

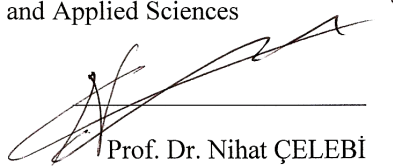
**CHARACTERIZATION OF PCBS, PAHS, AND
ORGANOCHLORINE PESTICIDES IN THE ATMOSPHERE OF
BOLU AND SOURCE APPORTIONMENT: GAS TO PARTICLE,
SOIL TO PARTICLE, SOIL TO GAS EXCHANGES**

**by
MUHAMMED ÖZ**

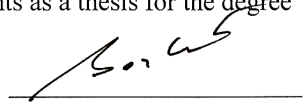
**THESIS SUBMITTED TO
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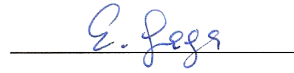
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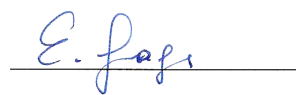
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ABSTRACT

CHARACTERIZATION OF PCBS, PAHS AND ORGANOCHLORINE PESTICIDES IN THE ATMOSPHERE OF BOLU AND SOURCE APPORTIONMENT: GAS TO PARTICLE, SOIL TO PARTICLE, SOIL TO GAS EXCHANGES

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In this study, 120 samples of particulate matter on glass fiber filters (GFF) and gas phase pollutants on polyurethane foam (PUF) were collected by using high volume air sampler. The sampler was placed on the roof of the presidency building in the campus of A.I.B.U., Bolu. Sixty daily samples were collected during 25th June-23rd August 2007 in summer time and 13th December 2007-10th February 2008 in winter time. Twenty-nine surface soil samples were collected from the 0.5 depth. The PUF and GFF samples were extracted by using soxhlet apparatus and soil samples were ultrasonically extracted. The extracted samples were eluted from the optimized Florisil and Alumina adsorption column. PCBs and PAHs were determined by gas chromatography-mass spectrometry (GC-MS) and OCPs were determined by gas chromatography-electron capture detector (GC-ECD).

Method validation was performed to determine PCBs, OCPs and PAHs. The concentrations of most of OCP compounds showed considerable increase in winter time. Generally, the concentrations of OCPs were found to be higher when the winds have blown from the sectors at which heavy agricultural activities were performed. The concentrations of OCP compounds were generally higher than the concentrations that were found in other agricultural and rural areas of the world. The winter time PAH concentrations were considerable higher than the summer time PAH concentrations. Although the concentrations were higher than the concentrations in rural areas in literature in winter season, the summer season concentrations were comparable. The important sources for PAHs in the sampling area were the domestic heating, traffic, asphalt production factory, and stubble burning. Total concentrations of PCBs were higher in winter season. Gas phase concentrations were higher than the particulate ones in both seasons. Although the concentrations of seven-eight chlorinated compounds were higher than the literature values, the others were comparable. Besides the local sources, there is an effect of long-range transport to the concentration of PCBs. The concentrations of low molecular weight persistent organic pollutants (POP) had generally higher than that of high molecular weight POPs in gas phase. Soil is a sink for all kinds of POP compounds.

Keywords: Bolu, Air Pollution, POPs, Source Apportionment, Gas-Particle Partitioning, Soil-Air partitioning, GC-MS, GC-ECD, Extraction

ÖZET

BOLU ATMOSFERİNDE PAH, PCB VE ORGANOKLORLU PESTİSİTLERİN BELİRLENMESİ VE KAYNAK DAĞILIMI: GAZ- PARTİKÜL, TOPRAK GAZ VE TOPRAK PARTİKÜL GEÇİŞLERİ

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Bu çalışmada, yüksek hacimli hava örnekleyicisi kullanılarak 120 adet partikül madde cam elyaf filtre (GFF) üzerine ve gaz fazı kirleticiler poliüretan köpük (PUF) üzerine toplanmıştır. Örnekleyici, A.İ.B.Ü., Bolu rektörlük binasının üzerine kurulmuştur. Atmış adet günlük örnek yaz sezonunda 25 Haziran ile 23 Ağustos 2007 tarihleri arasında ve kış sezonunda 13 Aralık 2007 ile 10 Şubat 2008 tarihleri arasında toplanmıştır. Toprak örnekleri 0,5 cm derinlikten alınmıştır. PUF ve GFF örneklerinin ekstraksiyonu sokslet düzeneği ile yapılmıştır ve toprak örneklerine de ultrasonik ekstraksiyon uygulanmıştır. Ekstraksiyonu yapılan örnekler optimize edilen Florisil ve Alumina adsorbsiyon kolonundan geçirilmiştir. PCB'ler ve PAH'lar gaz kromatografisi-kütle spektroskopisi (GC-MS) ile belirlenmiştir ve OCP'ler ise gaz-kromatografisi-elektron yakalama dedektörü (GC-ECD) ile belirlenmiştir.

PCB, OCP ve PAH'ların belirlenmesi için metodun validasyonu yapılmıştır. OCP bileşiklerinin büyük bir bölümünün derişimi kış aylarında belirgin bir artış göstermektedir. Genellikle, OCP'lerin derişimi rüzgâr, tarımsal faaliyetlerin yoğun yapıldığı sektörlerden estiğinde daha fazla bulunmuştur. OCP bileşiklerinin derişimi, dünyanın diğer tarımsal ve kırsal bölgelerinden daha yüksek bulunmuştur. Kış dönemi PAH derişimleri belirgin bir şekilde yaz döneminden yüksek bulunmuştur. Kış mevsimi PAH derişimleri literatürdeki diğer kırsal alanlardaki derişimlerden fazla olmasına rağmen, yaz mevsimi derişimleri karşılaştırılabilir seviyedir. Örnekleme alanında evsel ısınma, trafik, asfalt üretimi ve anız yangınları PAH'ların önemli kaynaklarındandır. PCB'lerin toplam derişimi kış mevsiminde fazladır. Her iki mevsimde gaz fazı derişimleri partikül fazından daha yüksektir. Yedi-sekiz klorlu bifenillerin derişimleri literatür değerlerinden yüksek olmasına rağmen diğerleri karşılaştırılabilir seviyededir. Yerel kaynakların yanı sıra uzun mesafe taşınımın PCB derişimleri üzerinde etkisi vardır. Gaz fazında, düşük moleköl ağırlıklı kalıcı organik bileşiklerin derişimleri genellikle yüksek olan kalıcı organik bileşiklerden (KOK) daha fazladır. Toprak KOK bileşiklerinin bütün türleri için alıcı bir ortamdır.

Anahtar Kelimeler: Bolu, Hava Kirliliği, KOK, Kaynak belirleme, Gaz-Partiköl

Dağılımı, Toprak-Hava Dağılımı, GC-MS, GC-ECD, Ekstraksiyon

DEDICATED TO MY MOTHER

FERİDE KILIÇ

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LIST OF ABBREVIATIONS

4,4'- DDD	: 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (Dichloro diphenyl trichloroethane)
4,4'- DDE	: 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (Dichloro diphenyl trichloroethylene)
4,4'- DDT	: 1,1-bis-(4-chlorophenyl)-2,2,2-trichloroethane
A.İ.B.U	: Abant İzzet Baysal University
Ace	: Acenaphthene
Ace-d10	: Acenaphthene-d10
Acy	: Acenaphtylene
AH	: Aliphatic hydrocarbons
Ant	: Anthracene
BaA	: Benzo(a)anthracene
BaP	: benzo[a]pyrene
BaP	: Benzo(a) pyrene
BbF	: Benzo(b)fluoranthene
BghiP	: Benzo(g,h,i)perylene
BkF	: Benzo(k)fluoranthene
CFC	: Chlorofluorocarbon
CH	: Chlorinated hydrocarbons
Chr	: Chysene
Chr-d12	: Chysene d12
DahA	: Dibenz(a,h) anthracene
DCM	: Dichloromethane
DF	: Digital filtration
ECD	: Electron capture detector
EPA	: Environmental protection agency
FA	: Factor analysis
f_A	: Fugacity in air
Flt	: Fluoranthene
Flu	: Fluorene
f_s	: Fugacity in soil
GC	: Gas chromatography
GC-ECD	: Gas chromatography-electron capture detector
GC-ECNIMS	: Gas chromatography-electron capture negative ion mass spectrometry
GC-FID	: Gas chromatography-flame ionization detector
GC-MS	: Gas chromatography-mass spectroscopy
GFF	: Glass fiber filter
GPP	: Gas particle partitioning
H	: Henry' s law constant
ha	: Hectare
HCH	: Hexachlorohexane
HFCF	: Hydrochlorofluorocarbons
HPLC	: High performance liquid chromatography

IADN	: Integrated atmospheric deposition network
Ind	: Indeno (1,2,3-cd) pyrene
IUPAC	: International union of pure and applied chemistry
K _{oa}	: Octanol-air partition coefficient
K _{ow}	: Octanol-water partition coefficients
K _p	: Particle/gas partition coefficients
K _{SA}	: Soil-air equilibrium partition coefficient
K' _{SA}	: Soot-air partition coefficient
K _{SW}	: Soot-warter partition coefficient
n.d.	: Not dedected
NAO	: North atlantic oscillation
Nap	: Naphthalene
Nap-d8	: Naphthalene-d8
NOAA	: National oceanic and atmospheric administration
OCPs	: Organochlorine pesticides
OECD	: Organisation for economic co-operation and development
PAH	: Polycyclic aromatic hydrocarbon
PBDE	: Polybrominated diphenyl ether
PCB	: Polychlorinated biphenyl
PCB-101	: 2,2',4,5,5'-Pentachlorobiphenyl
PCB-105	: 2,3,3',4,4'-Pentachlorobiphenyl
PCB-118	: 2,3,3',4,5'-Pentachlorobiphenyl
PCB-138	: 2,2',3,4,4',5'-Hexachlorobiphenyl
PCB-14	: 3,5-Dichlorobiphenyl
PCB-149	: 2,2',3,4',5',6-Hexachlorobiphenyl
PCB-153	: 2,2',4,4',5,5'-Hexachlorobiphenyl
PCB-166	: 2,3,4,4',5,6-Hexachlorobiphenyl
PCB-170	: 2,2',3,3',4,4',5-Heptachlorobiphenyl
PCB-18	: 2,2',5-Trichlorobiphenyl
PCB-180	: 2,2',3,4,4',5,5'-Heptachlorobiphenyl
PCB-194	: 2,2',3,3',4,4',5,5'-Octachlorobiphenyl
PCB-20	: 2,3,3'-Trichlorobiphenyl
PCB-204	: 2,2',3,4,4',5,6,6'-Octachlorobiphenyl
PCB-28	: 2,4,4'-Trichlorobiphenyl
PCB-30	: 2,4,6-Trichlorobiphenyl
PCB-31	: 2,4',5-Trichlorobiphenyl
PCB-44	: 2,4',5-Trichlorobiphenyl
PCB-52	: 2,4',5-Trichlorobiphenyl
PCB-65	: 2,3,5,6-Tetrachlorobiphenyl
PCDD	: Polychlorinated dibenzo-p-dioxin
PCDFs	: Polychlorinated dibenzofurans
PCHs	: Polychlorinated hydrocarbons
PCNs	: Polychlorinated naphthalenes
Per-d12	: Perylene-d12
Phe	: Phenanthrene
Phe-d10	: Phenanthrene- d10
P _L ^o	: Liquid-phase vapor pressures
PNA	: Pacific North American
PNHs	: Polynitrohydrocarbons

PO	: Percent observation
POP	: Persistent organic compound
ppLFER	: Polyparameter linear free energy relationship
PTFE	: Polytetrafluoroethylene
PUF	: Polyurethane Foam
Pyr	: Pyrene
Pyr-d10	: Pyrene-d10
RSD	: Relative standard deviation
SCOT	: Support-coated open tubular
SD	: Standard deviation
SIM	: Selected ion monitoring mode
SOC	: Semi-volatile organic compound
SPE	: Solid-phase extraction
TEQ	: Dioxin toxic equivalents
TMF	: Teflon membrane filters
TSP	: Total suspended particulate matter
UNEP	: United Nations Environment Program
USEPA	: United States Environmental Protection Agency
UWGB	: University of Wisconsin at Green Bay,
VOC	: Volatile Organic Compound
WCOT	: Wall Coated Open Tubular

CHAPTER 1

1. INTRODUCTION

Pollution is the introduction by man of substances or energy into the environment resulting in deleterious effects on human health, and other living sources, or interfere with amenities or other legitimate use of the environment (OECD, 1974). Many kind of pollution exists in nature such as noise, light, air, water, soil pollution, etc. Some kinds of pollution have some long-term or short-term dangerous effects on human beings as a result of direct exposure. Mostly human modification is observed in populous cities as well as a result of pollution, however rural areas, those are not greatly changed by humans, are also influenced from this modification because of the geographic structure and movement of earth especially meteorological parameters (Dickhut and Gustafson, 1995; Golomb *et al.*, 2001; Gryniewicz *et al.*, 2002; Vardar *et al.*, 2002; Motelay-Massei *et al.*, 2003; Vardar and Noll, 2003; Tasdemir and Esen, 2007).

Pollution has not been in public attention until several hundred years ago. After industrial revolution in the world, a large variety of synthetic chemicals has entered into the environment. The entry of these chemicals into the environment can be intentional, such as herbicides and pesticides, or unintentional, such as

polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) dibenzo-*p*-dioxins (PCDDs) and polybrominated diphenyl ethers (PBDEs) (Mclachlan and Hippelein, 1998). These groups of compounds have entered to the environment as by-products of the industrial manufacturing or combustion process, leakage, or leaching during the product's lifetime or after disposal (Garban *et al.*, 2002; Wu *et al.*, 2005; Domingo *et al.*, 2007).

The atmosphere is very important for the Earth and human beings because it is a protective blanket which sustenance life on the Earth and protects it from the hostile environment of outer space. The atmosphere is the source of carbon dioxide for plant photosynthesis, of oxygen for respiration and of nitrogen for nitrogen fixing bacteria and production of nitrogen derivatives. As a part of the hydrologic cycle the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still. Unfortunately, the atmosphere also has been used as a dumping ground for many pollutant materials, which causes damage to vegetation and other living species, shortens human life, and alters the characteristics of the atmosphere itself (Manahan, 2001).

Air contains very much amount of inorganic and organic pollutants in the form of either particulate or gaseous form. Particulate forms occur between the range of 0.001 μm to 100 μm and they are suspended liquid or solid species in the air. Gaseous pollutants include low vapor pressure, volatile, and semi-volatile aromatic and aliphatic organic compounds as well as inorganic compounds. It is approved as sink for organic and inorganic pollutants that is carried by the meteorological

conditions, especially by wind direction, wind speed, turbulence, and stability of atmosphere (Mayer, 1999; Sparks, 2003).

1.1. Organic Pollutants

Formerly inorganic pollution has been investigated because of visible effects. Nowadays pollution researches are concentrated on the organic pollutants due to their harmful health effects (Polkowska *et al.*, 2000; Gaga, 2004; Hung *et al.*, 2005; Wong *et al.*, 2005). All organic pollutants in the air, soil and water, which are derived from the exhaust gases, fossil fuel consumption, industrial processes and natural events such as forest fires and volcano eruption, have detrimental effect on many things including people, animals, plants and buildings (Odabaşı *et al.*, 1999; Esen *et al.*, 2007; Motelay-Massei *et al.*, 2006).

Organic compounds can be classified into two groups according to their vapor pressures. Generally, they are named as volatile and semi-volatile organic compounds. The class of volatile organic compounds (VOCs) includes species with different physical and chemical behaviors. Pure hydrocarbons containing C and H as the only elements (e.g., alkanes, alkenes, alkynes, and aromatics) are important VOC classes. However, VOCs containing oxygen, chlorine, or other elements besides carbon and hydrogen are also important. These latter classes include, for example, aldehydes, ethers, alcohols, ketones, esters, chlorinated alkanes and alkenes, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs) (Putaud *et al.*, 1999).

Semi-volatile organic compounds (SVOC or SOC) class includes hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, methoxyphenols and lactones, and other polar and nonpolar organic compounds with vapour pressures roughly between 10^{-6} and 10^1 kPa. The heavy hydrocarbons are often classified as SVOCs, but they are given a separate identity for precision and clarity (Watson *et al.*, 2001).

Especially, persistent organic compounds (POPs) are important class of organic pollutants, which are investigated as well as the group of semi-volatile organic compounds. Once released into the environment, they remain intact for exceptionally long periods of time as they resist photolytic, chemical and biological degradation. POPs in the environment are transported at low concentrations by movement of fresh and marine waters and, as they are semi-volatile, are transported over long distances in the atmosphere. The result is widespread distribution of POPs across the globe, including regions where they have never been used. POPs are characterized by low water solubility and high lipid solubility, resulting in their bioaccumulation in fatty tissues of living organisms, including humans, and they are found at higher concentrations at higher levels in the food chain. Thus, both humans and environmental organisms are exposed to POPs around the world resulting in both acute and chronic toxic effects to both humans and wildlife (Bidleman *et al.*, 1987).

1.1.1. Organochlorine Pesticides (OCPs)

A pesticide is a substance or mixture of substances used for preventing, controlling, or lessening the damage caused by a pest. Another definition for the

pesticides is any substance, preparation or organism prepared or used, to protect plants or wood or other plant products from harmful organisms; to regulate the growth of plants; to give protection against harmful creatures; or to render such creatures harmless (Coupe *et al.*, 2000). Many types of pesticides commercially has been produced to compete harmful species in the farmland and other terrestrial applications. The ideal pesticide should only attack the unwanted organism, leaving the non-targeted organism unaffected. However, hazardous effects of pesticides have been identified on people, therefore utilization of them has been banned or restricted by governments (Alegria *et al.*, 2006; Tuduri *et al.*, 2006).

Organochlorine pesticides (OCPs) are persistent organic pollutants (POPs) that have been widely used since World War II. They are highly bioavailable, can be bioaccumulated and biomagnificated in food chains. They can have adverse effects on human and animal health, causing nervous system damage, diseases of the immune system, reproductive and developmental disorders, and cancers (Harding *et al.*, 1997; Porta *et al.*, 1999; Dietz *et al.*, 2004; Harner *et al.*, 2006).

1.1.1.1. Molecular Structure of OCPs and Their Physical and Chemical Properties

The OCPs are generally stable in the environment and undergo limited decomposition or degradation. OCPs are not particularly volatile, but because they tend to persist in the environment, they can cycle among air, water, soil, vegetation, and animals. The common pesticide names, IUPAC names and chemical structures of some of the important pesticides are given in Appendix I. It represents a variety of

other names used to refer to each of the pesticides and illustrates their chemical structures. As given in Figure 1.1, chemical structures of dieldrin and heptachlor are very similar. Since these OCPs share many structural characteristics, they also share many chemical and physical properties. Due to higher volatilities, α - and γ -HCHs are the HCH isomers predominantly found in air, soil, and water, while β -HCH is found in high concentrations in animal fat, blood, and breast milk due to its slower metabolism (Willet *et al.*, 1998). For instance, DDT has a different type of structure, but it also shares some chemical and physical properties with dieldrin and heptachlor. DDT has two major metabolites in environment. One metabolite of DDT is DDD in reducing conditions and other, DDE is in oxidizing media. Figure 1.1 illustrates each of the OCPs. Their physical and chemical properties are given in Appendix II (<http://www.atsdr.cdc.gov/toxprofiles/>, 2008).

Since OCPs are fairly non-polar molecules, they tend to dissolve readily in hydrocarbon-like environments, such as the fatty material in living matter. They are only slightly soluble in water. Although OCPs can evaporate into the air, they adhere strongly to soils or sediments, where their concentrations can build up, often exceeding those of surrounding water (Taneja and Bhanti, 2005).

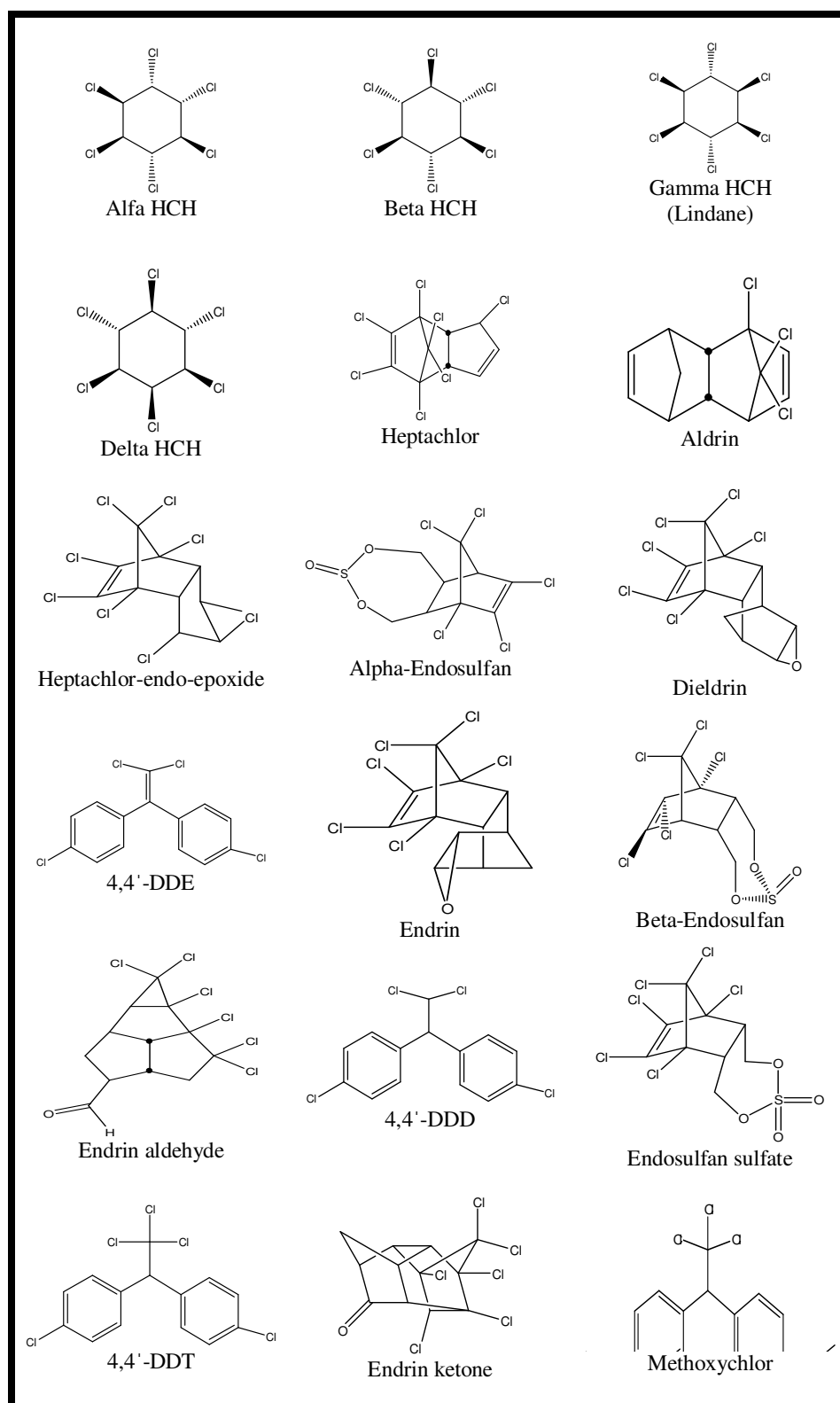


Figure 1.1. The molecular structures of OCPs

1.1.1.2. Sources of OCPs

When environmental contamination occurs, it is the result of either point-source or non-point-source pollution. Point sources are washing or cleaning water and spills, produced at equipment cleanup sites, improper disposal of OCP containers, pesticide storage sites where leaks and spills are not correctly cleaned up spills that occur while mixing concentrates or loading pesticides into application equipment. Non-point-source pollution comes from a wide area. The movement of pesticides into streams after broadcast applications is an example of non-point-source pollution (Waxman, 1998; Scheyer *et al.*, 2005).

Use of pesticides can have unintended effects on the environment. Most of the pesticides reach a destination other than their target species, including nontarget species, air, water, bottom sediments, and food. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides, that are applied to crops can volatilize and may be blown by winds into nearby areas (Gouin *et al.*, 2004; Tuduri *et al.*, 2006).

1.1.1.3. Toxicity and Carcinogenicity of OCPs

Pesticides may harm non-target organisms that are present during a pesticide application. Poorly timed applications can kill bees and other pollinators that are active in or near the target site. Pesticides may harm other wildlife, too. Even tiny amounts of some pesticides may harm them or destroy their source of food. Drift

from the target site may injure wildlife, livestock, pets, sensitive plants, and people (Waxman, 1998).

OCPs in water and sediments tend to bioaccumulate in living tissues, particularly in fish and other aquatic organisms. They also bioaccumulate in plants, birds, terrestrial animals, agricultural livestock, and domestic animals, where their concentrations increase by orders of magnitude as they rise through the food web, particularly as they reach higher organisms.

Pesticides can enter the human body orally, dermally or by inhalation resulting brain transmitter changes including neurological ‘kindling’; breast cancer (in test bacteria: genetic mutations; in mice: developmental learning deficits) and some undetermined effects. As long as the pesticide remains on the skin, wherever it is, then the chemical will continue to be dermally absorbed. The results of the inhalation of pesticides depend upon the nature of the chemicals involved (Stenersen, 2004). At low concentrations, OCPs exhibit relatively low acute toxicity to humans; however, they may mimic human hormones like estrogen, or have other properties that cause long-term health effects. At higher concentrations, OCPs can be very harmful, causing a range of problems including mood change, headache, nausea, vomiting, dizziness, convulsions, muscle tremors, liver damage, and death (Stenersen, 2004; Martinez-Haro *et al.*, 2008).

1.1.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic compounds are different groups of chemicals, which have only carbon and hydrogen atoms and simply identified containing two to eight fused aromatic rings (Vardar *et al.*, 2004). Also they have various functional groups, which may contain several elements. An important group of polycyclic aromatic compounds is the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzonoid rings and no elements other than carbon and hydrogen (Henner *et al.*, 1997).

PAHs are a group of over 100 different chemicals, which are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. Thus, they are present in high concentrations in the atmosphere in urban and industrialized areas (Garban *et al.*, 2002; Motelay-Massei *et al.*, 2003; Wu *et al.*, 2005).

PAHs can be released from their sources in gas phase or can be associated with particles by nucleation and condensation, forming particulate matter. The particulate form of PAHs are initially in the gaseous phase at high combustion temperature, however when the temperature decreases, gaseous phase PAHs adsorb or deposit on fly ash particles. The smaller the particle size provides the greater the surface area for the adsorption of PAHs. The ambient temperature is very important for the gas-particle distribution of PAHs. For instance naphthalene was 100 % found in the gas phase, while benzo[a]pyrene (BaP) and other compounds with 5 and 6 rings are adsorbed on particulate matter. However naphthalene was also found at

high levels in the ash from pulverized coal power generation therefore associated to the particulate matter (Mastral and Callen, 2000, Mandalakis *et al.*, 2002).

PAHs formation and emission mechanisms can be classified in two processes, pyrolysis and pyrosynthesis in any fuel combustion system. Pyrolysis is the formation of the smaller and unstable fragments from an organic compound upon heating. Fragments are the highly reactive free radicals with a very short average lifetime. By recombination reactions, these free radicals lead to more stable PAHs and this process is called pyrosynthesis (Mastral and Callen, 2000).

1.1.2.1. Molecular Structure of PAHs and Their Physical and Chemical Properties

The pure PAHs usually exist as colorless, white, or pale yellow-green solids and are relatively neutral and stable molecules. PAHs have low solubilities and low volatilities except small components like naphthalene. As molecular weight increases, aqueous solubility and vapor pressure decrease. The aqueous solubility decreases approximately one order of magnitude for each additional ring. Their lipophilicity is high, as measured by octanol-water partition coefficients (K_{ow}). Due to their hydrophobic nature, the concentrations of dissolved PAHs in water are very low (McLachlan and Hippelein, 1998).

PAHs have long half-lives in geological media. In aerobic sediment, for example, half lives range from three weeks for naphthalene up to 300 weeks for BaP. PAHs are regarded as persistent organic pollutants (POPs) in the environment and

their persistence increases with ring number and condensation degree (Henner *et al.*, 1997; Tsapakis and Stephanou, 2005).

Some of the commonly occurring PAHs which are listed on the hazardous material of United States Environmental Protection Agency (USEPA), are acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, fluoranthene, phenanthrene, fluorene, naphthalene, benzo[k]fluoranthene, pyrene, chrysene, indeno[1,2,3-c,d] pyrene and dibenz[a,h]anthracene. These molecular structures of PAHs are shown in Figure 1.2. and chemical and physical properties of them are given in Appendix III.

In the environment, we are most likely to be exposed to PAH vapors or PAHs that are attached to dust and other particles in the air. PAHs generally come from cigarette smoke, vehicle exhausts, asphalt roads, coal, coal tar, wildfires, agricultural burning, residential wood burning, municipal and industrial waste incineration, and hazardous waste sites. In the home, PAHs are present in tobacco smoke, smoke from wood fires, creosote-treated wood products, cereals, grains, flour, bread, vegetables, fruits, meat, processed or pickled foods, and contaminated cow's milk or human breast milk. Food grown in contaminated soil or air may also contain PAHs. Moreover, cook of foods at high temperature, which occurs during grilling or charring, increases the amount of PAHs in the food (Bi *et al.*, 2005; Hung *et al.*, 2005).

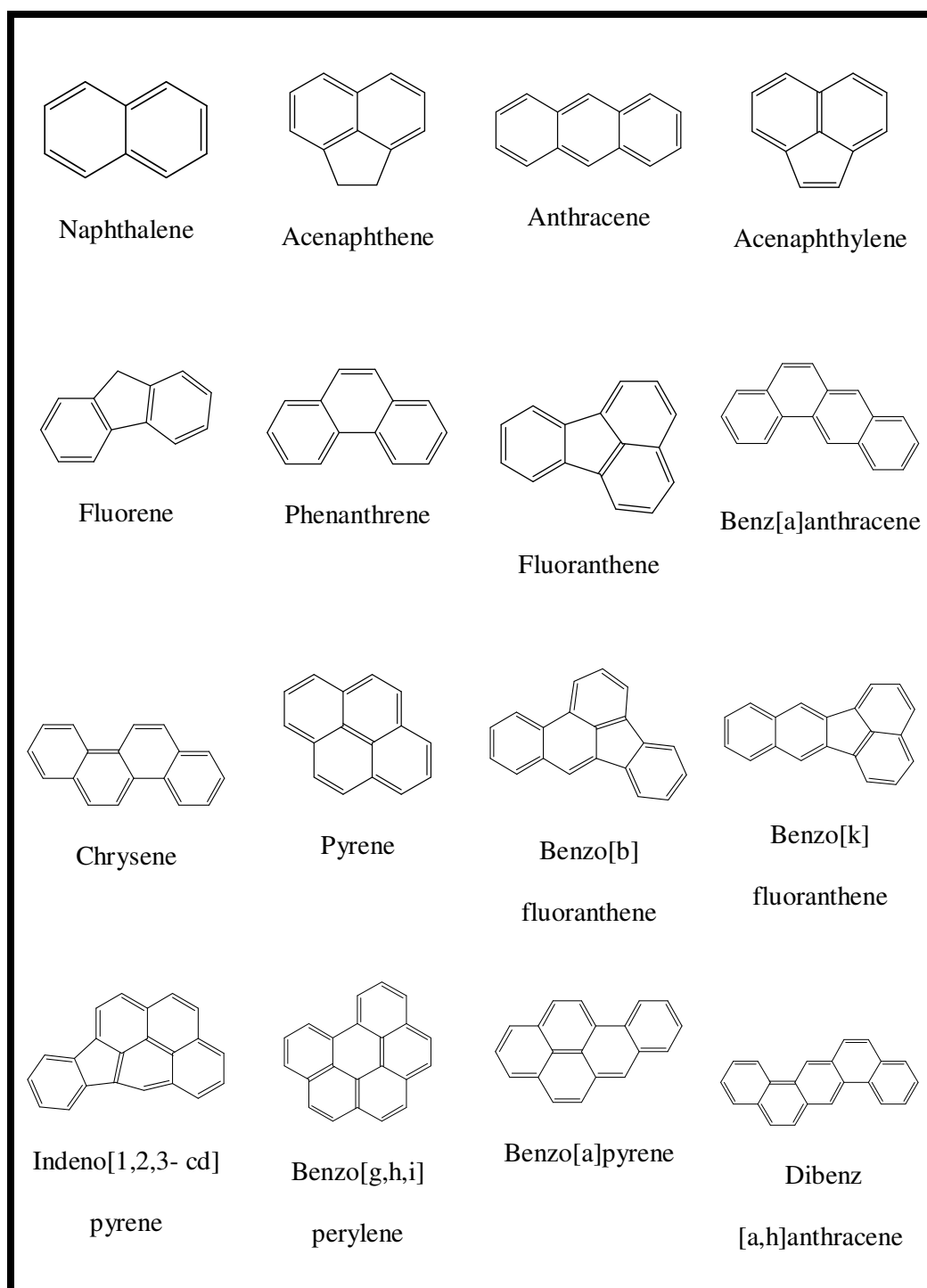


Figure 1.2. The molecular structures of PAHs

1.1.2.2. Sources of PAHs

PAHs arise from a number of sources. Some of them include hydrocarbon spillage (Benner *et al.*, 1990), incomplete products of combustion of fossil fuels, and power plants and blast furnaces (Brummelen *et al.*, 1996). However, the major pollution is likely to be from diffuse sources such as deposition from the atmosphere and there is evidence to indicate that PAHs are transported over long distances by atmosphere movement (Halsall *et al.*, 2001). Therefore most of the PAHs in soil are believed to result from atmospheric deposition after local and long-range transport. Other potential sources of PAHs in soil include sludge disposal from public sewage treatment plants, automotive exhaust, irrigation with coke oven effluent, leachate from bituminous coal storage sites, and use of soil compost and fertilizers (Sitaras *et al.*, 2004; Yang *et al.*, 1980). The other principal sources of PAHs in soils along highways and roads are vehicular exhausts and emissions from wearing of tires and asphalt (Sitaras *et al.*, 2004).

Molecular marker study has been used in distinguishing biogenic and anthropogenic sources of PAHs in the environment (Yunker and Macdonald, 1995). For example, the presence of primarily unsubstituted PAHs with the dominance of 2~5-ring compounds provides some evidence of combustion sources while the presence of alkyl substituted with the dominance of 2~3-ring compounds indicates some evidence of petroleum source.

1.1.2.3. Toxicity and Carcinogenicity of PAHs

PAHs are among the persistent environmental contaminants, deriving from incomplete combustion processes involving carbon fuels and materials. Since many of these compounds have proven to be mutagenic and/or carcinogenic, their widespread presence in ambient air is cause for cancer due to a likely causal correlation with deleterious health effects, proved by epidemiological findings.

Human PAH exposure is a function of several parameters, including levels in ambient air, partition coefficients between particles and gas and size of particulate matter. It is well documented that the effect of a PAH on the respiratory tract, such as BaP, is due to its association with small particles that can be inhaled and deposited in human bronchioles and alveoli (Lodovici *et al.*, 2003). Since BaP is well characterized toxicologically, whereas comparatively less information is available for most of the other PAHs, the health risks associated with respiratory PAHs uptake have often been calculated on the basis of BaP air concentration (Lodovici *et al.*, 2003).

1.1.3. Polychlorinated Biphenyls (PCBs)

PCBs are another persistent organic pollutant in the environment that have been widely used, and are generally known to have no natural sources. PCBs are commercially prepared by chlorination of biphenyl. PCBs have 209 possible different congeners and 10 homologues, depending on the ring chlorine substitution and the extent of chlorination. Due to the stability from biochemical attack and

flame, PCBs were used in dielectric fluids in transformers and capacitors, in transmission fluids, and in the manufacture of paints, lubricants, plastics, adhesives, and coating compounds (Kim and Masunaga 2005).

Although PCBs production was prohibited or restricted in certain application all over the world, these chemicals still pose a threat to public health due to their long-term environmental persistence and presence in some untreated materials. They can be released to the environment through leaching from landfills, previously contaminated soils and sediments or obsolete stockpiles (Tan *et al.*, 2007). Degradation of PCBs is dependent on the degree of chlorination and the position of chlorine atom on the biphenyl molecule (Tiedje *et al.*, 1993).

The high lipophilicity and persistence in the environment allows PCBs to bioaccumulate and biomagnify in the food chain and resist biodegradation. Therefore, PCBs have been found everywhere on the earth including the Arctic and Antarctic. They are considered priority soil contaminants because of their tendency to persist in soil and sediments. Long-term contaminated soil often displays a higher proportion of chlorinated congeners. PCBs in the air are commonly dominated by the lesser-chlorinated congeners due to their greater volatility, although higher chlorinated congeners are also regularly observed. Increasing concerns over PCBs have focused on reducing the environmental risk of PCBs to human beings (Fu, 2008).

The PCB compounds were not produced in Turkey, they have been exported from the other countries. Therefore the disposal sites and some PCB containing

compounds scavenging processes are the main sources of them. Leakages from the transformers and byproduct PCBs are still dominance in environment in Turkey (www.atikyonetimi.cevreorman.gov.tr/pcb/PCBs-Session1_2003.pdf).

1.1.3.1. Molecular Structure of PCBs and Their Physical and Chemical Properties

PCBs are a class of chemical compounds in which chlorine atoms replace some or all of the hydrogen atoms on a biphenyl molecule. The benzene rings can rotate around the bond connecting them, but the rings are forced towards either the same plane (called planar or coplanar) or perpendicular planes (termed non-planar) by the electrostatic repulsion of the electronegative chlorine atoms. The degree to which the rings can twist beyond these two extremes is a function of steric hindrance produced by chlorine atoms in different positions on the two rings (Jang, 2001).

The PCBs are very stable chemically against to acids, bases, and other reactive reagents. They also resist harsh conditions such as temperature and pressure. In general, PCBs are relatively insoluble in water, and the solubility decreases with increased chlorination. PCBs are also freely soluble in nonpolar organic solvents and biological lipids. In total, 209 different PCBs can be formed and different combinations are called congeners, each having a specific number of chlorine atoms located at specific positions. The PCBs with five chlorine substitutions have the largest number of isomers (number of isomers 46). The IUPAC names, abbreviations and cas numbers are given in the Appendix IV (Jang, 2001; www.iupac.org). Chemical structures of the selected PCB congeners are illustrated in Figure 1.3.

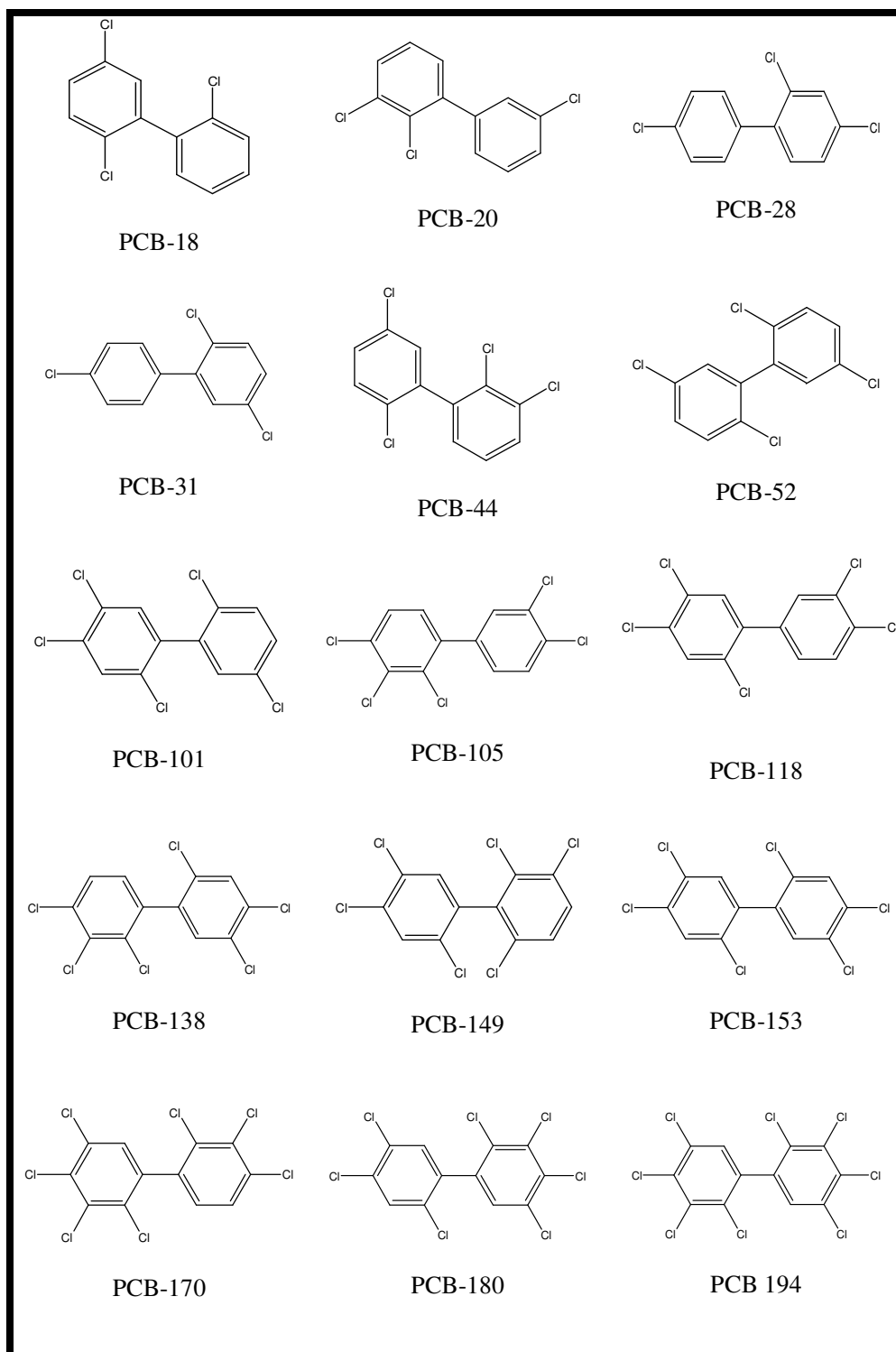


Figure 1.3. The molecular structures of PCBs

Depending on the degree of chlorination, their physico-chemical properties, like inflammability or electric conductivity, PCBs find a wide range of applications (Cindoruk *et al.*, 2007). Thus, some of their applications resulted in a direct or indirect release of PCBs into the environment. Relatively large amounts were released due to inappropriate disposal practices, accidents and leakages from industrial facilities. At high temperatures, PCBs are combustible, and the products of combustion may be more hazardous than the original material such as hydrogen chloride and PCDFs (Guerzoni *et al.*, 2005; Cindoruk *et al.*, 2007).

