Trajectories with different starting heights (50, 150, 300, 450, 600, 750, and 1000 m) for Izmir station at a specific sampling date (01/07/2014, ending at 08:00), trajectory length (5 day), and a maximum endpoint height (10 km) were applied and given in Figure 4.13. It might be used to clearly understand the influence of starting height on the trajectory analysis. It was seen that the trajectories with starting heights of 50 m and 150 m have very different patterns with direction changes along the way during transport due to most probably the effect of surface features. The stabilization of cluster patterns occurred with the increase of starting height from 300 m to 750 m. However, starting height of 1000 m exceeds boundary layer depth, and not representative of the air mass in the mixed layer. As a result, 300, 450, 600, and 750 m were chosen as starting heights in this study. This model with different starting heights was also applied at various combinations of sampling period, trajectory length, and maximum endpoint height, and similar phenomena was determined.

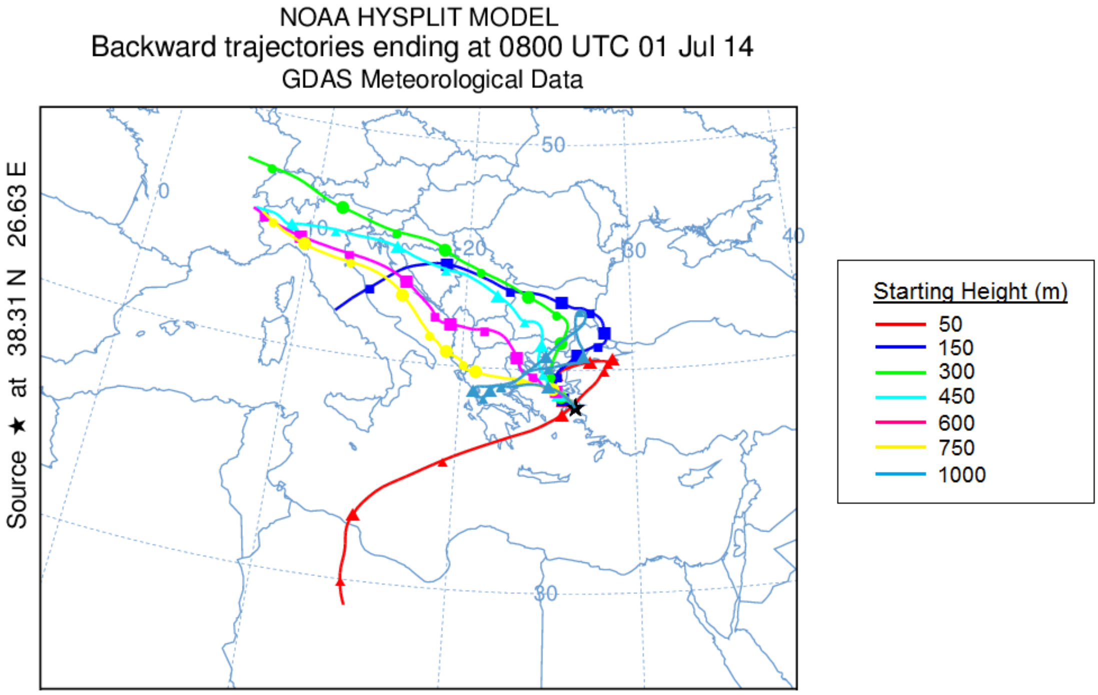


Figure 4.13. Comparison of back trajectories with different starting heights

4.2.1.1.4. Trajectory Length

Trajectory length is a significant input parameter in back trajectory analysis. Short trajectories might be suitable for pollutants that have ground-based sources or fast deposition rates (Gebhart et al. 2011). However, POPs can move long distances in the atmosphere without deposition thanks to their semi-volatile characteristics. Thus, long trajectories might be expected to give a better fit for POPs.

Trajectories at different trajectory lengths at many combination of input parameters for each station were compared. Trajectories with different trajectory lengths (1, 3, and 5 day) were computed for Istanbul station (41.05N-29.00E) at a specific sampling date (07/08/2014), trajectory height (300 m), and a maximum endpoint height (10 km), shown in Figure 4.14 as an example. Back trajectories computed for all trial days represent a nearly stable northeastward wind direction. However, the trajectories applied for 1 and 3 day might be short for the investigation of POPs source. The trajectories applied for 5 day reach more distant point with increasing trajectory length. Trajectory length is typically chosen as 5 day in the literature (Lammel et al. 2007, Garmash et al. 2013, Sofuoglu et al. 2013). As a result, trajectory length was chosen as 5 day in this study.

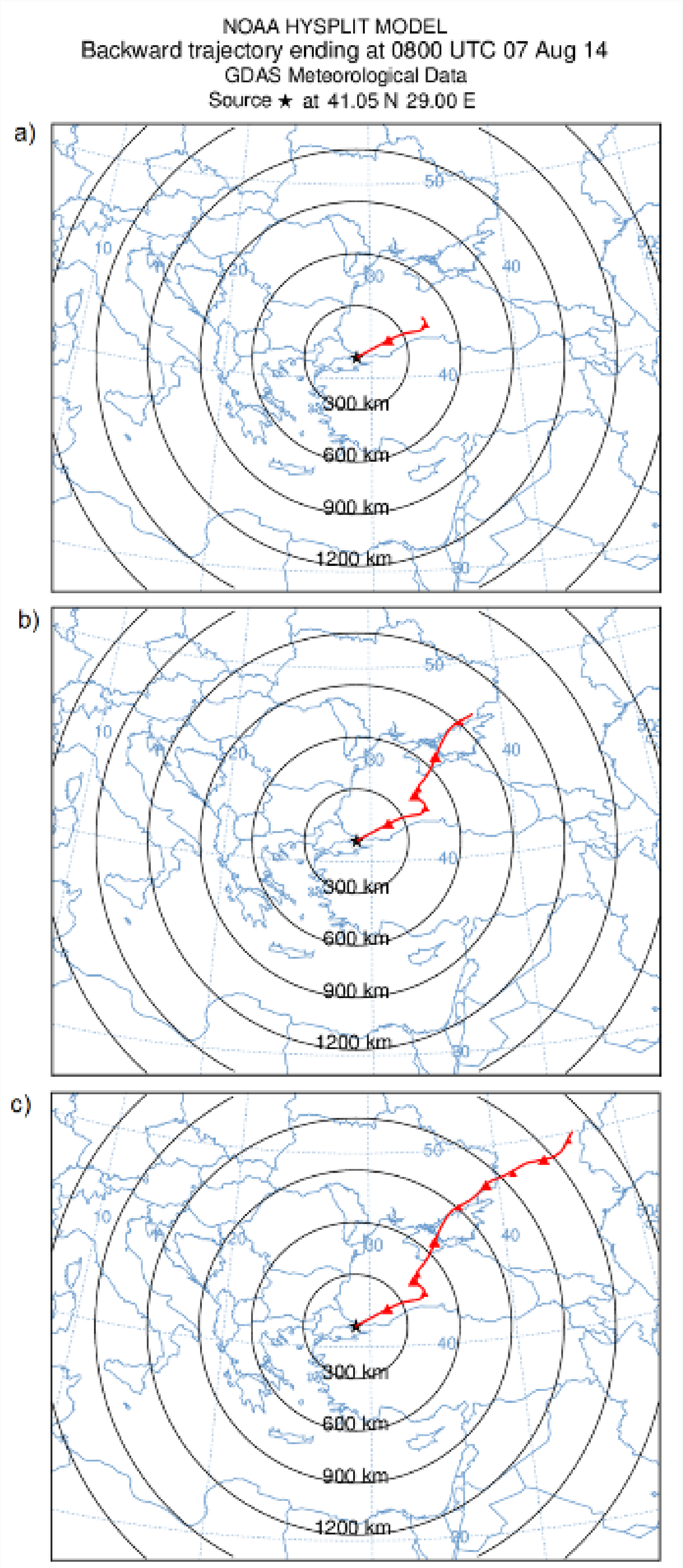


Figure 4.14. Comparison of back trajectories with different trajectory lengths of a) 1 day, b) 3 day, and c) 5 day computed for Istanbul station

4.2.1.2. Dominant Wind Directions for Each Station

Cluster analysis was applied to merge trajectories which are near each other by their mean trajectory, and then the dominant wind directions for Izmir and Istanbul station during the sampling period were obtained (Figure 4.15) for three different starting heights. The results of cluster analysis show that the dominant flow regime was N-NW for Izmir station. The dominant pathway followed Austria, Slovakia, Hungary, Serbia, Romania, Bulgaria, Greece, and Turkey. On the other hand, air masses traveled to Istanbul station from predominantly N-NE between May-Oct 2014. The air parcel movement passed from Belarus, Ukraine, Black Sea, and then reached Turkey to Istanbul station.

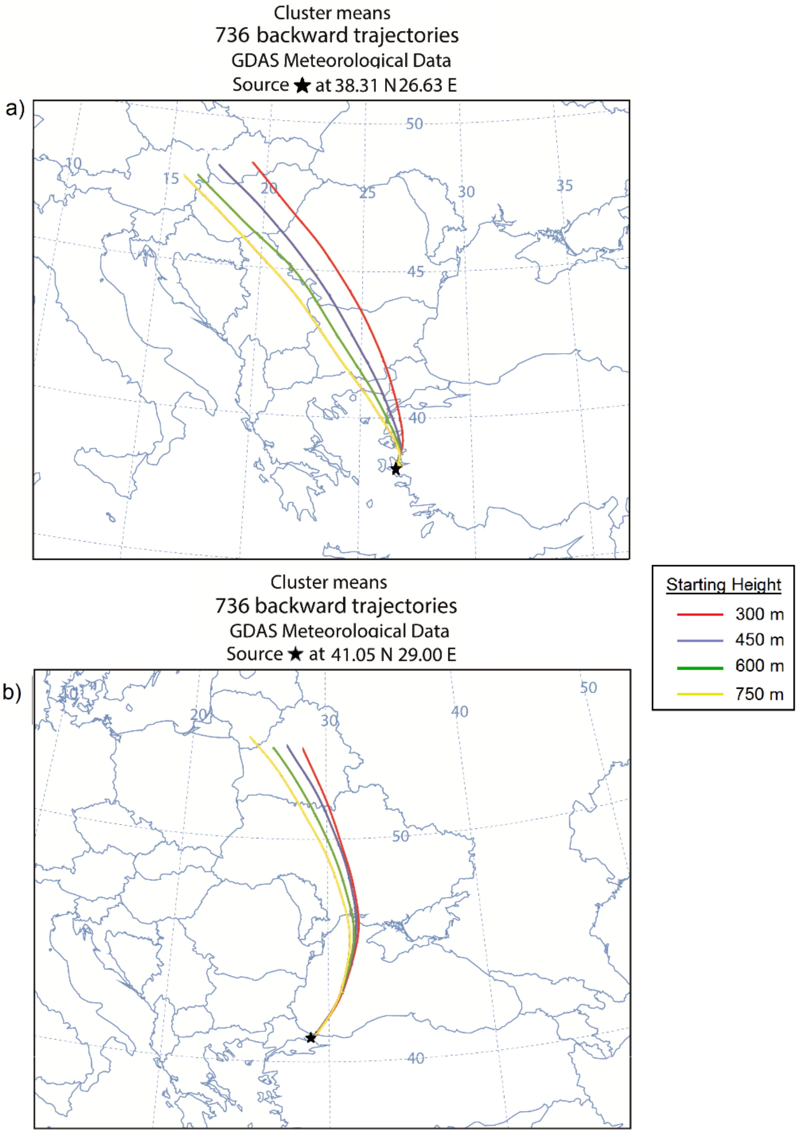


Figure 4.15. Clusters created for the trajectories with different starting height for a) Izmir and b) Istanbul station

4.2.2. Potential Source Regions (PSCF) of OCPs and PCBs

PSCF follows the behavior of a specific air mass with a known pollutant concentrations passing through a specific geographical cell and reaching to receptor site. In this study, the model was used to identify probable source regions for OCPs and PCBs by using back trajectories. PSCF analysis does not specify locations of sources, it rather points to probable source regions.

The ratio of α-HCH/γ-HCH during sampling period was calculated to estimate whether there is a fresh usage of HCH, and found as 0.20 and 0.70 for Izmir and Istanbul stations. Technical HCH was banned in 1970s/80s in different countries, while lindane was still used until 1990s (Breivik et al. 1999). Therefore, lindane at higher level was already expected, in comparison with α-HCH. The PCSF maps for HCH species measured at Izmir Station (Figure 4.16) showed that the area including Syria and Lebanon has the highest potential sources of lindane, whilst the potential sources of α-HCH extent over a wide area including Cyprus and Mediterranean Sea from the south; Black Sea, Ukraine, and Lithuania from the north with the possibility of >0.8, in addition to Syria and Lebanon. The main reason of determining Mediterranean and Black Sea as potential source regions might be short range atmospheric transport from potential sources near these regions. On the other hand, it was determined that the region including Greece, Macedonia, Bulgaria, Albania and Italy have the highest possibility to potential source of γ-HCH (>0.9), and western Russia, Romania, Moldova, and Ukraine are determined as having potential sources of α-HCH with higher possibility (>0.8) compared to the other countries for Istanbul station (Figure 4.17). Although all these countries signed to the Stockholm Convention, the convention was not entered into force only in Italy. Weiss et al. (2013) conducted a study to determine the levels of OCPs in butter samples collected from European countries, and showed that Ukraine, Romania, and Bulgaria have higher levels of HCH species, compared to central and northern Europe.

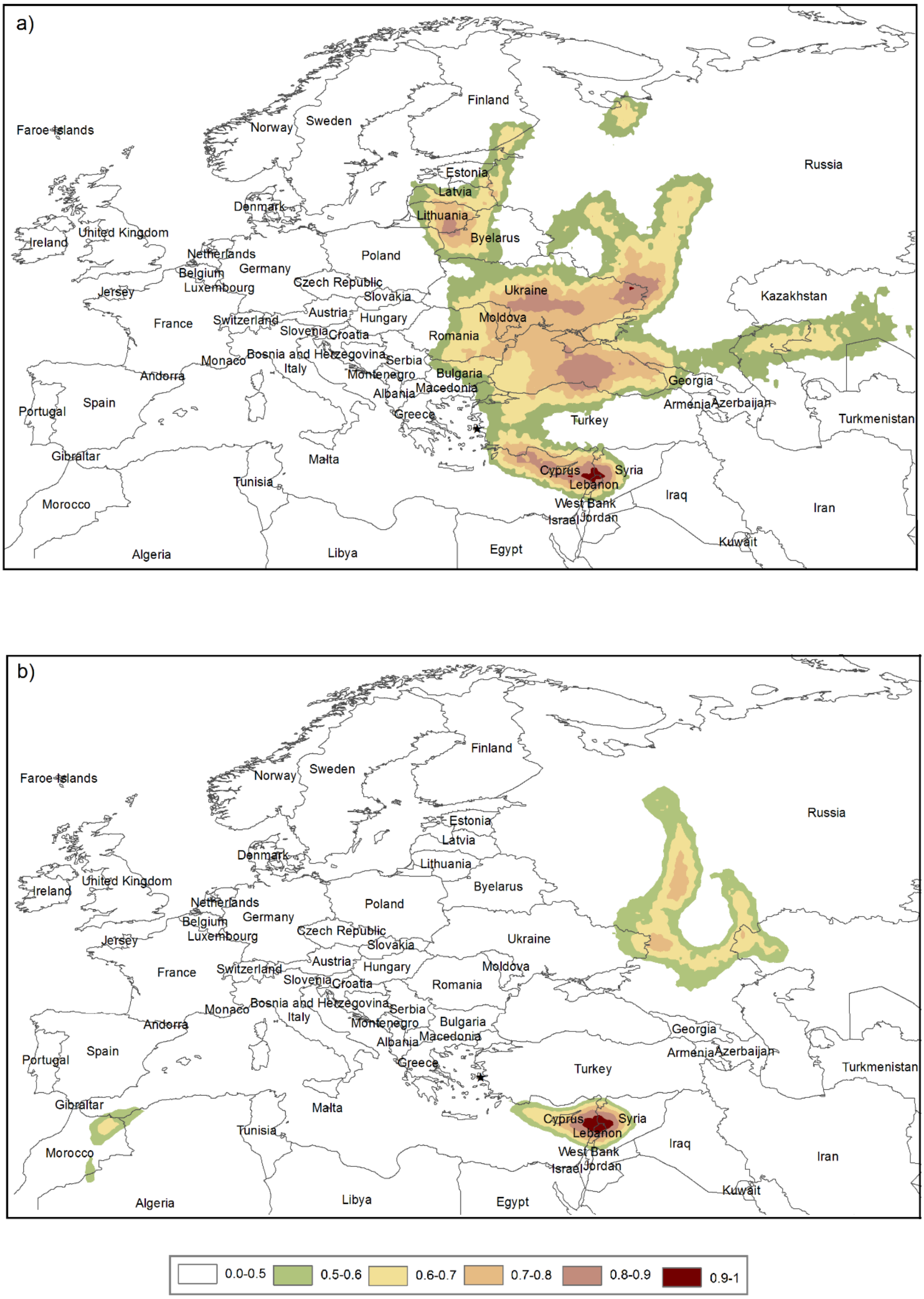


Figure 4.16. Potential source regions of a) α-HCH and b) γ-HCH for Izmir

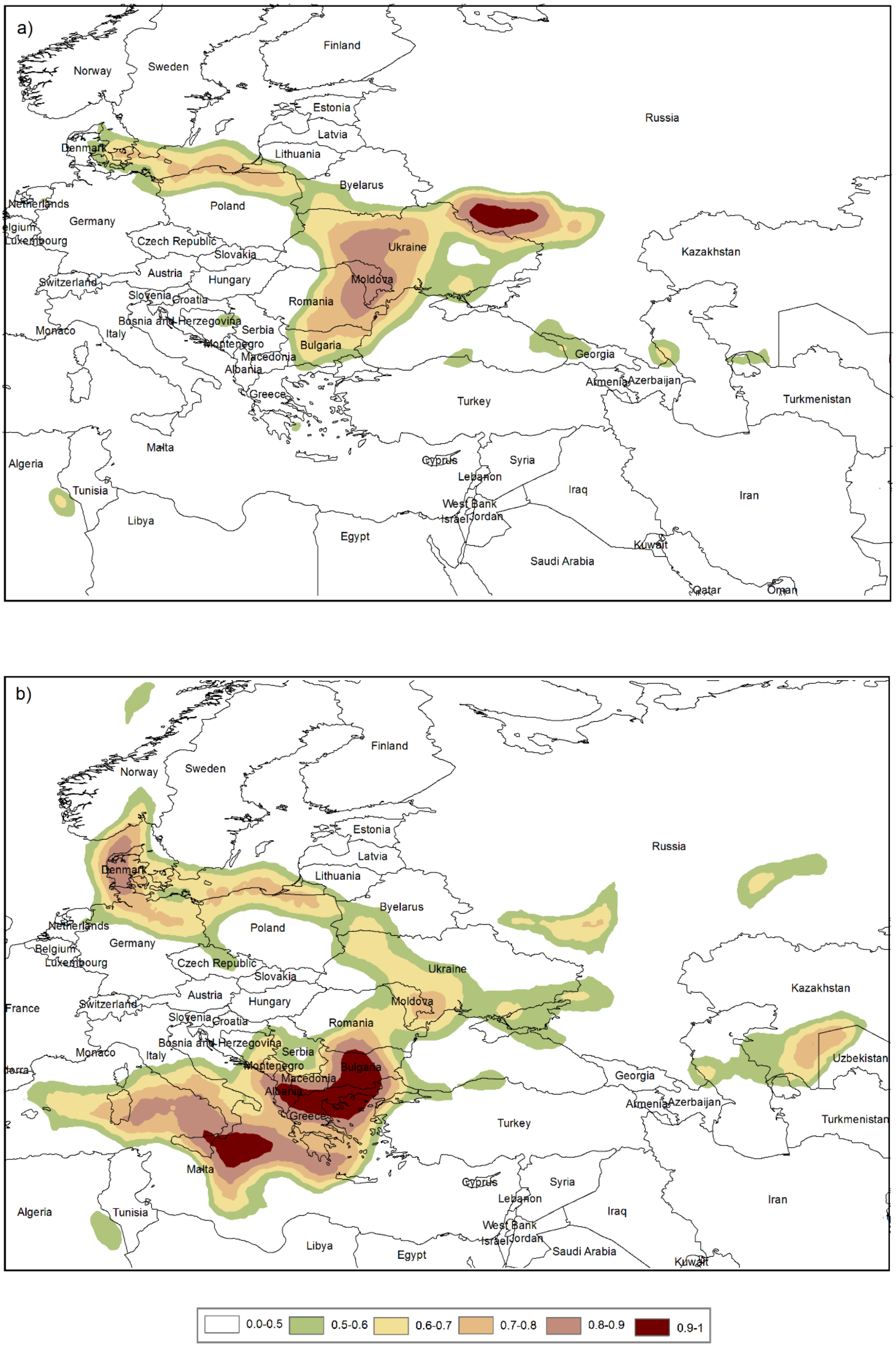


Figure 4.17. Potential source regions of a) α-HCH and b) γ-HCH for Istanbul

PSCF maps constructed for HCB pointed to different potential source regions for Izmir and Istanbul stations (Figure 4.18). High HCB concentrations measured in Izmir station were due to the influences of the areas in northeast, especially Rostov Oblast, Russian Republic of Kalmykia. However, southern west coastline of Turkey and Greece have the highest PSCF above 0.9 to potential HCB sources for Istanbul Station. The Stockholm Convention was entered into force in 2006 and 2011 in Greece and Russia Federation, respectively. Both being a new party compared to other parties, and HCB releasing as a by-product of many industrial applications might be strong reasons to identify Russia Federation as potential source region for HCB. The potential source area of HCB determined for Izmir Station, Rostov, is a headquarter in manufacturing of helicopter and farm machinery (Filatova 2011). Agricultural applications are dominant as well as heavy industry applications, one-third of Russia's vegetable oil is produced in the Rostov-on-Don from sunflowers (Novosti 2009). Besides, there is a developed agricultural sector in Kalmykia (Government of the Republic of Kalmykia 2002). Pribylova et al. (2012) also measured the maximum HCB level in the Russian Federation among other 22 countries of Central and Eastern Europe.

The constructed PSCF maps for the sum of HEPT and HEPX, as an oxidation product of HEPT (Figure 4.19) for Izmir station showed that the highest pollutant concentrations were originated from the areas in southeast (i.e., Syria and Lebanon). A wide area including Italy, Albania, Greece, Macedonia, Romania and Bulgaria was also determined as potential source region for HEPT and HEPX with a high possibility (>0.9), for Istanbul station. These countries were also found as potential sources of α-HCH. As mentioned before, all these countries signed the Stockholm Convention, but the convention was not entered into force only in Italy. Besides, European Union has banned the marketing and usage of HEPT since 1984 (EFSA 2007). Before that, Europe was the main consumer of HEPT with a high percentage of 60% in comparison with Asia, South America, Canada, USA and Africa (WHO-IPCS 1988).

High levels of one of the group of cyclodien pesticides (aldrin and its metabolite and insecticide dieldrin) were originated from both of Asian and European countries. It was shown that the contributions of the region including Cyprus, Syria, Lebanon, and a small part of northern coastline of Libya on aldrin+dieldrin levels are higher than others when considering the PSCF analysis of Izmir station. Although the two target OCP compounds have been forbidden in Turkey since 1970s, Mugla and surrounding area was found as having potential sources with a possibility between 0.50 and 0.70. On the other hand, the regions including Kazakhstan, Czech Republic, Slovakia, Hungary, and Romania were found as having larger potential sources of these pollutants, on the basis of PSCF analysis applied for Istanbul station (Figure 4.20). The PSCF results for endrin measured in Izmir and Istanbul stations were found as being similar with the results of aldrin+dieldrin (Figure 4.21).