Physical properties such as solubility, vapor pressure, and Henry's law constant have been reported for individual congeners. Experimentally determined octanol/water partition coefficients (K_{ow} values) for ten different substituted PCBs and other PCB congeners are available in Appendix V. Generally, PCBs are relatively insoluble in water, with the highest solubilities among the ortho-chlorinated congeners (5 mg L^{-1} for PCB 1), which may be due to hydrogen bonding associated with the more polar character of these molecules. Solubility decreases rapidly in ortho-vacant congeners, especially as the para positions are filled, which may result in greater and more uniform perimeter electronegativity and interference with hydrogen bonding. PCBs, especially the more chlorinated congeners, are also relatively non-volatile, with partial pressures and Henry's law constants that tend to decrease with increased chlorination, especially for meta- and para-saturated congeners (Moon *et al.*, 2006).

1.1.3.2. Sources of PCBs

General PCB sources are leakage from transformers; disposal of copy papers, paints/plasticizers, pesticide extenders, flame retardant, adhesives, coolants, inks, hydraulic fluids; to human, fish, and animal fat, groundwater. PCBs may enter the atmosphere from incineration plants combusting PCB containing materials, vaporization from waste disposal areas, sludge dewatering beds, electronic devices containing PCB content capacitors, transformers, and air-water-soil exchange (Biterna and Voutsas, 2005; Taşdemir and Holsen, 2005; Gambaro *et al.*, 2004; Simcik *et al.*, 1997).

Urban and industrial areas are major sources of atmospheric polychlorinated biphenyls (PCBs) to surrounding regions (Offenberg and Baker, 1997, 1999; Simcik *et al.*, 1997). Atmospheric transport from these areas can lead to significant PCB loading to surrounding terrestrial and aquatic ecosystems (Stevens *et al.*, 2001). Loading of atmospheric PCBs to aquatic and terrestrial ecosystems occurs through diffusive air-water exchange, air-vegetation exchange, wet deposition (rain, snow), and dry particle deposition. Once delivered, PCBs may be remobilized to the regional atmosphere by air-surface exchange processes (Brunciak *et al.*, 2001).

The combustion processes are reported as possible sources of PCBs as well as other POPs, which can be formed when a carbon and chlorine are combusted together. The presence of various POPs in emissions from the incineration of municipal, hospital and other wastes, domestic combustion, open burning of wastes, landfill fires and accidental fires is documented (Breivik *et al.*, 2002; Kakareka,

2002). The emissions from the combustion of different type of fuels (coal, wood, crude oil, leaded petrol, diesel), from various industrial-metallurgical activities and power generation processes were found to contribute to PCB inventions (Kakareka, 2002; Dyke *et al.*, 2003). Possible emissions of PCBs from vehicles or from residential heating facilities are scarce (Lohmann *et al.*, 2000; Biterna and Voutsas, 2005). However, the relative contribution of diffuse and small-scale sources to the regional inventories might be significant, especially after the reduction of the primary emissions from obvious sources (Dyke *et al.*, 2003; Biterna and Voutsas, 2005).

1.1.3.3. Toxicity and Carcinogenicity of PCBs

In humans, PCBs are believed to cause reduced male fertility, long-term behavioral and learning difficulties, particularly in children, and are classified as probable human carcinogens. They are insoluble in water but soluble in fats, and therefore do accumulate in the fatty tissues of animals. For example, PCBs have been detected at much greater than background levels in the blubber of whales and seals. Currently, it is likely that PCBs will continue to enter the human system via ingestion. PCBs are so persistent that the depositions on soil made many years ago can still enter the human food chain. Indeed, PCB emissions and re-deposition on soil continue (Meharg *et al.*, 2003; Liao *et al.*, 2008).

The relationship between exposure to PCBs and human health effects is reflective of the large variation in human exposure to the many different congeners and contaminants present in PCB formulations and to combustion by-products of

PCBs. The evidence suggests that exposure to PCBs is associated with increases in risk of cancers of the digestive system, notably of the liver, and of malignant melanoma. PCB exposure is also associated with reproductive deficiencies such as reduced growth rates, retarded development, and neurological effects; immunological changes, manifested as increased infection rates and changes in circulating lymphocyte populations; and dermatological changes, including chloracne and pigmentation disturbances of skin, nails, and gingivae, as well as nail deformation after exposure to highly chlorinated congeners (Scott *et al.*, 2008).

1.2. Chemical Fate and Transport of Persistent Organic Pollutants in the Environment (Air, Water and Soil)

POPs are chemicals that are resistant to degradation photochemically, biologically and chemically for a long period of time in the environment (Vagi, 2007). POPs cycle between the different environmental compartments and are capable of travelling long distances, thus becoming ubiquitous global pollutants (Scheringer and Wania, 2003) (Figure 1.4).

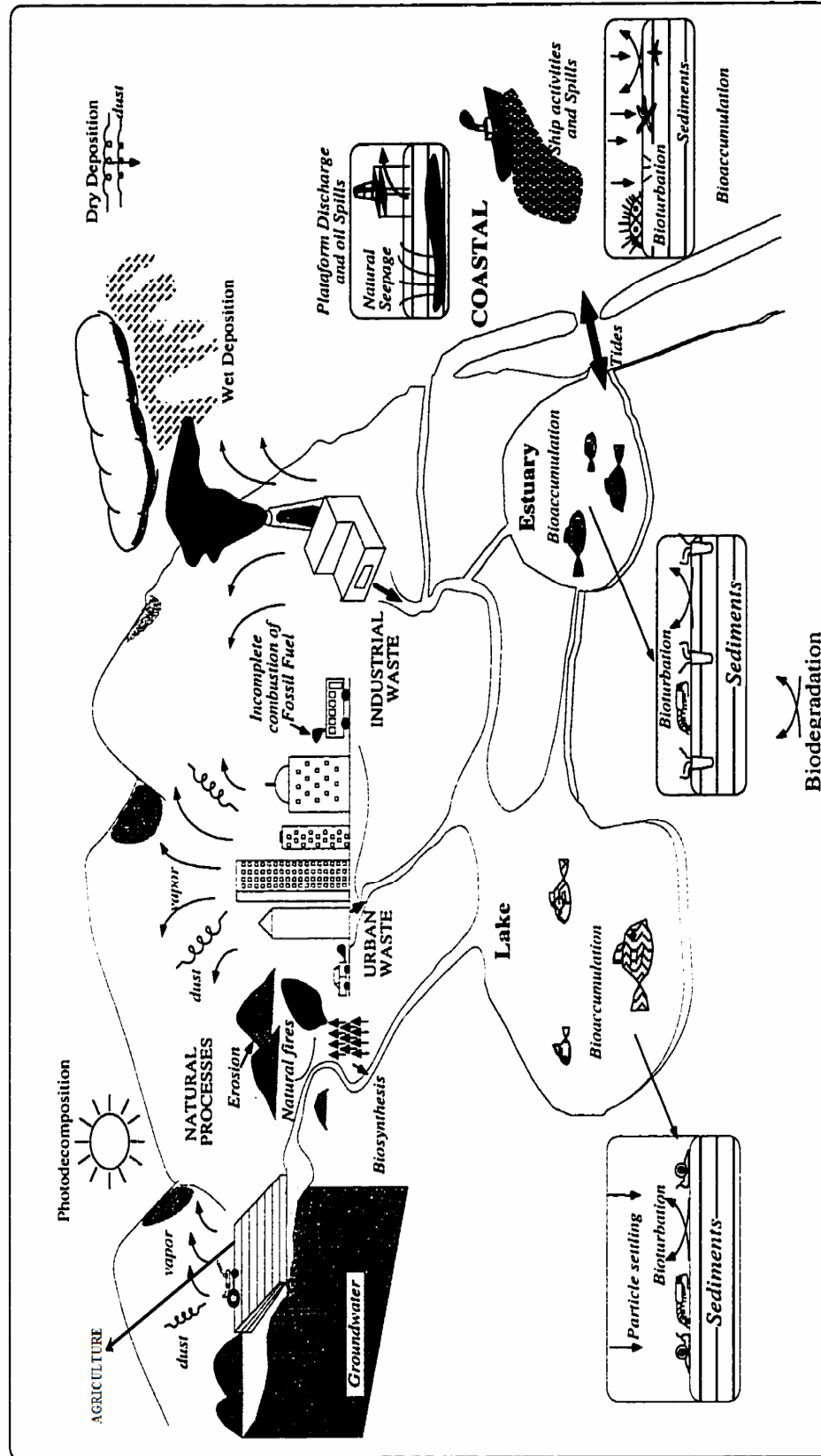


Figure 1.4. The fate of POPs in environment (Hemond and Fechner, 1994)

In principle, differences in the physico-chemical properties and environmental half-lives of different POPs would lead to a “fractionation” process, i.e., more volatile substances would be transported more rapidly and over larger distances than less volatile compounds. However, the fractionation pattern to be expected on the basis of chemical properties is often confounded by spatial and temporal variability of the emissions of the chemicals and by the conditions under which samples are taken in the field (Koumanova and Mehmetli, 2007). Researches are focused on the gas phase, the interaction of POPs with atmospheric aerosols (deposition and transport with aerosols; reactivity of the aerosol-bound fraction; air-aerosol partitioning), and the characterization of various surface media (soil, vegetation, ice-snow, and water) with respect to their sorptive capacity for POPs (Cousins *et al.*, 1999; Fenger, 1999; Koumanova and Mehmetli, 2007).

POPs in environment are determined by its partition between the water, the soil and sediment, and the atmospheric phases, and its potential for concentration in biota. These processes determine both the biological impact of the POPs and the extent of its dissemination. Procedures for determining the partition of POPs into biota are discussed, and attention is drawn to complicating factors, including the degradation of POPs, and to the important interdependence of adsorption and absorption on or into the species. Some equations used for correlating partition coefficients with physico-chemical parameters have been presented and some of their limitations have been noted in literature (Weiss *et al.*, 2000; Paasivirta *et al.*, 2000).

The atmosphere has an important role in the transport, deposition, and cycling of antropogenic POPs. Atmospheric deposition has been shown to be a significant

source of these pollutants to surface waters, especially coastal waters downwind of urban and industrialized source areas (Baker, 1994; Golomb *et al.*, 1997). The atmosphere is also a source of anthropogenic organic contaminants in large lakes, the remote ocean and remote Arctic areas (Halshall *et al.*, 2000). For instance, PAHs may be converted or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photo-oxidation (Marce and Borrull, 2000).

Soils are also important in the global cycling of POPs since they have a role in supplying and receiving chemicals to/from the atmosphere. It is well documented that agricultural soils are an important reservoir and emission source (Bidleman and Leone, 2004; Alegria *et al.*, 2006). POPs are retained in soils for several years due to their high affinity for soil organic matter, and are subject to losses through biological degradation, erosion, leaching and volatilization. Globally, soils have a huge storage capacity for POPs (Valle *et al.*, 2005), and therefore soil-air exchange may act to buffer atmospheric concentrations. The interaction between soil and air is one of the key issues in the global transport of POPs, and there are gaps in knowledge about the soil processes and the influence of physical and chemical properties on exchanges (Paassivirta *et al.*, 2000; Weiss *et al.*, 2000; Nam *et al.*, 2008).

To sum up the environmental fate and transport of persistent organic pollutants (POPs) require knowledge of the physical-chemical properties of the contaminants. The most important of these properties controlling the partitioning between different compartments are the octanol-water partition coefficient (K_{ow}), the vapor pressure of the solid substance (P_s) or the liquid (P_L), the aqueous solubility of the solid (S_s) or the (subcooled) liquid (S_L) and the air-water partition coefficient or

Henry's law constant (H) (Paassivirta *et al.*, 2000). Therefore, some of multimedia applications are developed for modelling the transport and the fate of POPs in a relation of air-water-soil exchanges.

1.3. Gas-Particle-Soil Distributions of Persistent Organic Compounds in the Atmosphere and Soil

The Earth's surface is the ultimate sink for trace gases and particles emitted at the surface or formed in the atmosphere. The transfer of trace gases and particles to the surface occurs through two pathways: wet and dry deposition. The relative importance of one pathway over the other depends on the nature of the substance (phase, reactivity and solubility), the occurrence of precipitation, and the nature of the surface cover. The nucleation and growth of aerosol particles from condensation nuclei are the first steps toward wet removal of both particles and gases (Hewitt and Jackson, 2003).

Soil as a reservoir is the main source of the gas and particle phase exchanges as well as the gas and particle in the air for soils besides the direct distribution from the pollutant sources. It exists in gas-particle and air-soil exchanges in environment. Principal deposition on soils occurs by wet and dry precipitation of the samples however in air gas-particle exchange and vaporization from the surface of the soil is the conveyance of the POPs.

1.3.1. Dry Deposition of Gases and Particles

Dry deposition occurs as trace gases and particles are adsorbed or reacted on objects at the Earth's surface. Factors that govern the dry deposition of gases include the level of atmospheric turbulence, the nature of the gas (solubility, reactivity, molecular diffusivity), and the nature of the surface itself. Obviously, a chemical or physical sink must exist for uptake to occur. Likewise, without turbulence even a perfectly adsorbing surface would be ineffective at removing gaseous material from the atmosphere because dry deposition would be limited by molecular diffusion (Hewitt and Jackson, 2003).

The processes involved in the dry deposition of particles are similar to those associated with gases, except that particles are also subject to gravitational settling. Both particles and gases are transported similarly through the aerodynamic layer. Diffusion in the laminar sub-layer occurs through Brownian motion, analogous to molecular diffusion for gases. Particles can interact with the surface through Brownian motion, impaction, interception, and gravitational settling. The relative importance of these processes is governed largely by the particle size. The “stickiness” of the particles is also important, but it is not as critical as the surface properties that influence the surface resistance for gases (solubility and reactivity). In general, the deposition of large particles ($D_p > 10 \mu\text{m}$) is dominated by gravitational settling. Large particles can have short lifetimes in the atmosphere, on the order of several hours to a day. Small particles ($D_p < 0.05 \mu\text{m}$) settle slowly, but are transported efficiently by Brownian motion and can also have short lifetimes (Hewitt and Jackson, 2003).

1.3.2. Wet Deposition

The processes by which gases and particles are incorporated into precipitation and subsequently removed from the atmosphere involve a large range of spatial and temporal scales: from the molecular scale to those associated with thunderstorms and fronts. The problem is complicated by the existence of multiple phases (gases, liquid water, ice), a size distributions of both aerosol pollutants and scavengers, and chemical reactions that can occur within the scavengers (Hewitt and Jackson, 2003).

The octanol-air partitioning coefficient, K_{OA} , is increasingly used as a descriptor of partitioning between the atmosphere and organic phases in soils and vegetation. A generator column technique is generally used in which an inert gas is flowed through a column containing a substance dissolved in octanol. The concentration in the equilibrated gas leaving the column is then measured. By this way, distribution and exchange of the POPs in octanol are determined experimentally in order to interpret the transfer in/into air and soil and related with the field samples (Harner and Mackay, 1996).

1.3.3. Gas to Particle Distribution of POPs

The distribution of POPs in the atmosphere between the gas and particulate phases is determined by several factors including the vapor pressure of the POPs, the amount of particles, the ambient temperature, POPs concentration, and the affinity of individual POP for the particles organic matrix (Baek *et al.*, 1991). Low molecular weight POPs were primarily in the gas phase while high molecular weight POPs were primarily found in the particulate phase. Gas phase percentages were generally

higher in summer than in winter due to increasing temperature with increasing the vapor pressure of the compounds (Odabaşı *et al.*, 1999; Kaupp and MacLachlan, 1999). The vapor pressure of a POP determines to a large extent, the phase (particulate or vapor) in which the chemical will be found. Junge (1977) showed that compounds with vapor pressures above 10^{-5} kPa should occur almost entirely in the gas phase, whereas compounds with vapor pressures less than 10^{-9} kPa should exist predominantly in the particulate phase. Any compound with a vapor pressure between these approximate limits would be expected to occur in both the vapor and particle phase (Henshaw and Eatough, 1991).

Gas-to-particle partition of POPs depends on the molecular weight of the compounds, temperature, humidity and precipitation as expressed formerly. Generally, low-volatile POPs with > 5 rings, identified by relatively high temperature of condensation, are adsorbed on the airborne particles. POPs present in the atmosphere are subject to complex physico-chemical reactions and transformations in the atmosphere; dry and wet deposition, photochemical transformations and reactions with other pollutants (Maliszewska *et al.*, 2000).

1.3.4. Soil to Air Distribution of POPs

Direct and indirect methods are used to measure particle phase dry deposition flux. In the direct method, a surrogate surface is used while in the indirect method measured ambient concentrations are multiplied by an assumed or modelled deposition velocity to determine the dry deposition flux (Odabaşı *et al.*, 1999). Deposition velocity is affected by the meteorological parameters, physical properties

of the particle (i.e., size, shape and density), and the type and roughness characteristics of the receptor surface (Golomb *et al.*, 2001). The selection of an appropriate deposition velocity is crucial since it may introduce large uncertainties in the calculation of dry deposition fluxes. Once deposited, POPs tend to accumulate in soil for a long period of time and they are subject to various partitioning, degradation and transport processes depending on their properties and microbiological degradability (Paassivirta *et al.*, 2000) (Figure 1.5).

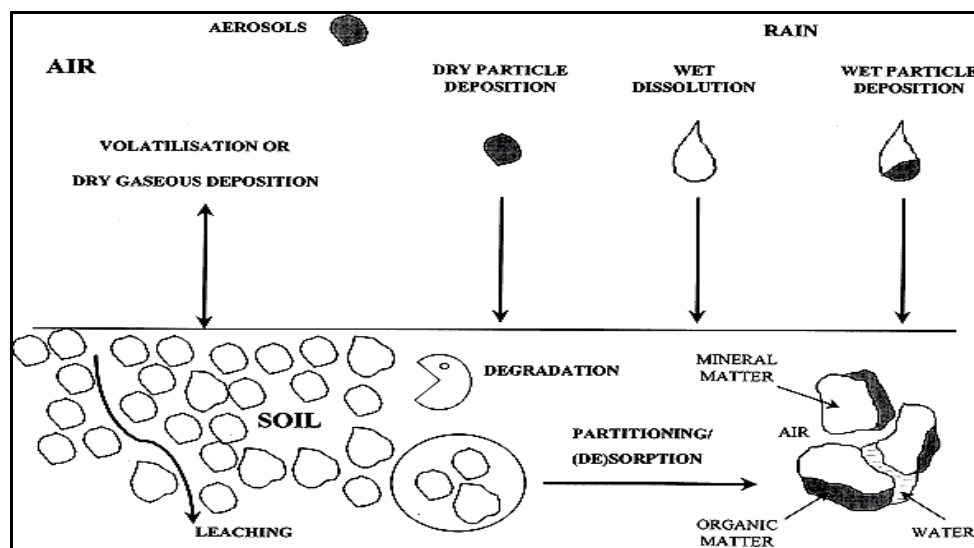


Figure 1.5. Air-soil exchange of POPs (Cousins *et al.* 1999)

Considering their large reservoir in soils, soil-air exchange is an important diffusive process affecting the fate and transport of POPs into the environment. K_{SA} values and soil-air equilibrium status for various POPs has been calculated in researches previously. Many variables can influence soil-air exchange: soil organic matter content, soil moisture, presence of a crop canopy and meteorological conditions (Taşdemir *et al.*, 2007).

Fugacity is a measure of chemical potential or partial pressure of a chemical in a particular medium that controls the transfer of chemicals between media (Ockenden *et al.*, 2003). Therefore the air soil exchange is expressed in terms of fugacity. Harner were calculated fugacities (P_a) of the POPs in soil (f_s) and air (f_a) and assuming that the fugacity capacity of soil is due entirely to the organic matter fraction. The direction of the net gas exchange at soil–air interface is determined by the fugacity ratio. A soil to air fugacity ratio [$(f_s/f_A) = (C_{sps}/K_{SA})/C_A$] greater than 1 indicates that the soil is a source with net gas volatilization to air, and a value less than 1 indicates that the soil is a sink with net gas deposition from air. For a system in equilibrium, f_s/f_A value is approximately equal to 1 (Harner and Falconer, 2000; Cousins and Jones, 1998).

In addition K_{oa} which is a function of temperature for all compounds (Harner *et al.* 2002) is combined with the soil air partition coefficient by the factor 0.411 (Karickhoff, 1981) which improves the correlation between the soil-air partition coefficient (K_{SA}) and K_{OA} (Hippelein and McLachlan, 1998; Ockenden *et al.*, 2003).

1.4. Methods of Analysis and Theory of Instruments

Broad range of instrumental methods and techniques have been used or developed for analysis and determination the content of the organic pollutants. That includes polyurethane foam sampler, pre-clean-up columns, ultrasonic extraction, gas chromatography-electron capture detector and gas chromatography-mass spectroscopy, etc.

1.4.1. Chromatography

Chromatography is the method of separation in which several chemicals to be separated for subsequent analyses are distributed between two phases. The first one is stationary (stationary phase), whereas the other moves in one direction (mobile phase). Chromatographic separation has many different forms, depending on the type of mobile and stationary phase, the type of equilibrium involved between mobile and stationary phase, and the physical means by which these two phases are brought into contact. Despite various forms, all chromatographic analyses are based on the establishment of equilibrium between a stationary phase and a mobile phase. Chemicals are separated according to their different affinities to the stationary phase. The technique through which the chemical components present in complex mixtures are separated, identified and determined is termed as chromatography. This technique is widely used like spectroscopy and is a very powerful tool not only for analytical methods but also for preparative methods (Sewell and Clarke, 1994).

According to mobile phase, this technique is classified into two categories as: Liquid Chromatography (LC) and Gas Chromatography (GC). The column, which holds the stationary phase (which in the form of small particles of the diameter of the order in microns), plays unique role in these processes. Usually silica is the base material for producing this phase.

1.4.1.1. Gas Chromatography

Gas Chromatography (GC) is made up of carrier gas, sample injection system, oven capillary column, referred detector and computer (Figure 1.6). GC becomes the premier technique for the separation and analysis of volatile compounds, and gas chromatographs have been the most widely used analytical instrument in the world. The most popular carrier gases are nitrogen, helium, and hydrogen. They must be very pure, and they are chosen for their inertness since, as we have seen, their only purpose is to carry the analyte vapors through the column (Fowlis, 1995).

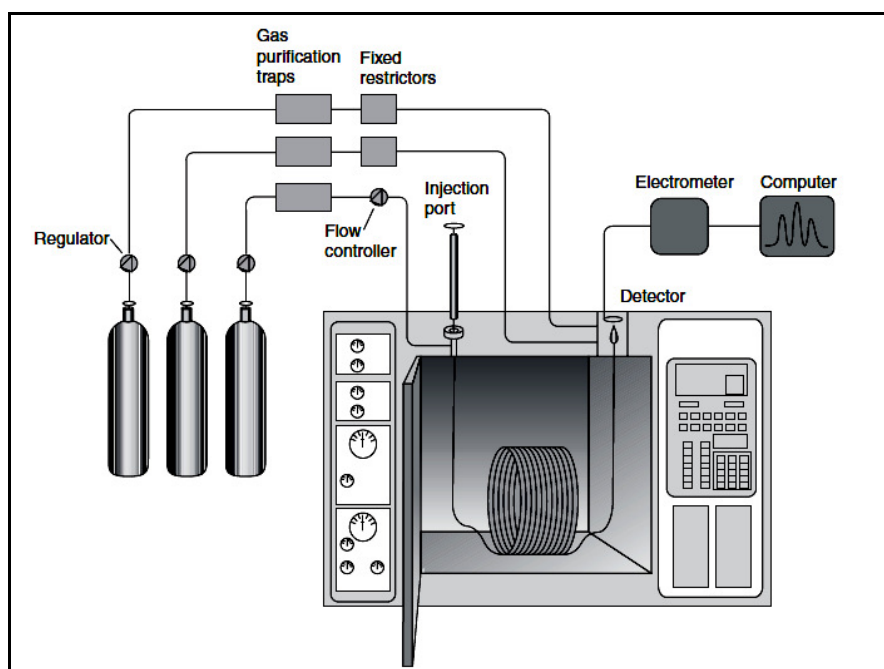


Figure 1.6. Schematic diagram of a typical GC system

GC is a very popular technique in organic analytical research, because of its very high selectivity and resolution, good accuracy, wide dynamic range and high sensitivity. Nevertheless, POPs with more than 24 carbon atoms cannot be analyzed

by GC because of their lack of volatility. Mixtures to be analyzed are injected into an inert gas stream and swept into a tube packed with a solid support coated with a resolving liquid phase. Sample was injected to the GC via split/splitless injector. Sample is vaporized in the injector throat the split valve is used to control the amount of sample allowed to enter the column. This is used to prevent overloading of the column. Since sample discrimination can occur during volatilization and splitting, a variety of throat liners are available that provide variations in surface area and composition to control these changes. The simplest throat liner is a plug of glass wool, but a variety of borosilicate glass and silica restricted tubes with constructions are available (Fowles, 1995).

There are two types of columns encountered in GC, packed and capillary columns. Chromatographic columns vary in length from less than 2 m to 50 m or more. They are constructed of stainless steel, glass, fused silica, or polytetrafluoroethylene (PTFE). Packed columns are densely packed with a uniform, finely divided packing material or solid support, that is coated with a thin layer (0.05 to 1 μm) of the stationary liquid phase. Capillary columns are of two basic types namely, wall coated open tubular (WCOT) and support-coated open tubular (SCOT). Wall coated columns are simply capillary tubes coated with a thin layer of the stationary phase. In SCOTs, the inner surface of the capillary is lined with a thin film ($\sim 30 \mu\text{m}$) of a support material. This type of column holds several times as much stationary phase as does a wall coated column and greater sample capacity. Generally, the efficiency of SCOT column is less than that of WCOT but significantly greater than packed column (Skoog, 1992). Many capillary GC stationary phases designed for optimally separate complex VOC mixtures are

commercially available from different suppliers. In general, nonpolar stationary phases, such as methyl polysiloxane or phenyl methyl polysiloxane, are the most suitable for the separation of these compounds (Santos and Galceran, 2002). Absorptive interaction between the components in the gas stream and the coating leads to a differential separation of the components of the mixture, which are then swept in order through a detector flow cell. GC suffers from a few weaknesses, such as its requirement for volatile compounds, but its major problem is the lack of definitive proof of the nature of the detected compounds as they are separated. For most GC detectors, identification is based solely on retention time on the column. Since many compounds may possess the same retention time, we are left in doubt as to the nature and purity of compound (s) in the separated peak (McMaster and McMaster, 1998).

1.4.2. Mass Spectroscopy (MS)

In mass spectroscopy chemical substances are bombarded with high energy electron beam causing total destruction and fragmentation of the molecules in the sample. This fragmentation results in small charged “pieces” or fragments of the molecules, which, because of their charge are made to move through a magnetic field. The magnetic field affects each fragments differently based on their mass and charge that they carry and thus they are separated (McMaster and McMaster, 1998).

Mass spectrometer consists of a source of high-energy electrons, ion accelerator, magnets, detector, recorder and high vacuum pumping system. In the instrumentation the entire path of the fragments, including the inlet system must be

evacuated. The reason is to avoid collisions of both the electron beam and the sample ions with contaminating foreign particles which would otherwise affect the sensitivity and hence the results. For this technique there are two different instrument designs as Magnetic Sector Mass Spectrometer and Quadrupole Mass Spectrometer (Figure 1.7).

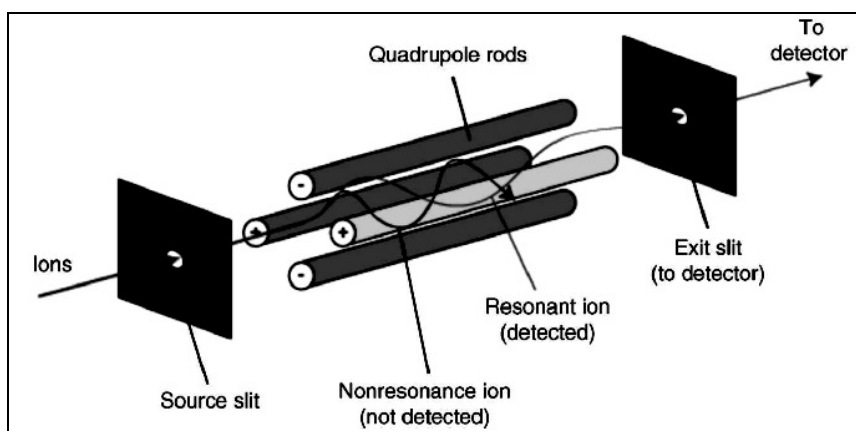


Figure 1.7. Quadrupole analyzer

The former is the older version which uses strong magnets to focus the fragmented ions to the detector plate, whereas, the latter uses four short parallel metal rods; wherein two vertical rods are connected to the positive pole and the other two to the negative pole of a variable power source. This will create a variable electric field and it is used to focus the fragments onto the detector slit. This quadrupole instrument is newer and more popular because of its compact design and also it provides a faster scanning capability.

1.4.3. Gas Chromatography-Mass Spectroscopy

The combination of gas chromatography for separation and mass spectroscopy for detection and identification of the components of a mixture of compounds is rapidly becoming the definitive analytical tool in the research of POPs. Because of its impressive sensitivity, GC-MS allows chemists to detect extremely small quantities of environmental contaminants in water, soil and air. One of the main areas of interest to environmental chemists is the identification and quantitation of organic substances, such as chlorinated compounds, polycyclic aromatic hydrocarbons, and pesticides, in water, air and soil. Selected or single ion monitoring (SIM) improves the sensitivity by limiting the mass of the ions detected to one or more specific fragment ions of known mass. Therefore it is highly selective and it eliminates the large portion of noise exist in the full scan mode. The great majority of the GC-MS application utilizes capillary GC with quadropole MS detection and electron ionization (EI). Nevertheless, there are substantial numbers of applications utilizing different types of mass spectrometers and ionization techniques coupled with multidimensional high-speed and pyrolysis-gas chromatographic methods (Ragunathan *et al.*, 1999).

The mass spectrometer takes the injected material, ionizes it in a high vacuum, propels and focuses these ions and their fragmentation products through a magnetic mass analyzer, and then collects and measures the amounts of each selected ions in a detector (McMaster and McMaster, 1998) (Figure 1.8).

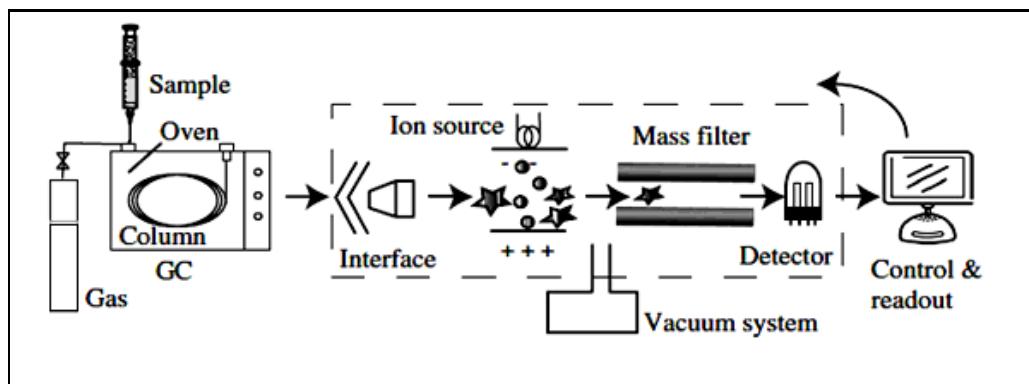


Figure 1.8. A schematic representation of GC-MS

1.4.4. Gas Chromatography-Electron Capture Detector

The electron capture detector (ECD) was an early high sensitivity gas chromatography detector invented by Lovelock in the late 1950s. It evolved from the development of the argon detector, although it worked on an entirely different principle. In its original form, it consists β -ray source that produces both of a cell containing a low energy electrons and ions. The original source was tritium absorbed into silver foil but, due to its inherent temperature instability, this was quickly replaced by the thermally stable ^{63}Ni source (Figure 1.9).

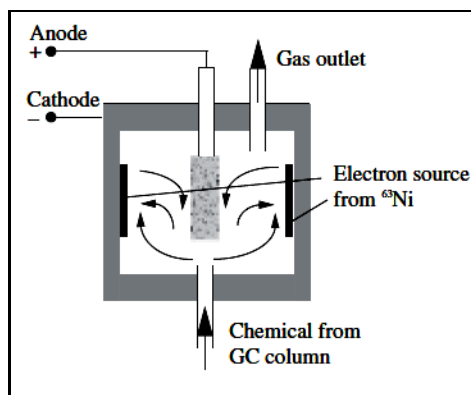


Figure 1.9. A schematic representation of working principle of ECD

Some more recent detectors generate the electrons by plasma discharge. The detector can function in two ways, either with a constant DC potential applied across the electrodes (the DC mode) or a pulsed potential applied across the electrodes (the pulsed mode). In the DC mode a constant potential of a few volts is applied across the electrodes that is just sufficient to collect all the electrons that are produced and, thus, provide a small standing current. When an electron capturing molecule enters the detector (e.g., a halogenated molecule) the electrons are captured by the molecules and the molecules become charged. The mobility of the electrons, captured by the halogenated material, is much smaller than the free electrons and the captured electrons are also more likely to be neutralized by collision with positive ions. As a consequence, the detector current falls dramatically. In the pulsed mode, the period of the pulsed potential is adjusted so that relatively few of the slow negatively charged molecules reach the anode but the faster moving electrons are all collected. During the off-period of the pulse the electrons re-establish equilibrium with the gas. The operating variables are pulse duration, the pulse frequency and the pulse amplitude. By appropriate adjustment of these pulse characteristics, the current can be made to indicate the mobilities of the different charged species in the cell and thus, provide some discrimination between different electron capturing materials.

The electron capture detector is one of the most sensitive gas chromatography detectors available. The electrons formed are attracted to a positively charged anode, generating a steady current. As the sample is carried into the detector by a stream of nitrogen or a 5 % methane, 95 % argon mixture, analyte molecules capture the electrons and reduce the current between the collector anode and a cathode. The analyte concentration is thus proportional to the degree of electron capture, and this

detector is particularly sensitive to halogens, organometallic compounds, nitriles, or nitro compounds.

1.5. Factor Analysis

Factor analysis is widely used multi-variate statistical method in environmental studies in order to identify pollution sources and to determine the effect of each source on total pollution.

It is necessary to have 70 or higher percentage of the samples to operate the system on selected compounds in FA. In principle, the FA classifies the compounds showing the similar changes and separates them into the factors (Henry *et al.*, 1984). Factor analysis comes out for the consideration of the changes in compounds derived from the common sources from the distribution of the environmental data sources. Ideally, each determined factor indicates a source of pollution that affects the samples. There are not common rules for the determination of the factors however, significant factor or higher eigen values more than one is generally selected. In theory, unrelated factors also have an eigen value and eigen values are smaller than one points less participation from the variable. Eigen values, which has a higher value is than one kept (Einax *et al.*, 1997).

The difficulties of the application of the factor analysis contain the effect that is the result of the combination of the multiple sources on the concentration of compounds. This distinction can be made correctly by means of a broad set of data. However, large data set of resources is not enough to distinguish. The usage of the

FA for the definition of sources on the receptor is entirely related to the transportation of compounds therefore, it is difficult to distinguish two sources close to each other although they have different kind of emissions. Therefore, the sources far from the sampling point tend to exist together and local winds mixing the air coming from different directions affect the results.

In this study, FA is performed by using Statgraphics Plus program package (Statgraphics 3.1, 1997). The first components are transformed by VARIMAX method (Schaug et al., 1990). First result is a factor matrix which each compound or variable associated with each factor. The numbers in matrix are named as factor loads and they show how much the variance of the compounds can be explained by factors. The factors at the matrix are in a decreasing row for the definition of the variation of the whole system. In general, only the high order factors are used for further analysis. The physical meaning of the factors is interpreted by compounds or variable showing high (> 0.20) loadings at the factors. There are no definite rules for the selection of the factors, however, the application of the selected factor must describe at least 70 % of total variance. Every time order of factors must be the same as the ability of being explained system variance by percentage. The number of parameters gives the total variance and each parameter has unit variance. The success of the FA solution is explained by all the factors described in percent variance. The higher is the percent of variance explained in the FA, the better is the solution of FA. Communality is the function of the variation of each compound explained by factors.

1.6. Gas-Particle Partitioning (GPP) Models

GPP is a parameter which can provide an indication about persistence of POPs in the atmosphere. Several processes might control the GPP of POP compounds: the first process is the evaporation and condensation. This process could be classified as a physisorption type which could be evaluated by the Junge–Pankow (J–P) model according to the vapor pressure of chemicals (Junge, 1977 and Pankow, 1987). The second process is the absorption and partition of POPs based on the octanol-air partition coefficient parameterized by the K_{OA} model (Finizio *et al.*, 1997). The third process depends on the adsorption principle which is explained by the soot-air partition coefficient (K_{SA}) (Harner and Bidleman, 1998) by utilization soot-water partition constant (K_{SW}). GPPs can also be governed by both adsorption and absorption mechanisms. Hence, polyparameter linear free energy relationships (ppLFERs) were proposed to predict the GPPs as a function of solvation parameters and van-der-Waals interactions (Götz *et al.*, 2007).

An experimental gas-particle coefficient (K_p) is used to describe the distributions of POPs. The absorption approach is explained by the following equation,

$$K_p = (C_p / TSP) / C_g = \frac{f_{OM}}{MW_{OM}} \frac{760RT}{\zeta P_L^o 10^6} \quad (1)$$

C_p : The concentration of compound in the particulate phase (ng m^{-3});

C_g : Concentration of compound in gas phase (ng m^{-3});

TSP: Total suspended particulate matter ($\mu\text{g m}^{-3}$);

f_{OM} : Fraction of the organic matter on the particulate matter;

T: Temperature (K);

R: Gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$);

MW_{OM}: Molecular weight of the organic compound (g mol^{-1});

ζ : Activity coefficient of pollutant absorbed in the organic matter;

P_L^o: Sub-cooled vapor pressure (Pa).

The experimental coefficient (K_p), which is related with the adsorption process, is developed for expression of gas-particle partitioning as given below (Simcik *et al.*, 1998).

$$K_p = (C_p / TSP) / C_g = \frac{N_s a_{PM} T_e^{(Q_1 - Q_v) / RT}}{2133 P_L^o} \quad (2)$$

C_p: The concentration of compound in the particulate phase (ng m^{-3});

C_g: Concentration of compound in gas phase (ng m^{-3});

TSP: total suspended particulate matter ($\mu\text{g m}^{-3}$);

N_s: Surface area concentration of adsorption region (mol cm^{-2});

a_{PM}: Surface area of the particulate matter ($\text{cm}^2 \mu\text{g}^{-1}$);

T: Temperature (K);

R: Gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$);

Q₁: Enthalpy of the desorption (kJ mol^{-1});

Q_v: Enthalpy of the evaporation (kJ mol^{-1});

P_L^o: Sub-cooled vapor pressure (Pa).

1.6.1. Junge-Pankow Model

Junge and Pankow (Junge, 1977 and Pankow, 1987) applied an adsorption model to determine the sorption of POPs to aerosols.

$$\phi = c\theta / (P_L^0 + c\theta) \quad (3)$$

Where ϕ , is the fraction of chemical adsorbed to particle, P_L^0 is the saturation liquid-phase vapor pressure of the adsorbing substance (Pa), θ is the aerosol surface area per unit volume of air ($\text{cm}^2 \text{ cm}^{-3} \text{ air}$) and the parameter c is related to the heat of desorption from the particle surface, the heat of vaporization of the compound and the moles of adsorption sites on the aerosol. Typical values for θ are 4.2×10^{-7} (continental air), 3.5×10^{-6} (rural air) and 1.1×10^{-5} (urban air) (Bidleman, 1999). The value of c is usually taken as 17.2 Pa cm (Harner and Bidleman, 1998). The fraction of the particle phase was expressed with the concentrations of the gas and particle phase by Falconer *et al.* (1995).

$$\phi = C_p / (C_p + C_g) \quad (4)$$

where, C_p is the concentrations of the pollutants in particle phase and C_g is the concentrations of the pollutants in gas phase.

1.6.2. Log K_p and Log P_L°

The following equation is successfully applied in order to determine the sorption (either adsorption or absorption) of on the particles in a time interval (Simcik *et al.*, 1998; Mandalakis *et al.*, 2002; Cindoruk *et al.*, 2007).

$$\log K_p = m_r \log P_L^\circ + b_r \quad (5)$$

The m_r values are approaches to one when the following assumptions are considered:

- the difference between desorption and H_{vap} , and the regions that are suitable for the adsorption must be constant for adsorption approach.
- activity coefficients must be constant for one group of compounds for the absorption.
- the difference between the desorption and the H_{vap} must be constant for one class of the compounds.

P_L° can be calculated by the following equation (Falconer *et al.*, 1995),

$$\log P_L^\circ = m_L/T + b_L \quad (6)$$

The slope m_L and b_L values can be found anywhere in literature for PAHs.

1.7. Back Trajectory Model

The transportation of the air mass can be calculated forward and backward by models. The back trajectory analysis is used to determine the source of the pollutants where they come from and what kind of effects cause the composition of them (Draxler and Rolph, 2003). Trajectory is the displacement of very small particles by the movement of air mass. The back trajectory modelling can be done by Hysplit models with desired heights, which refers long-range transport greater than 1000 m and short-term transport lower than 1000 m, respectively (<http://www.arl.noaa.gov/ready/hysplit4.html>, 2008).

1.8. General Information about Bolu

Bolu is a small city at the north west of the Turkey, which is in the western Black Sea Region. It is not a populous city and it has an average 32 person per kilometer. It is between the 30° 32' and 32° 36' east longitudes; and 40° 06' and 41° 01' north latitudes. The city has an average 1000 m altitude while the city center has a 725 m altitude. Sakarya and Düzce are at the west; Bilecik and Eskişehir are at the southwest; Ankara is at the southeast; Çankırı is at the east; Karabük is at the northeast; and Zonguldak is at the north direction. It has 9 cities, 4 districts, and 512 villages. 56 % of the area of province is covered with mountains. These mountains are arranged in northeast-southwest direction and divided by the plains forming with the effect of movement of Northern Anatolian Fault. Total size of the plains covering about 12 % of the area within the province is 102.000 ha, and the greatest one is the Bolu Plain with an area of 46.000 ha. 59 % of the Bolu is covered with the forest

areas, 18 % of it is covered with agricultural areas, and 15 % of the city is covered with grassland while the remaining part is useless areas. Southern winds are dominant in Bolu. The air masses from the sea to the landward and moderate temperature results the moisture.

In the agricultural regions, mostly grain is cultivated and mainly wheat is grown up in Bolu. The other kinds of grains are barley, oat, rice, and corn in Bolu. Tuber crops, potato, onion, garlic and animal beet are grown, and potatoes has significant economic value for Bolu.

Bolu do not have great industrial activities and most important ones are food, forest products and furniture, metal industry, thermal glass and tempered glass industry, electrical equipment production, the textile-clothing items, the cement and leather plants.

1.9. Objectives of the Study

The main objectives of the study are to make source region apportionment of persistent organic pollutants in the atmosphere of Bolu. Analyze particle and gas phase samples to determine the concentrations of Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs) and Organo Chlorine Pesticides (OCPs). To attain the main goal of the study, the following specific objectives will be realized.

- 1- to develop an extraction and clean-up method in order to separate and pre-concentrate all organic compounds as much as possible in one run,
- 2- to optimize the instrumental parameters to analyze the samples by GC-MS and GC-ECD,
- 3- to determine the concentrations of PAHs, PCBs and OCPs in air and soil samples,
- 4- to examine the temporal and seasonal variations of PAHs, PCBs and OCPs in the atmosphere,
- 5- to determine the effect of local meteorology on pollutants by making wind sector analysis,
- 6- to determine the gas to particle, air to soil exchange coefficients of PAHs, PCBs and OCPs,
- 7- to investigate the long range transport of pollutants by using Back Trajectory model,
- 8- to make source apportionment of pollutants by applying the receptor modelling (factor analysis, correlation analysis).

CHAPTER 2

2. LITERATURE SURVEY

2.1. Around the World

2.1.1. Literature Survey Related with Europe

In a study to establish the baseline contamination of the environment prior to the start-up of a new municipal incinerator, air samples were collected continuously over a period of one year at eight locations in southern Bavaria by Kaupp and McLachlan in 1998. The air samples were analyzed in six week intervals for the particle bound and gaseous concentrations of (PCDDs), (PCDFs), (PCBs) and (PCNs) as well as PAHs. Sampling was performed at a flow rate of $2.5 \text{ m}^3 \text{ h}^{-1}$ with a sampler consisting of a GFF backed up by XAD adsorbents. The logarithms of the K_p were closely correlated with the inverse mean ambient temperature. When $\log K_p$ at 25°C was plotted vs. the logarithm of the compounds P°_L , the investigated compounds separated out into two groups. Within each of the two groups a linear correlation between K_p and P°_L was observed, but for the PAHs and PCNs the particle bound fractions were always considerably higher than for the PCDD/Fs and PCBs with comparable P°_L . Due to these differences they showed that P°_L is not a

good parameter for describing the inter-chemical variability in gas-particle partitioning. Log K_p was also plotted against the logarithm of the K_{oa} and it is found that K_{oa} may be a better descriptor of partitioning behaviour for these substances. They also controlled possible loss of compounds from the adsorbent trap by several experiments and in all cases 20 g of XAD were sufficient for quantitative analysis (Kaupp and McLachlan, 1999).

Cousins and Jones discussed field experiment in which the air-soil exchanges of a range of PCBs and PAHs were measured and the use of the fugacity quotient PCDDs between the air and soil in the UK. They took soil and air samples periodically throughout the 9 month period and analyzed for PCBs and PAHs. The results from the experiment showed that the PCBs and PAHs in the soils were moving towards equilibrium partitioning conditions. They had previously spiked PAHs and PCBs in some of the samples and some of not spiked by these compounds. Statistically significant losses of the majority of PCB and PAH compounds occurred in the spiked soils. Volatilization was hypothesised to be the dominant loss mechanism. The PCBs in the unspiked soils were close to equilibrium with the air at the start of the experiment and there was, therefore, little change in their concentrations during the 9 months of exposure. For the PAHs there was also only a small change in the concentrations in the unspiked soils during the experiment, although there was a statistically significant loss of acenaphthene, fluorene and phenanthrene. They calculated soil-air fugacity quotients using the air and soil concentrations measured in the field experiment. The calculated soil-air fugacity quotients, together with the findings of the field experiment, indicate that the soil and air were close to equilibrium for PCBs. However, their study provided evidence that

the soil may be a source of some lighter weight PAHs to the atmosphere, whereas it appears to be still acting as a long-term sink for the heavier weight PAHs and the PCDDs. They carried out analysis of sample extracts for PCBs by GC-ECD. They listed the sum of 53 congeners in their article. They analyzed PAHs with high performance liquid chromatography (HPLC) with fluorescence detection (Cousins and Jones, 1999).

Concentrations of individual PCBs and some of OCPs were recorded in 62 air samples of 24 h duration taken every 1–2 weeks at an urban location in Birmingham, UK between April 1999 and July 2000 by Harrad and Mao, (2004). They collected samples using a high volume sampler fitted with a total suspended particulate (TSP) inlet modified to hold a GFF, and a pre-cleaned PUF plug. GFFs and PUFs were analyzed separately to yield concentrations in both particulate and vapor phases. Analyses were conducted using well-validated, containment enrichment, GC-MS procedures. They found the concentrations of PCBs 31/28, 52, 49, 47, 105, 149, 153, 138/164, 174, and 180 were significantly lower than those recorded at the same site in earlier measurements. Multiple linear regression analysis of all samples revealed concentrations of most PCB congeners to be influenced by a combination of reciprocal temperature, wind direction, and wind speed. However, when samples for which the wind speed $< 4.4 \text{ m s}^{-1}$ were analyzed; only temperature and atmospheric relative humidity were influential for most congeners. This absence of influence of wind direction under relatively calm atmospheric conditions implies that medium-to-long range transport rather than local sources exerts the greatest influence on PCB concentrations at their site (Harrad and Mao, 2004).

PCB concentrations were studied by Backe *et al.*, (2004) in different soils to determine the spatial variation over a region of approximately 11 000 km². They collected soil samples from 11 different areas, in the southernmost province of Sweden. They combined sampling with an air and precipitation study of POP, using the same sampling-sites. Air samples and rain samples were collected simultaneously from June 1992 to September 1993. They sampled air with air pumps through two PUF plugs, 2 m above ground. The relationship to different soil parameters was studied in their study. The large variation in PCB concentration in the soil between different sites (ranging between median 2.6 and 332 ng g⁻¹) explained by differences in soil properties, i.e. soil texture and organic matter content, but other environmental conditions such as proximity to secondary sources and wind direction also play a major role. PCB congener composition was shown to differ between sites, with congener patterns almost site-specific. PCB in air and precipitation was measured and the transfer of chemicals between the soil and air compartments was estimated. Soil-air fugacity quotient calculations showed that the PCBs in the soil consistently had a higher fugacity than the PCBs in the air, with a median quotient value of 2.7. The gaseous fluxes between soil and air were estimated using standard modelling equations and a net soil-air flux estimated by subtracting bulk deposition from gaseous soil-air fluxes. It was shown that inclusion of vertical sorbed phase transport of PCBs in the soil had a large effect on the direction of the net soil-air exchange fluxes (Backe *et al.*, 2004).

2.1.2. Literature Survey Related with America

One of the earliest studies about atmospheric organic pollutants began with Bidleman and Keller, and they had published an article related with the collection of the organic pollutants in air by GFF and PUF at a rural and an urban area between 1981 and 1982. They had found that PAHs with a 3 to 4 ring were on the PUF trap and higher ring PAHs were on the GFF. In addition, PUF was used as a trapping agent for PCB and OCP vapors. Sixteen samples of urban and four samples of rural air collected and separated into polar and non polar organic compounds. Total organic compounds that contain greater than nineteen carbons and PAHs were analyzed by flame ionization GC and reversed phase HPLC with fluorescence detection, respectively. As a result, the average non-polar concentration was found 629 ng m^{-3} and polar concentration was 234 ng m^{-3} for the urban area. In the rural area, the concentrations were found to be 292 ng m^{-3} and 139 ng m^{-3} , respectively, (Keller and Bidleman, 1984).

In 1989, Ligockit and Pankow measured the gas-particle distributions of PAHs and other organic compounds at ground level in Portland and at the Oregon coast. Their work was conducted to investigate the gas-particle distribution process with both GFFs and TMF. They found that measured particulate-phase concentrations of most PAHs and oxo-PAHs were virtually the same whether glass fiber or TMFs were used. They were determined the contributions to the measured particulate-phase concentrations made by gas adsorption to the GFFs. Backup glass fiber filter concentrations were measured and found to be quite variable, averaging 30-70 % of the primary filter values for alkanes, but less than 30 % for all PAHs. At

the coastal site, due to the lower concentrations of particulate matter, the gas-particle distributions of PAHs were shifted toward the vapor phase relative to what was observed in Portland. At both sites, the gas-particle distributions correlated with the supercooled liquid vapor pressures for the PAHs of low to intermediate volatility. The GFFs and TMFs were used for the particulate sampling and the PUF plugs were used for gaseous sampling. The GFFs used exhibit > 99 % collection efficiency for all particle sizes, any material found on a GFF backup filter in a blank-corrected quantity greater than ≈ 1 % of the front filter amount probably represented sorbed gas. The collected air samples were analyzed by GC-MS (Ligockit and Pankow, 1989).

In the paper published by Cotham and Bidleman in 1995, air samples were collected at an urban (Chicago, IL) and a rural (University of Wisconsin at Green Bay, UWGB) site to determine concentrations and particle-gas distributions of PAHs and PCBs. They drawn air volumes by the sampler through two GFF followed by two PUF plugs. They determined PCBs and PAHs by capillary GC-ECD and GC-MS respectively. As a result geometric mean Σ PAHs of molecular weights ≥ 166 were measured 195 ng m^{-3} in Chicago and 14 ng m^{-3} at UWGB. Ratios among PAHs suggested that some labile compounds were depleted during atmospheric transport. Geometric mean Σ PCBs (45 congeners) were found 1.3 ng m^{-3} in Chicago and 0.13 ng m^{-3} at UWGB. PCB profiles of most samples in Chicago and all at UWGB were skewed toward the lower molecular weight congeners, as in mixtures of Aroclors. They correlated apparent K_p with liquid-phase vapor pressures (P_L°) within a class of compounds (PAHs or PCBs). It was observed that PAHs were sorbed to a greater degree than PCBs for compounds of same volatilities (Cotham and Bidleman, 1995).

Simultaneous air samples were taken in Chicago and over southern Lake Michigan by Simcik *et al.*, (1998). The high volume air samplers were equipped with GFFs to collect particulate phase compounds and PUF plugs to collect the gas phase compounds in their study. Gas and particle phase concentrations of PCBs, PAHs, and TSP were measured in both regions. Due to the large number of PCBs analyzed, 55 peaks corresponding to 80 congeners, only the 40 most prominent had been reported. TSP concentrations ranged from 11 to 71 $\mu\text{g m}^{-3}$ in Chicago and 1.5 to 29 $\mu\text{g m}^{-3}$ over Lake Michigan. The GFF and PUF associated concentrations of PCBs and PAHs were a good estimate of the true gas and particle phase concentrations in these samples. Partitioning of PCBs and PAHs between gas and particle phases was well correlated with the subcooled liquid vapor pressure for individual samples. The matter under discussion of nonequilibrium represents a kinetic problem in which the lower molecular weight of PCBs and PAHs have higher diffusivities and, therefore, approach equilibrium faster than the higher molecular weight species in air resulting in their data that have a steep slope for PCBs and PAHs with higher vapor pressures and a decreasing slope as vapor pressure decreases. Their data do not exhibit a decreasing slope with decreasing vapor pressure, and a straight line best represents the correlation between partitioning and subcooled liquid vapor pressure. Another indication that kinetics are not affecting the slope is found when comparing regressions of samples representing air masses that originate in the urban/industrial complex, and ones that represent continental background. Regressions of $\log K_p$ vs $\log P^\circ_L$ for both Chicago and Lake Michigan samples gave high correlations for individual samples for both PAHs ($r^2 = 0.85\text{-}0.98$) and for most PCBs ($r^2 = 0.10\text{-}0.71$), but the slopes and intercepts amongst samples varied greatly. As a result,

PCBs and PAHs measured in Chicago and over Lake Michigan were apparently at equilibrium between the gas and particle phases (Simcik *et al.*, 1998).

Simcik *et al.*, (1999) had measured gas phase PCB concentrations in the atmosphere around the Great Lakes since November of 1990. In general, air samples were taken at each site using a high-volume air sampler equipped with a GFF and PUF plugs to collect the particle and gas phase PCBs, respectively. Then, these data were used to explore the temperature and time dependencies of gas phase PCB concentrations near Lakes Superior, Michigan, Erie and Chicago. Individual PCB concentrations were well correlated to temperature for the three remote sites using the Clausius-Clapeyron equation, but the calculated heats of surface-air exchange did not correlate (on a congener basis) with laboratory-measured heats of vaporization. On the other side, the heats of surface-air exchange for PCB congeners measured in Chicago are well correlated with laboratory-measured heats of vaporization. They conclude that the gas phase PCB concentrations measured at Chicago were controlled by short range transport, but at the three remote sites, these concentrations were controlled by long-range transport. Gas phase PCBs also exhibited decreasing concentrations over the period 1991-1997 near Lakes Michigan and Erie and in Chicago. Significant half-lives ranged from 0.5 to 7.5 years for individual congeners and 2.8 to 3.3 years for total PCBs. Gas phase PCBs near Lake Superior showed no general trend in gas phase concentration over this same time period (Simcik *et al.*, 1999).

Buehler *et al.* (2001) compared atmospheric concentrations of PAHs, PCBs, and pesticides at Brule River and Eagle Harbor, two rural sites on Lake Superior in

2001. They collected air samples using a modified Anderson high-volume sampler that pulls air through a filter and an absorbent at a rate of $34 \text{ m}^3 \text{ h}^{-1}$. The particles were collected on GFFs and gas phase compounds on XAD-2 resin. They analyzed the samples by GC-ECD and GC-MS. Pesticide and PCB concentrations were found similar at both sites. Day-by-day regression analyses of the data showed that PAH concentrations, an indication of urban contamination, were significantly higher at Brule River than at Eagle Harbor. Concentration ranges for all compounds at both sites were well within global background levels, despite the differences observed between the two sites. Clearly, pollution from industrialized area was influencing PAH concentrations at Brule River more than at Eagle Harbor. Despite the apparent influence of small city on Brule River concentrations PAH levels in the gas and particle phases in this study at both Brule River and Eagle Harbor were comparable to the levels at other rural locations, and they were well below urban PAH levels. Interestingly, while PAH levels at Brule River were, on average, 1-3 times greater than levels at Eagle Harbor and on some individual days 10 times greater. The Brule River sites were affected by nearby sources of PAHs; and Brule River site was affected less, presumably because it is further away (40 km) from a smaller city (Buehler *et al.*, 2001).

Data through 2001 from the Integrated Atmospheric Deposition Network (IADN) were used to investigate the causes of variability in gas phase PCB and pesticide concentrations measured near Lakes Michigan, Erie, and Superior in another study from Buehler *et al.*, (2004). They collected air samples using a modified high-volume sampler. Particles were collected on GFF and gas phase compounds were collected on XAD-2 resin. Both PCBs and pesticides were analyzed

by GC-ECD in gas phase and particulate phase by them. They used a multiple linear regression model that incorporates temperature and time to explain the variability in the concentrations. Their approach used autocorrelation analyses of the residuals to help them determine the effectiveness of the regression. Autocorrelation plots for the in-use pesticide lindane indicated that an agricultural application cycle was also present in the regression residual data at all sites. Similar analyses for the in-use pesticide endosulfan did not show an agricultural application effect. The banned compounds DDT and chlordane showed that temperature and time correctly accounted for the variability in the atmospheric concentrations of these compounds at all sites. In contrast to the other compounds, PCBs and hexachlorobenzene showed strong residual autocorrelation patterns near Lake Michigan of an unknown origin (Buehler *et al.*, 2004).

Bidleman and Leone collected soil samples from 30 farms in Alabama, Louisiana and Texas during 1999–2000 to determine residues of OCPs. 2.5 cm diameter and 8 cm deep soil samples were collected along a uniformly spaced grid. Soil cores from a field were pooled and sieved on site through a 2 mm steel mesh to provide a representative sample for analysis. In addition, they collected air samples by GFF and PUF plugs in the soil sampling region. Samples were analyzed by gas chromatography–electron capture negative ion mass spectrometry (GC–ECNI-MS). OCPs were measured in air at 40 cm above the soil at selected farms to investigate soil-air partitioning. Concentrations of OCPs in air were positively and significantly ($P < 0.001$ – 0.004) correlated to soil concentrations. Approach to soil-air equilibrium was assessed by calculating fugacities in the soil and air (f_s and f_a) for samples with quantifiable residues in both compartments. The fugacity fraction $f_s/(f_s+f_a) = 0.5$ at

equilibrium and is <0.5 or >0.5 for net deposition and net volatilisation, respectively. Mean fugacity fractions indicated near-equilibrium for some OCPs (p,p'-DDE, chlordanes, trans-nonachlor and dieldrin) and net volatilization for others (p,p'-DDT, o,p'-DDT, toxaphene, γ -HCH) (Bidleman and Leone, 2004).

2.1.3. Literature Survey Related with Arctic

In 1992, Stern *et al.*, established a long term program to measure the airborne concentrations of persistent organic pollutants (POPs) in the Arctic. To maximize spatial variation over a wide geographical area, three Arctic locations were selected; two sites in Canada, Alert on Ellesmere Island and Tagish in the western Yukon, and one in Russia at Dunai Island in eastern Siberia. Mean $\sum$ PCB concentrations in 1993, the year when all three sites were running simultaneously, were 27.4, 17.0, and 34.0 pg m^{-3} at the Alert, Tagish, and Dunai sites, respectively. With the exception of the Tagish site in 1993, where $\sum$ PCB concentrations were found to be weakly correlated with mean monthly temperatures, no correlation with temperature was observed. However, changes in the homolog group profile with temperature were apparent. On an annual basis, the trichlorinated congeners made the largest single contribution to the atmospheric concentrations of $\sum$ PCB, however, this contribution declined with the warmer months. This temperature-dependent homolog pattern was most clearly evident at Dunai, where the contribution of the pentachlorinated congeners matched or exceeded that of the trichlorinated congeners during May, June, and July of 1993. It was also evident at Alert and Tagish, but not to the same degree as in Dunai. Spatial and year-to-year differences at these Arctic sites were attributed to both the site's proximity to source areas and to the influence of air mass movement from

these source regions. For Alert and Dunai, cold and warm monitoring periods are defined by months in which mean weekly temperatures remain below and above -15 °C. At the Tagish site, they are defined by months in which mean weekly temperatures remain below and above 0 °C, respectively. Tagish had the lowest mean Σ PCB concentrations during both the warm and cold monitoring periods (Stern *et al.*, 1997).

Hung *et al.*, (2005) published an article discussing of the concentrations and transportation of PCB, PAH, and OCP at the Arctic atmosphere in the relation with the Northern Contaminants Program, in 2005. The NCP baseline monitoring project was established in 1992 to monitor for persistent organic pollutants (POPs) in Arctic air. Under this project, they were collected weekly samples of air at four Canadian and two Russian Arctic sites, namely Alert, Nunavut; Tagish, Yukon; Little Fox Lake, Yukon; Kinngait, Nunavut; Dunai Island, Russia and Amderma, Russia. Selected POPs, including PAHs, PCBs and OCPs, were analyzed in both the gas and particulate phases. Results obtained from this project in the past 5 years were summarized in their study. Temporal trends were developed for atmospheric PCBs and OCPs observed at Alert using a digital filtration (DF) technique. It was found that trends developed with 5 years of data (1993–1997) did not differ significantly from those determined with 7 years of data (1993–1999). This implies that with the DF technique, long-term trends can still be developed with less than 10 years of data. Occasional high trans-/cis-chlordane ratios and heptachlor air concentrations measured at Alert between 1995 and 1997 suggests sporadic fresh usage of chlordane-based pesticides. However, significant decreasing trends of chlordanes along with their chemical signatures had provided evidence that emission of old soil

residues was replacing new usage as an important source to the atmosphere. Measurements of OCP air concentrations conducted at Kinngait in 1994–1995 and 2000–2001 indicated faster OCP removal at this location than at Alert. This could be attributed to the proximity of Kinngait to temperate regions where both biotic and abiotic degradation rates were faster. The PAH concentrations observed at Alert mimic those at mid-latitudes and were consistent with long-range transport to the Arctic, particularly for the lighter PAHs. A decline in particulate PAH was observed, similar to atmospheric sulphate aerosol and could be attributed to the collapse of industrial activity in the former Soviet Union between 1991 and 1995. Spatial comparisons of OCP seasonality at Alert, Tagish, Dunai and Kinngait show elevated air concentrations of some compounds in spring. OCP and PCB air concentrations at Alert were found to be influenced by two climate variation patterns, the North Atlantic Oscillation (NAO) and the Pacific North American (PNA) pattern. The Σ PAH vapor phase concentrations ranged from 113 to 516 pg m^{-3} and the particle phase concentrations ranged from 38 to 392 pg m^{-3} at Alert from 1993 to 2000. The concentrations of Σ PAH observed at Spitsbergen were generally much higher than those found at Alert and Kinngait. For the dominant compounds, including fluorene, phenanthrene, fluoranthene and pyrene, the annual mean concentrations were higher at Spitsbergen by a factor of 2 to 3. As observed in 1993, the PCB levels for 1995–1996 were generally lower at Alert than those reported for other AMAP Arctic sites. α -, γ -HCHs and HCB, which are OCPs with the highest vapor pressures, achieved the highest levels in all 7 years and annual average air concentrations observed at Alert were similar to those found at Spitsbergen. Although DDT has been banned or severely restricted in many countries, it is still being used in others, especially those

in the tropical region, to control insects that carry diseases such as malaria and typhus (Hung *et al.*, 2005).

Weekly high volume air samples consisting of one GFF and two PUF plugs were collected at remote Arctic air monitoring stations. Weekly air samples collected at remote Arctic monitoring stations at Alert and Tagish, Canada, and Dunai Island, Russia, between 1994 and 1995 were analyzed for levels and seasonal trends of polychlorinated naphthalenes (PCNs) and non- and mono-ortho-substituted PCBs by Helm *et al.*, (2004). PCNs and non-/mono-o-PCBs were quantified by gas chromatography-electron capture negative ion mass spectrometry (GC-ECNIMS) using a GC-MS in selected ion monitoring (SIM) mode with methane as the reagent gas. Mean annual Σ PCN concentrations were 0.69, 0.82, and 0.38 pg m⁻³ at Alert, Dunai, and Tagish, respectively. PCNs exhibited a seasonal trend at Alert and Dunai, with higher levels occurring during winter when air masses originating over Eurasia influence the high arctic and coincide with the haze period. Episodic, trans- Pacific transport impacted PCN concentrations at Tagish. A seasonal trend was not evident for the non-/mono-o-PCBs. The contrary PCN and non-/mono-o-PCB trends indicate that the sources of these two compound classes to arctic air differ, and that atmospheric transport from source regions had a greater influence on PCN levels than for non-/ mono-o-PCBs. PCNs apparently originating from combustion sources contribute to levels in winter, as indicated by the presence of combustion marker congeners, but evaporative emissions from source regions were likely the dominant source. PCNs contributed 71 and 75% of dioxin toxic equivalents (TEQ) relative to the non-/mono-o-PCBs at Alert and Dunai and 30% at Tagish during the winter months, demonstrating the toxicological importance of PCNs as a compound class

relative to PCBs. Ranges (annual mean $\pm$ standard deviation) of Σ PCN were <0.01 - 1.3 (0.69 ± 0.36) pg m^{-3} at Alert, <0.01 - 1.7 (0.38 ± 0.51) pg m^{-3} at Tagish, and <0.01 - 2.9 (0.82 ± 0.94) pg m^{-3} at Dunai. PCB levels ranged from 0.05 to 0.20 (0.10 ± 0.05) pg m^{-3} at Alert, 0.002 - 0.11 (0.05 ± 0.03) at pg m^{-3} Tagish, and 0.19 - 0.82 (0.44 ± 0.19) pg m^{-3} at Dunai and were significantly different between all stations (Helm *et al.*, 2004).

2.1.4. Literature Survey Related with Asia

Yeo *et al.*, (2003) published an article on concentrations of PCB and OCP in rural air. They measured PCB and OCP concentrations every other week from July 1999 to February 2000 in the rural air of Ansong, Kyonggi-do in South Korea. They used a low volume PUF sampler to collect the ambient air PCB and OCP samples and they were analyzed by GC-MS. The average contribution of PCB homologs were tri-(44.5%), tetra-(23.6%), penta-(21.6%), hexa-(3.6%), hepta-(5.5%) and deca-CB (1.6%) therefore identifying tri-CBs as the main component of PCB homologs. They found that endosulfan was the most prevalent OCP because of its continuous usage as a pesticide in South Korea. The correlation coefficient between OCPs and temperature was significantly high which was partly due to the fact that major sources are re-volatilization from soil, vegetation and so on. The Clausius–Clapeyron equation was applied to atmospheric total PCBs and OCPs, relating partial pressure ($\ln P$) to inverse temperature ($1/T$). The partial pressure of total PCBs and OCPs were all significantly correlated with inverse temperature and the slopes of resulting plots of total PCBs and OCPs ranged from -2950 (total PCBs) to -6629 (α -HCH), -8106 (γ -HCH). The strong temperature effect and steep slopes of OCPs indicate the

predominant impact of local surroundings to these concentrations in the rural atmosphere. The distributions of PCB homologs during the sampling period were detected and the average concentration of 22 PCB (total PCBs) was found 19.9 pg m^{-3} with a range 6.13-71.9 pg m^{-3} (Yeo *et al.*, 2003).

2.2. Literature Survey Related with Turkey

Twenty successive daytime and nighttime air samples were collected and analyzed for 23 currently used and/banned organochlorine pesticides (OCPs) between 14 and 23 May 2003 in Izmir, Turkey by Sofuoğlu *et al.* They collected air samples using a modified high-volume sampler; particles on the GFF and the gas phase in a modified cartridge containing XAD-2 resin placed between layers of PUF. They collected particulate samples on 11-cm diameter glass fiber filters using another high volume sampler to determine total suspended particulate (TSP) matter and its organic matter (OM) content. They analyzed samples for OCPs with a gas chromatograph (GC) equipped with a micro-electron capture detector (μ -ECD). They found the average individual OCP concentrations in a range from $5 \pm 4 \text{ pg m}^{-3}$ (p,p'-dichlorodiphenyldichloroethane) to $391 \pm 306 \text{ pg m}^{-3}$ (chlorpyrifos). They did not observe strong diurnal cycling for most of the OCPs. They found the temperature dependence of gas phase statistically significant for β -HCH and endosulfan sulfate ($p < 0.1$) and was not significant for other compounds. They also investigated the effect of wind speed and direction using multiple linear regression analysis in addition to temperature dependency and these three parameters together explained the 2% (aldrin) to 72 % (endosulfan II) of the variability in gas phase OCP concentrations in their study. Results of the multiple regression analysis indicated that wind speed was

a statistically significant factor for most of the OCPs and wind direction was important for some compounds in that study. They interpreted the lack of correlation for heptachlor, aldrin, p-p'-DDE, and p-p'-DDT with temperature, wind speed and direction indication of the long-range transport. The partitioning of OCPs between particle and gas phases was investigated and compared to K_{OA} (octanol-air partition coefficient) absorption model in their study. They found that between experimental and modeled $\log K_p$ (gas-particle partition coefficient) values was good ($p < 0.01$, slope=0.94). They predicted that absorption model for particulate percentages was excellent for β -HCH, endosulfan I, and p-p'-DDT. However, the model underpredicted the particulate percentages for α,γ -HCHs, chlorpyrifos, and dieldrin, and overpredicted those for p-p'-DDE (Sofuoğlu *et al.*, 2004).

Atmospheric concentrations of polychlorinated biphenyls (PCBs) and trace elements were measured at two sites (industrial and urban) located around the Aliaga industrial region, Izmir, Turkey by Çetin *et al.* (2007). They collected PCB samples using a modified high-volume sampler; particles on GFF and the gas phase compounds in PUFs. They collected PM_{10} samples on cellulose acetate filters using a particulate matter sampler. They analyzed samples for PCBs with GC-MS and the elemental analysis of all samples was performed using an inductively coupled plasma-optical emission spectrometer (ICP-OES). They determined the average $\sum_{36}PCB$ concentrations as 3136 ± 824 and 1371 ± 642 $pg\ m^{-3}$ for summer and winter periods, respectively in the industrial site and the total PCB concentrations were 314 ± 129 and 847 ± 610 $pg\ m^{-3}$ in the Urban site. They found that the PM_{10} measured at the Industrial site was dominated by terrestrial elements and trace elements emitted by the iron–steel plants (Fe, Zn and Pb) from the elemental

analysis. The elemental profile at the Urban site was typical for Aegean Region that was dominated by terrestrial elements (Ca, Al, Mg) and sea salt (Na). They identified sources of particle phase PCBs and trace elements by using factor analysis (FA) and apportioned by chemical mass balance (CMB) model. FA suggested that the steel industry, fuel oil combustion, or the nearby vinyl chloride process in the petrochemical plant, and soil were significant PCB sources in their study. CMB results showed that at the industrial site, the contribution of steel industry and soil to particle phase PCBs were 71% and 22%, respectively, while at the urban site, the contributions were 33% and 49%, respectively. They found to be the steel industry the dominant contributor for trace elements around the site. They identified that the soil acts as a secondary source to the atmosphere for low molecular weight PCBs especially in summer and as a sink for the higher molecular weight ones according to the fugacity calculations in air and soil (Çetin *et al.*, 2007).

Ambient air and dry deposition, and soil samples were collected by Bozlaker *et al.* (2008) at the Aliağa industrial site in Izmir, Turkey. They collected air samples using a modified high-volume sampler. Particles were collected on 10.5 cm diameter GFFs while the gas phase compounds were collected using a cartridge containing XAD-2 resin placed between PUF plugs. Atmospheric total (particles+gas) $\sum_{41}$ -PCB concentrations were higher in summer ($3370 \pm 1617 \text{ pg m}^{-3}$) than in winter ($1164 \pm 618 \text{ pg m}^{-3}$), probably due to increased volatilization with temperature. Elevated ambient air concentrations during the summer months may be related to the increased volatilization rates of previously deposited PCBs on terrestrial surfaces. Average particulate $\sum_{41}$ -PCB dry deposition fluxes were 349-183 and 469-328 $\text{ng m}^{-2} \text{ day}^{-1}$ in summer and winter, respectively. Overall average particulate deposition

velocity was $5.5\text{--}3.5\text{ cm s}^{-1}$. The soil $\sum_{41}\text{PCB}$ concentrations measured at 48 different points in the study area were highly variable, and ranged between 0.23 and 805 mg kg^{-1} in dry weight. The spatial distribution of $\sum_{41}\text{PCB}$ soil concentrations showed that the iron-steel plants, ship dismantling facilities, refinery and petrochemicals complex are the major sources in the area. Calculated air-soil exchange fluxes indicated that the contaminated soil is a secondary source to the atmosphere for lighter PCBs and as a sink for heavier ones. Comparable magnitude of gas exchange and dry particle deposition fluxes indicated that both mechanisms are equally important for PCB movement between air and soil in Aliğa (Bozlaker *et al.*, 2008).

Gas and particle phase concentrations of atmospheric polychlorinated biphenyls (PCBs) were measured at an urban/industrial site in the city of Bursa, Turkey by Cindoruk *et al.* (2007). PCB concentration levels were presented between July 2004 and May 2005. They used a high volume air sampler equipped with a filter holder and a cartridge for the collection of samples. They took the samples by passing air through a GFF and then through a glass cartridge that contained PUFs. They determined the PCBs by GC-MS. They were presented that average particle and gas phase concentrations of individual PCB congeners ranged from 0.08 (PCB-183) to 6.86 (PCB-49) pg m^{-3} and from 0.01 (PCB-209) to 47.2 (PCB-33) pg m^{-3} , respectively. The mean concentration of total (gas + particle) PCBs varied between 24.27 and 666.21 pg m^{-3} with an average of $287.27 \pm 174.80\text{ pg m}^{-3}$. They had found that PCB concentrations at the sampling site were higher than the concentrations reported at non-urban sites. PCBs partitioned between gas and particle phases by them and they also examined partitioning according to different

approaches such as $\log K_p - \log P_L^0$, $\log K_p - \log K_{OA}$ and the Junge–Pankow model. They constructed a correlation matrix based on PCB congeners and meteorological parameters in order to present possible interactions. Application of the Clausius–Clapeyron equation yielded a low slope value indicating possible emissions from local and regional sources originating mainly from urban/industrial areas, landfill and waste incineration plant in their study (Cindoruk *et al.*, 2007).

Air concentrations of polychlorinated biphenyls (PCBs) in both gas and particle phases were measured in an urban site of the city of Bursa, Turkey between August 2004 and May 2005 by Cindoruk and Taşdemir (2007). They used a modified high-volume air sampler equipped with a filter holder and cartridge for sampling. Air samples were passed through the GFF and then through the PUF plugs. They conducted quantification of the PCB congeners using a GC-MS. The mean of total (particle + gas) PCB concentrations was about $491.8 \pm 189.4 \text{ pg m}^{-3}$. They also determined the main contributors for PCBs in the sampling site which were the local sources and long-range atmospheric transport supported by back trajectory analysis. They found that lower molecular weight PCB congeners generally dominated in the samples and particle phase of the measured PCBs accounted for 15% of the total PCB concentrations. Concentrations of individual PCB congeners in the air ranged from not detected to 9.86 pg m^{-3} (average $\pm$ SD, $1.78 \pm 3.28 \text{ pg m}^{-3}$) for particle phase and from 0.03 to 75.28 pg m^{-3} (average $\pm$ SD, $10.59 \pm 20.11 \text{ pg m}^{-3}$) for gas phase in their study. Average particle and gas phase PCB concentrations were $69.2 \pm 54.6 \text{ pg m}^{-3}$ and $434 \pm 162 \text{ pg m}^{-3}$, respectively. Average particle and gas phase percentages were about 15 and 85, respectively like the obtained values from the other industrial and suburban sites of the city of Bursa. The gas phase percentage

was lower than the reported values in literature; nevertheless, some reported a value of 60 % for gas phase while others reported 80 % for gas phase. The detected congeners were mostly in gas phase including lower molecular weight congeners. They investigated gas-particle distribution using different approaches such as $\log K_p - \log P_L^\circ$, $\log K_p - \log K_{OA}$ and the Junge–Pankow model. Regression analysis among $\log K_p$, $\log P_L^\circ$ and $\log K_{OA}$ exhibited significant correlation at $p < 0.05$ (Cindoruk and Taşdemir, 2007).

In a study published by Salihoğlu and Taşdemir (2009), the equilibrium soil concentrations and distributions of Σ_{41} PCB congeners from the air data measured at 4 sites (urban, suburban, residential, and industrial) in Bursa between 2004 and 2005. A modified high-volume air sampler equipped with a filter holder and cartridge was used for the sampling. They determined the PCB congeners by GC-MS. They used the soil–air partition coefficient (K_{SA}) for the predictions. Predicted soil concentrations ranged from 25 pg g^{-1} to 690 pg g^{-1} , while the atmospheric concentrations fluctuated between 35 pg m^{-3} and 1112 pg m^{-3} . They found soil concentrations to be in agreement with the lower range of European and global values, and below the regulatory limits. The urban and residential sites yielded higher PCB concentrations and a higher degree of heavier congeners than the sites characterized as suburban. The urban and residential sites were dominated by hexachlorinated biphenyls (CBs), followed by tri-CBs, while the industrial site was dominated by tri-CBs, followed by tetra-CBs. PCB congeners of 153, 180, 138, 118, and 101 were higher in all locations. They also determined the effect of the temperature changes on the concentrations which was found to be insignificant, as the correlations ranged between 0.0009 and 0.22 for all sites. The K'_{SA} approach

yielded reasonable results, and it is recommended to use this approach when there is limited data about the pollution levels of a certain media such as soil by using the measured levels of the other media such as air (Salihoğlu and Taşdemir, 2009).

2.3. Literature Survey Related with Types of the Method

In 1994, Raccanelli *et al.*, was set up a sample preparation procedure that allows simultaneous gas chromatographic determination of chlorinated hydrocarbons (CH, pesticides, PCBs), aliphatic (AH) and PAHs. They extracted contaminants from lyophilised samples with n-hexane/dichloromethane in a sonication bath and eluted extract through a multilayer clean-up-separation column, packed with sodium sulphate, activated copper, florisil, neutral alumina and silica and collected in three fractions. They obtained the mixtures of compounds that were quantifiable with GC-ECD, GC-FID and GC-MS. They had analyzed samples of sediment, particulate matter, macroalgae, and zoobenthos from the lagoon of Venice and industrial samples by this procedure. When analyzing halocarbons, they achieved sensitivity by the ECD and the separation attained by the column chromatography, enabled a precise and sensitive analysis. However, the qualification of PCB by GC-ECD and Aroclor formulations, even though the Aroclor pattern was enough reproduced in the samples, could lead to an overestimation of concentrations due to the inclusion of interferences. They compared Soxhlet and sonication bath which was showed the sonication procedure even though it gave a lower recovery, to have a number of advantages (solvent and time saving, blank and all procedure ease) that rendered it by far preferable. This methodology set-up for sample clean-up and separation enabled them to analyze four classes of compounds: PCBs, pesticides, aliphatic and

aromatic polycyclic hydrocarbons by a single column chromatographic procedure. They found the recoveries of reprocessed try better than the separated methodologies. In addition, some step of clean-up combined resulting low sample loss and less contamination. Analyses performed by GC-ECD for halocarbons and by GC-FID for alkanes and PAH are generally acceptable on a routine basis. When a more definitive peak was necessary, identification is required and a better sensitivity especially for PAH, the use of GC-MS is decisive (Raccanelli *et al.*, 1994).