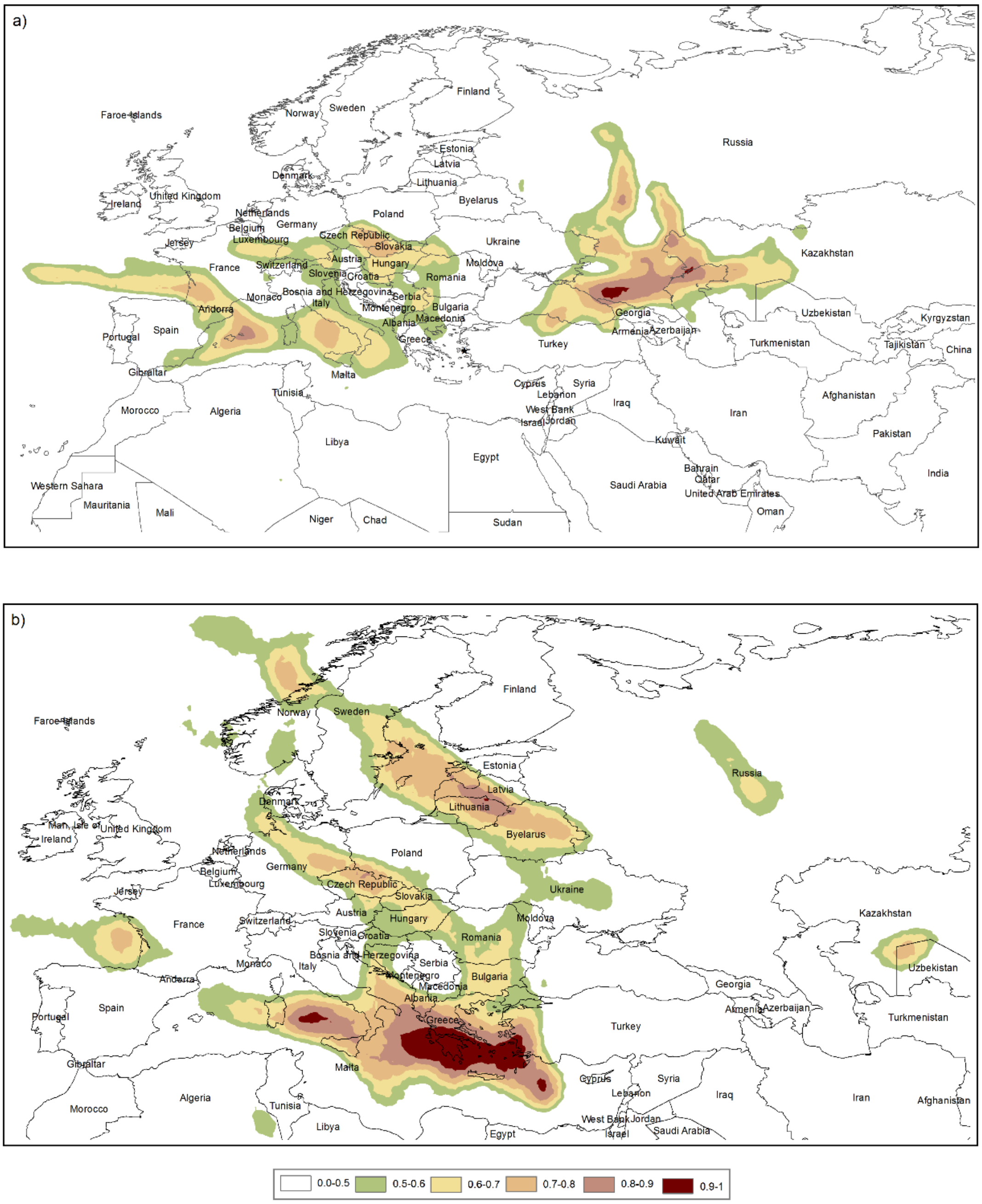


Figure 4.18. Potential source regions of HCB for a) Izmir and b) Istanbul

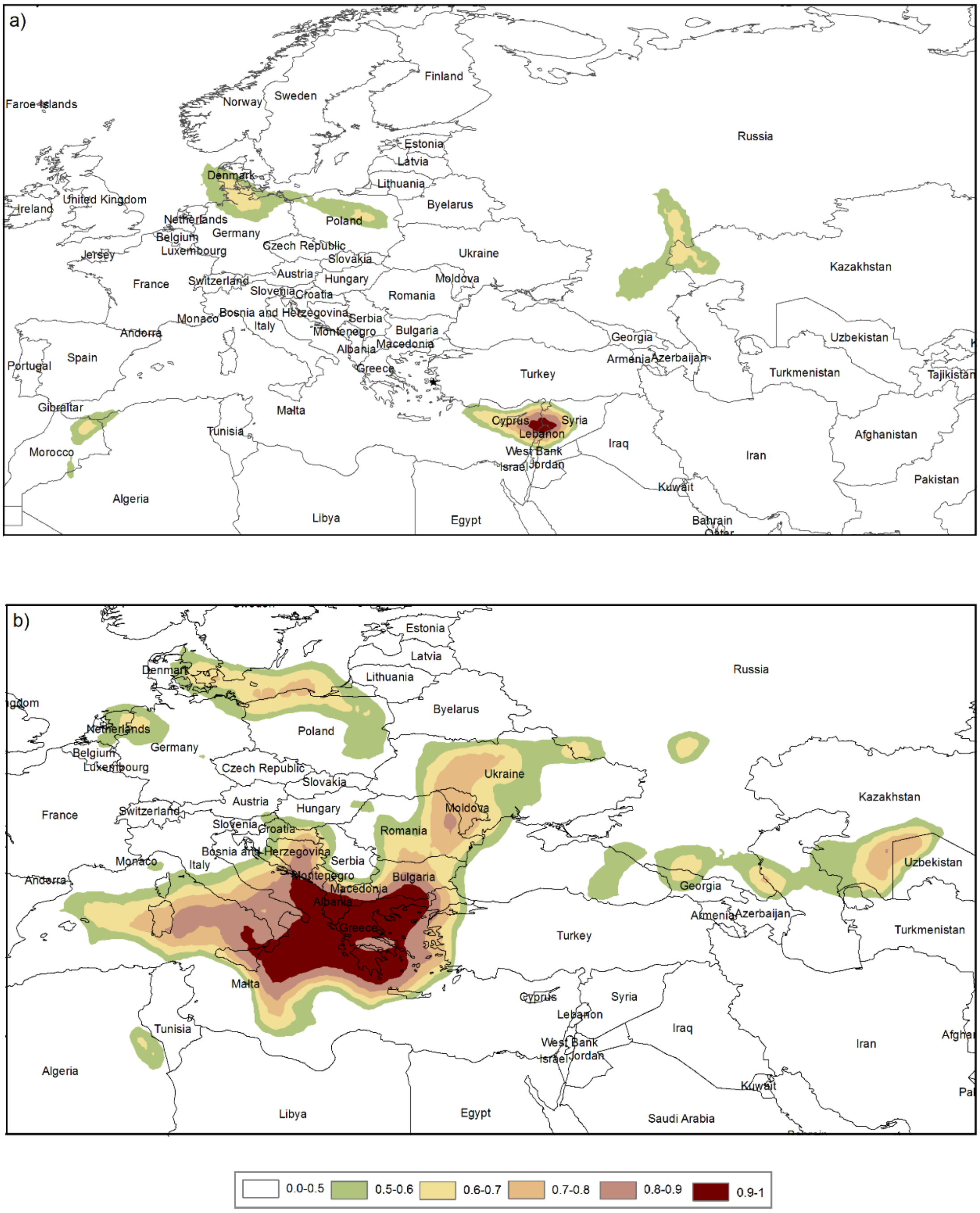


Figure 4.19. Potential source regions of HEPT+HEPX for a) Izmir and b) Istanbul

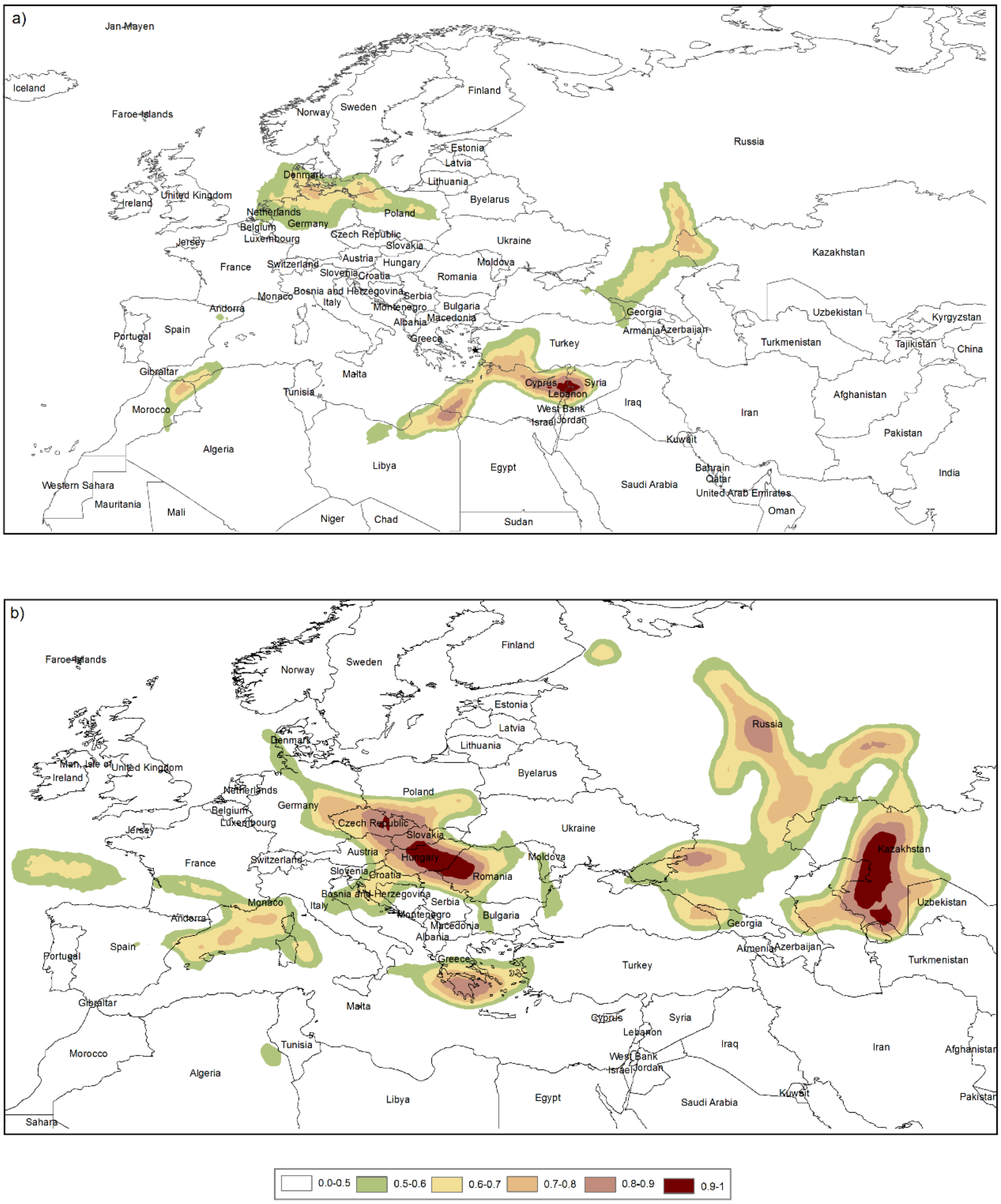


Figure 4.20. Potential source regions of aldrin+dieldrin for a) Izmir and b) Istanbul