In 1998, Singh *et al.* simultaneously analyzed a broad range of pollutants such as PAHs, PCBs, OC insecticides, polychlorinated hydrocarbons (PCHs) and polynitrohydrocarbons (PNHs) in spiked soil, water or plasma samples by using GC-MS. They extracted water and plasma samples containing the pollutants by a solid-phase extraction (SPE) method using florisil columns. The soil samples, fortified with the toxicants, were extracted with water, methanol or dichloromethane (DCM). The water extract was processed by the SPE method. The methanol and DCM samples were dried, dissolved in acetonitrile and subjected to the SPE extraction. The extracted samples were analyzed by GC-MS programmed to monitor selected ions. The chromatographic profile of total ions indicated complete separation of some compounds such as isophorone, naphthalene, all PCBs, most OC insecticides and PNHs; high molecular weight PAHs and some PCHs were partially or incompletely separated. The SPE method that provided 60–105 % recovery of pollutants from water samples, provided only 2–60% recovery from plasma samples. This may be due to the binding of pollutants to plasma proteins. Water recovered 1–30 %, while methanol or DCM recovered 65–100% of the pollutants added to the soil samples. GC-MS, in SIM mode, provides a simple, sensitive and confirmatory

analysis of targeted toxicants in environmental and biological samples as expressed in other researches. SPE by using florisil columns is suitable for the quantitative, multi-residue (50 compounds) analysis of soil, water or plasma samples. The HP-5 column provided clear separation of some compounds but partial to incomplete separation of others. However, by extracting selected ions from the total ion chromatogram, individual pollutant was identified and quantitated. Recovery from water and plasma samples were determined by using deuterium labelled internal standards. The results obtained with spiked samples indicate that the method can be used for the rapid screening of pollutants in soil, water and plasma samples (Singh *et al.*, 1998).

Ultrasonic solvent extraction of persistent organic pollutants including PAHs, PCBs, and OCPs from airborne particles was reported by Aydın *et al.*, in 2007. They optimized an extraction as functions of type and amount of solvent, sonication time, and number of extraction steps. Determination of PAHs and PCBs carried out by GC/MSD, while OCPs were determined using GC/ECD. The optimum extraction procedure was determined as three times consecutive extraction using a mixture of n-hexane:petroleum ether (1/1, v/v) for 15 min of sonication. Recoveries were obtained between 91 ± 2 and $96 \pm 1\%$ with Relative Standard Deviation (RSD) $\leq \pm 14\%$ for PCBs, for PAHs recoveries (except for naphthalene, $< 31\%$) were between 66 ± 6 and $90 \pm 4\%$ with RSD $\leq \pm 8\%$ while OCPs compounds recoveries were between 67 ± 5 and $120 \pm 7\%$ with RSD $\leq \pm 7\%$. When comparing the Soxhlet extraction method with optimized ultrasonic solvent extraction method, extraction time and solvent volume were reduced considerably with the ultrasonic solvent extraction method without reducing extraction efficiency. As a result of this work it was demonstrated

that optimized ultrasonic extraction method could be used in the analysis of PCBs, PAHs and OCPs compounds in airborne particles. They measured recoveries from the analyses of atmospheric air sampled GFF spiked with PCBs, PAHs and OCPs compounds were between 96 ± 7 and 108 ± 1 % with $RSD \leq \pm 9$ %, 72 ± 1 and 101 ± 1 % with $RSD \leq \pm 8$ % (except for naphthalene, 31 %) and 62 ± 5 and 110 ± 1 % with $RSD \leq \pm 6$ %, respectively (Aydın *et al.*, 2007).

CHAPTER 3

3. EXPERIMENTAL

3.1. Overview of BOLU

The geographical and general characteristics of the study area are important parameters for discussing pollution sources and chemical fate of pollutants in these type of studies.

3.1.1. The Geographical Information

Bolu is located between the two industrialized and populated cities, namely İstanbul and Ankara. The area of the city is about 8.276 km². 56 % of the area of city is covered with mountains arriving to latitudes about 2.499 m (Köroğlu Summit). These mountains are in northeast-southwest direction and divided by the plains forming with the effect of movement of Northern Anatolian Fault. Total size of the plains covering about 12 % of the area within the city is 102.000 ha, and the greatest one is the Bolu Plain with an area of 46.000 ha. The total population of Bolu is 270.417 people according to the results of General Census in the year of 2007 by State Statistics Institute (Figure 3.1) (www.tuik.gov.tr).

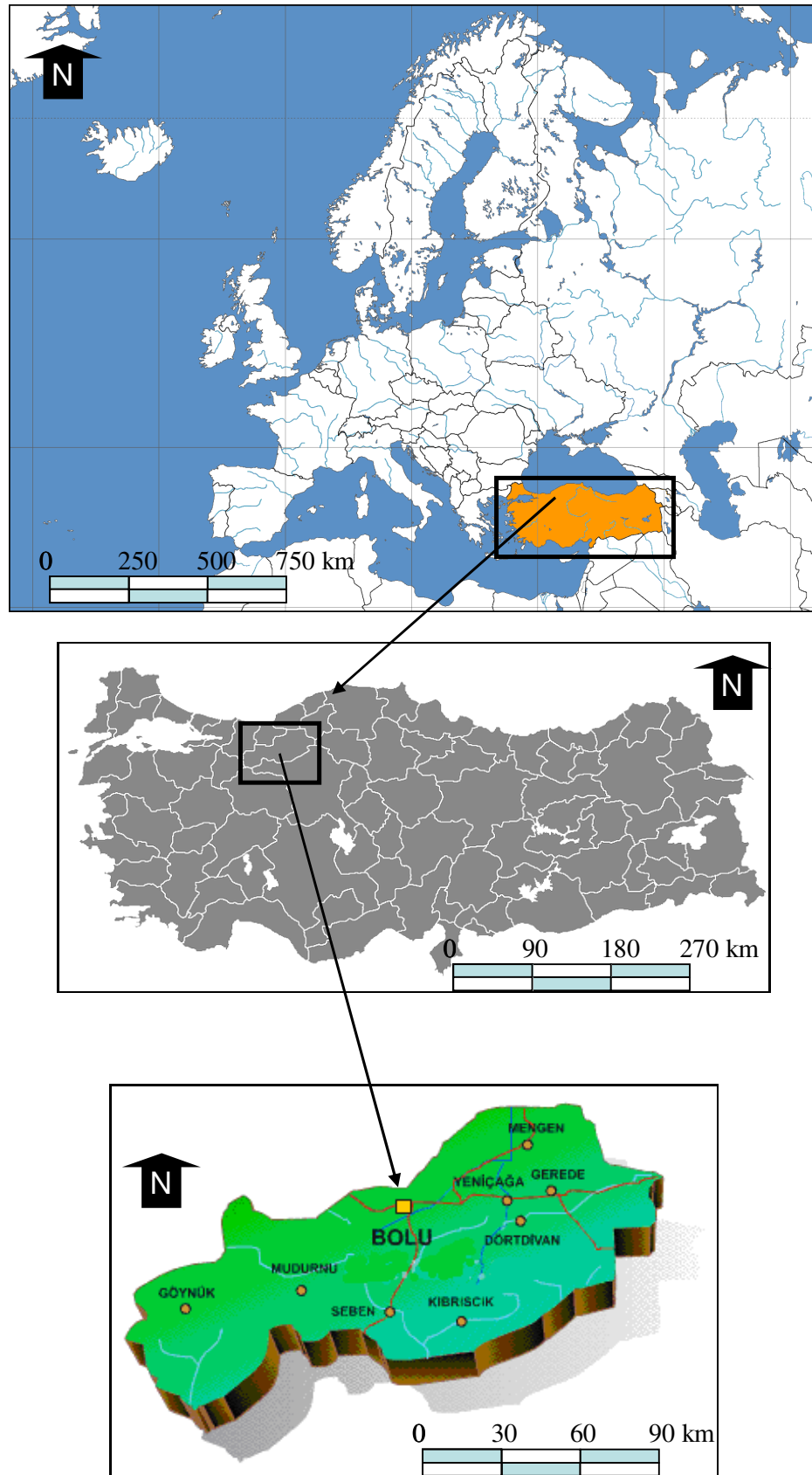


Figure 3.1. The map of Bolu

The weather is always very cold in winters (average temperature is 1.9 C°) and is warm in summer seasons (average temperature is 18.9 C°) in Bolu. It is primarily under the impact of the Black Sea Region, however, other neighboring regions affect the climate because of the geographical position. In Bolu, the climate is being affected from Black Sea, Marmara and Central Anatolia, which leads to differences of various agricultural products. Difference of surface structures and the effects of distance and also height from the sea level cause diversity of plant and agricultural applications.

The significant part of the city area is covered by the forests. The area of woodlands in the region is about 4.7×10^5 ha. The agricultural areas are in the form of small fragments.

3.1.2. Sources of Pollution

There exist many types of pollution sources that affect the urban and rural air quality therefore, the possible local source identification must be done by researchers. The possible major anthropogenic sources in Bolu thought to be domestic heating, industrial activities, the usage of pesticides and traffic. On the other hand, agricultural activities and forest fires as natural sources contributes the air pollution in this region. However, contribution of each source needs to be studied to take necessary control actions in Bolu.

3.1.2.1. Industrial Activities

Most abundant industrial activities in Bolu are food, wood, cement, machinery, leather and paper productions; in addition to motor oil and other chemical production plants. The industrial regions and the other properties of the surface structure are given in Figure 3.2. There are a slaughterhouse (before Çepni village), many poultry-processing plants, potato processing plant (Bolpat), fiberboard and laminate industry (Gentaş) constructed in Bolu. Moreover, there are cast plants, polyfoam and isopoly (the group name of the polyester and nylon) production plants. Gentaş produces 4.12×10^6 m² of fiberboard, 2.24×10^6 m² of laminated board and 745 tonnes of decoration paper in an annual base (TMMOB, 1998). In wood-pulping industry, conventional acid calcium sulfite cooking process is used. The active species in the sulfite process are sulfur dioxide, hydrogen sulfite, and sulfite varying their proportions depending on the actual pH of the cooking liquor. There are dissolved and colloidal substances in waste effluents of these plants (Eaton, 1993).

Potato-processing plants dissolve potato starch at 50-70 °C. Potatoes are saved in acid baths to prevent growing of solanine plant toxin in potato. In addition, discharging of hot solutions may cause thermal pollution. Recently, it was found that bark of potato includes carcinogenic dioxin (incorrect popular contraction of 2,3,7,8-tetrachlorodibenzo-p-dioxin) (Yıldırım, M., 2001).



Figure 3.2. Industrial and residence regions in Bolu

Bolu Cement plant uses dry furnace system with a capacity of 4.000 tonnes clinker day⁻¹. The electrostatic filters are used for dust collection, but some dust passes through. Dusts spreading out of chimney prevent the respiration and transpiration of forests and slow down growing up by decreasing photosynthesis. Also, they prevent water absorption by forming an impermeable layer on the surface of soil (Yıldırım, 2001).

3.1.2.2. Domestic Heating

LPG usage is limited and there was no natural gas usage at the time of the sampling period in Bolu. Most of the heating processes are achieved by fossil fuel and coal combustion. Domestic heating is important local source of pollutants. Coal is the major heating source in Bolu, therefore average 63.000 tonnes of coal were consumed in 2006-2007 and 2007-2008 in winter seasons. It is known that in literature, coal combustion is the main source of SO₂ and PAHs.

3.1.2.3. Traffic

D-100 motorway and TEM (E-83) highway are the most important roads between Ankara and İstanbul, passes through Bolu and approximately 3 km far away from the sampling point. Incomplete combustion products (NO_x and PAHs) exhausted from the vehicles can cause air and soil pollution. Relative emissions of different pollutants from petrol and diesel were shown in Table 3.1 (Harrison, 1996). At the sampling region, there are currently used approximately 1.100 otomobiles and midibus.

Table 3.1. Pollutant emissions from road traffic (Harrison, 1996)

Pollutants	Percent emission	
	Petrol cars	Diesel cars
NO _x	****	**
Hydrocarbons	****	***
Carbonmonoxide	****	**
Particulate matter	**	****
Aldehydes	****	***
Benzene	****	**
Polycyclic aromatic hydrocarbons	***	****
SO ₂	*	****
CO ₂	***	*
Lead (g Pb/L)	0.15 (normal), 0.4 (super), 0.013 (unleaded)	-
* Lowest emission **/** Intermediate emission **** Highest emission		

3.1.2.4. Agricultural Activities

Most of the agricultural product is the grain and a variety of the cereal includes wheat, barley, corn, oat and rice in Bolu. In addition, potato, sugar beet and sugar beet seed are the most important industrial plants grown up in Bolu. The sunflower plants can be cultivated in some part of the agricultural areas. Only some kinds of vegetables and fruits exist in Bolu. The common fruits are apple and grape. The apple is grown in Seben district. Vegetables are the secondary products that are rarely grown up in Bolu.

Endosulfan and chlorpyrifos are the most frequently applied pesticides in the study area. Endosulfan is mixed into irrigation water or mixed with soil before planting. Therefore it may remain in soil and mix underground water. In addition, it evaporates to air and persists in environment. If the pesticide vaporization from the water is considered, it will be expected that it is likely to be found in the air of Bolu.

Pesticides are applied to the agricultural areas between March and May and between September and October period for potatoes and wheat, respectively.

3.2. Sampling

Sampling methodology is very important and critical in air pollution studies. Sampling method and location is also significant importance for soil samples. First sampling campaign was carried out in between 25th June and 23rd August of 2007. Winter samples were collected in between 13th December of 2007 and 12th February of 2008.

3.2.1. Sampling Location

The sampling point was selected in the campus of the Abant İzzet Baysal University. The sampler was placed on the roof of presidency building that is 6 m above the ground level. A.İ.B.U is 12 km far from city the center and the major roads around the campus are D-100 motorway and TEM highway, which connect the Ankara and İstanbul.

A.İ.B.U presidency building is at the east of the campus and it is approximately 3 km far from the Ankara-İstanbul roads and 876 m high over the sea level. The sampling station has a 40° 42' of the north latitude and 31° 31' of the east longitude. Sampling station is shown in Figure 3.3.

(PCB-20), 2,4,4'-Trichlorobiphenyl (PCB-28), 2,4',5-Trichlorobiphenyl (PCB-31), 2,4',5-Trichlorobiphenyl (PCB-44), 2,4',5-Trichlorobiphenyl (PCB-52), 2,2',4,5,5'-Pentachlorobiphenyl (PCB-101), 2,3,3',4,4'-Pentachlorobiphenyl (PCB-105), 2,3,3',4,5'-Pentachlorobiphenyl (PCB-108), 2,2',3,4,4',5'-Hexachlorobiphenyl (PCB-138), 2,2',3,4',5,6-Hexachlorobiphenyl (PCB-149), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB-153), 2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB-170), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB-180), 2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB-194); for PAHs: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phe), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DahA), Indeno(1,2,3-cd)pyrene (Ind), Benzo(g,h,i)perylene (BghiP); for OCPs: Beta Hexachlorohexane (β -BHC), Heptachloroepoxide, Endosulfan I, 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (4,4'-DDE), Endrin, Endosulfan II, 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (4,4'-DDE), Endrin aldehyde, Endosulfan sulfate, Endrin ketone, and Methoxychlor. The usage of these compounds are restricted or entirely banned by many governments, and are declared as primarily important pollutants by EPA because of carcinogenicity of them.

3.2.3. Preparation for Sampling

Cleaning of Apparatus and Glassware: The glassware, used in sampling and preparation of samples for the analysis, were washed with commercial detergent (in hot water and rinsed with simultaneously tap water, deionized water, acetone and several times with hexane). Then they were dried in oven and were stored in closed

cupboards until usage. The mouth of glassware was closed with washed aluminum foil. Since the amounts of compounds were very low in samples, extreme precautions were necessary to eliminate the contamination. Also, other precautions were taken such as; the extractions were carried out in a fume hood that was used only for sample preparation for organic analysis.

Preparation of PUF: Two PUF plugs were pre-cleaned with acetone and wrapped with aluminum foil that was washed with hexane and acetone. Then they were stored in fume hood until dryness. When they were dried, they were placed into the glass cartridge. Then, top and bottom of the cartridges were closed with Teflon lips that were cleaned with hexane and acetone previously (Ari, 2008).

Preparation of GFF: The GFFs were baked in a muffle furnace at 400 °C for 5 hours before sampling in order to remove organic substances and conditioning and also were stored in a desiccator. Before collection of particles, the GFF was weighed and was wrapped with the precleaned aluminum foil (Cindoruk *et al.*, 2006)

3.2.4. Air Sampling

There are many sampling devices used for air sampling. In this study, high volume PUF sampler (Andersen PUF sampler, USA) (Figure 3.4) was used that is designed to simultaneously collect suspended airborne particulates as well as airborne organic vapors at flow rates up to 300 liters per minute. A dual chambered aluminum sampling module (Figure 3.5) contains both filtering systems. The upper chamber supports the airborne particulate filter media in a circular filter holder. The

lower chamber encapsulates a glass cartridge, which contains the polyurethane foam for vapor entrapment. Air flow rate is measured through the flow venturi utilizing a 0-100 Magnehelic Gage. Orifice calibration was done in order to eliminate the effect of pressure and temperature at the sampling site.

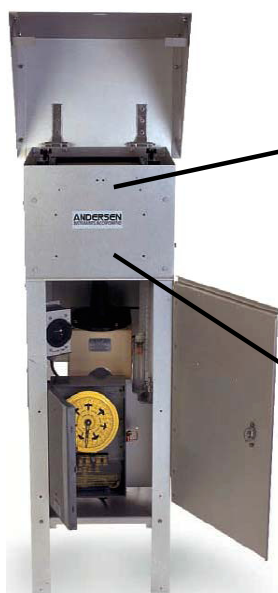


Figure 3.4. The PUF Sampler

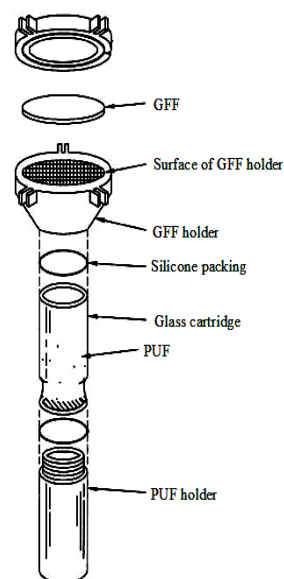


Figure 3.5. Sample collection part of sampler

Prefired GFF and precleaned PUF cartridges were brought to the sampling point and the head of PUF sampler was cleaned with acetone. After the GFF and PUF cartridge were placed into the sampler, flow rate was adjusted to $0.225 \text{ m}^3 \text{ min}^{-1}$ for 24 hours sampling duration. Twenty-four hours later, the samples were taken and wrapped with aluminum foil and also clean ones were put into sampler programming as the previous day. The GFF samples were stored in the desiccator until the extraction time and they were reweighed to calculate total suspended particle before the extraction.

3.2.5. Soil Sampling

In this study, total 29 surface soil samples were collected around the air sampling point. Surface soil samples (0.5 cm below surface) were collected by a steel scoop. Surface soil samples were collected at the beginning and at the end of winter period which would be used to observe deposition of pollutants. The sampling was repeated in May in order to interpret deposition behavior of PAHs in summer season. 19 soil samples were collected in winter, and 10 soil samples were collected in summer. All samples were enclosed in an aluminum foil, dried in an oven at 40 °C for one day, and saved at room temperature. Organic matter in soil (0.11) was determined by ignition at 600 °C and density was found to be 2.01 g cm⁻³. Density of the soil was obtained from the division of known amount of soil sample with its volume that was determined by graduated cylinder. The sampling points around the air sampling station are given in Figure 3.6 and 3.7.

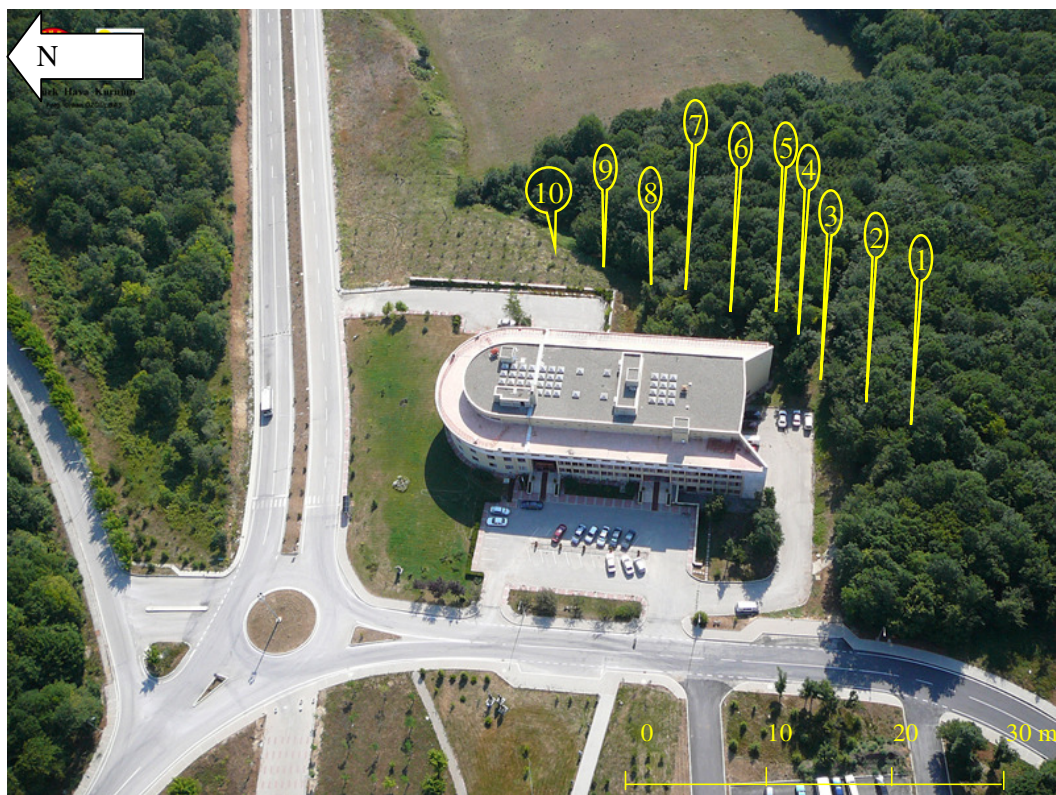


Figure 3.6. Sampling points in soil in summer

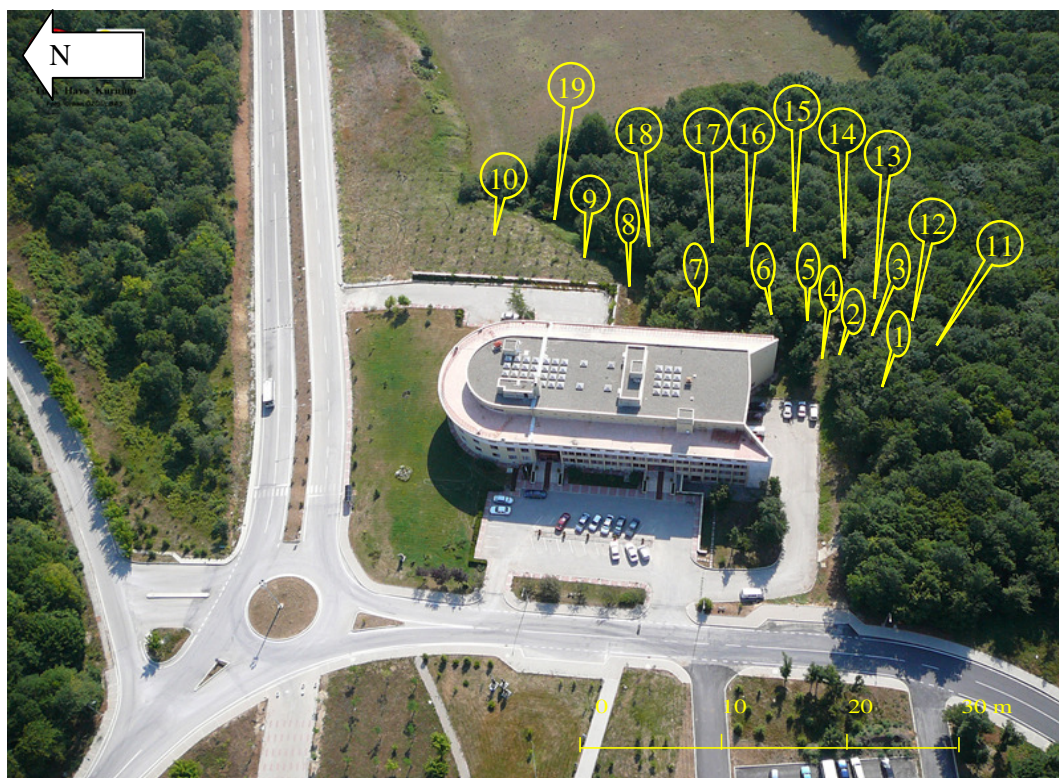


Figure 3.7. Sampling points in soil in winter

3.2.6. Field Blank for Air Samples

Field blanks were collected twice in a month and a total of seven blank samples were obtained in the study period. Prefired GFF and precleaned PUF cartridges were brought to the sampling point and placed into the sampler. After waiting ten minutes and without operating the sampler, those blanks were transferred back to the laboratory to extract and analyze in the same manner as air samples.

3.2.7. Samples for Method Validation

All steps of preparation and analysis were validated. For that purpose, the standard mixtures were used and the same preparation and analysis procedure were applied as samples. For air, six standard samples of 0.01 ppm, 0.5 ppm and 2 ppm were prepared and analyzed in a day to found out the short-term repeatability. Three standard mixtures of 0.01 ppm, 0.1 ppm and 1.0 ppm were used for long-term repeatability measurements during four weeks. For soil samples, 0.01 ppm, 1 ppm and 2 ppm standard mixtures were prepared. Then 30 grams from nine samples were weighed and three subsamples from each of nine samples were used as a matrix for each level of standard mixtures.

3.3. Preparation of the Samples for the Analysis

In the relevant sections, procedures for the preparation of the samples for the analysis were described. The flow chart of the general overview of the sampling procedure is given in Figure 3.8.

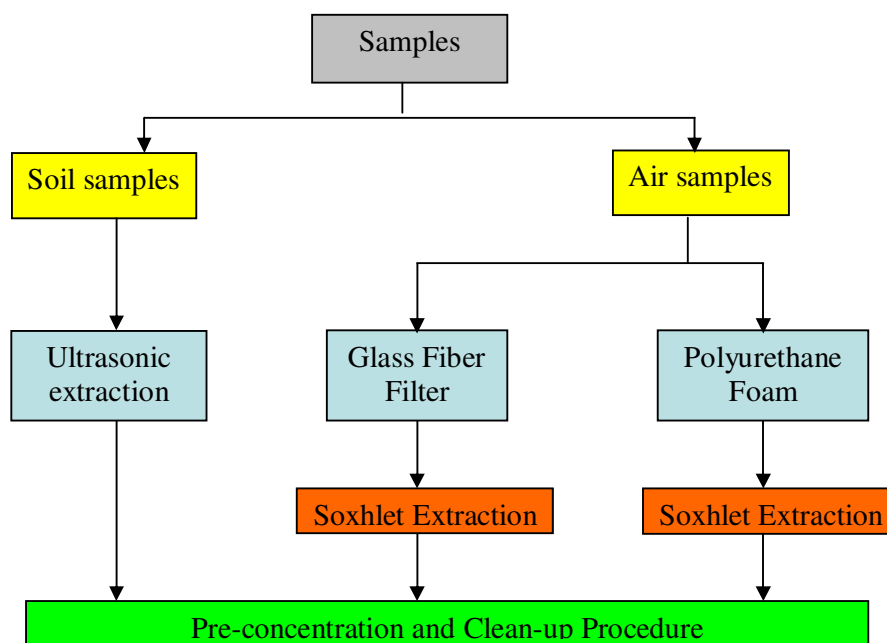


Figure 3.8. Sampling and extraction scheme

3.3.1. Reagents and Materials

Dichloromethane, Acetone, Toluene, Ethyl acetate, and n-Hexane were GC grade (99.99 % purity) and were purchased from Merck Company (Germany) as well as Petroleum benzene 40-60°C range with 90 % purity. Sodium sulfate, florisil (0.150- 0.250 mm) and neutral aluminum oxide (0.063-0.2 mm) were purchased from Merck Company (USA). The granulated sodium sulfate was anhydrous and has 99 % purity for drying of solvents and gases. Glass microfiber filters (90 mm) were from Whatman Company (USA). N₂ gas was pure grade (99 %) and purchased from

Habaş Company (Turkey). Standard reference materials (SRM 1649a) were purchased from National Institute of Standards (NIST, USA).

Certified PAH deuterated surrogate standard solutions and standard solution were purchased from Accu Standards (USA) and Ultra Scientific (USA), respectively. PCB congener standard, internal standard and surrogate standard were purchased from Absolute Standards (USA). OCP standard solution was obtained from Dr. Ehrenstorfer (Germany). Surrogate standard solution and internal standard solution was purchased from Ficsher Scientific (USA) and Absolute Standards (USA), respectively (Table 3.2).

Calibration standards solutions and intermediate stock solutions were prepared from the main stock standards with appropriate dilutions with n-hexane. All of the stock, intermediate and standard solutions were stored in a refrigerator. 1000, 500, 100, 50, 25, and 10 μ L gas tight glass syringes (Hamilton,USA) were used in the preparation of the standards in 2 mL amber vials from Agilent company (USA).

Ultrasonic extractions were preformed by using an ultrasonic bath (Elma, Germany). A rotary evaporator (Heidolph, Germany) was used to reduce the volumes of extracts. The extracted air samples were transferred by an automatic pipette (Brand transferpette, UK) (1000-100 μ L/100-10 μ L) to 10 mL amber glass vials.

An oven (Nüve, Turkey), (0-250°C), was used to dry glasswares. A heating mantle (Medline, UK) was used for soxhlet apparatus in order to heat solvent mixtures. A muffle furnace (Elektro-mag, Turkey) was used to baking organics on

the glassware and conditioning of the analytes as well as GFFs. A sieve (Retsch, Netherlands) (mesh number 30) was used to separate the sizes of soil samples. The analytical balance (0.1 mg) (And, Japan) was used for all weighing processes.

All the samples were spiked with surrogate standards prior to their extraction. 20 µL of 32 ppm deuterated PAH mixture, 40 ppm OCP surrogates, and 50 ppm PCB surrogate were added to the samples prior to extraction in order to determine analytical recovery efficiencies. Standards, surrogate standards and internal standards used in this study were listed in Table 3.2.

Table 3.2. All Standard Solutions

For Group	Compounds	Stock Solution (ppm)	Part Number
PCBs	PCB-18, PCB-20, PCB-28, PCB-31, PCB-44, PCB-52, PCB-101, PCB-105, PCB-108, PCB-138, PCB-149, PCB-153, PCB-170, PCB-180, PCB-194, PCB-30, PCB-204	100	Absolute Standards, 94567
PCBs (IS)		100	Absolute Standards, 94569
PCBs (Surr)	PCB-14, PCB-65, PCB-166	100	Absolute Standards, 94568
PAHs	Nap, Acy, Ace, Flu, Ant, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, Ind, BghiP,	100	Accu Standards, PM 610
PAHs (Surr)	Acenaphthene-d10, Crysene-d12, Perylene-d12, Phenanthrene-d10	1000	Ultra Scientific, M-525-IS
OCPs	Alpha-HCH, Beta BHC, Gamma-HCH, Delta-HCH, Heptachlor, Aldrin, Dieldrin, Heptachloroepoxide, Endosulfan I, 4,4'-DDE, Endrin, Endosulfan II, 4,4'-DDE, Endrin aldehyde, 4,4'-DDT, Endosulfan sulfate, Endrin ketone, Methoxychlor.	2000	Dr. Ehrenstorfer, 08080100
OCPs (IS)	Pentachloronitrobenzene	100	Absolute Standards, X9176
OCPs (Surr)	2,4,5,6-Tetrachloro-m-xylene, Dibutylchorendate	2000	Fischer Scientific, US-ISM-300

3.3.2. Extraction

In analytical applications, extraction is an important step, which depends on the polarity of the analyte and the solubility ranges of the different compounds in the solvent. Most common extraction applications are soxhlet extraction (SOX), liquid-liquid extraction (LLE), solid-phase extraction (SPE), solid-phase micro-extraction (SPME), matrix solid-phase dispersion (MSPD), supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE). In this study, the soxhlet extraction was applied for air samples of GFF and PUF plugs. Ultrasonic extraction was preferred for soil samples.

3.3.2.1. Soxhlet Extraction (SOX)

Soxhlet apparatus with an organic solvent (e.g. hexane, acetone, dichloromethane, methanol, and methanol-water) has been still used for the determination organic compounds in solid matrices as well as in gaseous phase. The size of the system can vary, but the most common configurations change from 100 mL to 1000 mL of solvent or solvent mixture (Figure 3.9).

At the extraction part of this experiment, the GFF and PUF samples were soxhlet-extracted with a mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) for 24 hours after addition of all surrogate standards.

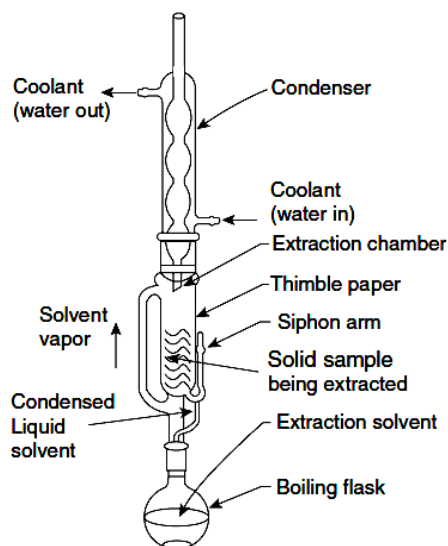


Figure 3.9. The soxhlet apparatus

3.3.2.2. Ultrasonic Extraction (UE)

In this study, approximately one kilogram soil samples were collected around the air sampling station, were sieved from mesh number 30, which has pore width 0.595 mm to remove bigger part-stones and organic fossils. Then two 30 g sub-samples were weighed and the surrogate standards were added. All soil samples were waited in a 30 mL mixture of dichloromethane (DCM) and petroleum ether (PE) (1:4) for 24 hours following 30 minutes ultrasonic extraction. Finally, sodium sulfate was added into the filter paper so as to remove traces of water. The samples were concentrated under the nitrogen flow and transferred to the 10 mL vials. The samples were stored at 4 °C in the refrigerator.

3.3.2.3. Pre-concentration and Concentration of Samples

The collected PUF and GFF samples were extracted in approximately 650 mL and 150 mL solvent mixture, respectively. The excess solvent must be removed in order to analyze samples. Therefore, the rotary evaporator was used to preconcentrate them at 500 mbar and at 40 °C water bath. All air and soil sample extracts were concentrated to 10 mL by evaporator. They were transferred into 15 mL vials by washing the walls of the balloons with solvent mixture (DCM : PE) several times. Afterwards they were concentrated to 1 mL in the fume hood under the nitrogen flow. Extracted soil samples also contained high volume solvent mixture (ca. 30 mL) therefore the volumes decreased under the nitrogen flow before the analysis.

3.3.3. Clean-up

A “Clean-up” procedure was applied to samples after extraction to remove interfering chemicals from the sample while keeping target analyte(s) in the sample matrices prior to an instrumental analysis. That is the clean-up is to remove as much garbage as possible from complex sample matrices. Clean-up is critical to the analysis of trace analyte of interest (ppm–ppt or lower), because the analyte is often masked by high background concentration of various types of organics and the removal is essential for further analyses by instruments. Clean-up will also avoid the rapid deterioration of expensive capillary GC columns and instrument downtime caused by cleaning and rebuilding of detectors and ion sources. Many of the clean-up procedures are performed after extraction (Zhang, 2007).

As a result, when multiple clean-up procedures are necessary, additional care is recommended to minimize analyte loss during each individual clean-up procedure. Therefore, clean-up techniques are combined with several chromatographies such as; Gel Permeation Chromatography (GPC), Florisil Column Chromatography (FCC), Alumina Column Chromatography (ACC), Charcoal/Celite Column Chromatography (CCC) and Solid Phase Extraction (SPE).

3.3.3.1. Preparation of Chemicals for Column

Preparation of Sodium Sulfate and Glass Wool: Sodium Sulfate (Na_2SO_4) was used to dry the extracts and it is precleaned before its usage. For that purpose, Na_2SO_4 was put into a beaker, and washed with hexane. It was filtered into a large beaker, covered loosely with solvent rinsed aluminum foil and oven dried at $50\text{ }^\circ\text{C}$ for 1 hour and conditioned at $225\text{ }^\circ\text{C}$ overnight. Dry Na_2SO_4 was transferred to an amber glass bottle with a Teflon lined cap and stored in a desiccator.

Glass wool used in the experiments was also cleaned before use. A quantity of a glass wool was placed into a beaker and washed sequentially hexane and dichloromethane. It is dried in oven and stored in a desiccator.

Preparation of Florisil and Alumina: Alumina is a highly porous granular aluminium oxide (Al_2O_3). The alumina solid is packed into a column topped with a water-absorbing substance over which the sample is eluted with a suitable solvent, which leaves interference on the column. Alumina is used to separate pesticide

residues chlorinated hydrocarbons and aromatic hydrocarbons from interfering compounds such as metal and water (Zhang, 2007).

Florisil is an activated form of magnesium silicate with basic properties. Florisil has been used for the clean-up of pesticide residues and other chlorinated hydrocarbons, for the separation of nitrogen compounds from hydrocarbons, and for the separation of aromatic compounds from aliphatic-aromatic mixtures. Florisil is also good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Zhang, 2007).

Both neutral aluminum oxide (0.063-0.2 mm) and Florisil (149-250 μm) were activated at 400 °C for 20 hours. Aluminum oxide was deactivated with 1.5% Milli-Q water (Raccanelli *et al.*, 1994).

3.3.3.2. Preparation of Adsorption Column

Adsorption column may contain one or more type of compounds depending on separation of the compounds under research of interest. In this study, combination of the Florisil Column Chromatography (FCC) and Alumina Column Chromatography (ACC) was the most effective method for the fractional separation of the PAHs, PCBs and OCPs because of the high recoveries and less chemical usage.

Column was 10 cm long and 0.5 cm width (diameter), and prepared by putting glass wool, one gram aluminum oxide, one gram florisil and one gram sodium sulfate into the column, respectively (Figure 3.10). Aluminum oxide (known

as an alumina) is a white oxide of aluminum. It was used for adsorbing metal oxides and water. Florisil (known as a magnesium silicate) is also white substance that contains magnesium oxide–silicon dioxide with the ratio (15:85). It was used for separation of volatile or semi-volatile organic substances as well as removal of impurities in samples. The sodium sulfate was used for reducing water and moisture in the samples.

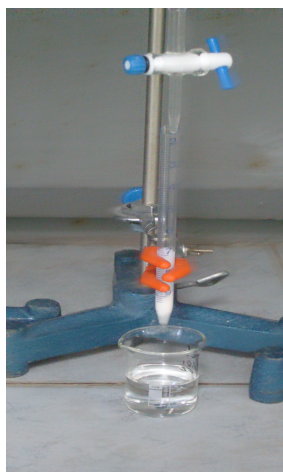


Figure 3.10. Clean-up column

3.3.3.3. Optimization of the Column

One of the EPA method (EPA Method-LMMB 029) was modified for the three organic pollutants groups of PAH, OCP and PCB. Therefore, one ppm mixture of standard and surrogate solutions of PAH, PCB and PCB was prepared and different elution solvents or solvent mixtures and also different amounts of florisil were used to collect the groups of compounds in either one or two fractions. Both fractions in separate beakers and one fraction in a beaker were collected and concentrated to 300-500 μ L under nitrogen flow. Then the concentrated fractions were transferred to amber vials by gas tight syringe and to concentrate samples were

continued under nitrogen blow down until nearly dryness. Finally, the fractions were diluted to one mL with n-hexane.

The column was prepared from glass wool, aluminium oxide, florisil and sodium sulphate. The tip of column was closed by glass wool. Simultaneously, one gram of aluminium oxide, one or two grams (determined one gram after optimization) of florisil and one gram of sodium sulphate were poured into the column. The column was activated with the 10 mL n-hexane. The sample was loaded to the column and solvent or solvent mixtures were eluted from the column. Individually many experiments were performed in order to determine the most suitable solvent and most efficient amount of solid matrices. Also, recoveries of the compounds were calculated which is given in Appendix VI.

Collection of the Samples in One Fraction

Different solvent mixtures (Table 3.3) were tried for optimum recovery of compounds from the clean-up column. Initial attempts were made to recover all types of compounds in one fraction. In first set of experiments, PCBs, PAHs and OCPs were eluted in one fraction by using different solvent combinations to adjust polarity of the elution solvent. Following solvent mixtures were tried: i) hexane-toluene (4:1), ii) hexane-dichloromethane (4:1), and iii) hexane-ethyl acetate (1:1). However, the recoveries of one fraction were not enough for OCPs, PAHs, and PCBs. Thus, it was not suitable for the collection of the whole compounds in one fraction. Since OCPs and PCBs interfere with each other and the higher recoveries for some OCPs were obtained.

Table 3.3. Solvent and solvent mixtures of elution from column

One Fraction		Two Fraction	
Solvents (For Elution)		Fraction 1	Fraction 2
	Hexane - Toluene (4:1)	Hexane	Hexane - Ethyl acetate (1:1)
	Hexane - Dichlorometane (4:1)	Hexane	Ethyl acetate - cyclohexane (1:1)
	Hexane - Ethyl acetate (1:1)	Hexane	Hexane - Toluene (4:1)
		Hexane	Hexane - Dichlorometane (4:1)

Collection of the Samples in Two Fractions

The second method was the collection of the PCBs, PAHs, and OCPs in two fractions. PCBs and some of the OCPs were collected in fraction I with hexane. PAHs and some of OCPs were collected in fraction II with hexane-ethyl acetate, cyclohexane-ethyl acetate, hexane-toluene and hexane-dichloromethane mixtures. In addition, different amounts (1 g or 2 g florisil) of the adsorbents were used to obtain higher efficiency in separation. Recoveries of the individual groups are given in Figure 3.11., 3.12, and 3.13. Hexane was most convenient solvent for separation of the PCBs because of polar property of them. Different types of solvent systems were used for the second fraction as expressed before. Cyclohexane-ethyl acetate mixture had large ranges in recoveries for PAHs and OCPs as well as hexane-dichloromethane and hexane-toluene. It was found that the collection of samples in two fractions which elution was performed with hexane for the first fraction and hexane-ethyl acetate (1:1) mixture for the second fraction had the high recoveries with respect to others. The detailed recovery data are presented in Appendix VI.

The optimized column, determined as hexane (25 mL) for the first fraction and hexane-ethyl acetate (40 mL) for the second fraction, was utilized for all

collected samples. As it is expressed before, the compounds were separated and collected in two fractions and PCBs were completely in the first fraction. However it was not possible to separate and collect OCPs in one fraction. Some of them were eluted in the first fraction like alpha BHC, gamma BHC, delta BHC, heptachlor, aldrin, dieldrin and 4,4'-DDT. Therefore they were not analyzed in this study. For the analysis of these compounds, further studies are required. The remaining compounds in the OCP group, were collected in the second fraction, were determined exactly and recoveries of them are given in Figure 3.13.

Fifteen PAH compounds were collected in the second fraction with very little loss however, recovery of naphthalene was very low for the second fraction. Since it has high vapor pressure and evaporates at room temperature.

Efficiencies of the extraction procedure by the standard mixtures were calculated and the percent recoveries of almost all compounds were generally between 70-118 % except for Ace, Acy and endosulfan sulfate. The average recoveries of Ace, Acy and Endosulfan sulfate were 66 %, 56 % and 128 %, respectively. The relatively low recoveries of Ace and Acy were probably due to their high vapor pressure. High recovery of the endosulfan sulfate might be derived from the interferences by the other compounds. The complete sample preparation procedure is shown in the Figure 3.14.

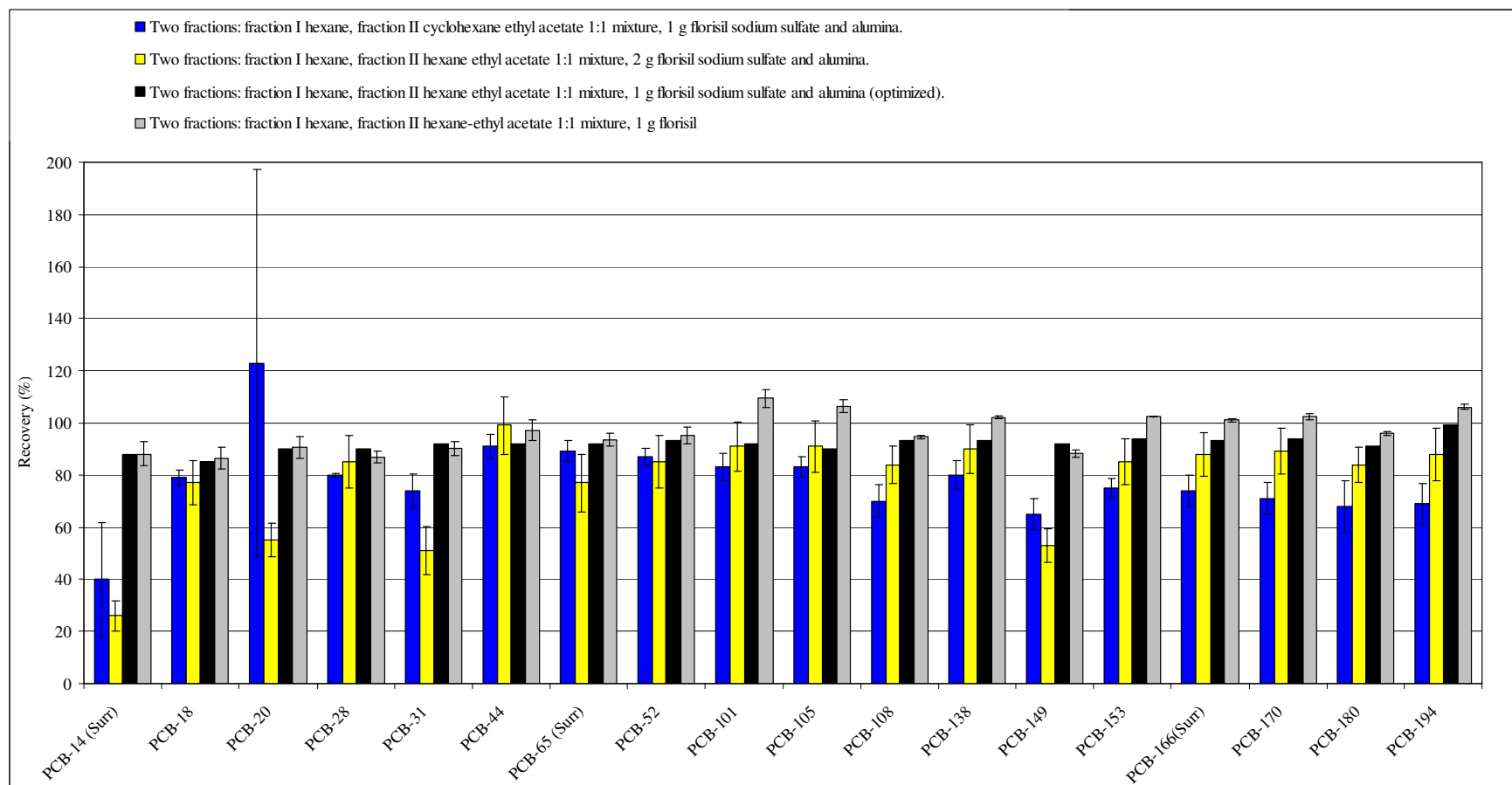


Figure 3.11. Recoveries of PCB compounds

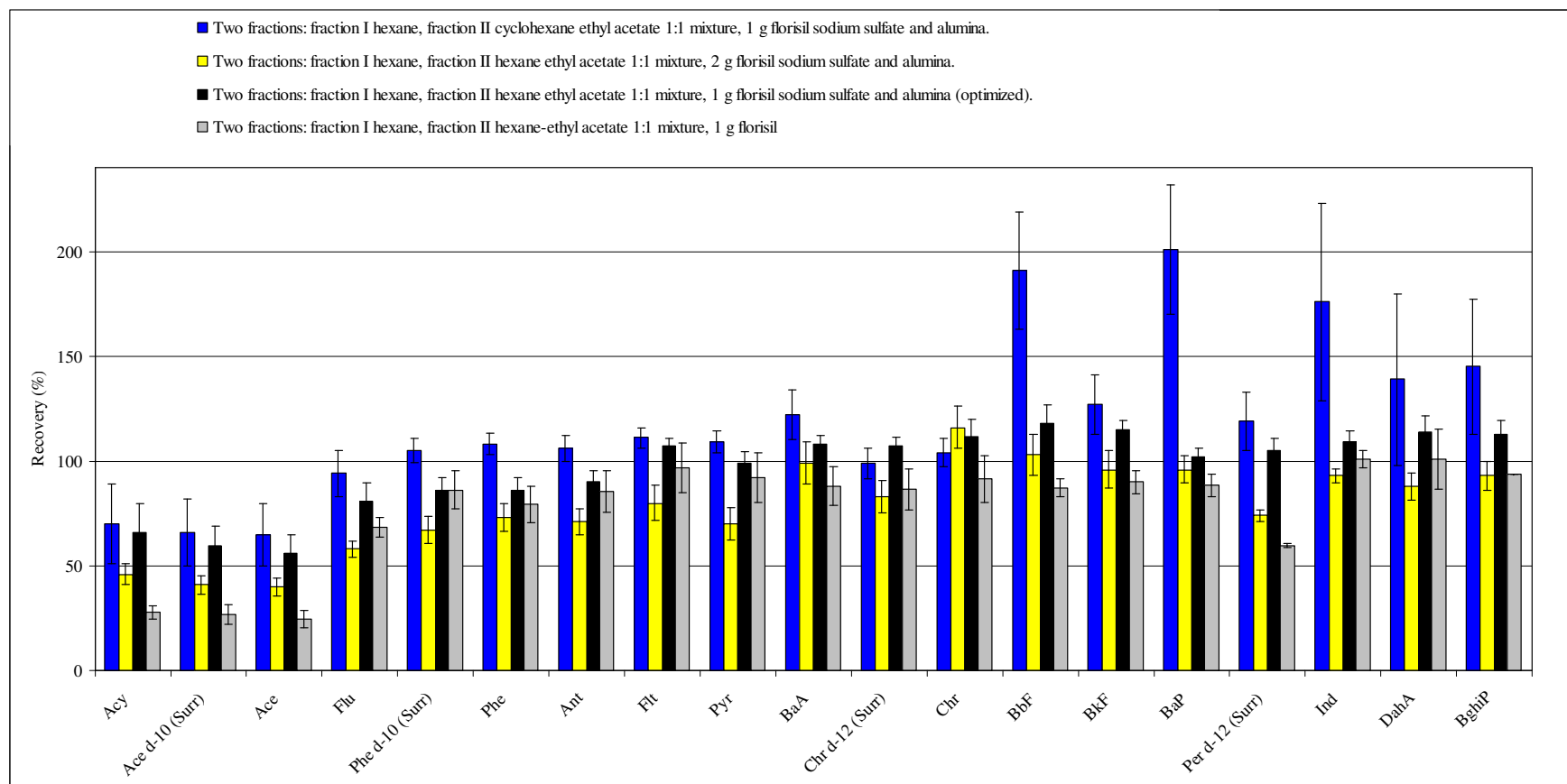


Figure 3.12. Recoveries of PAH compounds

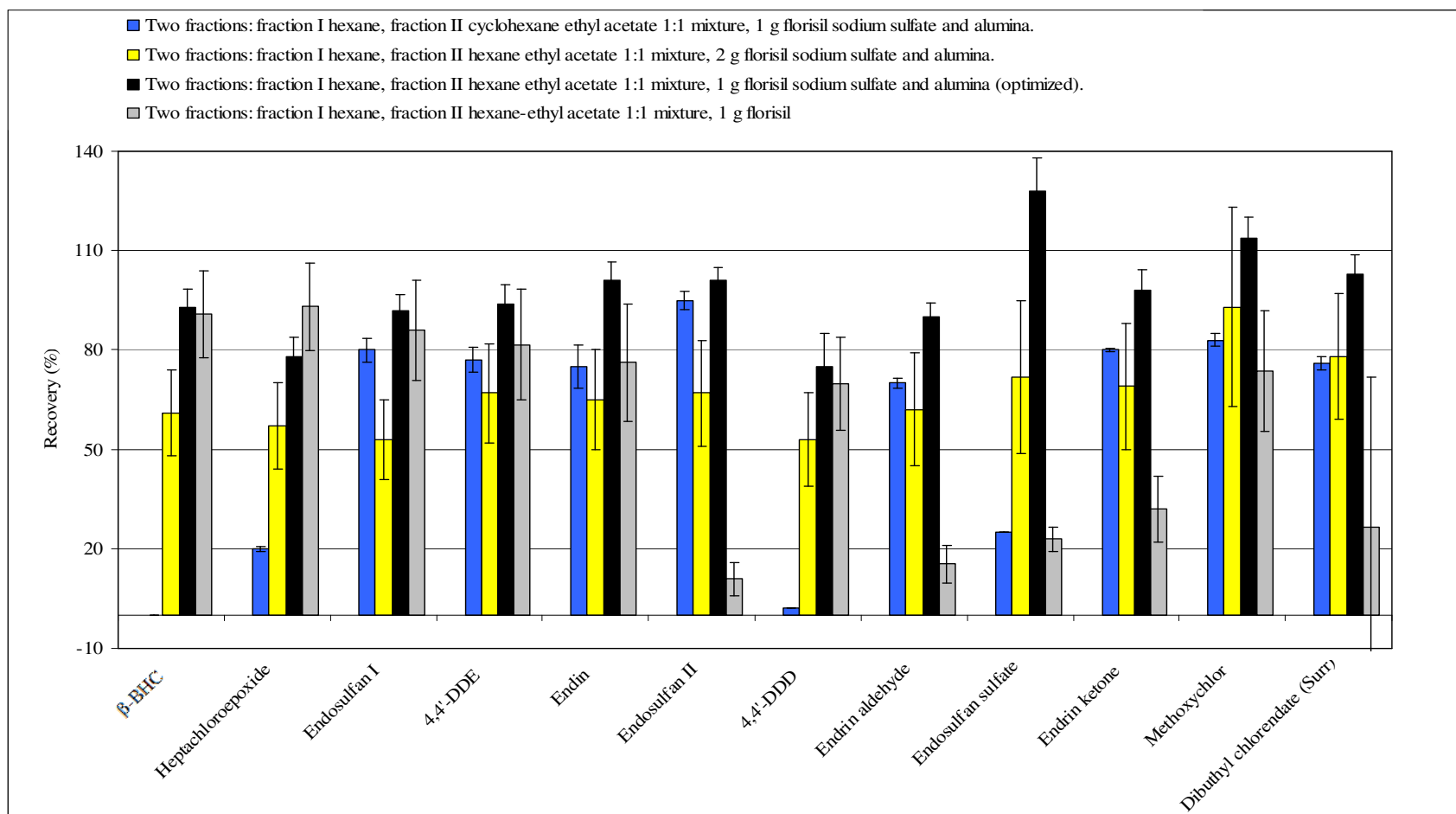


Figure 3.13. Recoveries of OCP compounds

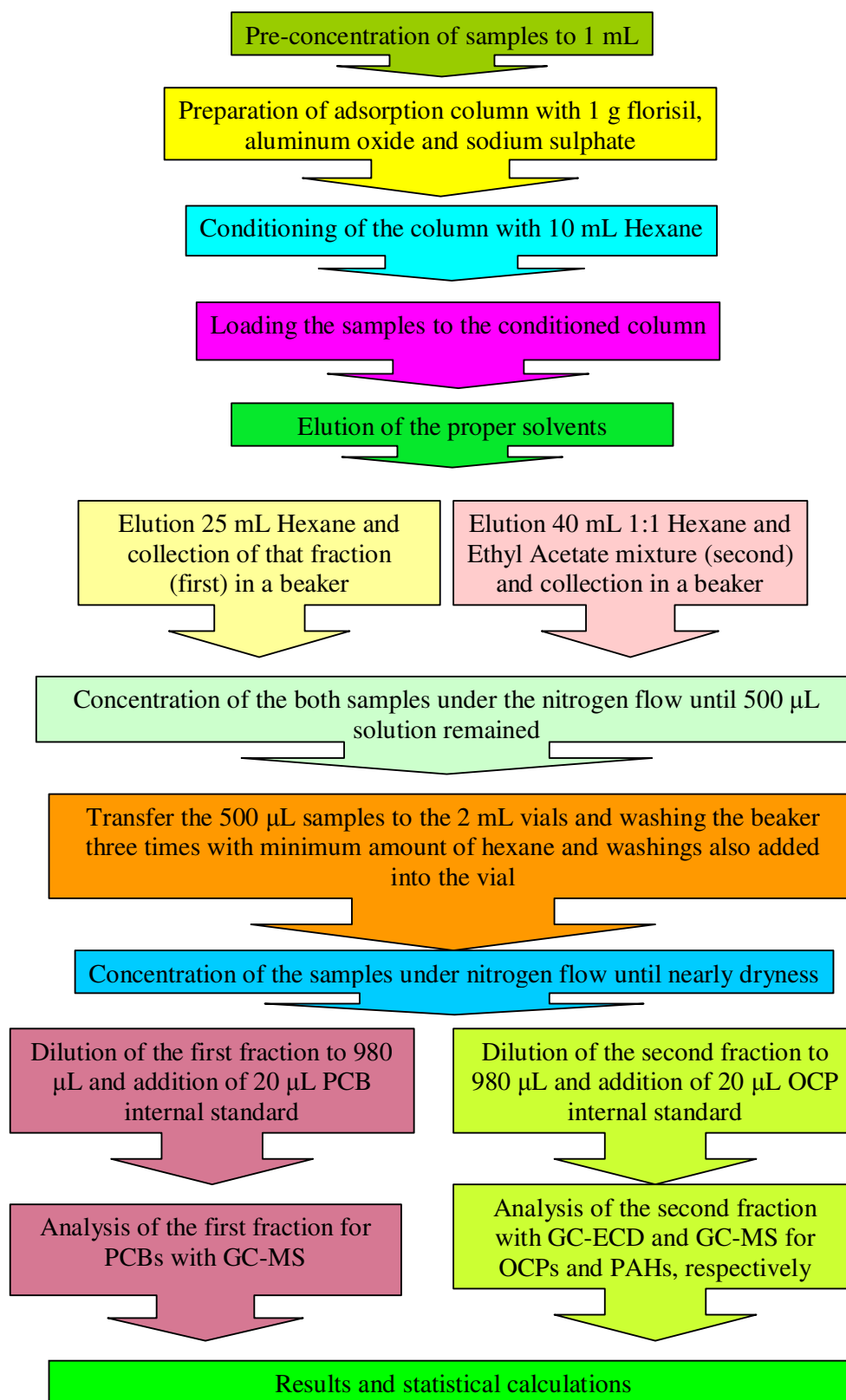


Figure 3.14. Preparation of samples after extraction step

3.4. Meteorological Parameters

Temperature, moisture, wind direction and daily fall has great influences on the pollutants transportation. Therefore the meteorological parameters were obtained from the nearest meteorology station (Appendix VII), which is 743 m high from sea level, located at 40° 44' of north latitude and at 31° 36' of east longitude. The parameters were measured at the station is given in figures below (Figure 3.15, Figure 3.16, Figure 3.17, Figure 3.18, Figure 3.19, Figure 3.20).

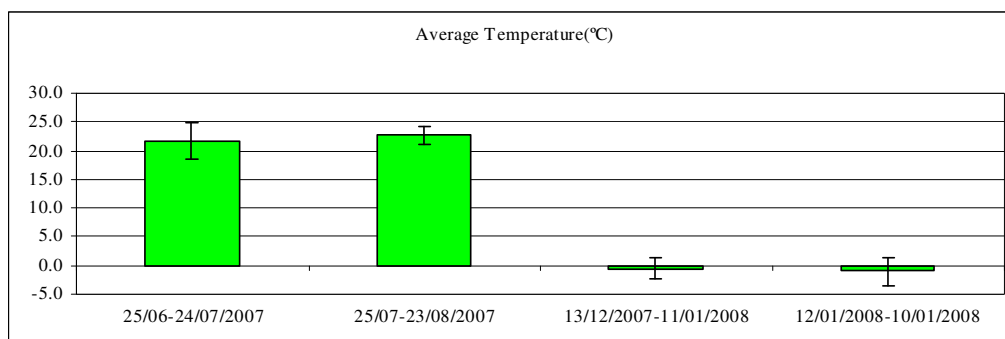


Figure 3.15. Average temperature of the sampling period

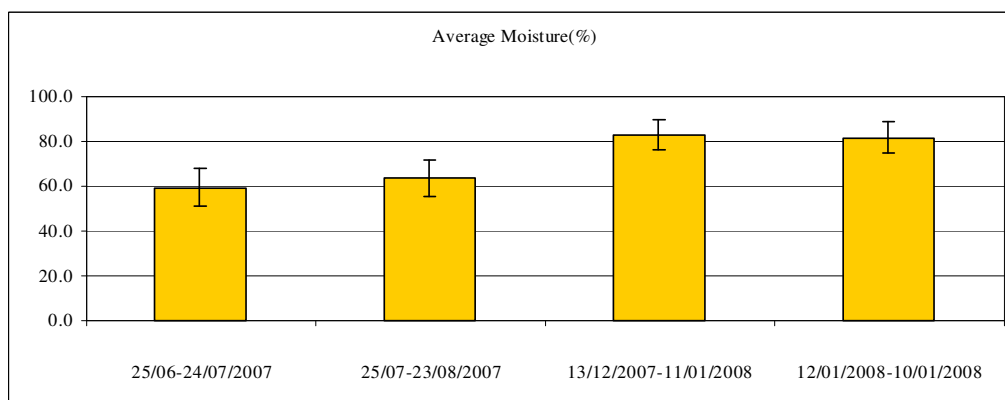


Figure 3.16. Average moisture of the sampling period

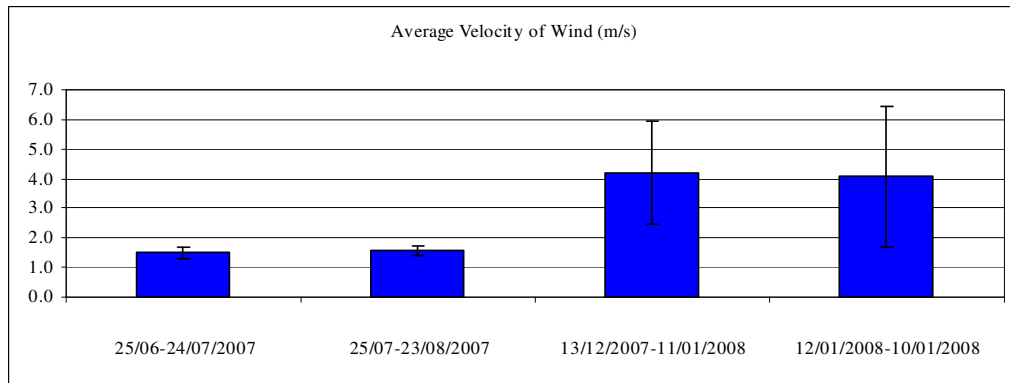


Figure 3.17. Average wind velocity of the sampling period

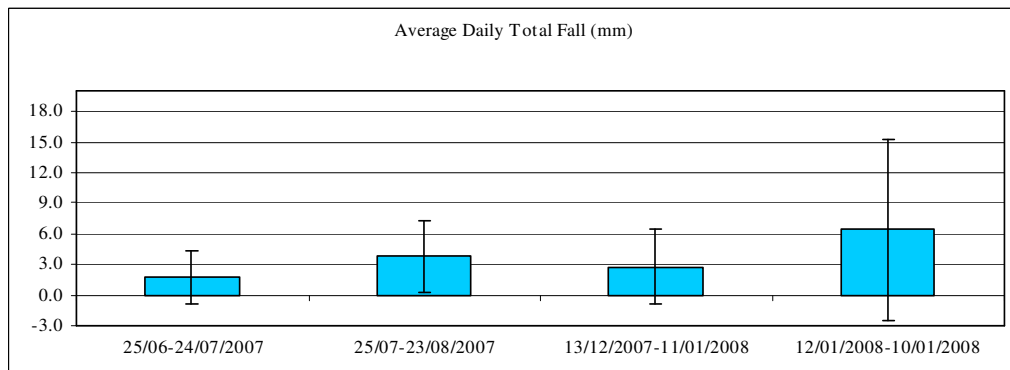


Figure 3.18. Average amount of fall during the sampling period

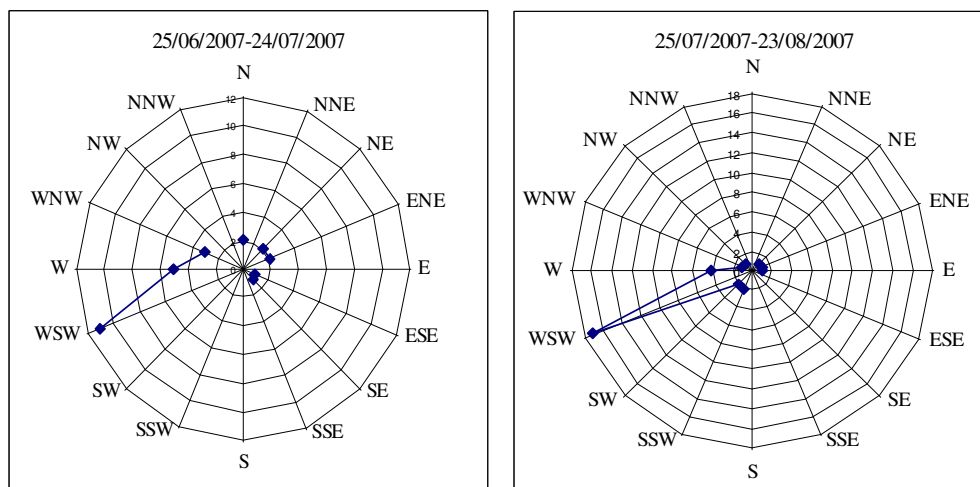


Figure 3.19. Wind direction of the summer sampling period

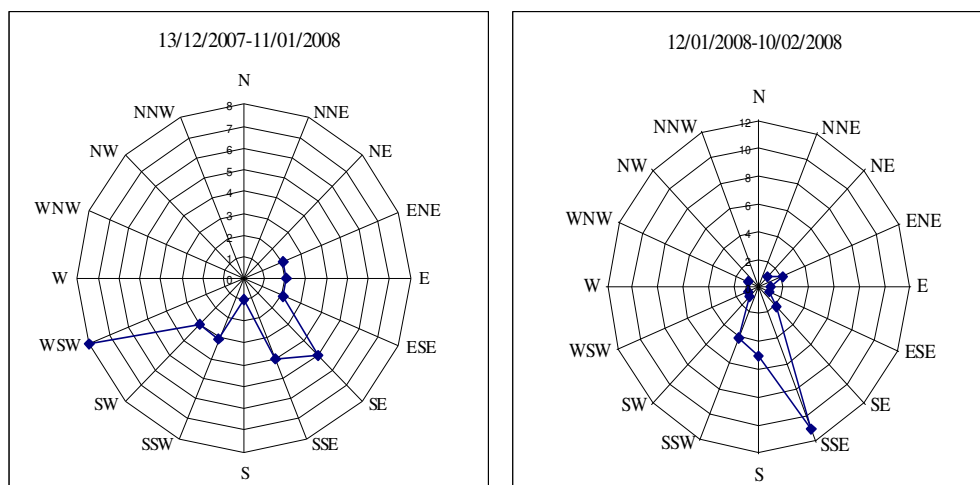


Figure 3.20. Wind direction of the winter sampling period

3.5. Analysis of the Samples

Most of the chemical analyses were carried out by the state of the art instruments. Thus very low amount of chemicals can be analyzed such as nano, pico and lower amounts. Air analysis also includes very low amounts of compounds and these instrumental studies require more attention and patience. In this study, the samples were analyzed in the air laboratory of the Environmental Engineering Department at the Anadolu University.

3.5.1. Instruments and Apparatus for Analysis

The complex organic matrix analysis requires sensitive and comprehensive instrumental studies. Therefore, we had to utilize two kinds of instruments to analyze all compounds. A HP (Hewlett Packard) 6890N series gas chromatograph equipped with the electron capture detector (Agilent, USA) was utilized for analysis of the OCPs. A 60 m, 0.25 mm id., 0.25 mm film thickness, cross linked 5 % phenyl

methyl siloxane, HP1 MS, capillary column (Agilent Tech.) and 15 millicuries of nickel 63 type ECD detector was used for the separation and detection of OCPs.

A HP 6890N series gas chromatograph (Agilent, USA) coupled with HP 5973 mass spectrometer (Agilent, USA) was used for the analysis. A 30 m, 0.25 mm id., 0.25 mm film thickness, cross linked 5% phenyl methyl siloxane, HP 5MS, capillary column (Agilent Tech.) was used for the separation of PAHs and PCBs throughout the study. Agilent 7683B series automatic injector (Agilent, USA) was used in both instruments.

3.5.2. Parameters of the GC-MS and GC-ECD

GC-MS parameters were optimized before analysis of samples. A splitless glass liner was chosen and injection port temperature was set at 280 °C. Several temperature programs were tried to obtain the best resolution parameters of the compounds given in Table 3.4. The temperature program was adjusted for PCB, PAH and OCP compounds as the mobile phases were an inert gas that was ultra purified helium for PAHs and PCBs, and nitrogen gas for OCPs. Electron impact was 70 eV for PAHs and PCBs and quadrupole and source temperatures were 150 °C and 230 °C at mass spectroscopy, respectively.

Table 3.4. Operating GC-MS and GC-ECD conditions for PAHs, PCBs and OCPs

Operation Parameters	PAHs	PCBs	OCPs
GC Column	30 m x 250 μ m x 0,25 μ m nominal film thickness, %5 Phenyl Methyl Siloxane, HP 5MS, capillary column	30 m x 250 μ m x 0,25 μ m nominal film thickness, %5 Phenyl Methyl Siloxane, HP 5MS, capillary column	60 m x 250 μ m x 0,25 μ m nominal film thickness, %5 Phenyl Methyl Siloxane, HP 1MS, capillary column
Liner	Splitless glass liner, deactivated	Splitless glass liner, deactivated	Splitless glass liner, deactivated
Mobile Phase (Carrier gas)	Ultra purified Helium, 99.999 %, 1 mL min ⁻¹	Ultra purified Helium, 99.999 %, 1 mL min ⁻¹	Ultra purified Helium, 99.999 %, 1 mL min ⁻¹
Type of Injection	Splitless	Splitless	Splitless
Temperature of the Injection Port	280°C	280°C	250°C
Temperature of Oven (Temperature Programs)	70°C (4 min), 7 °C min ⁻¹ to 250°C (5 min), 5 °C min ⁻¹ to 300°C (8 min)	70°C (2 min), 25 °C min ⁻¹ to 150°C (1 min), 3 °C min ⁻¹ to 200°C (1 min), 8 °C min ⁻¹ to 280°C (5 min)	50°C (1 min), 25°C min ⁻¹ to 170°C (5.8 min), 5 °C min ⁻¹ to 300°C (2 min)
Volume of the Injection	1 μ L	1 μ L	1 μ L
Detector	MS	MS	ECD
Quadrupole temperature of the Mass Spectroscopy	150 °C	150 °C	
Source Temperature of the Mass Spectroscopy	230 °C	230 °C	

3.5.2. Calibration of the GC-MS

Perflourotributylamine (PTFBA) was used to check to current status of the mass spectrometer. PTFBA has been the predominant calibration gas used in mass spectrometry because of the mass range of its fragments, their evenly spaced major fragments, and the volatility of the gas under the analyzer vacuum. PTFBA is ionized in the mass spectrometer's source by the electron beam from the filament and passed into the analyzer where its fragments are separated and detected. The major masses for calibration compound are 69, 131, 219, 264, 414, 464, 502, 614. In a well-tuned mass spectrometer, the 69 mass is the base mass; fragments 131 and 219 have approximately the same heights, equal to 45-60 % of the 69 peak; the 414 peak is about the 3-6 % of the 69 peak; and 502 will be 3 % or less than 69 peak height (Gaga, 2004).

Current status of the instrument was always monitored by autotune. Autotune report also provides information about the possible leaks. If 28 (N₂) or 44 (CO₂) exist in high percentages in the autotune report, source of leak was investigated. Usually leaks may occur in the GC inlet or MS interface parts. Electron multiplier voltage is another parameter showing the status of the ion source. Higher voltage is an indication of polluted ion source. If the voltage is around 2000 eV, MS is vented and ion source is cleaned. Polluted ion source causes greater deviations of concentrations than the original ones. If the instrument is working properly analysis can be started.

The standard mixtures were analyzed in scan mode first in order to see the fragmentation pattern of each PAH and PCB compounds. All the ions in between 35 and 550 amu were scanned. By this way standard purity can be determined before starting analyses. If the standard contains impurities and decomposition products, both are monitored in SCAN mode. After scanning the standard, target and qualifier ions were determined for each PAH and PCB compounds. One target and one or more qualifier ions were selected and were usually monitored for quantitative analysis.

SIM mode increases sensitivity by limiting the mass of the ions detected to one or more specific fragment ions of known mass. As a result, it is highly selective and it decreases a large portion of the noise in full scan detection mode. Entire chromatogram was divided in 7 time intervals for PAHs and 2 time intervals for PCBs in which specific ions were monitored, by this way sensitivity of the measurements were increased by decreasing backgrounds in the entire chromatogram. The monitored ions and SIM windows are given separately for PCBs and PAHs in Table 3.5 and Table 3.6.

Table 3.5. SIM windows for PCBs

SIM Window	Time Period (min)	Monitored Ions (m/z)	Compounds
1	6-22	150, 151, 152, 186, 220, 222, 224, 256, 258, 260, 290, 292, 294	PCB-14, PCB-30, PCB-18, PCB-28, PCB-31, PCB-20, PCB-52, PCB-65, PCB-44,
2	22-40	158, 254, 256, 288, 290, 324, 326, 328, 358, 360, 362, 394, 396, 398, 428, 430, 432	PCB-101, PCB-149, PCB-108, PCB-153, PCB-105, PCB-138, PCB-166, PCB-204, PCB-180, PCB-170, PCB-194.

Table 3.6. SIM windows for PAHs (Gaga, 2004)

SIM Window	Time Period (min)	Monitored Ions (m/z)	Compounds
1	8-12	127, 128, 129, 136, 137, 134	Nap, Nap-d8
2	12-15	151, 152, 153, 154, 160, 162, 164, 165, 166, 167	Acy, Ace d-10, Ace, Flu
3	15-21	176, 178, 179, 184, 187, 188, 189	Phe d-10, Phe, Ant
4	21-25	101, 200, 202	Flt, Pyr
5	25-30	120, 226, 228, 229, 236, 240, 241	BaA, Chr-d12, Chr
6	30-35	126, 132, 252, 253, 260, 264, 265	BbF, BkF, BaP, Per-d12
7	35-47	138, 139, 276, 277, 278, 279	Ind, DahA, BghiP

Mass software performs automatic integration of the peaks with respect to the method written in data analysis. Nevertheless, visual review of the produced chromatogram is essential since sometimes automatic integrations produce wrong results especially for closely eluting compounds. Each time, for each analysis, all the chromatograms were reviewed before further calculations. Figure 3.21 and Figure 3.22 represent the PAHs and PCBs SIM chromatograms, respectively.

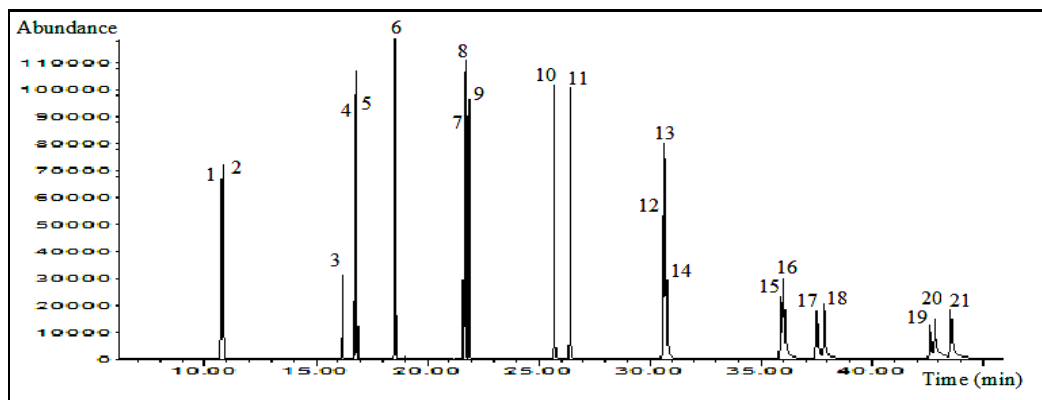


Figure 3.21. SIM chromatogram of 0.5 ppm of PAHs and surrogates 1. Nap-d8, 2. Nap, 3. Acy, 4. Ace-d10, 5. Ace, 6. Flu, 7. Phe-d10, 8. Ant, 9. Phe, 10. Flt, 11. Pyr, 12. BaA, 13. Chr-d12, 14. Chr, 15. BbF, 16. BkF, 17. BaP, 18. Per-d12, 19. Ind, 20. DahA, 21. BghiP

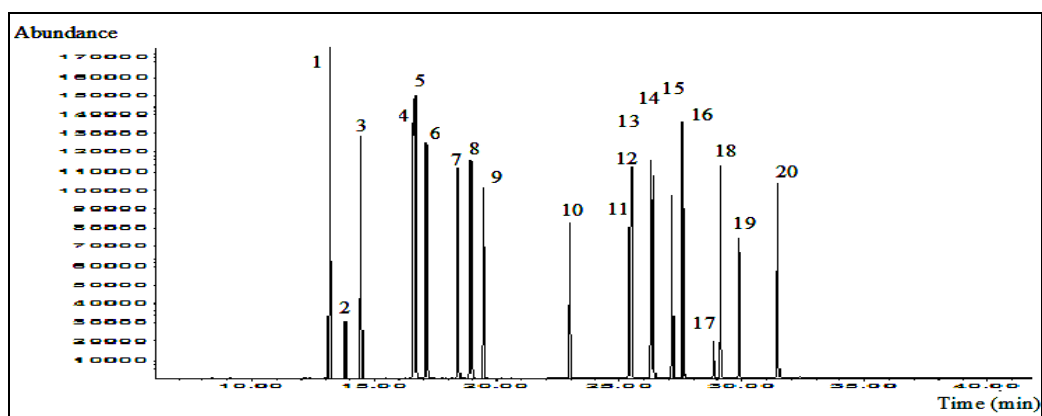


Figure 3.22. SIM chromatogram of 0.5 ppm of PCBs standards, internal standard and surrogates 1. PCB-14, 2. PCB-30, 3. PCB-18, 4. PCB-28, 5. PCB-31, 6. PCB-20, 7. PCB-52, 8. PCB-65, 9. PCB-44, 10. PCB-101, 11. PCB-149, 12. PCB-108, 13. PCB-153, 14. PCB-105, 15. PCB-138, 16. PCB-166, 17. PCB-204, 18. PCB-180, 19. PCB-170, 20. PCB-194.

Before the analysis of the unknown, a calibration curve is prepared by running at least five standards for both PAHs and PCBs. There are two ways in which calibration is performed: external standard calibration method and internal standard calibration method. External standard method involves preparation of a calibration curve by plotting area or height response against concentrations of

analyte(s) in the standards. The internal standard method is more reliable than the external standard method. Equal amounts of one or more internal standards are added onto equal volumes of sample extracts and the calibration standards.

3.5.2.1 Calibration for PCBs

Internal standard calibration was used for quantification of PCBs. PCB-30 and PCB-204 were used as internal standards which were added to the final extracts in the same amount with standards. Then they were used to calculate the concentrations of samples by correcting sample volumes.

Ten lowest amount of calibration standard, that was 5 ppb, were analyzed and results of each component divided by average volume of air sampling period. The concentration of individual compounds calculated as well.

Detection limit (LOD) is expressed as the concentration of analytes which gives a signal that is 3σ above the mean signal (where σ is the standard deviation of the lowest level standard). The quantification limits (LOQ), expressed as the concentration of analyte which gives a signal 10σ above that lowest level standard (Table 3.7).

Table 3.7. Calibration parameters, selected ions, LOD and LOQ values for PCBs

Compounds	Retention times	Linear Range (pg mL ⁻¹)	r ²	LOD (pg m ⁻³)	LOQ (pg m ⁻³)	Target ion	Ions (m z ⁻¹)
PCB-14 (SURR)	13.201	5-500	0.9994	0.00429	0.0143	222	152, 224, 151
PCB-18	14.475	5-500	0.9993	0.00477	0.0159	186	256, 258, 150
PCB-31	16.620	5-500	0.9990	0.0299	0.0997	256	258, 186, 260
PCB-28	16.679	5-500	0.9903	0.00418	0.0139	256	258, 186, 260
PCB-20	17.158	5-500	0.9992	0.00394	0.0131	256	258, 186, 260
PCB-52	18.435	5-500	0.9985	0.00378	0.0126	292	220, 290, 222
PCB-65 (SURR)	18.974	5-500	0.9996	0.00422	0.0141	292	290, 220, 293
PCB-44	19.488	5-500	0.9987	0.00440	0.0147	292	220, 290, 222
PCB-101	22.989	5-500	0.9986	0.00513	0.0171	326	254, 256, 328
PCB-149	25.451	5-500	0.9985	0.00302	0.0101	360	362, 290, 288
PCB-118	25.513	5-500	0.9983	0.00381	0.0127	326	328, 324, 254
PCB-153	26.303	5-500	0.9988	0.00328	0.0109	360	362, 290, 358
PCB-105	26.406	5-500	0.9978	0.00266	0.0089	326	328, 324, 254
PCB-138	27.172	5-500	0.9985	0.00555	0.0185	360	362, 290, 288
PCB-166 (SURR)	27.602	5-500	0.9988	0.00316	0.0105	360	362, 358, 290
PCB-180	29.123	5-500	0.9975	0.00221	0.00737	394	396, 324, 326
PCB-170	29.890	5-500	0.9989	0.00920	0.0307	394	396, 324, 326
PCB-194	31.463	5-500	0.9990	0.0164	0.0547	430	428, 358, 432

3.5.2.2 Calibration for PAHs

Since internal standards were not available PAHs, analytes were quantified by external calibration method. GC-MS was calibrated with for standard mixtures of PAHs from 0.1 ppm to 4 ppm for PAHs and good correlation coefficients were obtained for all the PAHs and surrogates. The LOQ and LOD values were also determined as PCB compounds for each PAH compounds (Table 3.8). The retention times of the all compounds are also given in Table 3.8.