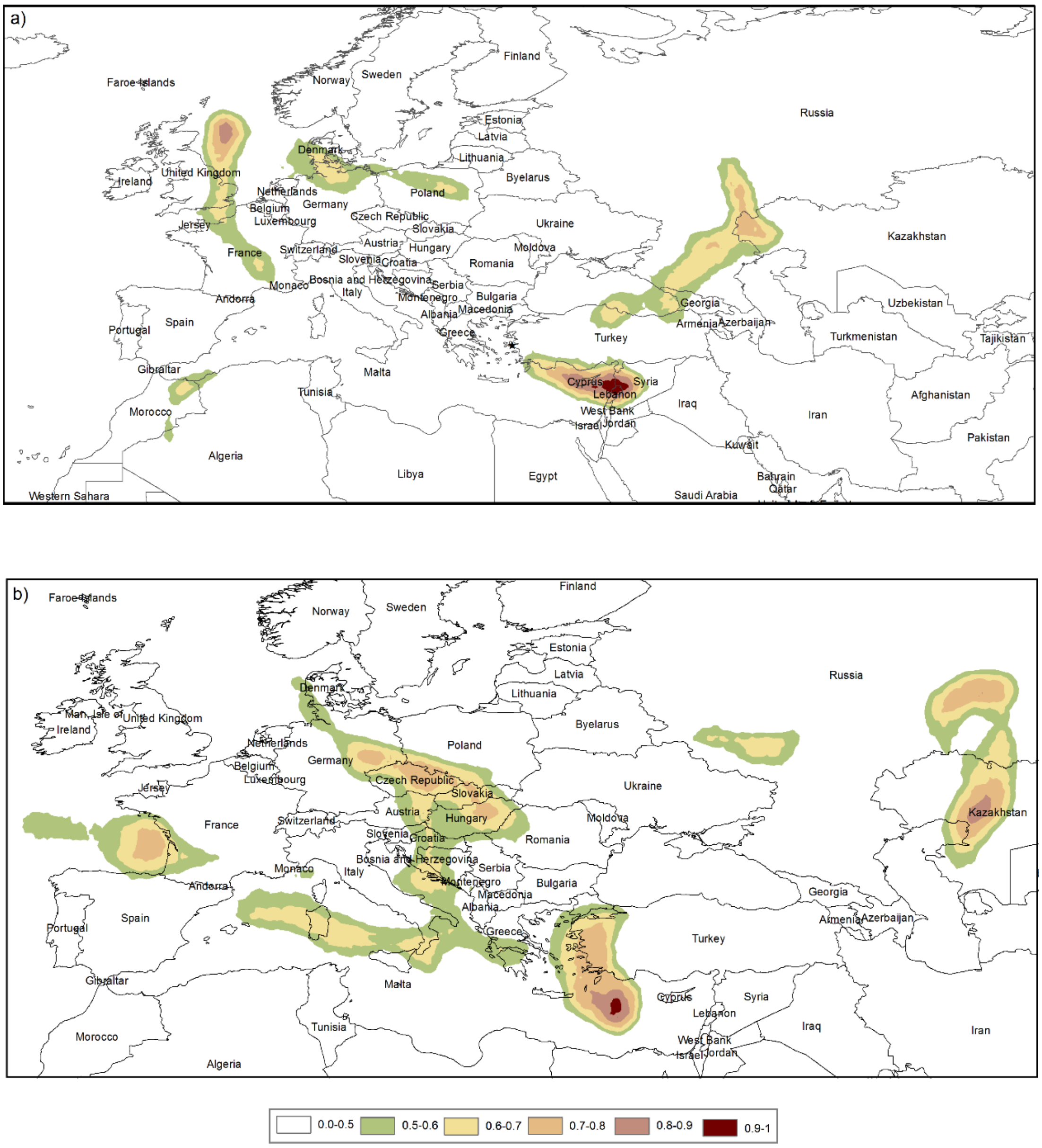


Figure 4.21. Potential source regions of endrin for a) Izmir and b) Istanbul

The PSCF maps constructed for the sum of the dominant DDT species (*o,p′*-DDE and *p,p′*-DDE) showed that the contribution possibility of the area including Cyprus, Syria, and Lebanon on the DDEs emission were above 0.80, based on PSCF results applied for Izmir station (Figure 4.22). Besides, similar to aldrin+dieldrin, Mugla and surrounding area was found to be a potential source with a PSCF between 0.70 and 0.80. Kazakhstan was determined as another potential source region for DDEs. The Stockholm Convention was entered into force in 2007 in Kazakhstan, and in 2011 in Russia Federation which is neighboring country of Kazakhstan. The higher concentration of DDE in this study might be explained with historical usage of DDT in this region. DDT most probably broke down with time and converted into DDEs. When compared to literature studies about the level of DDTs in soil conducted before ban and restriction, it was shown that the concentration of DDTs in soil ranged from Queensland, Australia to Russia Federation and Uzbekistan which are neighboring countries of Kazakhstan (Galiulin and Bashkin 1996, Cavanagh et al. 1999).

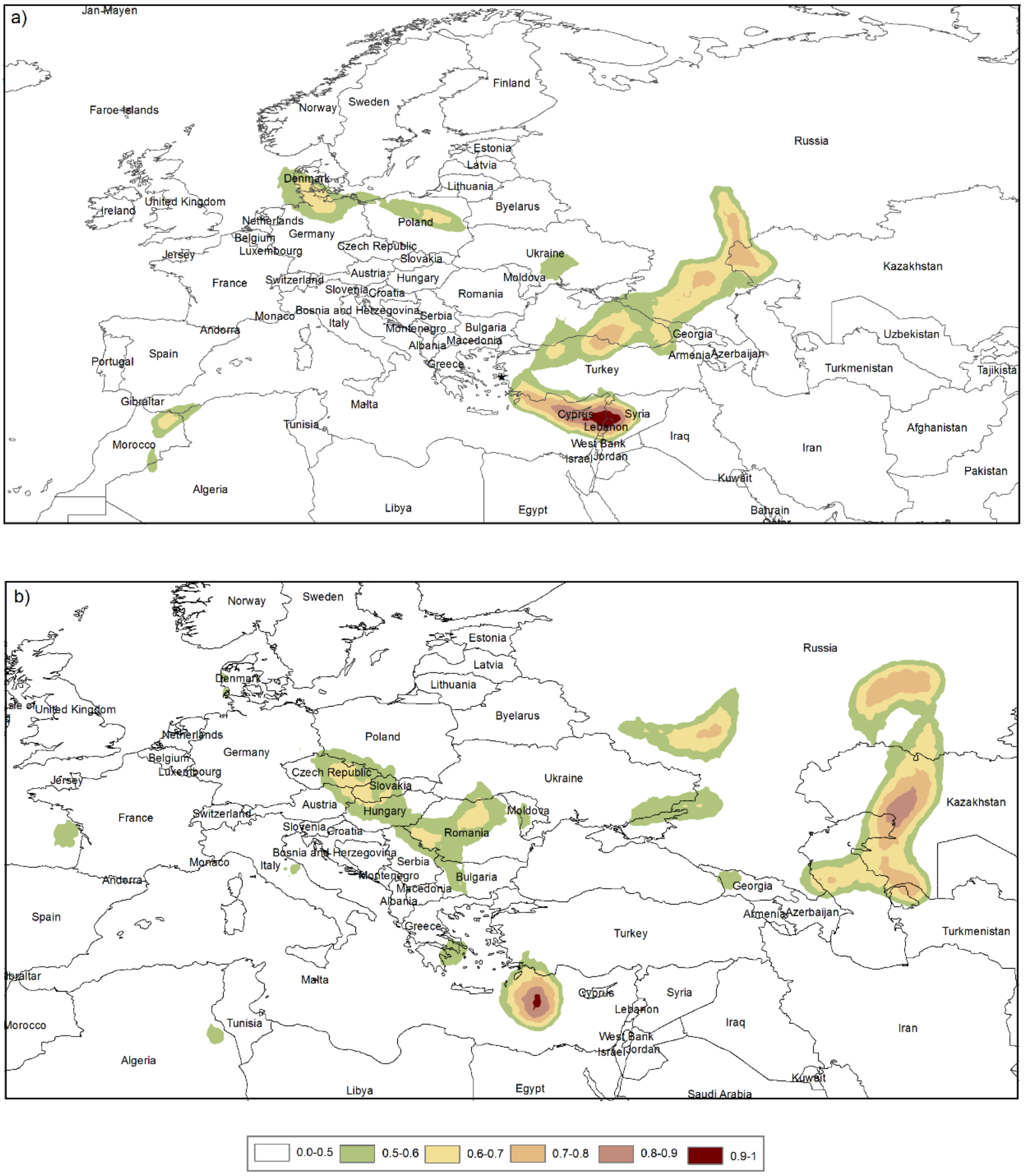


Figure 4.22. Potential source regions of DDEs for a) Izmir and b) Istanbul

Cyprus, Syria, Lebanon (based on PSCF results for Izmir station), Mugla, and surrounding area (based on PSCF results for Istanbul station) were again found as the potential source regions for the targeted endosulfans (Figure 4.23). The ratio of Endo-I/Endo-II is used to support that there is no usage of recent commercial endosulfan. Commercial endosulfan is a mixture of Endo-I and Endo-II with a ratio of 2.33 (Rice et al. 1997). It is known that Endo-II is more persistent and stable in the environment in comparison with the Endo-I. The ratio was calculated as 1.55 for Izmir, indicating that there was no fresh endosulfan input. The ratio for Istanbul was found as 2.30 which was close to the value of 2.33. Endosulfan has been banned since 2011 in order to eliminate production and use of it. The endosulfans adsorbed on the soil due to recent history usage in southwestern Aegean Region might be most probably vaporized with warmer temperature and found as a potential source.

The ratio of CC/TC was used to determine whether there is no usage of technical chlordane, or not. The ratio of CC/TC in technical chlordane is 0.77 (Sovocool et al. 1977). The degradation rate of TC is higher than CC, thus the conversion of TC occurs more rapidly in comparison with CC. Therefore, the ratio < 0.77 refers fresh usage of technical chlordane. The calculated ratio for Izmir station (0.39) were found below 0.77 in this study, implied recent usage of technical chlordane. If there was no illegal use near the station, these compounds might be released to the atmosphere anywhere in which are still used, then reached the sampling site thru long range atmospheric transport. The PSCF map of chlordane (CC+TC) for Izmir station (Figure 4.24) showed that the prevailing source regions appear from Russia, Syria, Lebanon, and Tunisia with the possibility of >0.9. Air masses transported from Kazakhstan and Italy, contributed to the higher levels of chlordanes. According to results of PSCF model applied for Istanbul Station, Bosnia-Herzegovina, Poland, and Moldova were found as other potential source regions for chlordanes with a PSCF from 0.50 to 0.80. All of these countries are parties of Stockholm Convention. This chemical is still used in China (except Hong Kong and Macau Special Administrative Regions of the People's Republic of China) as a termiticide, and it is produced in eastern China (Jaward et al. 2005). Therefore, chlordane might have been transported from China to Russia and Kazakhstan.

Syria and Lebanon were found the most probable potential source regions on the basis of PSCF results for Mirex measured in Izmir station, like for the most of targeted pollutants (Figure 4.24.c). Mirex was detected in the gas phase with a <25%

percent of the samples collected from Istanbul station, thus PSCF map was not constructed for Istanbul Station.