Table 3.8. Calibration parameters, selected ions, LOD and LOQ values for PAHs

Compounds	Retention times	Linear Range (ng mL ⁻¹)	r^2	LOD (pg m ⁻³)	LOQ (pg m ⁻³)	Target ion	Ions (m z ⁻¹)
Nap-d8 (Surr)	10.732	0.1-4	0.9994	0.07	0.22	136	137, 134
Nap	10.789	0.1-4	0.9999	0.06	0.19	128	127, 129
Acy	16.203	0.1-4	0.9986	0.06	0.19	152	151, 153
Ace	16.746	0.1-4	0.9991	0.11	0.35	164	162
Ace-d10(Surr)	16.845	0.1-4	0.9999	0.08	0.27	153	154, 152
Flu	18.556	0.1-4	0.9991	0.09	0.28	166	165, 167
Phe-d10(Surr)	21.651	0.1-4	0.9984	0.12	0.41	188	189, 184
Phe	21.725	0.1-4	0.9999	0.08	0.28	178	176, 179
Ant	21.874	0.1-4	0.9995	0.09	0.28	178	176, 179
Flt	25.724	0.1-4	0.9989	0.24	0.82	202	200, 101
Pyr	26.427	0.1-4	0.9991	0.18	0.59	202	200, 101
BaA	30.582	0.1-4	0.9934	0.56	1.88	228	226, 229
Chr	30.654	0.1-4	0.9968	0.53	1.75	240	241, 236
Chr-d12(Surr)	30.726	0.1-4	0.9958	0.22	0.73	228	226, 229
BbF	35.892	0.1-4	0.9953	0.46	1.55	252	250, 253
BkF	36.031	0.1-4	0.9963	0.32	1.05	252	253, 126
BaP	37.525	0.1-4	0.9962	0.73	2.43	252	253, 250
Per-d12(Surr)	37.844	0.1-4	0.9937	1.76	5.86	264	260, 265
Ind	42.591	0.1-4	0.9920	0.53	1.77	276	277, 274
DahA	42.807	0.1-4	0.9910	0.38	1.26	278	276, 279
BghiP	43.528	0.1-4	0.9892	0.21	0.69	276	277, 138

Acenaphthene-d10 and phenanthrene-d10 were used for the recovery calculations of 3 ring PAHs, Chrysene-d12 for 4 ring PAHs and Perylene-d12 for the 5 and 6 ring PAHs. Calculated average recoveries of surrogates for the air samples were 43 %, 67 %, 97 %, 77 % for Ace-d10, Phe-d10, Chr-d10, Per-d12, respectively. The compounds whose concentrations were determined by surrogate recovery and the representative compounds by surrogates are given in Table 3.9.

Table 3.9. Surrogates and representative PAHs compounds

Surrogate	Representative PAH compounds
Ace d-10	Nap, Acy, Ace, Flu
Phe d-10	Phe, Ant
Chr d-12	Flt, Pyr, BaA, Chr
Per d-12	BbF, Ind, DahA, BghiP, BaP, BkF

3.5.2. Calibration of the GC-ECD

GC using an electron capture detector is a very sensitive method and is well suited for analysis of such polyhalogenated organic compounds. In the ECD, a beta emitter, such as radioactive tritium or ^{63}Ni , is used to ionize the carrier gas. Fast beta particles generated by the radioactive source collide with the molecules of the carrier or make-up flow gas. By impact ionization, free slow-moving electrons are produced, which generate a measurable and steady current. If the GC effluent contains organic molecules with electronegative functional groups, electrons will be captured and the current will be reduced. In comparison to a signal without sample compounds, the reduction in electron flow is proportional to the quantity of electrophile sample components. In this study, chlorinated pesticides were discussed to determine the concentration and fate. Therefore GC-ECD was used which was previously calibrated by standard solutions. A chromatogram of 1 ppm solution is given in Figure 3.23 and the r^2 of calibration graphs are given in Table 3.10.

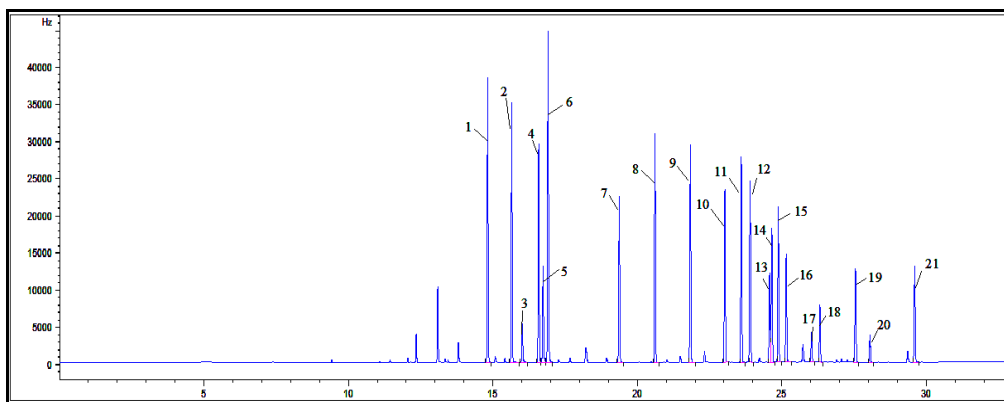


Figure 3.23. Chromatogram of 1 ppm mixture of OCP standard, surrogate and internal standard 1. 2,4,5,6-tetrachloro-m-xylene, 2. Alpha-HCH, 3. Beta-HCH, 4. Gamma-HCH, 5. Delta-HCH, 6. Pentachloronitrobenzene, 7. Heptachlor, 8. Aldrin, 9. Heptachlor-endo-epoxide, 10. Alpha-Endosulfan, 11. Dieldrin, 12. 4,4'-DDE, 13. Endrin, 14. Beta-Endosulfan, 15. 4,4'-DDE, 16. Endrin aldehyde, 17. Endosulfan sulfate, 18. 4,4'-DDT, 19. Endrin ketone, 20. Methoxychlor, 21. Dibutylchloredate.

Table 3.10. Retention times and regression coefficients of OCPs

Compound	Retention Times	Linear Range (pg mL ⁻¹)	r^2	LOD (pg m ⁻³)	LOQ (pg m ⁻³)
2,4,5,6tetrachloro-m-xylene (Surr)	14.81	5-1000	0.9999	0.73	2.42
Alpha-HCH	15.64	5-1000	0.9992	1.80	6.00
Beta-HCH	16.01	5-1000	0.9999	1.56	5.20
Gamma-HCH	16.57	5-1000	0.9992	2.03	6.75
Delta-HCH	16.72	5-1000	0.9951	3.90	13.0
Heptachlor	19.36	5-1000	0.9994	4.03	13.4
Aldrin	20.63	5-1000	0.9999	0.98	3.26
Heptachlor-endo-epoxide	21.85	5-1000	0.9999	1.40	4.66
Alpha-Endosulfan	23.05	5-1000	0.9999	1.28	4.28
Dieldrin	23.62	5-1000	0.9999	2.20	7.34
4,4'-DDE	23.92	5-1000	0.9999	1.56	5.20
Endrin	24.60	5-1000	0.9995	2.65	8.82
Beta-Endosulfan	24.67	5-1000	0.9998	1.46	4.86
4,4'-DDD	24.90	5-1000	0.9999	1.79	5.97
Endrin aldehyde	25.17	5-1000	0.9998	1.27	4.22
Endosulfan sulfate	26.04	5-1000	0.9927	4.59	15.3
4,4'-DDT	26.34	5-1000	0.9943	5.10	17.0
Endrin ketone	27.57	5-1000	0.9993	1.84	6.14
Methoxychlor	28.07	5-1000	0.9991	7.82	26.1
Dibutylchlorendate (Surr)	29.62	5-1000	0.9991	2.01	6.71

The OCP compounds were analyzed by GC-ECD and internal standard calibration was done by the standard solutions and pentachloronitrobenzene. Seven standard solutions from 0.005 ppm to 1.0 ppm were prepared and injected to the GC-ECD. The LOD and LOQ values were calculated with the similar methods used in PAHs and PCBs. Lowest level of the calibration standards was analyzed ten times and divided by the daily average volume of air at the sampling point and standard deviation was used to find LOD and LOQ as well as PAHs and PCBs.

CHAPTER 4

4. RESULT AND DISCUSSION

4.1. Organochlorine Pesticides (OCPs)

The usage of the most OCP compounds generally have been banned by governments as well as in Turkey, however, some of them are still in use or illegally used. In this study, both the air and soil samples were analyzed in order to determine the source of the pollutants and exchange relationships between them.

4.1.1. OCPs in Air

OCP compounds intentionally used compounds for medication to get rid of some harmful insect, however OCPs persists in environment resulting any harm to other organisms. At the sampling period, 60 summer and 60 winter samples were collected in both gas and particle phase by PUF plugs and GFFs, respectively. Although 18 OCP compounds were validated and used in optimization process, it was possible to determine 11 OCPs in samples.

4.1.1.1 Statistical Interpretation of the Data

The statistical evaluations of total OCP concentrations are given in Table 4.1. The percent observation of compounds was in the range of 31 % and 73 %. Heptachloroepoxide had the lowest observation percentage in samples and endrin and endosulfan sulfate were the highest ones in the air samples. In this study, the relative atmospheric level of the various OCPs was as follows: beta BHC > endrin > methoxychlor > endosulfan.

Mean value of the samples were higher than the median and geometric mean because of the abruptly changes in concentrations. The mean value of the samples generally lower than standard deviation that is because the composition of the samples influenced from the various type of sources and chemical and physical transformation as well as wind direction. If the data of the measured samples are affected from the different kinds of sources, the log-normal distribution is observed (Figure 4.1). The log-normal distribution can be calculated by the geometric mean therefore the tables of statistical calculations contain that value. Average log-normal distribution was generally given by geometric mean. Moreover, it was understood from the closeness of the median to geometric mean that is different from the mean. Therefore, the analyzed compounds in this study had generally the log-normal distribution except for endosulfan sulfate. The meteorological parameters in these calculations had high effects on the atmospheric pollutants. The normal distribution of the endosulfan sulfate can be explained by the conversion of parents with the photochemical oxidation.

Table 4.1. Statistical assessment of total (gas and particle phase) OCP concentrations (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
beta BHC	42	35	0.366	0.0696	0.107	0.552	0.000562	1.842	1.842
4,4'-DDD	48	40	0.0269	0.0239	0.0208	0.0188	0.00362	0.0943	0.0907
4,4'-DDE	40	33	0.00997	0.00428	0.00468	0.0184	0.000305	0.116	0.116
endosulfan II	87	73	0.0429	0.0371	0.0331	0.0313	0.00571	0.184	0.178
endosulfan sulfate	49	41	0.0958	0.0860	0.0882	0.0393	0.0177	0.213	0.195
endosulfan I	75	63	0.0739	0.0406	0.0323	0.149	0.000494	1.219	1.218
endrin	88	73	0.188	0.149	0.139	0.141	0.00938	0.753	0.744
endrin aldehyde	43	36	0.0424	0.0291	0.0281	0.0390	0.00106	0.172	0.171
endrin ketone	36	30	0.0607	0.0506	0.0491	0.0494	0.0181	0.285	0.267
heptachloroepoxide	37	31	0.0220	0.0176	0.0123	0.0221	0.000227	0.108	0.108
methoxychlor	51	43	0.208	0.172	0.148	0.205	0.0218	1.357	1.335

*Total analyzed samples: 120

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

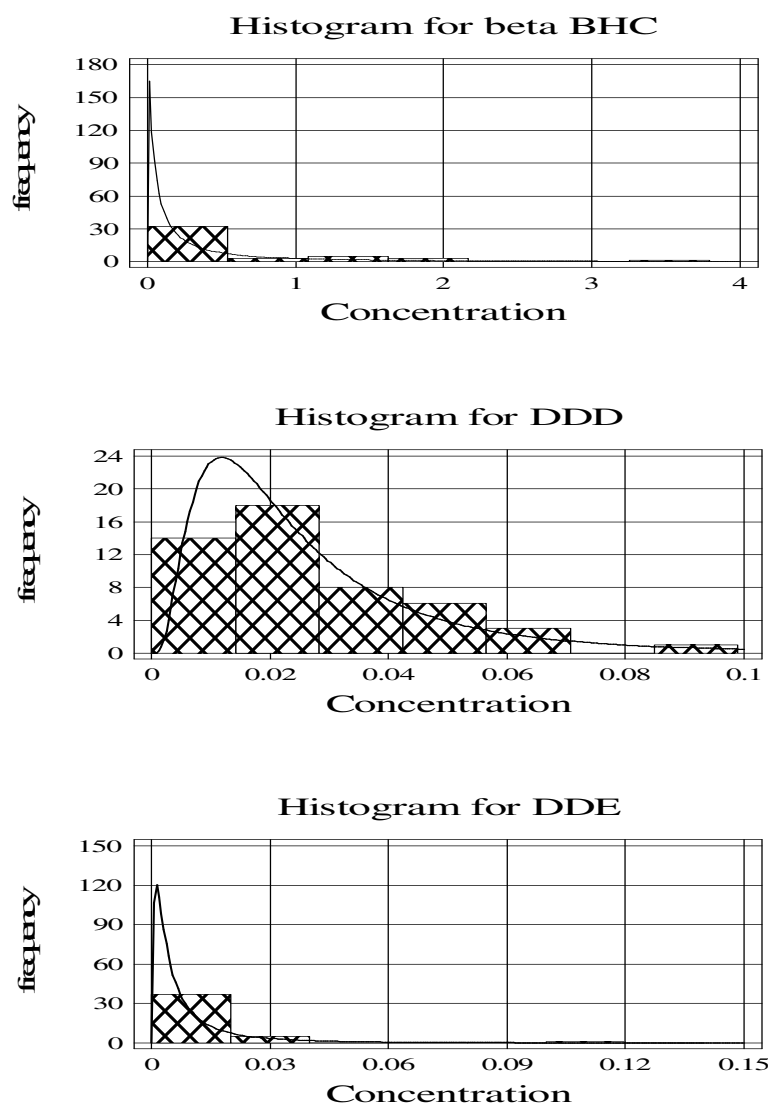


Figure 4.1. The statistical distribution of OCP concentrations (ng m⁻³)

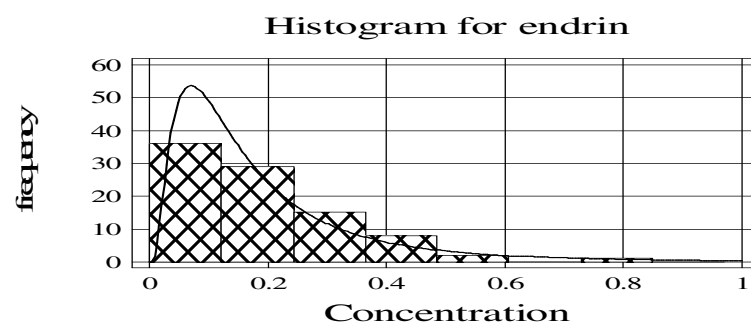
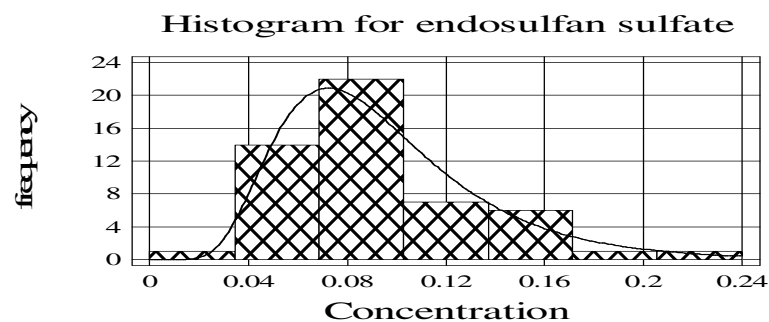
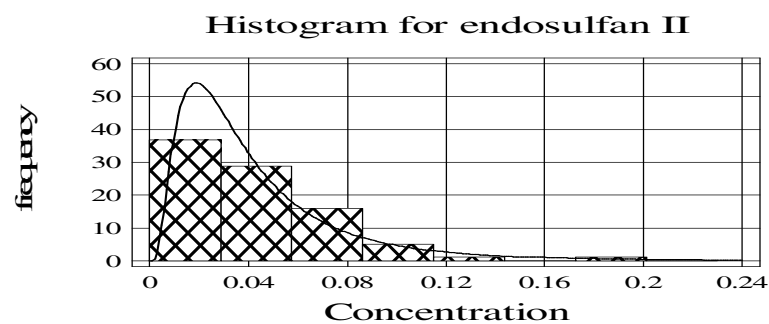
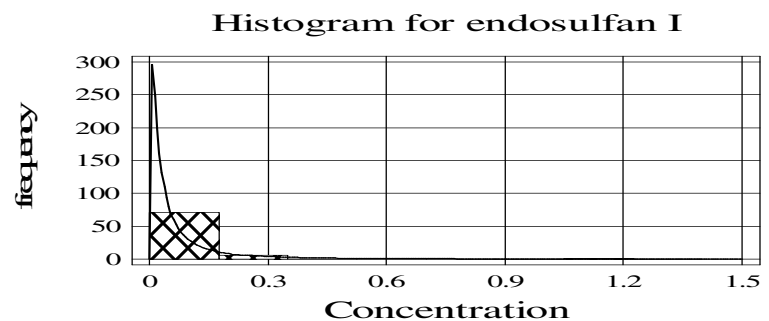


Figure 4.1. The statistical distribution of OCP concentrations (ng m^{-3}) (Continued)

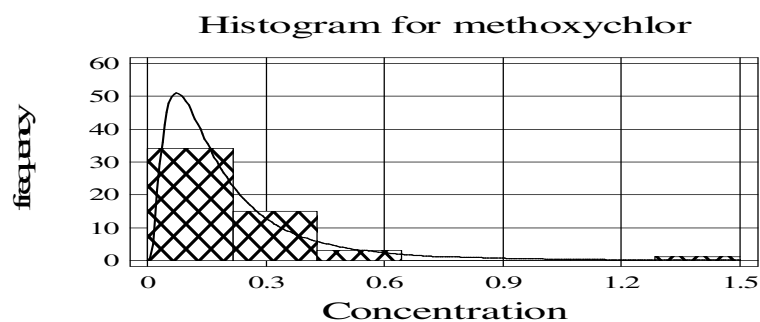
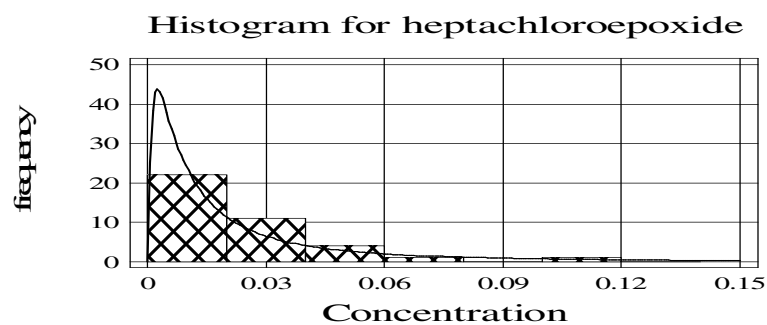
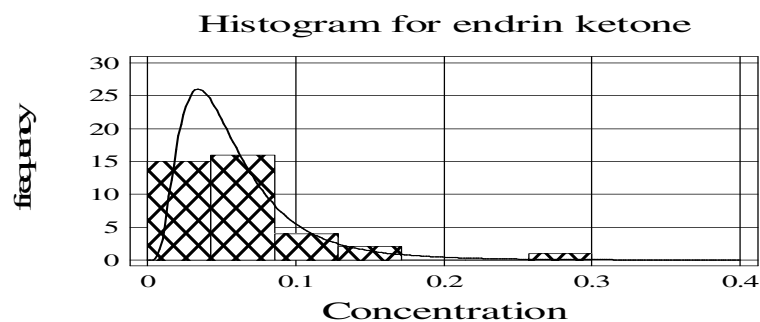
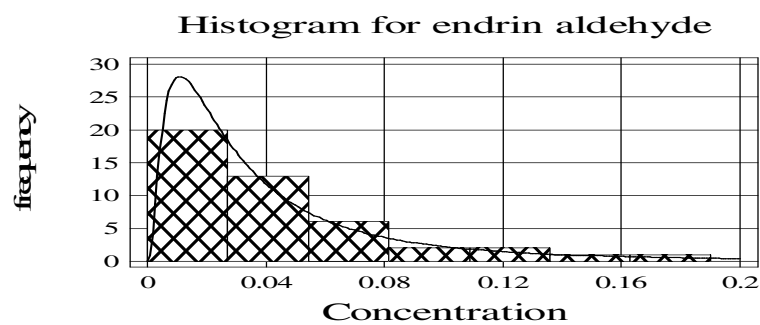


Figure 4.1. The statistical distribution of OCP concentrations (ng m^{-3}) (Continued)

4.1.1.2. Diurnal Distribution of OCPs

Daily concentrations of the OCPs are given in Figure 4.2 and distribution of the OCP compounds was determined. The concentrations of beta BHC and methoxychlor had the highest value whereas endosulfan II and 4,4'-DDD had the lowest ones. Unlike other OCPs, beta BHC had abrupt changes, which might be derived from daily usage or transportation. The minimum concentration of OCPs belonged to the 4,4'-DDE. According to the daily concentrations of the OCPs, the winter season showed significant increase except for beta BHC.

Table 4.1 presents average concentrations of OCPs in Bolu. Although the use of most of the OCPs ceased all over the world as well as in Turkey, these chemicals have been still observed in the atmosphere even now. Most OCPs were observed in the samples whereas heptachloroepoxide had the lowest observation percentage. Heptachloroepoxide and 4,4'-DDE, that can be as toxic as their parent compounds, (Yeo *et al.*, 2004). Endrin and beta-BHC showed the highest concentrations at sampling point with values typically ranging from 10s to 1000s of pg m^{-3} , while the others show values ranging from 1s to 100s of pg m^{-3} . The higher values of these compounds might result from their usage, duration used in the past and physicochemical properties. Endosulfan is one of the OCPs registered in Bolu to be used for controlling wide spectrum of insect pests on fruits and vegetables, and commonly used pesticide in agricultural applications in Bolu. Endosulfan and parent compounds such as endosulfan sulfate, alpha and beta isomers commonly observed in our samples that are called as a “soft” organochlorine because of their chemical properties, degradation rate, and metabolism in plants and animals. Its biologically

active oxidation product, endosulfan sulfate, is also significant as a residue as its concentration is found to be higher than the endosulfan I and II. BHCs are also very resistant to biodegradation (Yeo *et al.*, 2004). Beta BHC which is the most stable compound in the family had the highest average concentration in the samples. It had the lowest vapor pressure and solubility in its parents. Although it had moderate observation frequency its daily concentration exhibited higher values in the observed samples. Determination of 4,4'-DDD and 4,4'-DDE in samples, which are the oxidation and reduction product of DDT, indicates the former usage and persistence of DDT.

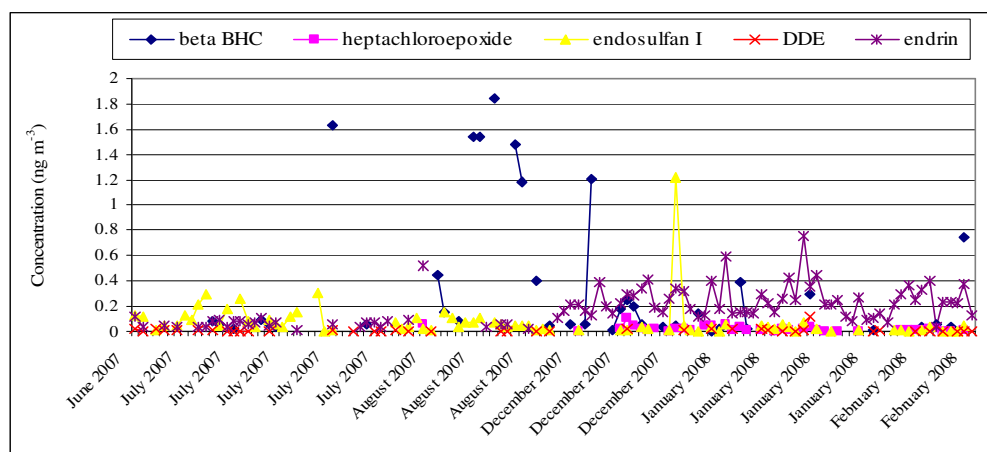


Figure 4.2. Daily concentrations of five OCP compounds

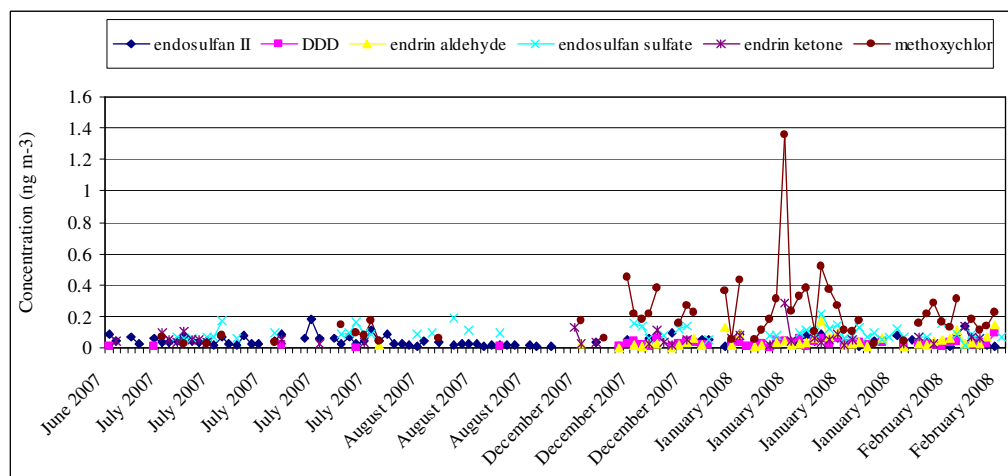


Figure 4.3. Daily concentrations of six OCP compounds

4.1.1.3. Seasonal Changes of the OCPs

Seasonal variations can be seen when the winter and summer samples were individually discussed. Gas and particle phase samples are also interpreted in terms of seasonal changes. Gaseous summer samples are given in Table 4.2. The nine OCP compounds had an observation range between 5 % and 78 % in summer. Endosulfan II had the highest arithmetic mean and 4,4'-DDD had the lowest arithmetic mean. Endrin aldehyde and heptachloroepoxide were not observed in gaseous phase at the sampling period. The range from higher to lower concentration is as follows: beta BHC > endosulfan sulfate > endosulfan I > methoxychlor.

Table 4.2. Statistical evaluation of gas phase OCP concentrations for summer samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
beta BHC	17	28	0.572	0.0844	0.191	0.730	0.0217	1.85	1.82
4,4'-DDD	3	5	0.00984	0.0105	0.00910	0.00438	0.00517	0.0139	0.00869
4,4'-DDE	19	32	0.00688	0.00483	0.00518	0.00595	0.00120	0.0223	0.0211
endosulfan II	47	78	0.0374	0.0287	0.0301	0.0296	0.00836	0.184	0.175
endosulfan sulfate	9	15	0.0904	0.0923	0.0897	0.0119	0.0675	0.110	0.0428
endosulfan I	39	65	0.0880	0.0682	0.0581	0.0765	0.00223	0.304	0.302
endrin	23	38	0.0467	0.0434	0.0441	0.0132	0.00938	0.0770	0.0675
endrin ketone	8	13	0.0495	0.0516	0.0484	0.0106	0.0337	0.0673	0.0336
methoxychlor	7	12	0.0830	0.0787	0.0780	0.0323	0.0418	0.145	0.103

*Total analyzed samples: 60

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Statistical evaluation of the particle phase summer samples is given in Table 4.3. The percent observations of nine OCP compounds had a range between 3.3 % and 32 % in the 60 samples. Beta BHC had the highest and 4,4'-DDD had the lowest percent observation. The highest concentrations were determined for beta BHC and rank of the other concentrations high level to low level as follows: endosulfan sulfate > methoxychlor > endrin.

Table 4.3. Statistical evaluation of particle phase OCP concentrations for summer samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
beta BHC	4	6.7	0.527	0.397	0.0780	0.601	0.00100	1.183	1.182
4,4'-DDD	2	3.3	0.00446	0.00447	0.00440	0.00108	0.00370	0.00523	0.00152
4,4'-DDE	7	12	0.000843	0.000692	0.000672	0.000548	0.000236	0.00149	0.00125
endosulfan II	17	28	0.0208	0.00923	0.0126	0.0290	0.00482	0.1143	0.1094
endosulfan sulfate	11	18	0.0846	0.0728	0.0799	0.0360	0.0592	0.1864	0.1272
endosulfan I	5	8.3	0.0393	0.0252	0.0315	0.0311	0.0139	0.0915	0.0775
endrin	19	32	0.0596	0.0373	0.0414	0.1006	0.0240	0.4746	0.4506
endrin ketone	5	8.3	0.0361	0.0337	0.0357	0.00611	0.0301	0.0457	0.0156
methoxychlor	4	6.7	0.0650	0.0305	0.0446	0.0729	0.0249	0.1742	0.1492

*Total analyzed samples: 60

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Statistical calculations for winter were performed in gaseous phase and data is given in Table 4.4. The whole optimized OCP compounds were observed in winter samples however percent observation range changed between 10 % and 98 %. Endrin ketone and methoxychlor had the lowest percent observation whereas endrin had the highest. Highest percent observation of endrin can be explained by its persistence in the air as well as its chemical properties and usage. The arithmetic mean concentrations were in the order of beta BHC > methoxychlor > endrin > endosulfan sulfate > endrin ketone.

Table 4.4. Statistical evaluation of gas phase OCP concentrations for winter samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
beta BHC	18	30	0.215	0.0577	0.0680	0.321	0.000562	1.202	1.202
4,4'-DDD	18	30	0.0107	0.00837	0.00916	0.00735	0.00361	0.0317	0.0281
4,4'-DDE	16	27	0.0161	0.00642	0.00633	0.0279	0.000788	0.116	0.115
endosulfan II	20	33	0.0204	0.0139	0.0158	0.0151	0.00571	0.0533	0.0476
endosulfan sulfate	15	25	0.0713	0.0695	0.0703	0.0124	0.0507	0.0917	0.0409
endosulfan I	8	13	0.00851	0.00391	0.00540	0.0112	0.00196	0.0357	0.0337
endrin	59	98	0.0768	0.0636	0.0679	0.0471	0.0227	0.247	0.225
endrin aldehyde	14	23	0.0115	0.00540	0.00368	0.0142	0.0000167	0.0453	0.0453
endrin ketone	6	10	0.0312	0.0232	0.0287	0.0160	0.0215	0.0624	0.0409
heptachloroepoxide	13	22	0.0268	0.0180	0.0161	0.0274	0.00235	0.0998	0.0974
methoxychlor	6	10	0.102	0.0905	0.0697	0.0836	0.0218	0.214	0.193

*Total analyzed samples: 60

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Statistical calculations were performed for particle phase OCP concentrations in winter season given in Table 4.5. Eleven compounds were also observed in winter samples and percent observation range changed between 6.7 % and 98 %. These were the 4,4'-DDE and endrin, respectively. 4,4'-DDE had the lowest arithmetic mean concentrations whereas methoxychlor had the highest value. Methoxychlor, endrin, endosulfan sulfate and endrin ketone had the highest arithmetic mean concentrations.

Table 4.5. Statistical evaluation of particle phase OCP concentrations for winter samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
beta BHC	5	8.3	0.0386	0.0335	0.0334	0.0202	0.0120	0.0590	0.0470
4,4'-DDD	41	68	0.0258	0.0219	0.0209	0.0176	0.00463	0.0943	0.0896
4,4'-DDE	4	6.7	0.00378	0.00291	0.00294	0.00310	0.00107	0.00825	0.00717
endosulfan II	30	50	0.0406	0.0352	0.0324	0.0286	0.00678	0.142	0.135
endosulfan sulfate	23	38	0.0858	0.0766	0.0781	0.0351	0.0177	0.158	0.140
endosulfan I	30	50	0.02203	0.0170	0.0146	0.0176	0.000494	0.0734	0.0729
endrin	59	98	0.167	0.153	0.136	0.111	0.0337	0.545	0.512
endrin aldehyde	40	67	0.0410	0.0255	0.0244	0.0389	0.000277	0.157	0.157
endrin ketone	22	37	0.0646	0.0450	0.0496	0.0592	0.0181	0.285	0.267
heptachloroepoxide	27	45	0.0152	0.0107	0.00917	0.0135	0.000227	0.0640	0.0637
methoxychlor	38	63	0.2407	0.1988	0.1866	0.2203	0.04293	1.3571	1.3142

*Total analyzed samples: 60

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

4.1.1.3.1. Seasonal Ratios

Seasonal variations can be explained better when the gas-particle ratios discussed. Hence, total OCP concentrations were calculated in gas and particle phase as well as median values given in tables above. The ratios of total concentrations of OCPs were given in Figure 4.4. According to the mean values of gas phase concentrations, the winter concentrations of the OCPs were significantly ($p = 0.05$) higher than the summer except for 4,4'-DDE, endrin and methoxychlor. The high

concentration of these exceptional compounds in winter might be mainly related to transportation, duration of usage and their chemical properties. When the particle phase concentrations of winter were compared to summer season, all OCP compounds under discussion were significantly ($p = 0.05$) high in winter except for beta BHC. Since beta BHC is not only more stable but also is a by-product of lindane and PVC production, the high gas phase concentration of the beta BHC mainly derived from the near pollution source.

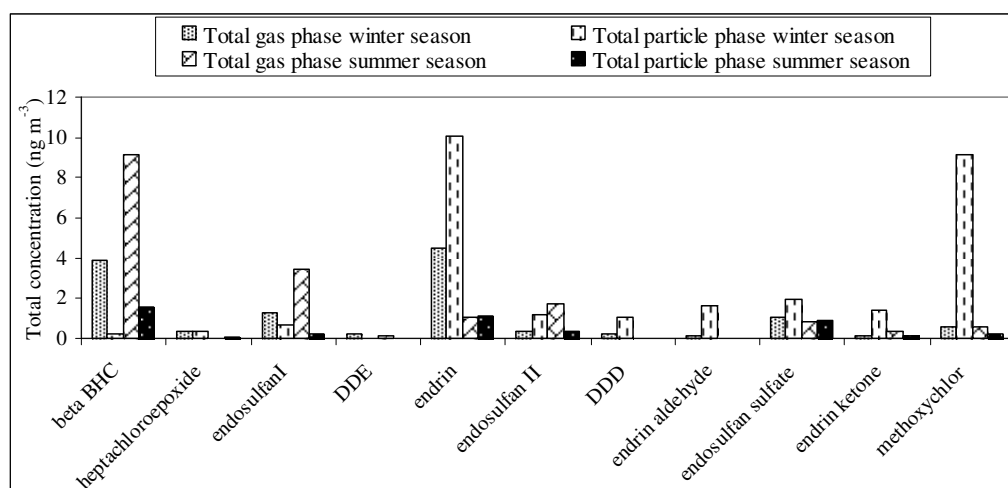


Figure 4.4. Mean concentrations of gas and particle phase OCPs

The gas-particle ratio was investigated in both seasons in order to determine the fractional distribution in either particle or gas phase. Gas phase concentrations of the all compounds were significantly high in summer as it is expected from the effect of the rise in temperature. On the contrary, all compounds except for beta BHC, 4,4'-DDE and heptachloroepoxide were significantly ($p = 0.05$) high in particle phase in winter. The OCP molecules that evaporate in summer bound to the surface or into the particles, therefore the particle phase concentrations were found to be higher in winter. Since atmospheric levels of some OCPs are influenced by meteorological

factors such as; volatilization, deposition and degradation. These results had also been reported in several studies that the examined relationship between atmospheric concentration and ambient temperature (Halsall *et al.*, 1998; Sofuoğlu *et al.*, 2001; Yeo *et al.*, 2004).

Generally, maximum values were obtained in summer at the gas phase and at the particle phase in winter. Current usage of endosulfan exhibited moderate concentration however distribution of the parent compounds that are oxidation or degradation products were also determined. The most stable parent of endosulfan group is the endosulfan I and moreover, endosulfan II is converted to the endosulfan I in ambient air (Burgoyne and Hites, 1993). In this study, endosulfan I concentration was higher than endosulfan II as well. Moderate concentration of the endosulfan derived from the limited usage and mainly transports to sampling point from the very close agricultural areas. Although beta BHC had low observation percentage, the concentration had high values in both seasons in gas phase. This could be explained by instantaneous spreading of this compound from the local sources.

4.1.1.4. A Comparison of OCP Concentrations with Related-Literature Values

The concentrations of the OCPs were compared with literature values in order to determine the OCP loadings in Bolu. The data for similar regions in the literature is given in Table 4.6. and was compared with this study. Sampling places and gas phase or particle phase or total concentrations are given in the first column of the table.

Table 4.6. A comparison of OCP concentrations with related-literature mean values (pg m⁻³)

Referance	β-BHC	heptachlor epoxide	endosulfan I	4,4'-DDE	endrin	endosulfan II	4,4'-DDE	endrin aldehyde	endosulfan sulfate	endrin ketone	methoxychlor
This study (Bolu, Turkey), rural, agricultural, particle	283 ± 635	16.6 ± 15.3	24.5 ± 20.4	1.9 ± 2.3	143 ± 118	33.5 ± 30.0	24.8 ± 17.8	41.2 ± 38.9	85.5 ± 34.9	59.4 ± 54.5	224 ± 217
This study (Bolu, Turkey), rural, agricultural, gas	393 ± 597	26.8 ± 27.4	97.6 ± 177	11.1 ± 19.6	68.4 ± 42.7	32.3 ± 27.1	10.6 ± 6.9	11.7 ± 13.7	78.5 ± 15.3	41.7 ± 15.7	91.9 ± 59.4
This study (Bolu, Turkey), rural, agricultural, total	366 ± 552	22.0 ± 22.0	73.9 ± 14.8	9.97 ± 18.4	188 ± 141	42.9 ± 31.3	26.9 ± 18.7	42.4 ± 39.0	95.8 ± 39.3	60.7 ± 49.4	208 ± 205
Hung <i>et al.</i> , 2005 (Canada), rural, total	0.59 (0.03-2.39)	1.42 (0.03-2.50)	5.81 (2.05-13.4)	0.42 (0.12-0.92)	0.20 (0.08-0.70)						0.23 (0.12-0.46)
Hung <i>et al.</i> , 2005 (Canada), rural, total	0.47 (0.02-7.99)	1.47 (0.04-16.2)	8.33 (0.08-88.6)	0.71 (0.03-13.6)	0.29 (0.07-1.52)						0.40 (0.09-6.53)
Hung <i>et al.</i> , 2005 (Canada), rural, total	0.36 (0.06-1.99)	1.15 (0.11-2.98)	6.25 (0.06-384)	0.38 (0.10-0.85)	0.27 (0.18-0.59)						0.37 (0.26-0.63)
Sadiki and Poissant, 2008 (Canada), rural, agricultural, gas		24 ± 13	451 ± 315	39 ± 26	7 ± 1	38 ± 24	11 ± 5				
Sadiki and Poissant, 2008 (Canada), rural, agricultural, particle	4 ± 3		3 ± 2	1 ± 1		1 ± 1					
Alegria <i>et al.</i> , 2008 (Mexico), rural, agricultural, total			182 ± 121	334 ± 95		38 ± 33	42 ± 18		7.3 ± 2.2		
Alegria <i>et al.</i> , 2008 (Mexico), rural, agricultural, total			77 ± 51	39 ± 21		12 ± 7	13 ± 9.9		3.2 ± 1.1		
Sofuoğlu <i>et al.</i> , 2004 (İzmir, Turkey), urban, total	320 ± 176	34 ± 35		20 ± 8	16 ± 10	20 ± 7	5 ± 4	48 ± 38	369 ± 375	41 ± 26	220 ± 255
Gouin <i>et al.</i> , 2008 (Canada), rural, agricultural, total			820 ± 30			125 ± 7			8 ± 3		
Park <i>et al.</i> , 2000 (USA), rural, gas	4.1 ± 10.3	13.1 ± 7.5		11.3 ± 9.0	1.4 ± 2.9		2.1 ± 1.9				102.3 ± 83.6
Park <i>et al.</i> , 2000 (USA), rural, particle	0.3 ± 0.5			0.5 ± 0.5	4.6 ± 6.1		0.8 ± 1.8				240.7 ± 220.3
Yao <i>et al.</i> , 2006 (Canada), rural, agricultural, total			717	28.9		162					65.1 ± 72.9
Yeo <i>et al.</i> , 2004 (South Korea), rural, agricultural, total		21.3±34.8		34.6±51.3			6.2±18.3		334±911		

The data collected in İzmir has significant importance because of similar beta BHC concentrations whereas other studies have 100 fold lower. Although the usage of this compound was banned in Turkey in 1985, the high concentrations show that beta BHC is still in use or used at extremely high application rate in the past. Although heptachloroepoxide concentration found in this study was higher than the one in Canada by Hung *et al.*, (2005), the studies in İzmir, South Korea and other parts of Canada had comparable results with this study. Endosulfan I and endosulfan II are used commonly and they are legal OCP compounds. In addition, potatoes and crops (wheat, barley, etc.) are treated with them in Bolu. The usage of endosulfan I and endosulfan II level have decreased for the last three years. On the other hand, endosulfan I and endosulfan II concentrations had similar or lower values in all rural and agricultural areas except for the rural area of Canada. Endosulfan sulfate concentration was lower than South Korea and İzmir whereas it was higher than other studies. Endosulfan sulfate is the oxidation product of endosulfan I and endosulfan II, therefore, its concentrations were higher as a result of long-term applications.