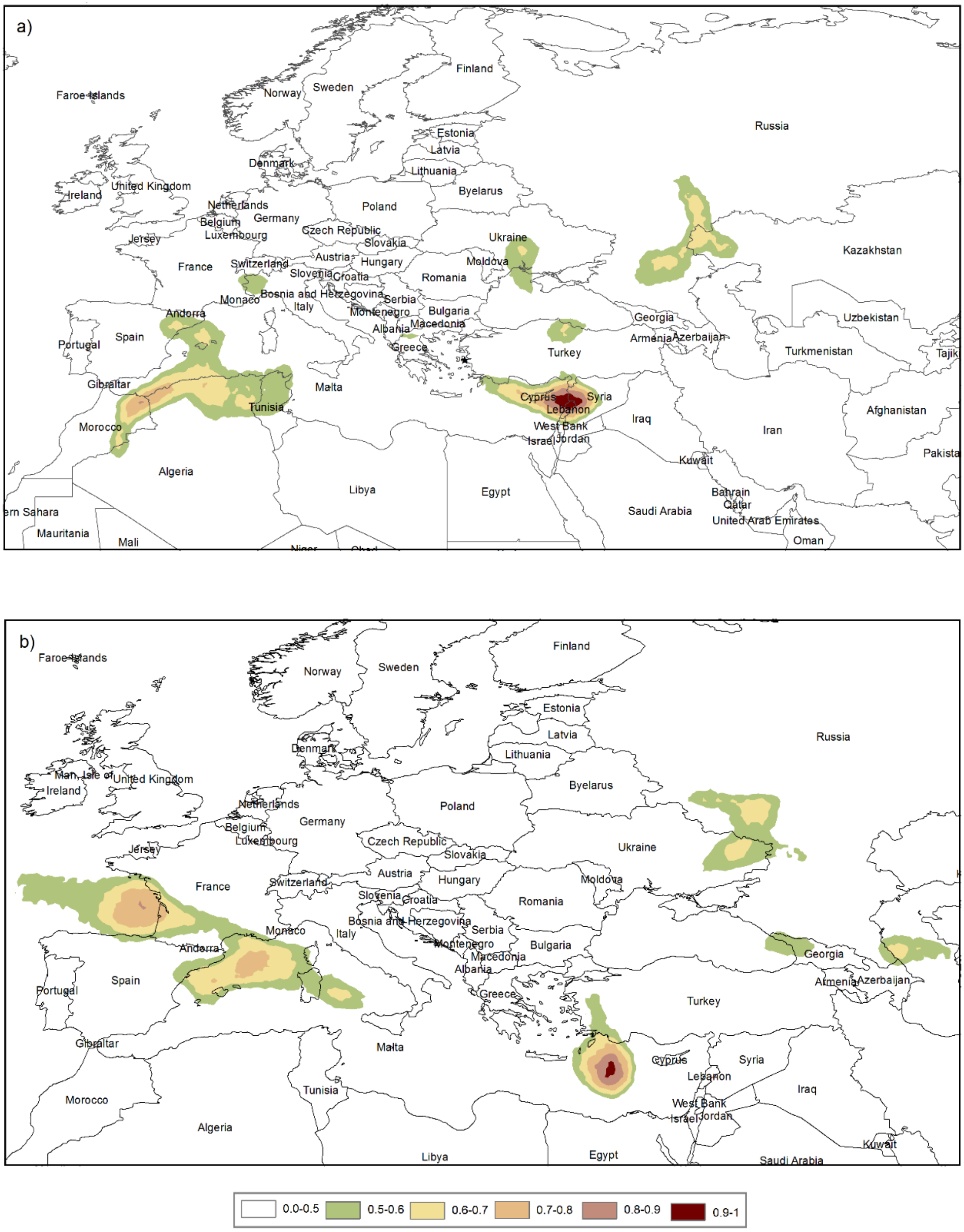


Figure 4.23. Potential source regions of endosulfans for a) Izmir and b) Istanbul

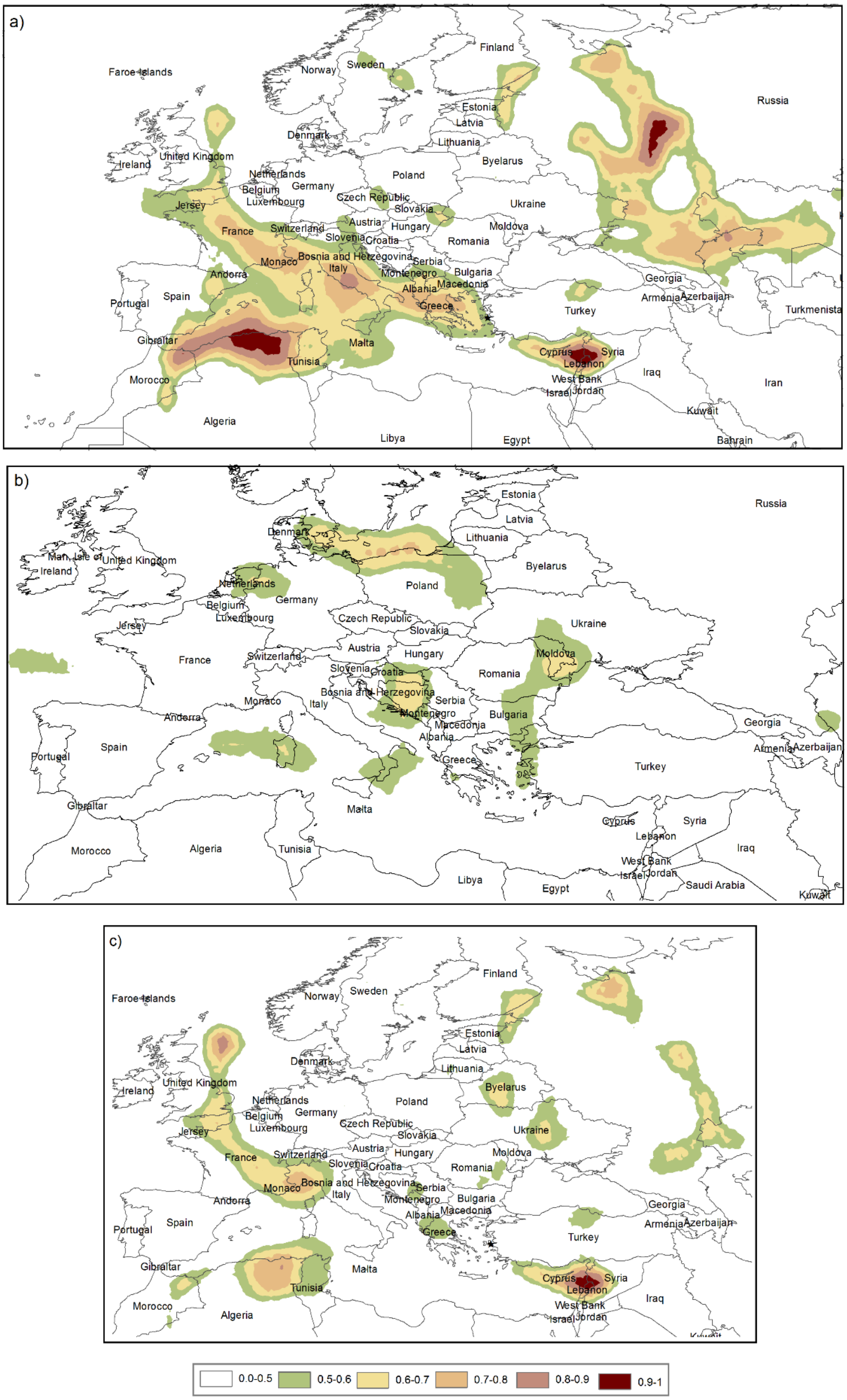


Figure 4.24. Potential source regions of CC+TC for a) Izmir and b) Istanbul, and c) potential source regions of Mirex for Izmir

The constructed PSCF maps for Σ_{43}PCBs pointed to the region where Syria and Lebanon is as having potential sources with the highest possibility of >0.90, according to Izmir station data. In addition, regions of Russia Federation and Kazakhstan (Asian), Denmark and Poland (Europe), and Tunisia and Morocco (African) were found as the following potential source regions with higher PSCF from 0.50 to 0.70. When PCB homolog groups are considered individually, Syria and Lebanon have the highest contribution of potential sources of each PCB homolog group, except octa-CBs. The high level concentrations of tri-CBs were dominantly originated from Russia Federation, where Stockholm Convention was entered into force in 2011, as well as Syria and Lebanon. The industrial applications in Rostov region might be the reason for the levels of tri-CBs, as it also was the probable region for the HCB levels. The PSCF results for the remaining PCB homolog groups were similar to those found for Σ_{43}PCBs. For Istanbul, the high possibility of potential sources of Σ_{43}PCBs was found in regions of Czech Republic, Slovakia, Hungary, Romania, and Albania with the value of >0.9, followed by those around Italy and Kazakhstan with the possibility from 0.80 to 0.90. When considered tetra-CBs homolog group, regions in Southern Europe including Albania, Greece and Italy was remarkable with the highest PSCF (>0.90) and spreading over a wide area. Pribylova et al. (2012) was also found the highest PCB level in Ust-Kamenogorsk, Kazakhstan, followed by an urbanized/industrialized site in Romania in a study that considered a wide area that covers the Central and Eastern Europe.

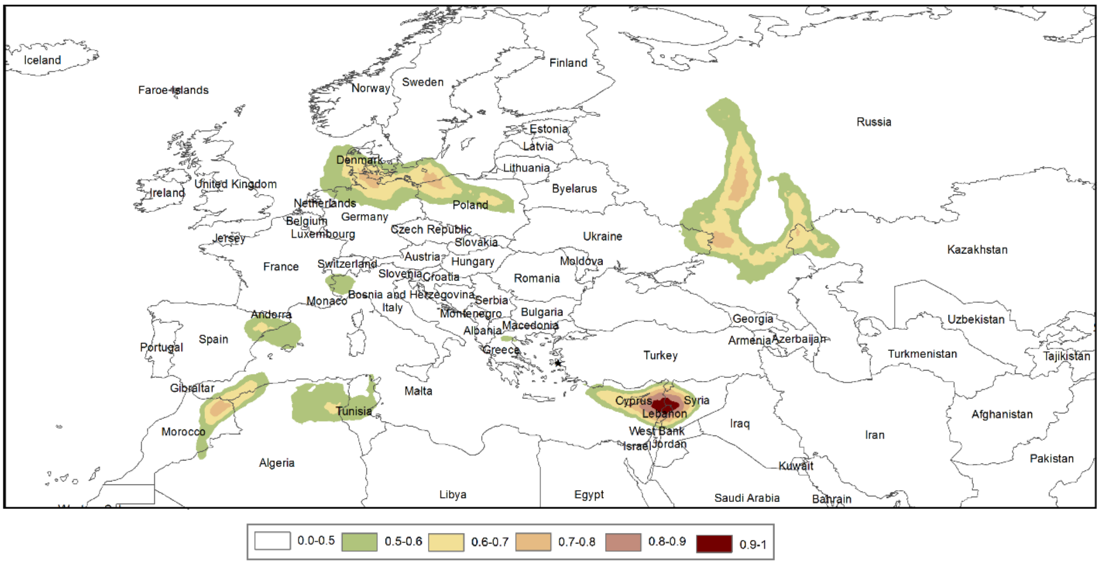


Figure 4.25. Potential source regions of Σ_{43}PCBs for Izmir

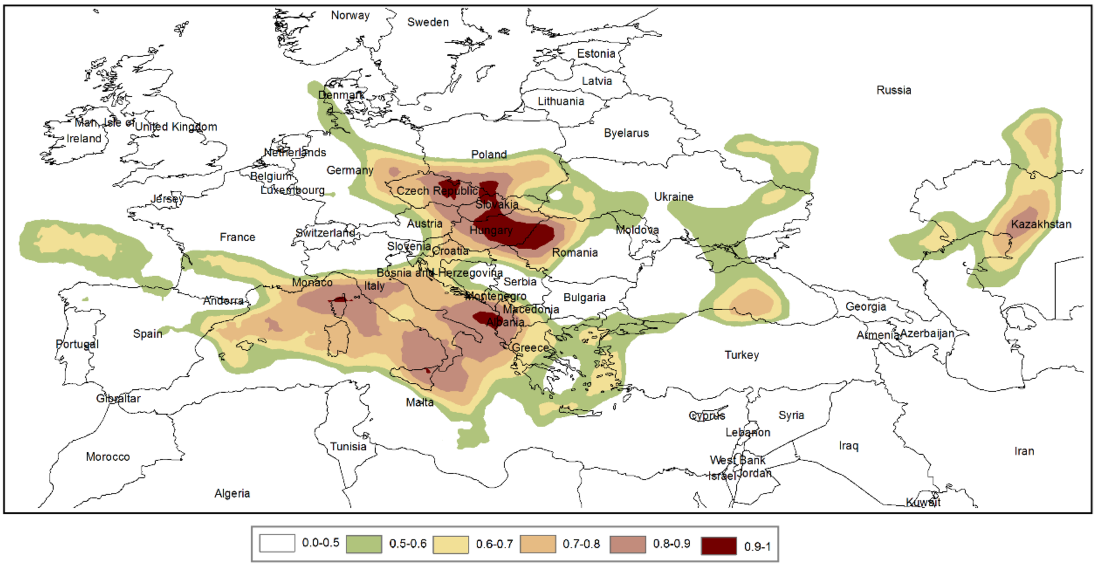


Figure 4.26. Potential source regions of Σ_{43}PCBs for Istanbul

It was found that the air masses came to Izmir and Istanbul stations predominantly from N-NW and N-NE during sampling period, respectively. However, the results of PSCF modelling pointed to different potential source regions for targeted pollutants in different continents. This case can be explain with the principle of PSCF analysis. PSCF is used to the ratio of the number of high concentration endpoints to the number of total endpoints in a specified grid cells, though the back-trajectory analysis is not used to the concentration levels of pollutants, only to the meteorological data.