4,4'-DDD and 4,4'-DDE which were the derivatives of the 4,4 DDT were not significantly different from other regions. Endrin concentration was 30-50 fold higher than literature values except for rural area in Canada and 10 fold higher than the value measured in İzmir. Although the usage of that compound was banned in 1979, it was found at high levels in the atmosphere and observed nearly in all samples. Endrin aldehyde and endrin ketone had the similar concentrations in the study conducted in İzmir. Methoxychlor, which is not restricted by government, was found same as in literature values except for some regions in Canada.

4.1.1.5. Wind Sector Analysis

Wind sector analysis is generally used to explain the transportation of pollutants from local sources. Total concentrations of gas and particle phase will be examined for wind sector analysis (Table 4.8). The dominant wind direction in summer was blowing down from the south, the south east, and the west. It was compatible with most of the compounds, which had high concentrations in this direction. High concentrations are shown in bold in the tables. Beta BHC concentrations were high in the SSW, the SW and the W directions. Concentrations of endosulfan I, endrin, and endosulfan II were high in the W and the WNW, the WSW and the SW, respectively. High concentrations of endosulfan sulfate and metoxychlor were detected at the SW, the WSW and the W directions. Endrin ketone was found high at the WSW and the WNW. As can be seen in Table 4.7, there are highly agricultural regions such as Mudurnu, Seben, Kıbrıscık, and villages that are close to the sampling point.

The dominant wind directions were from the west, the southwest and the southeast in winter (Table 4.9). Beta BHC concentration was high at the WSW and the ESE, while, heptachloroepoxide was high in the WSW and the SE directions. Maximum effect to the concentration of endosulfan I was attributed by the SE winds meanwhile, the SSW winds highly affected the 4,4'-DDE concentrations. Endrin and endosulfan sulfate concentrations were observed higher at the S and the SE directions and also, all directions had significant contributions to endrin. The air masses transported from the SE and the E winds carried the endosulfan II pollutant. The ESE winds affected the 4,4'-DDD and endrin aldehyde concentrations. The SSE

winds were more effective on the concentrations of the endrin ketone and methoxychlor.

Table 4.7. Types of the sources and regions on the wind sectors with respect to the sampling point

Sector	Types of Sources
South, S	Agricultural Region (Seben), Gölköy Lake
South South West, SSW	Forestry and Agricultural Region (Mudurnu, Göynük)
South West, SW	Agricultural Region (Mudurnu, Göynük), Heating Center of University, Forestry Region, Residential Area (Gölköy), Forestry Region
West South West, WSW	Residential Area, Adapazarı
West, W	Traffic (TEM and D-100 roads), Forestry Regions
West North West, WNW	Traffic (TEM and D-100 roads), Forestry Regions, Düzce
North West, NW	Traffic (TEM and D-100 roads), Forestry Region
North North West, NNW	Traffic (TEM and D-100 roads), Residential Area (Public Houses), Forestry Region
North, N	Traffic (TEM and D-100 roads), Residential Area (Public Houses), Forestry Region
North North East, NNE	Traffic (TEM and D-100 roads), Forestry Region
North East, NE	Residential Area (Bolu), Agricultural Regions, Residential Area (Karaköy), Industrial Area (Cast, Isopoly, Steel, PVC and Aluminum Carpentry, Petrochemical, Motor oil, Chemical, Polyfoam Plants), Agricultural Regions (Yeniçağa, Mengen)
East North East, ENE	Residential Area (Bolu), Agricultural Regions, Asphalt Manufacturing Plant
East, E	Residential Area (Bolu), Agricultural Regions (Dörtdivan), Industrial Area, Leather Factories (Gerede)
East South East, ESE	Industrial Area (Potato Plant), Residential Area (Karaköy, Doğançı Village)
South East, SE	Agricultural Regions (Karacasu, Seben, Kırıcık), Industrial Area (Wood-pulp Industry)
South South East, SSE	Industrial Area (Wood-pulp Industry), Agricultural Regions

Table 4.8. Mean and standard deviations of the total concentrations of OCPs in summer with respect to the wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	NW	N	NE	ENE	E	SE
N*	2	2	28	9	4	1	2	3	2	1	1
beta BHC	1.18		1.21±1.16	0.80±0.83			0.061	0.041±0.0017	0.022		0.022
heptachloroepoxide			0.056								
endosulfanI	0.043		0.074±0.072	0.11±0.09	0.15±0.13	0.025	0.066	0.074±0.076		0.039	
4,4'-DDE		0.0014	0.0047±0.0037	0.0057±0.0044	0.0060		0.0055	0.0027	0.0012	0.0048	0.0012
endrin	0.026	0.058	0.100±0.133	0.064±0.029	0.040±0.0040		0.046	0.041±0.045	0.078	0.064	0.078
endosulfan II	0.016	0.081	0.040±0.036	0.038±0.020	0.050±0.036		0.024	0.040±0.040	0.017	0.021	0.017
4,4'-DDD			0.0071±0.0048	0.0052				0.014			
endrin aldehyde		0.014									
endosulfan sulfate		0.082	0.100±0.038	0.12±0.074	0.060				0.068		0.068
endrin ketone			0.049±0.023	0.042±0.0087	0.10			0.052			
methoxychlor		0.11	0.084±0.043	0.072±0.013	0.026						

N*: Number of windy days

Table 4.9. Mean and standard deviations of the total concentrations of OCPs in winter with respect to the wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
N*	6	7	4	9	1	4	3	3	8	15
beta BHC		0.14		0.26±0.43			0.034	0.38±0.52	0.12±0.12	0.11±0.12
heptachloroepoxide	0.019±0.026	0.014±0.0044	0.0045	0.039±0.0098		0.0027	0.029	0.0056±0.0046	0.028±0.037	0.019±0.014
endosulfanI	0.025±0.023	0.012±0.017	0.016	0.017±0.021		0.0153		0.024±0.025	0.18±0.42	0.024±0.019
4,4'-DDE	0.0031	0.012±0.015		0.010±0.012	0.00856			0.0043	0.012±0.0095	0.026±0.046
endrin	0.34±0.15	0.19±0.11	0.24±0.12	0.180±0.089	0.143	0.15±0.10	0.14±0.057	0.25±0.12	0.33±0.18	0.27±0.11
endosulfan II	0.047±0.029	0.047±0.035		0.038±0.029		0.049±0.0022	0.073±0.026	0.0074	0.048±0.025	0.040±0.039
4,4'-DDD	0.036±0.013	0.014±0.0053	0.024	0.015±0.0089	0.010	0.037	0.011	0.060±0.049	0.034±0.017	0.031±0.017
endrin aldehyde	0.052±0.036	0.022±0.011	0.016	0.038±0.060	0.0076	0.062	0.0036	0.061±0.075	0.052±0.051	0.042±0.027
endosulfan sulfate	0.10±0.038	0.075±0.024	0.095	0.12	0.072	0.075±0.027	0.074		0.12±0.059	0.092±0.042
endrin ketone	0.063±0.030	0.052		0.047±0.018	0.024		0.027±0.011	0.023	0.044±0.021	0.089
methoxychlor	0.22±0.12	0.24±0.19	0.11	0.23±0.21	0.043	0.022		0.17±0.057	0.26±0.12	0.32±0.31

N*: Number of windy days

Wind sector analysis for the gas and particle phase concentrations were assessed. According to the wind sectors, the distribution of the gas phase concentration in summer is given in Table 4.10 and the dominant wind directions were from the WSW and the W directions. Accordingly, most pollutants were moved from the west and south west winds to the sampling point. Particulate pollutants were in the same manner as gaseous ones. According to wind sector, the particle phase concentrations of OCPs were given in Table 4.11. It was found that OCP concentrations were mainly high at the WSW, the SW and the W winds in both phases.

The evaluation of the concentrations of gas phase OCPs with respect to the wind sectors are given in Table 4.12 for winter. Different from the summer period, the number of the SSE windy days was high and great concentrations were observed at this sector. The SSE had high effects on the concentration of 4,4'-DDE, endrin ketone and metoxychlor, while, the SE had high contribution to endosulfan I, endosulfan sulfate and endrin aldehyde in gas phase samples. The concentrations of the beta BHC, endosulfan II, heptachloroepoxide and endrin were affected by the ESE, the E, the WSW and the S wind sectors, respectively. In addition, the south winds were effective on 4,4'-DDE. The wind sector analysis of the particle phase was given in Table 4.13. It had been observed that high concentrations of particle phase are at the S, the E, the SE, and the SSE, which means that the air masses carried by these winds.

Table 4.10. Mean and standard deviations of the gas phase concentrations of OCPs in summer with respect to the wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	NE	ENE	SE
N*	2	2	28	9	4	3	2	1
beta BHC	1.18		2.13	0.40		0.0010		
heptachloroepoxide			0.056	0.056				
endosulfan I	0.043		0.057±0.049	0.057±0.049				
4,4'-DDE		0.00071±0.0010	0.00030±0.00020	0.00034±0.00015				
endrin	0.026	0.036±0.0016	0.091±0.155	0.091±0.155	0.037	0.035	0.037	0.039
endosulfan II		0.061±0.075	0.021±0.027	0.021±0.028	0.0083	0.0068	0.0075	0.0078
4,4'-DDD			0.0037	0.0037				
endosulfan sulfate		0.041±0.058	0.093±0.048	0.093±0.048	0.059		0.092	0.068
endrin ketone			0.034±0.004	0.034±0.0040	0.034			
methoxychlor		0.087±0.123	0.025	0.078	0.026		0.036	

N*: Number of windy days

Table 4.11. Mean and standard deviations of the particle phase concentrations of OCPs in summer with respect to the wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	N	NE	ENE	E	SE
N*	2	2	28	9	4	2	3	2	1	1
beta BHC			1.10±1.18	0.72±0.90		0.061	0.040±0.0024	0.089		0.022
endosulfan I	0.043		0.072±0.073	0.13±0.085	0.15±0.13	0.066	0.074±0.076	0.118	0.039	
4,4'-DDE			0.0052±0.0036	0.0053±0.040	0.0060	0.0055	0.0027			0.0012
endrin		0.043	0.056±0.032	0.044±0.0064	0.043	0.046	0.024±0.021	0.064	0.064	0.038
endosulfan II	0.016	0.039	0.036±0.035	0.037±0.016	0.046±0.030	0.024	0.037±0.042	0.056	0.021	0.0089
4,4'-DDD			0.010	0.0052			0.014			
endrin aldehyde		0.014	0.0050							
endosulfan sulfate			0.093±0.0092	0.083±0.022						
endrin ketone			0.048±0.0097	0.042±0.0087	0.067		0.052			
methoxychlor		0.042	0.099±0.033	0.072±0.013						

N*: Number of windy days

Table 4.12. Mean and standard deviations of the gas phase concentrations of OCPs in winter with respect to the wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
N*	6	7	4	9	1	4	3	3	8	15
beta BHC		0.14		0.29±0.45		0.060	0.034	0.38±0.52	0.15±0.14	0.13±0.14
heptachloroepoxide	0.0024	0.006±0.008		0.032±0.013			0.014±0.020	0.0077	0.099	0.018±0.023
endosulfan I		0.0020						0.0043	0.40±0.68	0.013±0.016
4,4'-DDE		0.012±0.015		0.010±0.012	0.0086			0.0043	0.012±0.011	0.026±0.045
endrin	0.096±0.052	0.063±0.011	0.055±0.035	0.071±0.016	0.048	0.052±0.011	0.052±0.017	0.066±0.019	0.080±0.054	0.084±0.061
endosulfan II	0.0094±0.0031	0.042±0.016		0.020±0.010		0.047	0.047	0.0074	0.014±0.013	0.012±0.0076
4,4'-DDD	0.015±0.011	0.007±0.002		0.010				0.0057	0.0095±0.0027	0.011±0.0088
endrin aldehyde	0.013±0.019			0.0019				0.0058	0.015	0.014±0.016
endosulfan sulfate	0.070±0.0091	0.033±0.046	0.040	0.064	0.072	0.053±0.0038			0.084±0.010	0.079±0.014
endrin ketone				0.035				0.023	0.022	0.036±0.023
methoxychlor	0.098±0.10					0.022				0.132±0.086

N*: Number of windy days

Table 4.13. Mean and standard deviations of the particle phase concentrations of OCPs in winter with respect to the wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
N*	6	7	4	9	1	4	3	3	8	15
beta BHC				0.012					0.059	0.040±0.016
heptachloroepoxide	0.023±0.028	0.017	0.0045	0.028				0.0046±0.0060	0.014±0.010	0.016±0.0091
endosulfan I	0.025±0.023	0.017±0.020	0.016	0.017±0.021		0.015		0.022±0.022	0.026±0.025	0.021±0.012
4,4'-DDE	0.0031								0.0040±0.0038	
endrin	0.24±0.16	0.12±0.11	0.13±0.079	0.11±0.087	0.096	0.12±0.088	0.084±0.044	0.18±0.12	0.25±0.13	0.20±0.076
endosulfan II	0.042±0.025	0.029±0.028		0.030±0.021		0.050	0.050±0.007		0.038±0.025	0.047±0.042
4,4'-DDD	0.031±0.013	0.011±0.0060	0.024	0.0097±0.0066	0.0010	0.037	0.011	0.038±0.050	0.029±0.015	0.028±0.014
endrin aldehyde	0.046±0.041	0.022±0.011	0.016	0.030±0.053	0.0076	0.062		0.059±0.071	0.050±0.046	0.041±0.029
endosulfan sulfate	0.074±0.019	0.077±0.028	0.12	0.059		0.044	0.074		0.11±0.040	0.085±0.043
endrin ketone	0.063±0.030	0.052		0.060	0.024	0.13	0.027±0.011		0.038±0.021	0.087±0.088
methoxychlor	0.22±0.13	0.24±0.19	0.11±0.063	0.23±0.21	0.043			0.17±0.057	0.26±0.12	0.29±0.32

N*: Number of windy days

4.1.1.6. Back Trajectories

Three dimensional back trajectory models are drawn everyday for the sampling station. READY HYSPLIT models are used that is developed by NOAA (National Oceanic and Atmospheric Administration) in USA (Draxler and Rolph 2003, Rolph, 2003). Back trajectories were run at different heights and three day (72 hours) backward to observe the long-range transport. Therefore, they were drawn as 500 m, 1000 m and 1700 m. The 500 m, is used for short-range transport, 1000 m and higher heights represent long-range transport. The three day backward trajectory drawings give important information about the sources of pollutants, where the air mass starts its journey from the source, where it passes through until it reaches to the sampling station. The trajectories were drawn for the days of the high concentration are shown in Figure 4.5. As it is seen in the wind sector analysis, the dominant wind directions were from the south, the east and the west. These air masses were usually from the local sources. Effect of long-range transport on the concentration of pesticides was not high, because the number of winds from the north was very small. According to the trajectories, the conversion was dominant at the sampling region, therefore the local sources had high effect on the concentrations of the OCPs.

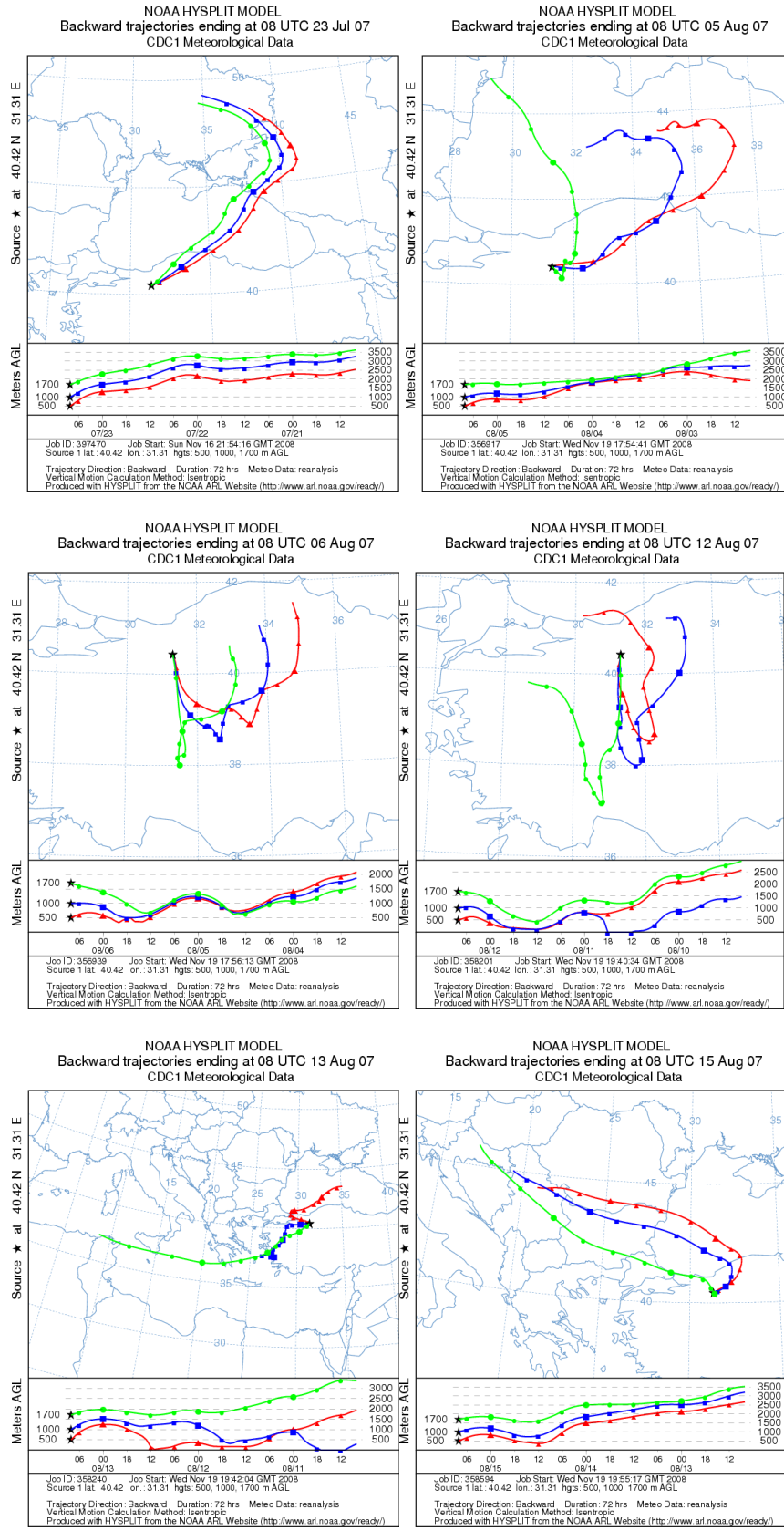


Figure 4.5. Back trajectory models for OCPs

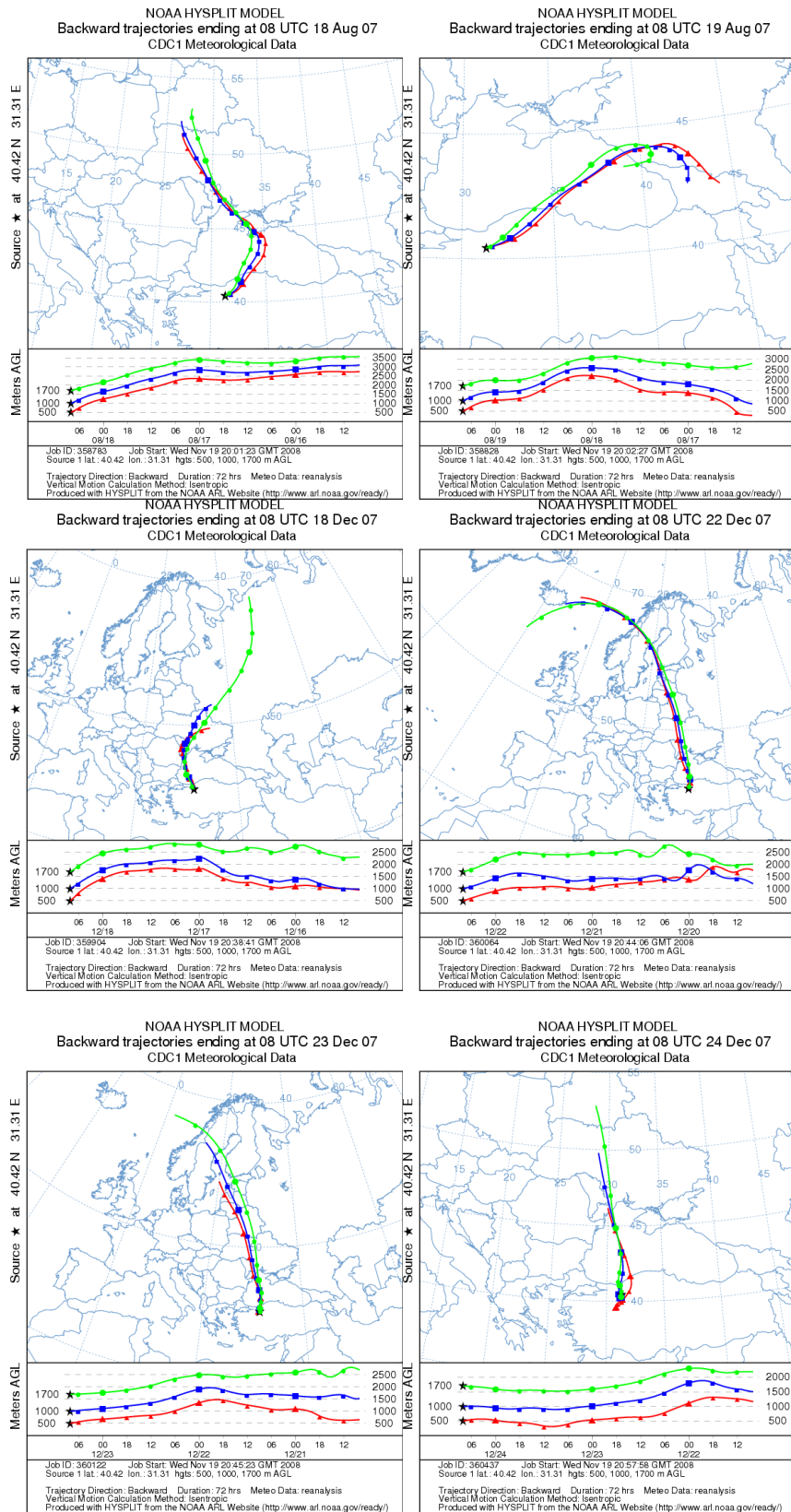


Figure 4.5. Back trajectory models for OCPs (continued)

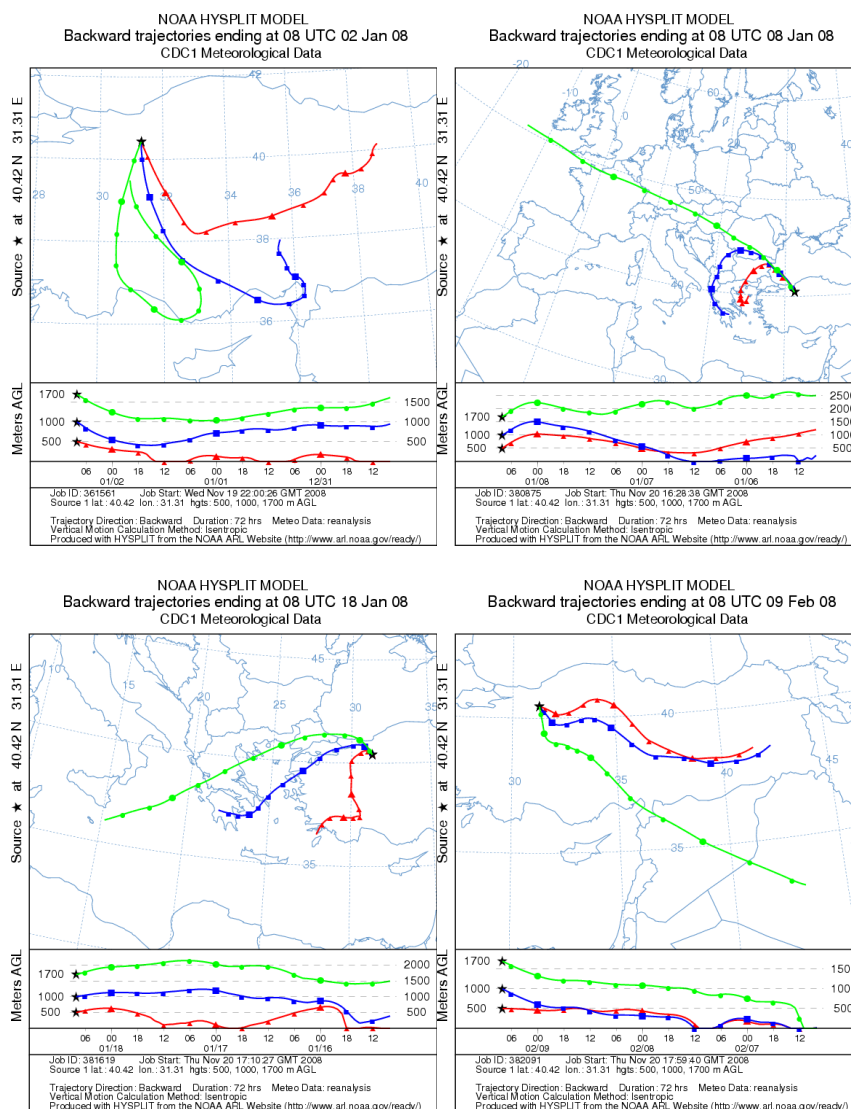


Figure 4.5. Back trajectory models for OCPs (continued)

4.1.1.7. Correlation Analysis

The aim of this analysis is to determine the sources of compounds. Binary correlation (pearson) between the compounds is generally used in environmental studies so as to determine sources and the movement or pathways of the compounds to the sampling point. Binary correlation was determined from total concentrations of the OCPs (gas and particle phase) due to identification of sources. It was not possible

to search the gas and particle phase concentrations separately because of low observation percentages. High correlation between two compounds shows emission from the same source and/or the derivation of the same pattern. Correlation values were calculated from the Statgraphics Plus Version 3.1 (Table 4.14) at the 95 % confidence level. Correlation coefficients lower than 0.25 are not shown in the table. Beta BHC, 4,4'-DDE, endrin ketone and heptachloroepoxide were not calculated because of low number of data.

Table 4.14. Pearson correlation matrix of OCPs

Compounds	4,4'-DDD	4,4'-DDE	Endo-sulfan I	Endo-sulfan II	Endo-sulfan Sulfate	Endrin	EA	EK	Hepta chloro-epoxide	M
4,4'-DDD	1.00				0.31	0.62	0.68	0.47		0.33
4,4'-DDE		1.00				0.30				
Endosulfan I			1.00							
Endosulfan II				1.00						
Endosulfan Sulfate					1.00	0.42	0.52		0.31	0.40
Endrin						1.00	0.75		0.28	0.42
EA							1.00			0.28
EK								1.00		0.77
Heptachloro epoxide									1.00	0.29
M										1.00

$p < 0.05$, EA: Endrin Aldehyde, EK: Endrin Ketone, M: Methoxychlor.

In Table 4.14 the correlation constants are given and strong relation was found between 4,4'-DDD with endrin, 4,4'-DDD with endrin aldehyde and 4,4'-DDD with methoxychlor. It has also been determined that there were strong relations between endosulfan sulfate with endrin and endrin aldehyde with methoxychlor. There were other significant relations between compounds such as; endrin with endrin aldehyde, endrin with methoxychlor, endrin aldehyde with methoxychlor.

This means that, the compounds influenced from the similar types of pathways and/or came from the same sources.

4.1.1.8. Factor Analysis (FA)

The results of FA for total concentrations are given in Table 4.15. The 4,4'-DDE, endosulfan II, endosulfan sulfate, endosulfan I, endrin, endrin aldehyde, methoxychlor compounds can be analyzed, because the number of data for these compounds was appropriate. The number of undetected samples is high; therefore, the filling of data was not applied. 84.2 % of total variance was explained by selected two factors. The first factor that explained the 70.7 % of the total variation, identified as representing the south east directions to the sampling point. The OCP compounds that had high loadings under this factor were endosulfan II, endosulfan I, endrin, endrin aldehyde, and methoxychlor. When the wind sector analysis was reviewed, the compounds under factor 1 had the highest concentration values at the south east directions (ESE, SE, SSE). The second factor affecting the concentration of samples was identified as in the south, the west, and the south west directions. The loadings of 4,4'-DDE, endosulfan sulfate, endrin aldehyde under that factor were high. These compounds had high concentrations at the WSW (generally in summer) when the wind sector analysis was reviewed. This factor explained the 13.5 % of the total variance. The regions close to the sampling point have intensive agricultural applications. These applications occur in Mudurnu in the south west, Seben in the south and south east, Dörtdivan in the east and Kırıcık in the south directions.

Table 4.15. The result of the factor analysis applied to total concentration of the compounds

Compounds	Factor 1	Factor 2	Communality
4,4' -DDE		0.95	0.91
Endosulfan II	0.92		0.85
Endosulfan sulfate	0.47	0.74	0.77
Endosulfan I	0.78	0.36	0.73
Endrin	0.85	0.45	0.92
Endrin aldehyde	0.65	0.62	0.81
Methoxychlor	0.89	0.31	0.89
% Variance	70.7	13.5	
Source	The South, East Directions	The South, The Southwest and The West Directions	

4.1.2. OCPs in Soil

Soil behaves as an environmental reservoir for semi-volatile organic compounds in the terrestrial environment. Soil is polluted directly when insecticides are removed by medications while some of the OCPs are transferred from air by meteorological parameters.

4.1.2.1. Statistical Evaluation of the OCPs

The surface layer concentration of total OCPs in all soil samples ranged from under the detection limit to 9.28 ng g^{-1} with an average value of 2.51 ng g^{-1} . The major groups of OCPs in the soil belonged to the endosulfan sulfate, methoxychlor, endrin, and beta BHC. The total (sum of concentrations of each compound in all samples) concentrations of endosulfan I, endosulfan II, and endosulfan sulfate were 0.71 , 6.80 and 12.7 ng g^{-1} , respectively, and endrin ketone, endrin aldehyde, and endrin were 2.09 , 2.73 and 11.2 ng g^{-1} , respectively. Although the use of some OCPs

has been banned in Turkey, the results disclosed in this study show that residues still persist in the soil at considerable concentrations.

The beta BHC content was the second highest in soil samples (Table 4.16) Commercial BHC contains 4-15 % Beta BHC. Moreover, other kinds of BHC are converted to each other by chemical transformations. Since thermodynamically most stable structure with all of the chlorine atoms are in equatorial positions, beta-BHC is the least reactive and the most persistent one among the four other isomers. Since, this isomer has the highest stability with low solubility and vapor pressure.

Table 4.16. Statistical evaluation of summer and winter term soil samples (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
beta BHC	9	31	1.11	0.968	0.819	0.756	0.153	2.06	1.91	9.96
4,4'-DDD	6	21	0.499	0.607	0.384	0.301	0.091	0.844	0.753	2.99
4,4'-DDE	5	17	0.620	0.470	0.563	0.335	0.382	1.19	0.807	3.10
endosulfan II	14	48	0.485	0.335	0.320	0.506	0.048	1.96	1.91	6.80
endosulfan sulfate	9	31	1.41	1.49	1.38	0.290	0.919	1.74	0.817	12.7
endosulfan I	2	7	0.353	0.353	0.337	0.148	0.248	0.458	0.210	0.706
endrin	22	76	0.511	0.307	0.397	0.478	0.225	2.21	1.98	11.2
endrin aldehyde	8	28	0.341	0.167	0.234	0.441	0.145	1.42	1.28	2.73
endrin ketone	4	14	0.524	0.585	0.495	0.175	0.266	0.657	0.391	2.09
heptachloroepoxide	4	14	0.409	0.377	0.397	0.123	0.300	0.584	0.284	1.64
methoxychlor	12	41	0.945	0.957	0.875	0.372	0.539	1.41	0.876	11.3

*Total analyzed samples: 29

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

The endosulfan sulfate was derived from the last transformation product of the endosulfan family. Therefore, the concentration percentage had comparable values with the other parents. For instance, endosulfan I had very low observation percentage and the lowest concentration among its parents and whole OCPs. The usage of endosulfan parents is not completely restricted and most medication is done by the endosulfan I. As it was found in air samples, observation percentage of the

endrin in soil samples denoted that it is still in use or persistent after a long time application in the past at the agricultural medications.

DDT can be transformed to 4,4'-DDE by soil microorganisms under aerobic conditions while under anaerobic conditions it is transformed to 4,4'-DDD in soil (Chen *et al.*, 2005). In this study, total soil concentration of the 4,4'-DDE was higher than 4,4'-DDD, since the surface soil directly exposed to the air. However, we could not determine the concentrations of the DDT in soil samples as with in air samples. The presence of the 4,4'-DDE and 4,4'-DDD indicated the former usage of this compound. There is also exceptional usage of the DDT, endrin and BHC for beet seed medications in Turkey (<http://www.kkgm.gov.tr/teblig/2003-43.html>). As expressed before, the beet seed growing has application at the agricultural areas in Bolu.

When the frequency diagrams were drawn for all OCPs, they showed normal distribution (Figure 4.6). The mean, geometric mean and median values in Table 4.16 also indicated normal distribution as well. Median and geometric mean were very close to each other and both are approximately similar with arithmetic mean. Standard deviations of the OCPs were generally lower than the arithmetic mean, which means that the OCP concentrations were not affected from the chemical and physical transformations and from different sources.

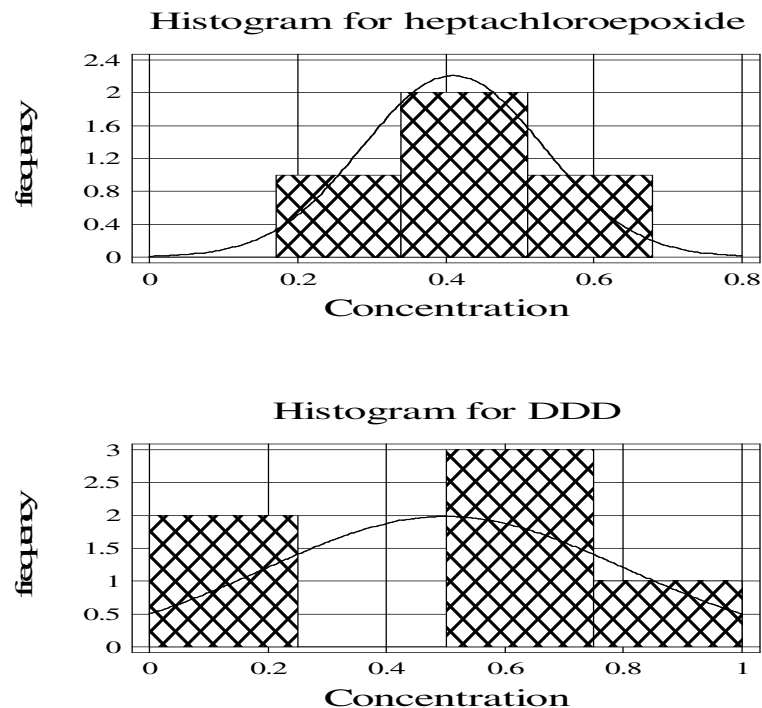


Figure 4.6. The statistical distribution of OCP concentrations in soil (ng g^{-1})

4.1.2.2. Seasonal Differences of OCPs

The eleven OCPs were determined in summer while eight OCPs were determined in winter. Although endosulfan I is the major isomer in the environment it could not be determined in winter samples since winter samples were collected in January and February with low ambient temperature. It is known that the endosulfan II is converted to endosulfan I at high temperature (Burgoyne and Hites, 1993; Yao *et al.*, 2006; Sadiki and Poissant, 2008). The presence of the endosulfan I was proved in summer samples with increasing in temperature as it can be seen in Table 4.17 and Table 4.18. The other compounds which were not detected in winter were heptachloroepoxide, and 4,4'-DDE. 4,4'-DDE is the dehydrochlorination product of the DDT as well (Hao *et al.*, 2008; Yeo *et al.*, 2004). Therefore,

undetected period indicated the lower medium temperature, which can prevent the transformation of DDT. Heptachloroepoxide is the oxidation product of the heptachlor and has the highest solubility in its parents. Hence, deposition of the heptachloroepoxide on soil was removed by mixing to ground water or it remained in the air sorbed to the particles (Venier and Hites, 2007).

Table 4.17. Statistical evaluation of winter term soil samples (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
beta BHC	5	26	1.01	0.555	0.701	0.836	0.153	2.02	1.87	5.07
endrin	16	84	0.343	0.295	0.318	0.176	0.225	0.956	0.731	5.49
endosulfan II	6	32	0.220	0.212	0.182	0.129	0.048	0.429	0.381	1.32
4,4'-DDE	2	11	0.365	0.365	0.308	0.277	0.169	0.561	0.392	0.730
endrin aldehyde	7	37	0.186	0.164	0.180	0.056	0.145	0.298	0.153	1.3
endosulfan sulfate	3	16	1.46	1.49	1.45	0.196	1.25	1.64	0.387	4.38
endrin ketone	2	11	0.425	0.425	0.394	0.225	0.266	0.584	0.318	0.850
methoxychlor	8	42	0.766	0.613	0.717	0.322	0.539	1.315	0.777	6.13

*Total analyzed samples: 19

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Table 4.18. Statistical evaluation of summer term soil samples (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
beta BHC	4	40	1.22	1.25	0.995	0.748	0.321	2.06	1.74	4.88
heptachloroepoxide	3	30	0.446	0.391	0.436	0.121	0.362	0.584	0.222	1.34
endosulfanI	2	20	0.353	0.353	0.337	0.148	0.248	0.458	0.210	0.71
4,4'-DDD	4	40	0.679	0.560	0.621	0.355	0.408	1.19	0.780	2.72
endrin	6	60	0.960	0.905	0.715	0.732	0.230	2.21	1.98	5.76
endosulfan II	8	80	0.673	0.505	0.448	0.610	0.092	1.96	1.87	5.39
4,4'-DDE	4	40	0.566	0.665	0.429	0.328	0.091	0.844	0.753	2.26
endrin aldehyde	2	20	0.810	0.810	0.528	0.869	0.196	1.42	1.23	1.62
endosulfan sulfate	6	60	1.39	1.53	1.35	0.342	0.919	1.74	0.817	8.35
endrin ketone	2	20	0.622	0.622	0.621	0.050	0.586	0.657	0.071	1.24
methoxychlor	4	40	1.30	1.30	1.30	0.094	1.19	1.41	0.219	5.21

*Total analyzed samples: 10

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

The average concentrations of all OCP compounds were high in summer except for endosulfan sulfate, which had the approximately similar concentrations (Figure 4.7). Endosulfan sulfate had the highest values among its parents in both

seasons while endosulfan I had the lowest in summer and not detected in winter. Beta BHC had the high concentrations in both seasons as it was observed high concentrations in the air samples. The observation percentage of the endrin was high in winter with a very low concentration, while it had moderate observation percentage (60 %) in summer. In addition, the concentration of the endrin increased in summer. 4,4'-DDD had low concentration and observation percentage in both seasons. The factor analysis and the Pearson correlations were not determined in the soil contaminants because of high set of not-detected compounds and missing data.