Regions around Syria and Lebanon were determined as having the largest potential sources for all of the targeted pollutants except for HCB. Lebanon and Syria enforced the Stockholm Convention in their countries in 2003 and 2004, respectively. However, there is not any study about the levels and sources of the targeted pollutants in these countries. It was also not found any formal information about usage of these chemicals or their formations as by-products in this region at war. Regions in Russia Federation and Kazakhstan were found as other significant potential source regions for α-HCH, HCB, chlordane, aldrin+dieldrin, DDEs, and PCBs. Russia Federation have started to enforce the Stockholm Convention in 2011, which is a later year compared to the other countries. The targeted OCPs are still used in China which is neighboring country that may be the main source. It was also showed that there are many other potential sources for different pollutants in Europe such as Ukraine, Romania, Italy, Greece, Bulgaria, Macedonia, Sweden, Poland, etc.) which indicates that OCPs and PCBs are current problems in Europe, in agreement with (Pribylova et al. 2012).

4.3. Population Exposure and Carcinogenic Risks

Monte Carlo simulation was implemented to estimate population exposure and risks for inhalation route. Fitted distributions for each input variable to the exposure-risk models, and their parameter values are presented in Table 4.1.

Table 4.1. Fitted distributions for exposure-risk model input variables

Input Variable^a	**Fitted Distribution**	**Distribution Parameters^b**	**AD^c**	**KS^d**
Izmir Station				
α-HCH concentration	Gamma	Loc=1.23 Scale=18.19 Shape=0.63	0.4301	0.1181
γ-HCH concentration	Lognormal	Mean=46.58 SD=151	1.8243	0.2105
HCB concentration	Beta	Alpha=2.34 Beta=5.00 Scale=149.85	0.4356	0.1112
HEPT concentration	Lognormal	Mean=62.89 SD=218.14	0.4678	0.1080
DDEs concentration	Lognormal	Mean=57.78 SD=175.42	0.2955	0.0864
CC+TC concentration	Gamma	Loc=0.63 Scale=4.62 Shape=1.31	0.2160	0.0829
Dioxin-like PCB concentration	Weibull	Loc=-0 Scale=0 Shape=0.81	0.4166	0.1112
Nondioxin-like PCB concentration	Gamma	Loc=0 Scale=167.91 Shape=1.30	1.1540	0.1572
α-HCH CDI	Lognormal	Mean=1.15 SD=1.84	2.7601	0.0417
γ-HCH CDI	Lognormal	Mean=4.43 SD=16.03	0.4319	0.0216

(Cont. on next page)

Table 4.1 (Cont.)

Input Variable[a]	**Fitted Distribution**	**Distribution Parameters**[b]	**AD**[c]	**KS**[d]
Izmir Station				
HCB CDI	Gamma	Loc=0.11 Scale=1.88 Shape=2.22	0.3171	0.0163
HEPT CDI	Lognormal	Mean=6.09 SD=24.23	0.1487	0.0143
DDEs CDI	Lognormal	Mean=5.61 SD=19.47	0.2913	0.0173
TC CDI	Gamma	Loc=0.03 Scale=0.50 Shape=1.19	0.9035	0.0306
Σ_{43}PCBs CDI	Gamma	Loc=0.01 Scale=18.02 Shape=1.08	1.0809	0.0254
Istanbul Station				
α-HCH concentration	Extreme Value	Mode=10.36 Scale=8.47	0.2787	0.0950
γ-HCH concentration	Logistic	Mean=21.47 Scale=9.29	0.5029	0.1160
HCB concentration	Triangular	Min=-1.59 Likeliest=37.54 Max: 86.64	0.1681	0.0879
HEPT concentration	Gamma	Loc=0.85 Scale=22.10 Shape=0.54	0.9486	0.1677
Dieldrin concentration	Gamma	Loc=3.23 Scale=43.99 Shape=0.43	0.6737	0.1648
p,p′-DDE concentration	Exponential	Rate=0.02	0.3061	0.1058
TC concentration	Extreme Value	Mode=2.14 Scale=1.59	0.9545	0.1421
Dioxin-like PCB concentration	Weibull	Loc=-0 Scale=0 Shape=1.14	0.4377	0.1157
Nondioxin-like PCB concentration	Weibull	Loc=-104.27 Scale=220.14 Shape=5.09	0.2515	0.0860

(Cont. on next page)

Table 4.1 (Cont.)

Input Variable[a]	**Fitted Distribution**	**Distribution Parameters**[b]	**AD**[c]	**KS**[d]
Istanbul Station				
α-HCH CDI	Extreme Value	Mode=0.92 Scale=0.79	4.0461	0.0526
γ-HCH CDI	Extreme Value	Mode=1.09 Scale=1.57	6.1224	0.0598
HCB CDI	Weibull	Loc=-0.07 Scale=4.26 Shape=1.67	1.1196	0.0291
HEPT CDI	Weibull	Loc=0.03 Scale=0.92 Shape=0.76	4.0701	0.0497
Dieldrin CDI	Lognormal	Mean=1.77 SD=2.69	6.6184	0.0644
p,p′-DDE CDI	Gamma	Loc=0.01 Scale=5.59 Shape=0.91	0.6504	0.0252
TC CDI	Extreme Value	Mode=0.18 Scale=0.15	4.1168	0.0427
Σ_{43}PCBs CDI	Extreme Value	Mode=6.54 Scale=4.55	0.3562	0.0193

[a] Unit of Concentration : pg/m^3, unit of CDI: pg/kg/day
[b] SD: Standard Deviation
[c] AD: Anderson- Darling
[d] KS: Kolmogorov-Smirnov

The estimated 95th percentile inhalation exposure for individual OCPs ranged from 1.80 to 23.14 pg/kg/day and from 0.74 to 16.47 pg/kg/day for Izmir and Istanbul stations, respectively (Table 4.2). Minimum CDI values were found for chlordanes for both of the two stations, whilst exposures to HEPT and *p,p′*-DDE were estimated at the highest values, compared to that of other OCPs. The estimated 95th percentile inhalation exposure for Σ_{43}PCBs was also found as 60.78 and 19.49 pg/kg/day for Izmir and Istanbul stations, respectively. However, these values are underestimations since they are based on the six month measurement survey which covers from May to Oct 2014. Because these compounds are generally found at higher concentrations during the warmer months compared to the colder months, it would be a reasonable conservative to assume an equal exposure for the remainder of the year, which would approximately double the listed levels in Table 4.2.

Table 4.2. The estimated mean and 95th percentile inhalation exposure (CDI, pg/kg/day) and risk for individual OCPs and Σ_{43}PCBs

	Izmir Station				**Istanbul Station**			
	Mean		**95th percentile**		**Mean**		**95th percentile**	
Pollutant	**CDI**	**Risk**	**CDI**	**Risk**	**CDI**	**Risk**	**CDI**	**Risk**
α-HCH	1.11	6.99×10^{-9}	3.93	2.47×10^{-8}	1.41	8.87×10^{-9}	.57	2.25×10^{-8}
β-HCH	5.85	7.60×10^{-9}	14.8	1.92×10^{-8}	1.94	2.53×10^{-9}	5.59	7.27×10^{-9}
HCB	4.28	6.85×10^{-9}	9.54	1.53×10^{-8}	3.74	5.99×10^{-9}	8.30	1.33×10^{-8}
HEPT	6.06	2.73×10^{-8}	23.14	1.04×10^{-7}	1.11	5.02×10^{-9}	4.31	1.94×10^{-8}
Dieldrin	-	-	-	-	1.88	3.01×10^{-8}	7.19	1.15×10^{-7}
DDEs[a]	6.13	2.08×10^{-9}	21.4	7.26×10^{-9}	5.11	1.74×10^{-9}	16.47	5.60×10^{-9}
Chlordane[b]	0.62	2.17×10^{-10}	1.80	6.31×10^{-10}	0.24	9.54×10^{-10}	0.74	2.57×10^{-10}
Σ_{43}PCBs	19.55	4.46×10^{-8}	60.78	1.27×10^{-7}	9.11	2.11×10^{-8}	19.49	4.45×10^{-8}

[a] For Izmir station: o,p′-DDE+p,p′-DDE, for Istanbul station: p,p′-DDE

[b] For Izmir station: CC+TC, for Istanbul station: CC

The estimated 95th percentile inhalation risk levels for Izmir station ranged from 6.31×10^{-10} (CC+TC) to 1.04×10^{-7} (HEPT), whereas these statistics ranged from 2.57×10^{-10} (TC) to 1.15×10^{-7} (dieldrin) for Istanbul station. Zhang et al. (2013) investigated the population risks due to OCPs exposure in an industrialized and urbanized area in eastern China, and reported cancer risks of HCB, ∑DDTs, ∑HCHs, chlordane, and mirex levels as $< 10^{-6}$, in agreement with this study. In another study conducted in China by Wang et al. (2013), the cancer risk estimates for DDT, HCH, HCB, chlordane, and HEPT ranged between 1×10^{-6}-1×10^{-4}, higher than estimation of Zhang et al. (2013) and this study probably because in addition to inhalation, they also considered dermal exposure route which contributed with 82% to the overall exposure to OCP compounds, whereas this percentage was 1.57% for inhalation route. However, the dermal contact route was not considered in this study because the majority of particle phase concentrations of OCPs were BDL. The estimated 95th percentile inhalation risk levels associated with exposure to Σ_{43}PCBs were 1.27×10^{-7} and 4.45×10^{-8} for Izmir and Istanbul station, respectively. It was reported the cancer risk levels due to PCBs as $< 10^{-6}$ in the study conducted by Zhang et al. (2013) in China and $< 10^{-8}$ in the study conducted by Vilavert et al. (2014) in Spain. Estimated risk frequency histograms and fitted distributions for simulated population risks due to inhalation exposure of HEPT for Izmir station, dieldrin for Istanbul station, and Σ_{43}PCBs for both of the stations are shown in Figure 4.27.

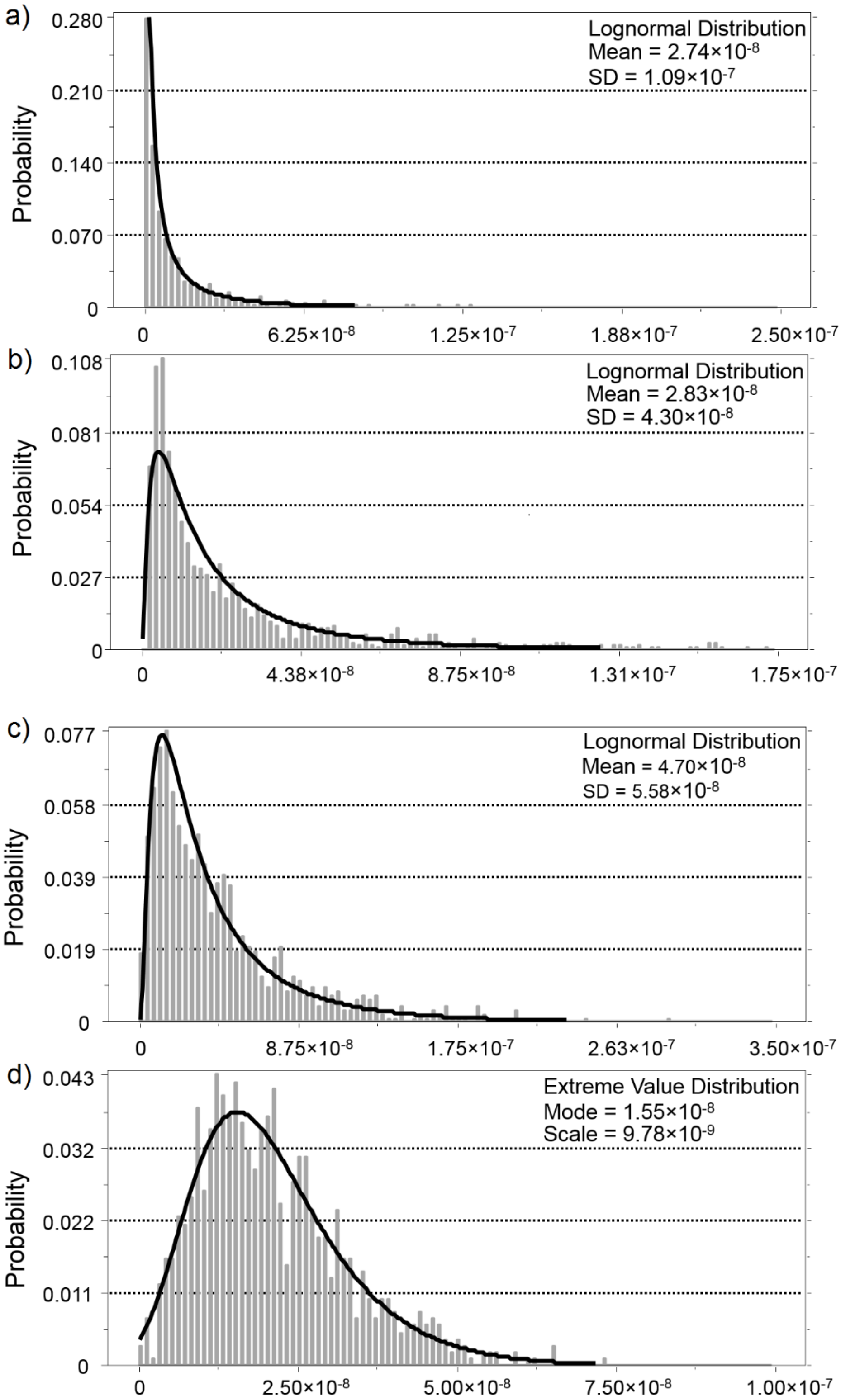


Figure 4.27. Fitted probability distributions of cancer risk due to exposure of a) HEPT for Izmir and b) dieldrin for Istanbul, and exposure of Σ_{43}PCBs for c) Izmir and d) Istanbul

The acceptable carcinogenic risk is defined as one in a million chance of additional human cancer over a 70 year lifetime (10^{-6}) by USEPA. Whilst the risk levels below 10^{-6} are acceptable, the risk levels above 10^{-4} indicates considerable potential health risks. In this study, all the estimated risk levels based on both of the mean and 95% percentile values for individual OCPs and Σ_{43}PCBs were found as $<10^{-6}$, indicating acceptable risk levels.

When the risk levels estimated for Izmir and Istanbul stations are compared, the ranges of risk levels due to exposure of individual OCPs are similar to each other whereas this range for exposure of Σ_{43}PCBs in Izmir station was about 3 times higher than that in Istanbul station, based on their 95% percentile risk levels. The main reason for the difference between the risk levels associated with exposure of Σ_{43}PCBs in Izmir and Istanbul station was the difference between concentrations of Σ_{43}PCBs in Izmir (232±224 pg/m^3) and Istanbul (104±48 pg/m^3) stations.

4.3.1. Sensitivity Analysis

Sensitivity analysis was conducted to determine the influence of each input variable on exposure-risk as the percent contribution to variance. HEPT and dieldrin were selected as model OCPs for sensitivity analysis in Izmir and Istanbul stations, respectively. The risk level due to exposure of HEPT in Izmir station was predominantly affected from total (gas+particle) concentration of HEPT with the percentage of 93%. Besides, total (gas+particle) concentration of dieldrin played the most important role on the risk level associated with exposure of dieldrin in Istanbul station with the contribution of 90%. It was also shown that variation in the total (gas+particle) concentrations of non-dioxin like PCBs is the largest source of variation in exposure-risk, therefore, they play the most important role in determining the exposure-risks for both of the Izmir and Istanbul stations and with the contributions of 78% and 53%, respectively.

4.3.2. Uncertainty Analysis

Results of the uncertainty analysis in the simulated risk are given in Table 4.3 as descriptive statistics for a chosen set of distribution percentiles and the mean. Coefficient of variation (CV) was calculated as 8 % for the median and mean in Izmir station, while this value was found as 14 % and 10 % for the 5th and 95th percentiles, respectively. CV was also calculated as <7 % for all of the median, mean, 5th percentile, and 95th percentile for OCPs in Istanbul station. The uncertainty for the Σ_{43}PCBs was lower with CV <3 % for the median, mean, and 95th percentile in both of the sampling stations, whereas it was 6 % in Izmir station and 10 % in Istanbul station for the 5th percentile, indicating uncertainties arisen from the Monte Carlo process were low.

Table 4.3. Uncertainty in the estimated percentiles of estimated carcinogenic risk

	Statistic	**5th percentile**	**50th**	**Mean**	**95th**
Izmir Station					
	Minimum	2.33×10^{-10}	4.67×10^{-9}	2.17×10^{-8}	7.57×10^{-8}
	Maximum	5.05×10^{-10}	7.17×10^{-9}	3.47×10^{-8}	1.31×10^{-7}
OCP	Median	3.31×10^{-10}	5.68×10^{-9}	2.72×10^{-8}	9.72×10^{-8}
	Mean	3.44×10^{-10}	5.65×10^{-9}	2.74×10^{-8}	9.85×10^{-8}
	SD[a]	4.78×10^{-11}	4.28×10^{-10}	2.25×10^{-9}	1.02×10^{-8}
	Minimum	4.49×10^{-9}	2.91×10^{-8}	4.05×10^{-8}	1.05×10^{-7}
	Maximum	5.97×10^{-9}	3.49×10^{-8}	4.76×10^{-8}	1.38×10^{-7}
PCB	Median	5.26×10^{-9}	3.18×10^{-8}	4.41×10^{-8}	1.16×10^{-7}
	Mean	5.27×10^{-9}	3.19×10^{-8}	4.40×10^{-8}	1.17×10^{-7}
	SD	3.13×10^{-10}	1.08×10^{-9}	1.31×10^{-9}	4.17×10^{-9}
Istanbul Station					
	Minimum	2.83×10^{-9}	1.26×10^{-8}	2.97×10^{-8}	1.04×10^{-7}
	Maximum	3.65×10^{-9}	1.77×10^{-8}	3.68×10^{-8}	1.52×10^{-7}
OCP	Median	3.25×10^{-9}	1.49×10^{-8}	3.24×10^{-8}	1.29×10^{-7}
	Mean	3.21×10^{-9}	1.50×10^{-8}	3.26×10^{-8}	1.28×10^{-7}
	SD	1.53×10^{-10}	9.98×10^{-10}	1.28×10^{-9}	9.04×10^{-9}
	Minimum	3.58×10^{-9}	1.73×10^{-8}	1.94×10^{-8}	3.96×10^{-8}
	Maximum	6.14×10^{-9}	1.95×10^{-8}	2.12×10^{-8}	4.73×10^{-8}
PCB	Median	5.03×10^{-9}	1.84×10^{-8}	2.04×10^{-8}	4.37×10^{-8}
	Mean	4.84×10^{-9}	1.83×10^{-8}	2.03×10^{-8}	4.33×10^{-8}
	SD	4.88×10^{-10}	3.85×10^{-10}	3.54×10^{-10}	1.51×10^{-9}

[a] SD: Standard Deviation

CHAPTER 5

CONCLUSION

The concentration profiles of 22 targeted OCPs and 43 targeted PCBs were obtained for the ambient air of Izmir and Istanbul. Gas and particle phase samples were collected on weekdays for a 24-hour period between May and October 2014 from a background site in Izmir and an urban site in Istanbul. Potential source regions were estimated by applying back-trajectory modeling along with the use of PSCF. Exposure and carcinogenic risk levels associated with the route of inhalation were assessed by using Monte Carlo simulation.

The mean concentration of Σ_{22}OCPs was measured as 316 pg/m^3 in Izmir station and 216 pg/m^3 in Istanbul station. The most dominant OCP compound for Izmir was determined as HEPT (mean concentration of 61±126 pg/m^3), followed by γ-HCH, HCB, and DDEs. For Istanbul, p,p′-DDE and HCB (mean concentration of 54±57 and 41.27±18.38 pg/m^3) were found abundantly, compared to the other targeted OCPs. The detection of the targeted OCPs in gas phase were higher than in particle phase for both sampling stations. It was seen that higher levels of many targeted OCP compounds were measured in Izmir station. The main reason for the spatial variation might be the location of Izmir station which is in a background site where agricultural practices were applied more than in an urban site of Istanbul. The other reason might be the temperature difference between Izmir and Istanbul, thus quantity of volatilization from the soil into the air.

The mean total concentration of Σ_{43}PCB was calculated as 232±224 and 104±48 pg/m^3 in Izmir and Istanbul stations, respectively. PCB 28 and 18 (mean concentration of 22.26±18.79 and 19.30±13.63 pg/m^3, respectively) were found as the most dominant congeners for Izmir, PCB 18 had the highest mean concentration (15.82±10.44 pg/m^3), followed by PCB 44, 60, and 28 for Istanbul. The targeted PCBs were widely detected in gas phase. The abundance of lower chlorinated PCB congeners (especially tri- and tetra-CBs) can be associated with their high vapor pressures caused easier volatilization compared to PCBs with larger chlorine atoms which prefer to deposit and retain close to point of source. The contribution on total amount of PCBs decreased with an increase in number of chlorine atoms. The higher tri-, tetra-, and penta-CB levels were detected in Izmir in comparison with in Istanbul.

PSCF model was used to identify probable source regions for OCPs and PCBs by using back trajectories. The results of PSCF modelling pointed to different potential source regions for targeted pollutants in different continents. The largest potential sources for all of the targeted pollutants except for HCB were originated from regions around Syria and Lebanon. Another major potential source regions for α-HCH, HCB, chlordane, aldrin+dieldrin, DDEs, and PCBs were found as an area in Russia Federation and Kazakhstan. It was also determined that European countries Ukraine, Romania, Italy, Greece, Bulgaria, Macedonia, Sweden, and Poland have potential sources for different targeted pollutants.

Monte Carlo simulation was applied to estimate exposure and population risks via the route of inhalation. The estimated 95th percentile inhalation exposure for individual OCPs ranged from 1.80 to 23.14 pg/kg/day and from 0.74 to 16.47 pg/kg/day for Izmir and Istanbul, respectively. These statistics for Σ_{43}PCBs was found as 60.78 and 19.49 pg/kg/day, respectively. The carcinogenic risks associated with inhalation did not exceed the acceptable risk levels (10^{-6}) for any estimated risk levels based on the 95% percentile values for individual OCPs and Σ_{43}PCBs in both sampling stations. Sensitivity analysis suggests that the total (gas+particle) concentrations of targeted pollutants played the most important role on the risk levels for both sampling stations.

Simultaneous collection of soil, water, sediment, and air samples could give more detail idea about the deposition and volatilization processes, thus the correlations among the environmental surfaces. Probable source regions were just estimated in this study. Studies about the levels of OCPs and PCBs conducted in the probable source regions could give more information on whether there are any sources for the targeted pollutants, and help to assess accuracy of PSCF modelling. Besides, longer sampling period could be cause to reach more accurate results for PSCF modeling and Monte Carlo simulation.

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APPENDIX A

DETAILS ABOUT ANALYTICAL QUALITY ASSURANCE / QUALITY CONTROL

Table A.1. Results of laboratory control samples

Congener /Compound	PUF (pg/µL)		Filter (pg/µL)	
	Mean	SD[a]	Mean	SD
PCB 30	0.05	0.02	0.04	0.01
PCB 18	0.09	0.04	0.08	0.04
PCB 31	0.06	0.02	0.06	0.03
PCB 28	0.04	0.02	0.04	0.02
PCB 22	0.06	0.02	0.05	0.02
PCB 54	0.05	0.03	0.06	0.03
PCB 52	0.07	0.03	0.08	0.04
PCB 49	0.09	0.03	0.07	0.02
PCB 44	0.08	0.03	0.08	0.03
PCB 41/60	0.03	0.01	0.03	0.01
PCB 74	0.06	0.02	0.05	0.02
PCB 70	0.05	0.02	0.06	0.03
PCB 60	0.13	0.05	0.16	0.07
PCB 56	0.02	0.01	0.03	0.01
PCB 104	0.09	0.03	0.10	0.04
PCB 95	0.08	0.03	0.09	0.04
PCB 90/101	0.06	0.03	0.05	0.02
PCB 99	0.07	0.03	0.10	0.03
PCB 87	0.10	0.05	0.10	0.05
PCB 110	0.09	0.03	0.06	0.03
PCB 123	0.08	0.02	0.06	0.02
PCB 118	0.07	0.05	0.07	0.03
PCB 114	0.12	0.03	0.13	0.04
PCB 105	0.11	0.04	0.14	0.04
PCB 155	0.03	0.01	0.03	0.01
PCB 151	0.04	0.02	0.06	0.03
PCB 149	0.05	0.03	0.05	0.02
PCB 153	0.08	0.02	0.07	0.02
PCB 132	0.07	0.02	0.09	0.03
PCB 141	0.10	0.03	0.10	0.04
PCB 138	0.10	0.03	0.10	0.05
PCB 158	0.06	0.02	0.06	0.03
PCB 167	0.11	0.04	0.13	0.08
PCB 156	0.10	0.04	0.04	0.09
PCB 157	0.12	0.06	0.06	0.06
PCB 188	0.08	0.08	0.08	0.02
PCB 187	0.11	0.07	0.07	0.04
PCB 183	0.09	0.04	0.04	0.04
PCB 174	0.14	0.08	0.08	0.04
PCB 180	0.13	0.06	0.06	0.07
PCB 170	0.13	0.02	0.02	0.08
PCB 189	0.10	0.04	0.04	0.07
PCB 199	0.15	0.03	0.03	0.18
PCB 203	0.23	0.12	0.12	0.17
HCB	0.34	0.11	0.29	0.003
α-HCH	ND[b]		3.23	0.04
β-HCH	ND		ND	
γ-HCH	0.69	0.04	ND	
δ-HCH	ND		ND	
HEPT	ND		ND	
Aldrin	ND		ND	
HEPX	ND		ND	
CC	ND		ND	
TC	ND		ND	
o,p′-DDE	ND		ND	
TC	ND		ND	
Dieldrin	ND		ND	
o,p′-DDD	ND		ND	
p,p′-DDE	ND		ND	
Endrin	2.44	0.40	ND	
Endo-II	ND		ND	
o,p′-DDT	ND		ND	
p,p′-DDD	ND		ND	
EndoSO$_4$	ND		ND	
p,p′-DDT	ND		ND	

[a] SD: Standard Deviation
[b] ND: Not detected

Table A.2. Detailed information about GC/MS analysis

Congener/ Compound	Retention time (min)	Target ion	Qualifier ion 1	Regression Coefficient	Min conc. in calibration
PCB 30	12.047	256	258	0.998498	0.2
PCB 18	12.609	256	258	0.996501	0.2
PCB 31	14.549	256	258	0.998196	0.2
PCB 28	14.606	256	258	0.998633	0.2
PCB 22	15.373	256	258	0.999574	0.2
PCB 54	13.931	290	292	0.997652	0.2
PCB 52	16.177	290	292	0.998515	0.2
PCB 49	16.383	290	292	0.999104	0.2
PCB 44	17.165	290	292	0.999354	0.2
PCB 41/64	17.762	290	292	0.999556	0.2
PCB 74	18.949	290	292	0.998870	0.2
PCB 70	19.141	290	292	0.998340	0.2
PCB 60	20.015	290	292	0.999254	0.2
PCB 56	20.172	290	292	0.999048	0.2
PCB 104	19.652	324	326	0.998593	0.2
PCB 95	19.355	324	326	0.998157	0.2
PCB	20.570	324	326	0.997539	0.2
PCB 99	20.841	324	326	0.997961	0.2
PCB 87	21.942	324	326	0.998750	0.2
PCB 110	22.479	324	326	0.998646	0.2
PCB 123	23.747	324	326	0.999531	0.2
PCB 118	23.888	324	326	0.997480	0.2
PCB 114	24.454	324	326	0.998668	0.2
PCB 105	25.281	324	326	0.994432	0.2
PCB 155	20.051	360	362	0.999888	0.2
PCB 151	23.120	360	362	0.998454	0.2
PCB 149	23.761	360	362	0.988911	0.2
PCB 153	25.106	360	362	0.996875	0.2
PCB 132	25.178	360	362	0.996760	0.2
$^{13}C_{12}$PCB	25.288	338	-	-	-
PCB 141	25.774	360	362	0.998459	0.2
PCB 138	26.505	360	362	0.997271	0.2
PCB 158	26.609	360	362	0.998997	0.2
PCB 167	27.691	360	362	0.998316	0.2
PCB 156	28.472	360	362	0.994854	0.2
PCB 157	28.659	360	362	0.999221	0.2

(Cont. on next page)

Table A.2. (Cont.)

Congener/ Compound	**Retention time (min)**	**Target ion**	**Qualifier ion 1**	**Regression Coefficient**	**Min conc. in calibration**
PCB 188	24.692	394	396	0.997869	0.2
PCB 183	27.431	394	396	0.996033	0.2
PCB 174	28.087	394	396	0.996858	0.2
PCB 180	29.013	394	396	0.997005	0.2
PCB 170	29.859	394	396	0.991004	0.2
PCB 189	30.620	394	396	0.997722	0.2
PCB 199	29.340	426	428	0.997672	0.2
PCB 203	30.229	426	428	0.993854	0.2
PCB 194	31.459	426	428	0.996177	0.2
$^{13}C_{12}$PCB	14.663	268	270	0.999967	0.2
$^{13}C_{12}$PCB	16.219	302	304	0.999911	0.2
$^{13}C_{12}$PCB	20.584	336	338	0.999974	0.2
$^{13}C_{12}$PCB	25.105	374	372	0.999833	0.2
$^{13}C_{12}$PCB	26.494	374	372	0.999741	0.2
$^{13}C_{12}$PCB	29.382	406	408	0.999504	0.2
$^{13}C_{12}$PCB	32.891	508	510	0.999345	0.2
HCB	8.832	284	286	0.999761	1
α-HCH	8.837	255	253	0.993100	1
β-HCH	9.391	253	255	0.990847	1
γ-HCH	9.524	255	253	0.999704	1
δ-HCH	10.207	255	253	0.997076	1
HEPT	10.907	266	268	0.997586	1
Aldrin	11.538	237	235	0.999855	1
CC	12.774	410	412	0.999681	1
o,p′-DDE	12.939	246	248	0.999498	1
Endo-I	12.966	406	408	0.999327	1
TC	13.000	410	412	0.998765	1
Dieldrin	13.461	237	235	0.998784	1
o,p′-DDD	13.661	248	246	0.999424	1
p,p′-DDE	13.573	318	316	0.999943	1
Endrin	13.805	380	382	0.997534	1
Endo-II	14.047	406	408	0.996295	1
o,p′-DDT	14.310	248	246	0.996839	1
p,p′-DDD	14.338	248	250	0.998791	1
$EndoSO_4$	14.767	386	388	0.998809	1
p,p′-DDT	14.979	248	250	0.997181	2
Mirex	16.544	368	370	0.999452	1

Table A.3. Summary of recovery efficiencies (%) of target analytes

Analyte	Mean	SD[a]	Min	Max	Analyte	Mean	SD	Min	Max
PCB 30	87.14	8.72	75.42	101.08	PCB 114	80.90	9.86	68.08	91.42
PCB 18	68.17	6.79	59.83	76.67	PCB 105	77.65	19.75	62.50	114.9
PCB 31	81.43	11.03	64.83	98.42	PCB 155	73.35	7.53	65.17	83.08
PCB 28	65.17	6.56	59.08	77.08	PCB 151	76.15	8.70	65.75	86.25
PCB 22	71.56	8.30	61.75	82.75	PCB 149	76.97	8.21	68.25	86.25
PCB 54	70.32	8.09	59.58	81.67	PCB 153	64.71	7.63	56.42	74.33
PCB 52	72.57	8.13	61.17	82.25	PCB 132	72.28	8.81	62.58	82.50
PCB 49	70.58	6.70	63.33	80.50	PCB 141	79.54	8.77	67.58	88.58
PCB 44	72.68	8.44	63.00	81.75	PCB 138	100.1	13.00	74.08	108.3
PCB 41/60	71.64	7.70	61.75	81.58	PCB 158	76.97	7.37	68.33	84.33
PCB 74	77.47	8.75	66.92	91.17	PCB 167	84.57	11.66	69.92	98.25
PCB 70	73.85	8.76	64.25	87.58	PCB 156	87.58	9.83	76.92	99.08
PCB 60	79.35	5.99	71.42	85.42	PCB 157	84.33	9.58	73.75	96.75
PCB 56	72.49	6.47	66.33	81.83	PCB 188	78.07	8.29	68.33	86.50
PCB 104	70.01	8.18	59.42	79.17	PCB 187	86.08	10.74	75.75	99.50
PCB 95	74.10	8.50	64.08	82.92	PCB 183	86.46	10.09	73.92	97.00
PCB90/10	73.33	6.91	63.92	82.50	PCB 174	86.31	8.80	77.58	96.42
PCB 99	77.78	7.95	68.17	88.17	PCB 180	87.68	10.66	75.58	99.58
PCB 87	74.74	5.97	67.33	81.17	PCB 170	93.24	15.44	76.33	112.2
PCB 110	76.64	8.13	67.17	85.92	PCB 189	85.32	11.48	70.17	96.75
PCB 123	82.15	9.09	70.42	93.42	PCB 199	90.58	12.79	75.83	104.6
PCB 118	75.78	8.67	65.33	86.67	PCB 203	92.51	8.23	79.50	104.1
HCB	81	10	65	93	TC	88	10	72	99
α-HCH	74	13	59	90	Dieldrin	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	Endrin	103	13	84	115
HEPT	67	5	59	73	Endo-II	99	21	69	127
Aldrin	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	EndoSO_4	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] SD: Standard Deviation