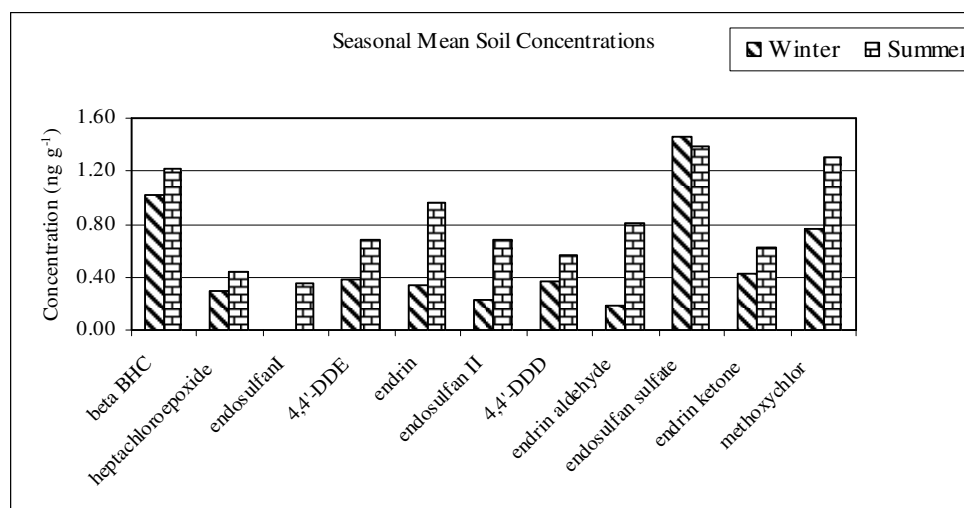


Figure 4.7. A comparison of the seasonal soil concentrations of OCPs

4.1.2.3. A Comparison of OCP Concentrations with Related-Literature Values

In Table 4.19 the average (mean) concentrations of the OCPs is given for this study and others. The heptachloroepoxide, endosulfan I, endosulfan II, endosulfan sulfate and methoxychlor concentrations were higher than the other studies while endrin ketone and endrin aldehyde were lower ones. 4,4'-DDE, and 4,4'-DDD concentrations were lower than the studies in China and Russia whereas it was higher

in the study in Hong Kong. Endrin concentration had higher level in Czech Republic and China soils than this study however, it was lower in study in Hong Kong. Beta BHC concentration in this study was higher than the studies in China and Russia, while it had lower values than the Hong Kong.

Table 4.19. A comparison of the soil concentration (mean) of OCPs with related-literature (ng g⁻¹)

Reference	β-BHC	heptachlor epoxide	endosulfan I	4,4'- DDE	endrin	endosulfan II	4,4'- DDD	endrin aldehyde	endosulfan sulfate	endrin methoxy ketone	methoxy chlor
This study (Bolu, Turkey), rural, agricultural	1.11	0.41	0.35	0.62	0.51	0.48	0.50	0.33	1.41	0.52	0.94
Li <i>et al.</i> , 2008 (China). rural, agricultural				167			69				
Fu <i>et al.</i> , 2009 (China), urban	0.4-8.2 ¹	n.d. ¹	n.d	0.6-27 ¹	n.d.-12 ¹	n.d.	0.1-5.7 ¹	n.d-0.1 ¹	n.d.	n.d.- 1.3 ¹	
Franzle et. al. 2008 (Russia)	0.38±0.37			20.3±66.9			0.56±0.45				
Shegunova et. al., 2007 (Czech Republic), rural					1.05						0.19
Zhang et. al., 2006 (Hong Kong), Forest, rural	5.66±1.17			0.20±0.19	0.01±0.01		0.01±0.01				

n.d: not detected, 1: range of concentrations

4.1.3. Exchanges of OCPs

The OCP compounds are found in gas phase, particle phase or both due to their physico-chemical properties. However the determination of phases at which the OCPs are in high concentration is not explained well. Therefore some models are used for determination high concentrated phase of the OCPs.

4.1.3.1 Application of Clausius-Clapeyron Equation for Gas Phase Concentrations

The temperature dependency of the gas phase OCPs are determined by the Clausius-Clapeyron equation. That is $\ln P = m\left(\frac{1}{T}\right) + b$, where the $\ln P$ is natural logarithm of partial pressure and T is the temperature in Kelvin and m is slope and b is the intercept of the line. In addition, the partial pressures are calculated from the ideal gas equation for each compound. Afterwards, graphs of the $\ln P$ vs $1/T$ are drawn to determine the m and b values. The low value of the slope signs the remoteness of the sources whereas the high value of the slope indicates closeness of the sources. Mainly negative results corresponds the long-range transportations from the local sources and dominance of evaporation (Esen *et al.*, 2008). The slope was found -1529 and intercept was -26.8 in this study (Figure 4.8). Since the OCP compounds, which were determined at the sampling area, indicates the transportation from the local sources that are highly agricultural regions and the most of them are far from the sampling area.

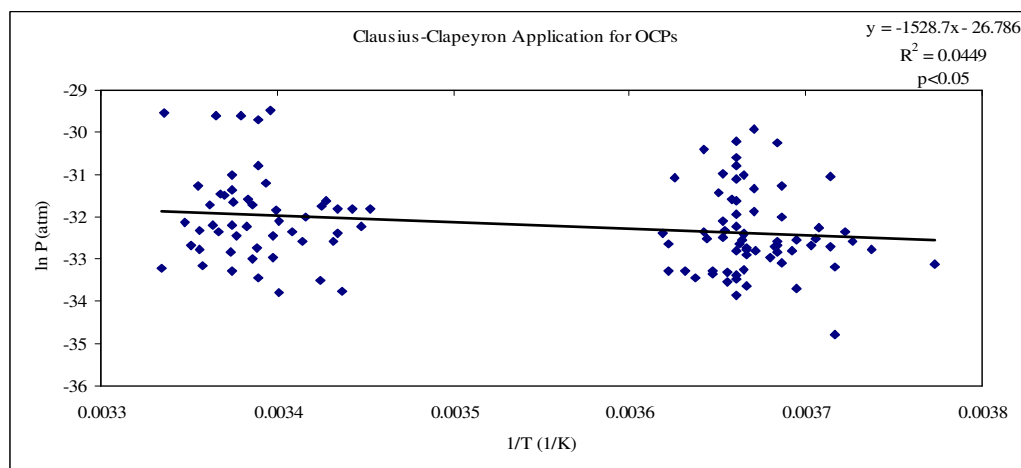


Figure 4.8. Temperature relationship with partial pressure of gas phase OCPs

4.1.3.2. Gas to Particle Exchange

Gas-particle partition of the OCPs explains the behaviour which they are either in gaseous or in particulate form. As it is seen in Figure 4.9 and Figure 4.10, the particulate form of most of OCPs are dominant in winter, whereas the gaseous form of most OCP compounds are high in summer as a function of rise in temperature.

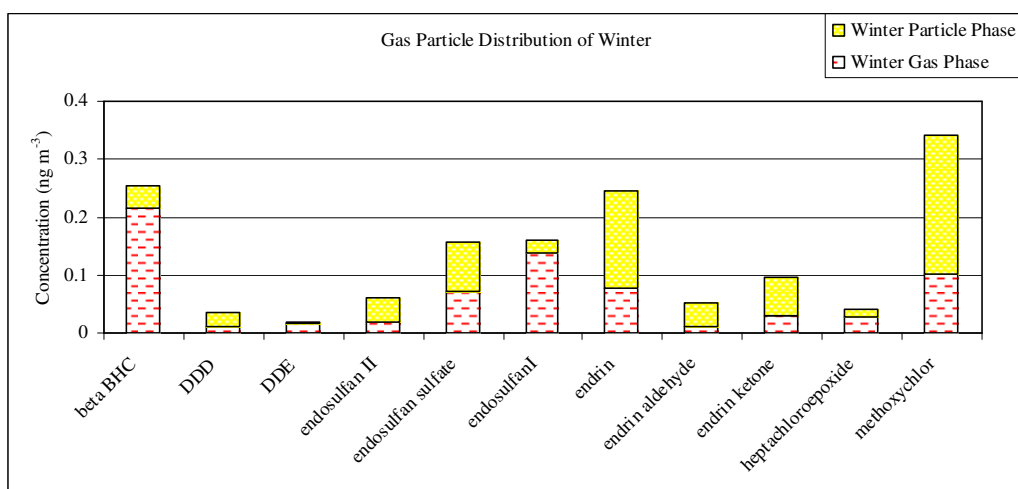


Figure 4.9. Gas-particle distribution of the OCPs in winter

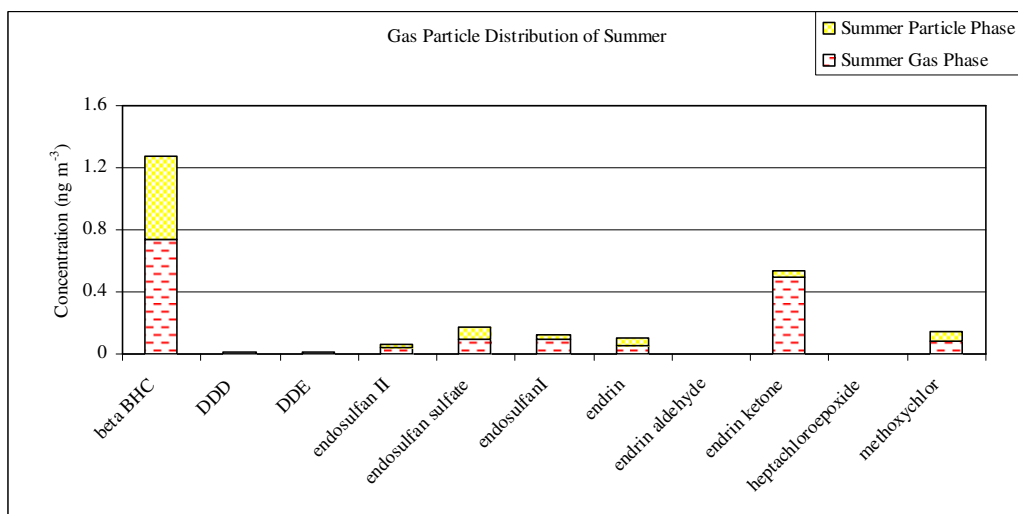


Figure 4.10. Gas-particle distribution of the OCPs in summer

In this study, it is not possible to determine the partitioning constants because of small data set of both gas and particle phase concentrations. Therefore, the partitioning models did not applied to OCP compounds. Experimentally determined $\log K_p$ values of the OCPs in the range of -0.42 to -3.02 with an average value -1.57.

4.1.3.3. Air-to-Soil Exchange

The equilibrium partitioning of a chemical between air and soil is described by the dimensionless soil–air partition coefficient (K_{SA}). If the system is in equilibrium, the use of the term K_{SA} is correct otherwise, the values obtained from above equation are defined as soil–air quotients (Meijer *et al.*, 2003).

K_{SA} is dependent on temperature, humidity and the properties of the chemical and the soil (Meijer *et al.*, 2003). Partitioning of POPs to soil occurs by the absorption to the organic carbon fraction. The K_{OA} is a descriptor of chemical partitioning between the atmosphere and organic phases (Harner *et al.*, 2000). Hippelein and McLachlan (1998) found a linear relationship that relates the K_{SA} to K_{OA} and to the organic carbon fraction of the soil. The factor 0.411 improves the correlation between the K_{SA} and K_{OA} (Hippelein and McLachlan, 1998; Bidleman and Leone, 2004). Temperature dependent K_{OA} values can be measured directly for compounds of interest, while K_{SA} is soil-specific.

The direction of the net gas exchange at soil–air interface is determined by the fugacity ratio. A soil to air fugacity ratio $[(f_s/f_A) = (C_s \rho_s / K_{SA}) / C_A]$ greater than 1 indicates that the soil is a source with net gas volatilization to air, and a value less

than 1 indicates that the soil is a sink with net gas deposition from air. For a system in equilibrium, f_S/f_A value is equal to 1 (Harner *et al.*, 2000).

In this study, the fugacity ratios were calculated at the air sampling site using the air ($N = 120$) and soil OCP concentrations ($N = 29$) corresponding to the same sampling seasons. The average organic matter content of soil samples was 10.8 % (in dry sample). The density of soil solids was experimentally determined as 2.01 g cm^{-3} like Bozlaker *et al.* (2008) was used a similar value. The experimentally determined K_{SA} values and fugacity ratio for OCPs were given in Table 4.20 and Table 4.21, for winter and summer seasons, respectively. Very low f_S/f_A ratio of the OCPs indicated the deposition from air to soil rather than from soil to air. From these ratios it was found out that soil was a sink for OCP compounds.

Table 4.20. Calculated soil-air exchange parameters for winter

Compound	K_{SA}	Log K_{SA}	f_S/f_A	Log f_S/f_A
beta BHC	9.47E+06	6.98	3.38E-09	-8.47
DDD	6.83E+07	7.83	1.27E-09	-8.90
DDE	4.78E+07	7.68	1.49E-09	-8.83
endosulfan II	2.16E+07	7.34	5.99E-07	-6.22
endosulfan sulfate	4.12E+07	7.61	1.21E-06	-5.92
endrin	8.97E+06	6.95	7.95E-11	-10.10
endrin aldehyde	3.25E+07	7.51	7.81E-13	-12.11
endrin ketone	2.74E+07	7.44	2.71E-11	-10.57
heptachloroepoxide	2.25E+07	7.35	1.38E-08	-7.86
methoxychlor	1.50E+07	7.18	9.61E-09	-8.02

Table 4.21. Calculated soil-air exchange parameters for summer

Compound	K_{SA}	Log K_{SA}	f_S/f_A	Log f_S/f_A
beta BHC	3.30E+06	6.52	1.09E-09	-8.96
DDD	1.16E+08	8.06	1.97E-09	-8.70
DDE	1.98E+08	8.30	5.67E-09	-8.25
endosulfan II	3.62E+07	7.56	9.21E-07	-6.03
endosulfan sulfate	3.09E+07	7.49	8.35E-07	-6.08
endosulfanI	8.07E+06	6.91	5.26E-08	-7.28
endrin	4.14E+07	7.62	3.37E-10	-9.47
endrin ketone	2.53E+06	6.40	2.30E-12	-11.64
methoxychlor	3.16E+07	7.50	1.85E-08	-7.73

4.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Concentrations, sources, and air-soil exchanges of the PAHs will be discussed in the following sections.

4.2.1. PAHs in Air

Air is a sink for PAHs. Once PAHs are emitted from their sources, they redistribute themselves in air, soil and water bodies. Due to their semi-volatile nature, they exist in gas and particulate phase in the atmosphere. Bolu has a cold winter season which requires the consumption of fossil fuels, particularly coal, for heating in residential and industrial areas. As a result, concentrations of PAHs are expected to be high in the atmosphere of Bolu.

In this study, gas and particle phase concentrations of 15 PAHs were measured in a rural and agricultural site in Bolu. Two sampling campaigns were conducted. Although we aimed at the analysis of 16 PAHs, we were able to analyze

15 PAHs, except for naphthalene which was very volatile and had a very little recovery at the clean-up and extraction steps at the laboratory.

4.2.1.1. Statistical Interpretation of Data

Statistical interpretation is of great importance for the evaluation of PAH concentrations. The Statgraphics Plus 3.1 and Excell package programs were used for the calculation of descriptive statistics (mean, median, standard deviation, etc.). Statistical evaluation of the data was given in Table 4.22 for total (gas and particle phase) PAHs.

Table 4.22. Statistical assessment of total (gas and particle phase) PAHs concentrations (ng m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
ACY	107	98.2	18.1	4.93	6.19	33.8	0.327	240	239
ACE	108	99.1	13.2	4.77	4.35	31.8	0.215	203	203
FLU	109	100	43.1	10.3	13.3	85.6	1.36	561	560
PHE	109	100	48.2	24.5	20.5	66.5	0.731	394	394
ANT	109	100	9.07	3.64	4.02	12.2	0.637	57.0	56.3
FLT	109	100	17.3	7.88	8.13	24.7	0.692	185	184
PYR	109	100	12.4	4.94	6.11	18.0	0.692	129	129
BaA	109	100	7.80	3.73	4.71	8.80	0.826	53.3	52.5
CHR	109	100	8.00	3.16	4.35	9.41	0.572	56.8	56.2
BbF	106	97.2	17.4	6.79	8.96	22.5	0.606	126	125
BkF	108	99.1	9.83	5.91	6.52	10.4	0.602	58.2	57.6
BaP	106	97.2	10.7	5.38	6.48	11.7	0.602	68.7	68.1
IND	105	96.3	13.7	2.73	3.35	23.0	0.0322	106	106
DahA	65	59.6	3.00	1.48	1.17	3.86	0.0344	16.2	16.2
BghiP	105	96.3	9.67	5.17	5.90	11.3	0.805	69.9	69.1

*Total analyzed samples: 109

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of the Observed Samples

Fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), Benz[a]anthracene (BaA), and chrysene (CHR) were observed in either gas or particle phase or both, while dibenz [a,h]anthracene (DahA) had the lowest observation percentage in the samples. Fluorene (FLU) and phenanthrene

(PHE) contribute more to the total PAH concentrations with high average concentrations of 43.1 ng m^{-3} and 48.2 ng m^{-3} , respectively. Dibenz [a,h]anthracene (DahA) had the lowest concentration (3.00 ng m^{-3}). The relative concentrations of the other PAHs were as follows: Acenaphthylene (ACY) > benzo(b) fluoranthene (BbF) > flouranthene (FLT) > indeno (1,2,3-cd) pyrene (IND) > acenaphthene (ACE) > pyrene(PYR) > benzo(a)pyrene (BaP) > benzo(k)fluoranthene (BkF) > benzo(g,h,i)perylene (BghiP) > anthracene (ANT) > chrysene (CRY) > benz(a)anthracene (BaA).

Standard deviations of the PAHs were greater than their mean values which means that several factors such as meteorological factors, source strength and physico-chemical properties of PAHs contribute to their concentrations. Moreover, geometric mean value was close to median, as shown in Table 4.22. The statistical evaluation of the total concentrations indicated log-normal distribution of PAHs. Log normal distribution of pollutants have been widely reported in the literature due to various contributing factors such as meteorology, types of pollutant sources and their source strengths as seen in Figure 4.11.

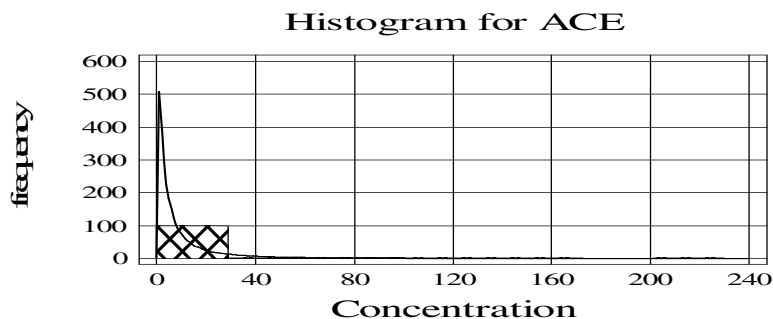


Figure 4.11. The statistical distribution of PAH concentrations (ng m^{-3})

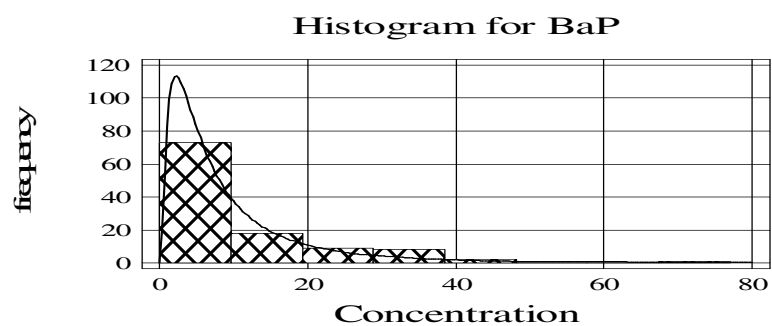
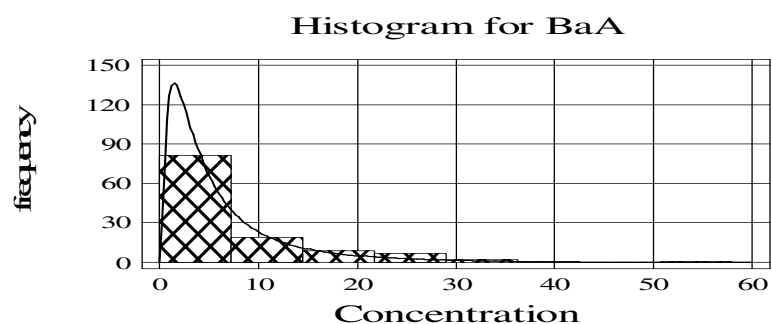
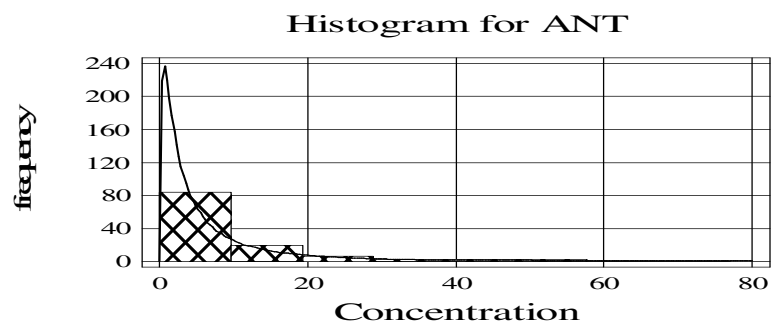
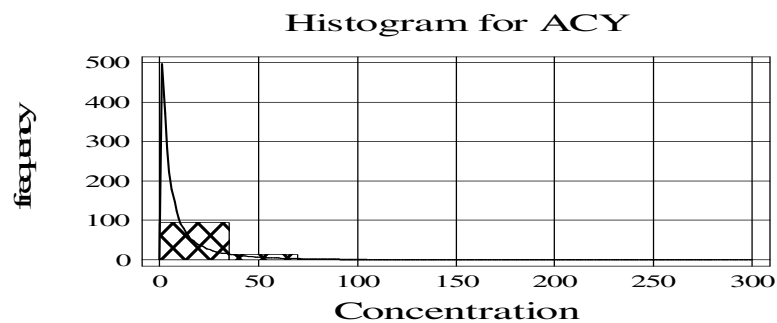


Figure 4.11. The statistical distribution of PAH concentrations (ng m^{-3}) (Continued)

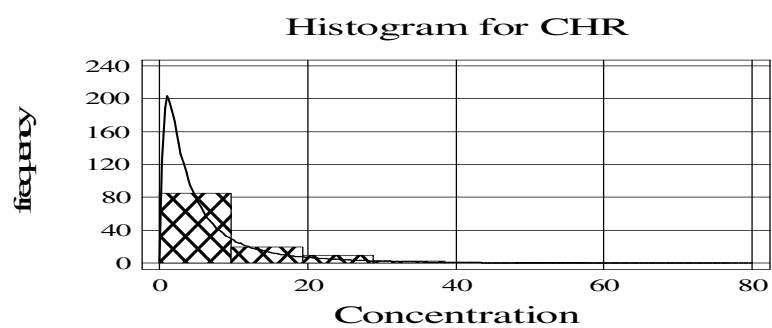
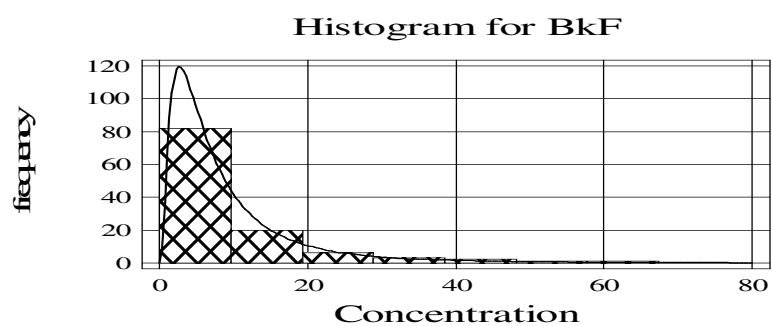
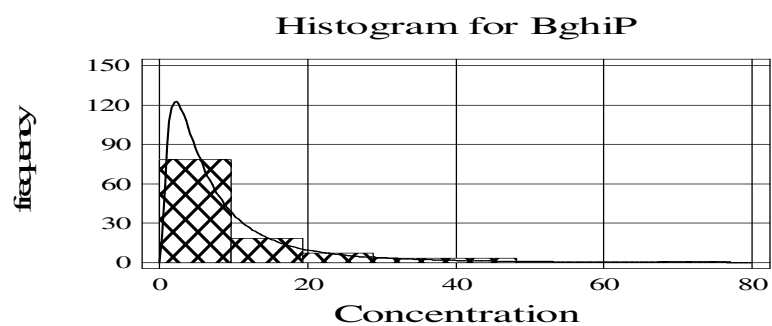
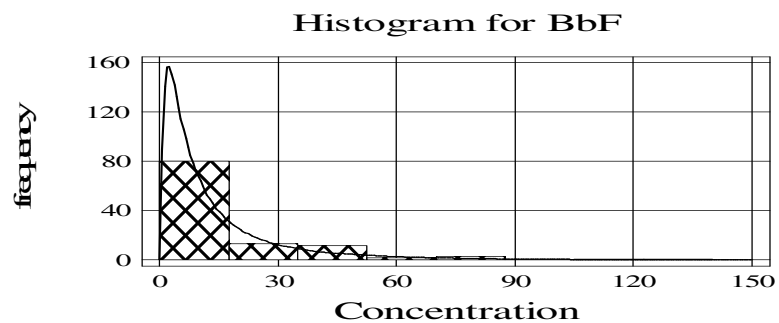


Figure 4.11. The statistical distribution of PAH concentrations (ng m^{-3}) (Continued)

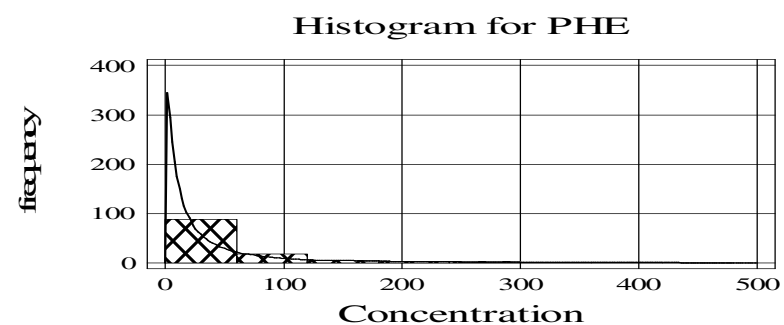
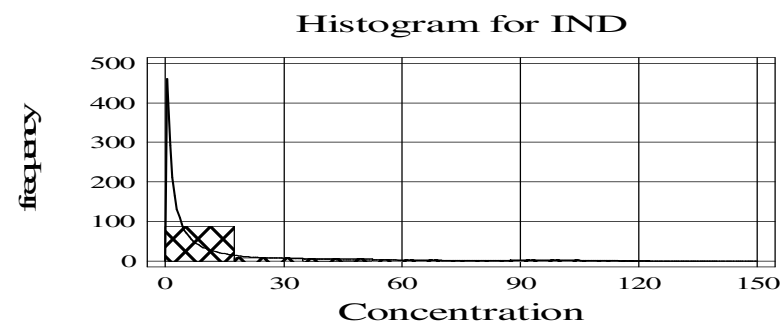
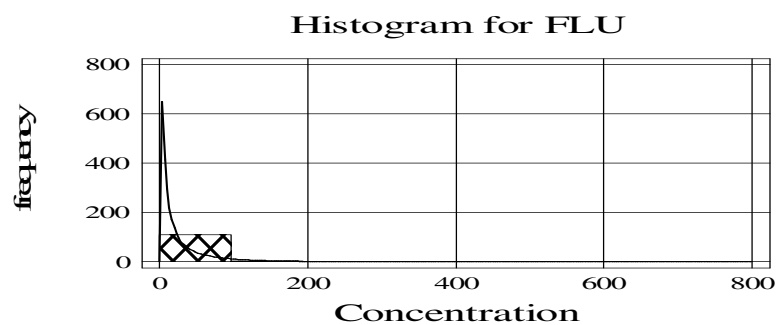
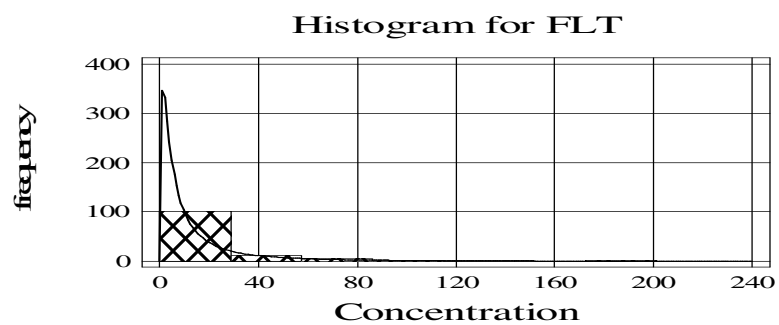


Figure 4.11. The statistical distribution of PAH concentrations (ng m^{-3}) (Continued)

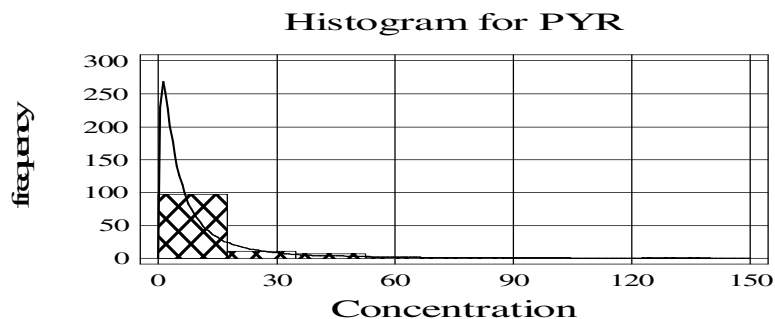


Figure 4.11. The statistical distribution of PAH concentrations (ng m^{-3}) (Continued)

4.2.1.2. Diurnal Distribution of PAHs

Daily concentrations of the PAHs were measured and the average concentrations were given in Figures 4.12 and 4.13. As can be clearly understood from figures, PHE and FLU had the highest concentrations under the daily measurements, with instantaneous peaks. However, the dibenz (a,h) anthracene had the lowest percent observation with a low daily contribution to the total concentrations of the PAHs.

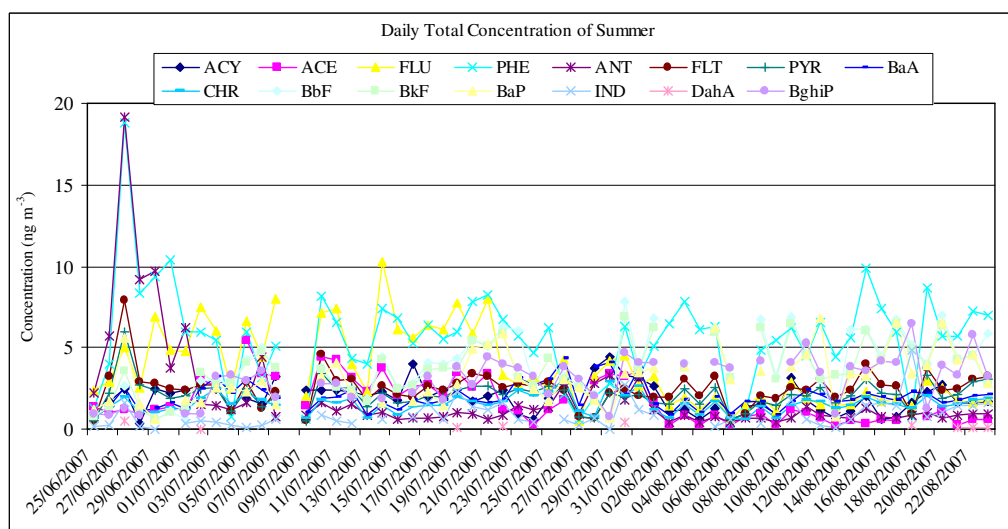


Figure 4.12. Daily concentrations of PAHs in summer

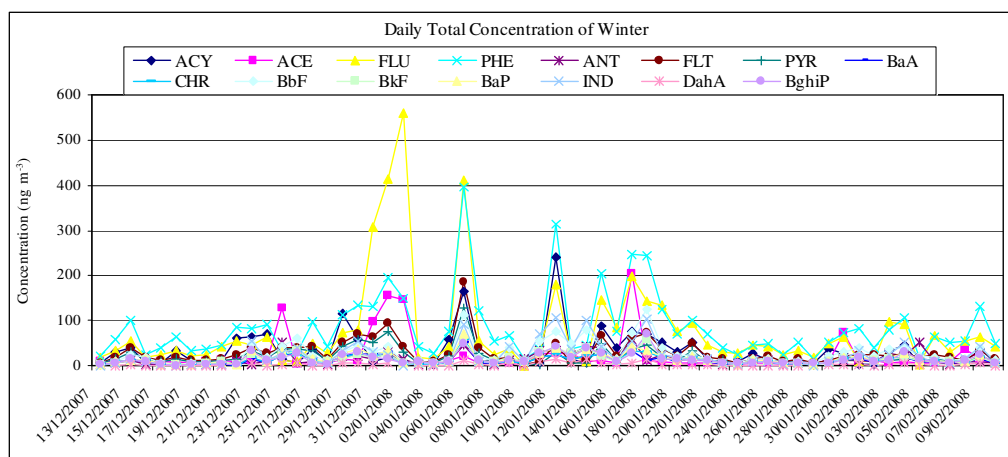


Figure 4.13. Daily concentrations of PAHs in winter

The concentrations of $\sum$ PAHs in the air ranged from 9.3 to 1849 ng m^{-3} , with a mean value of 222 ng m^{-3} . The detected concentrations of PAHs ranged from the detection limit (in the range from 0.06 to 0.11 pg m^{-3}) to 561.5 ng m^{-3} for 3-ring PAHs (ACY, ACE, FLU, PHE, and ANT), from the detection limit (in the range from 0.18 to 0.56 pg m^{-3}) to 185.1 ng m^{-3} for 4-ring PAHs (FLT, PYR, BaA, and CHR), from the detection limit (in the range from 0.32 to 0.73 pg m^{-3}) to 125.7 ng m^{-3} for 5-ring PAHs (BbF, BkF, BaP, and DahA), and from the detection limit (in the range from 0.21 to 0.38 pg m^{-3}) to 105.9 ng m^{-3} for 6-ring PAHs (IND and BghiP). The compositional profiles of PAHs at the sampling point indicated that 3-ring and 4-ring PAHs were abundant. ACY, ACE, FLU, PHE, ANT, FLT, PYR, BaA, and CHR had relative high vapor pressure and a low phase transition temperature. Hence, their concentrations mainly depended upon the instantaneous spreading and high temperatures in the summer. Daily results showed that concentrations of PAHs increased in winter time most probably due to extensive use of coal and wood for domestic heating. Although domestic heating contributes to highest concentrations in winter period, meteorological conditions also affect the

concentrations. Unfavorable meteorological conditions such as lowering mixing height and solar activity may also enhance the concentrations of PAHs. Since the PAH concentrations mainly come from the local sources and the dispersion in the atmosphere decreases at the lower mixing heights. The solar activities were relatively small at sampling area which resulted in the decrease in the decomposition of PAHs by photochemically.

4.2.1.3. Seasonal Changes of PAHs

Gas and particle phase concentrations of the 15 PAHs were evaluated separately for summer and winter seasons to examine seasonal variation and contributing sources. In Table 4.23, PHE and FLU had the highest concentrations with high percent observation, while CHR and IND had the lowest gas concentrations in the summer. Moreover, BghiP had also a high mean concentration; however, it had very low percent observation (2 samples). This situation was an expected result for high molecular weighed-PAHs that are mainly in particle phase. DahA was not detected in the gas phase samples either. Mean concentration range of PAHs in the gas phase summer samples were between 0.87 ng m^{-3} and 4.98 ng m^{-3} , CHR and PHE, respectively.

Table 4.23. Statistical evaluation of gas phase PAH concentrations in summer samples (ng m⁻³)

Compound	<i>N</i>	PO (%)	Mean	Median	Geo M	SD	Min	Max	Range
ACY	48	85.7	1.35	1.25	1.15	0.728	0.327	2.86	2.54
ACE	50	89.3	1.25	0.609	0.801	1.11	0.191	4.41	4.22
FLU	52	92.9	2.63	2.03	1.96	2.14	0.468	10.29	9.82
PHE	52	92.9	4.98	5.33	3.90	2.86	0.372	18.01	17.6
ANT	52	92.9	1.40	0.483	0.701	2.79	0.267	18.26	18.0
FLT	51	91.1	1.89	1.84	1.67	0.961	0.180	7.08	6.90
PYR	51	91.1	1.51	1.46	1.37	0.731	0.162	5.64	5.48
BaA	52	92.9	1.12	0.877	1.01	0.581	0.413	2.91	2.50
CHR	50	89.3	0.874	0.744	0.819	0.350	0.305	1.96	1.65
BbF	33	58.9	2.17	2.58	1.87	1.05	0.574	5.22	4.65
BkF	36	64.3	2.01	2.28	1.72	1.00	0.574	4.95	4.38
BaP	18	32.1	1.89	1.74	1.56	1.10	0.570	3.78	3.21
IND	3	5.4	0.951	0.259	0.292	1.72	0.033	4.81	4.78
BghiP	2	3.6	3.49	3.45	3.10	1.78	1.27	6.46	5.19

*Total analyzed samples: 56

**PO: Percent Observation, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, *N*: Number of the Observed Samples

Particle phase concentrations of the PAHs were statistically evaluated in Table 4.24 for the summer period. The 15 PAHs, with an observation range of 15.4 % to 100 % were monitored in the 52 samples. PHE, ANT, and BaA were observed in the entire samples, while DahA had the lowest percent observation (15.4 %). Although DahA was not observed in the gas phase samples, it was observed in several particle phase samples due to its relatively high molecular mass. The significantly high mean concentrations observed for BghiP and BbF, and the lowest one for DahA. The mean concentrations of the PAHs varied between 0.186 and 2.97 ng m⁻³. Maximum found concentrations of the PAHs belong to PHE, BghiP, and BbF, respectively.

Table 4.24. Statistical evaluation of particle phase PAH concentrations in summer samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
ACY	32	61.5	1.08	0.897	0.898	0.666	0.264	2.73	2.46
ACE	44	84.6	0.681	0.510	0.530	0.472	0.0960	1.91	1.82
FLU	51	98.1	1.36	1.36	1.09	0.790	0.222	2.73	2.51
PHE	52	100.0	0.999	0.555	0.683	1.41	0.231	8.08	7.85
ANT	52	100.0	0.737	0.483	0.604	0.579	0.307	3.19	2.88
FLT	51	98.1	0.820	0.710	0.756	0.437	0.428	2.79	2.36
PYR	51	98.1	0.788	0.700	0.737	0.337	0.340	2.29	1.95
BaA	52	100.0	1.05	0.952	0.999	0.348	0.573	2.21	1.64
CHR	51	98.1	0.862	0.785	0.830	0.243	0.435	1.55	1.11
BbF	42	80.8	2.97	2.98	2.76	0.980	0.612	5.06	4.44
BkF	47	90.4	2.56	2.73	2.25	1.09	0.644	4.62	3.98
BaP	47	90.4	2.59	2.64	2.37	0.991	0.676	4.62	3.95
IND	44	84.6	0.884	0.634	0.623	0.652	0.0322	2.73	2.70
DahA	8	15.4	0.186	0.104	0.133	0.172	0.0344	0.504	0.470
BghiP	45	86.5	2.95	3.26	2.61	1.22	0.805	5.25	4.45

*Total analyzed samples: 52

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of the Observed Samples

The statistical evaluation of the PAHs in gas phase samples for the winter is given in Table 4.25. The entire samples in the winter included most of the PAHs with a high percent observation (100 %); however, high molecular weighed-IND, DahA, and BghiP compounds had a low percent observation in gas phase. FLU and PHE had significantly high mean concentrations, whereas IND and DahA had the lowest ones. The concentrations of the PHE and FLU were 70.6 and 71.3 ng m⁻³ and were 2-to-100 fold higher than the other PAHs. Relatively high concentrations of the other PAHs were ACY (29.1 ng m⁻³), ACE (20.1 ng m⁻³), FLT (14.6 ng m⁻³), and ANT (11.3 ng m⁻³).

Table 4.25. Statistical evaluation of gas phase PAH concentrations in winter samples (ng m⁻³)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
ACY	60	100	29.1	12.7	12.7	40.1	0.284	234	234
ACE	60	100	20.1	6.15	8.42	40.0	0.536	201	201
FLU	60	100	70.6	38.8	34.7	102.7	0.466	561	560
PHE	60	100	71.3	52.5	51.7	62.7	6.66	298	291
ANT	60	100	11.3	7.18	6.81	12.1	1.12	50.4	49.2
FLT	60	100	14.6	11.2	10.5	11.5	0.723	58.4	57.6
PYR	60	100	8.69	6.06	6.00	6.92	0.542	26.8	26.3
BaA	60	100	1.38	1.14	1.20	1.44	0.702	12.1	11.4
CHR	60	100	1.33	1.08	1.12	1.70	0.607	14.0	13.4
BbF	60	100	2.30	1.64	1.75	3.28	0.632	25.8	25.2
BkF	60	100	1.93	1.50	1.61	1.81	0.632	14.3	13.6
BaP	60	100	1.90	1.45	1.56	1.93	0.598	15.3	14.7
IND	40	66.7	0.715	0.152	0.193	2.50	0.043	15.7	15.7
DahA	7	11.7	0.409	0.094	0.156	0.792	0.051	2.20	2.15
BghiP	50	83.3	2.22	1.87	1.92	1.57	0.813	11.2	10.4

*Total analyzed samples: 60

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Actual Samples

The air samples collected in the particle phase included all the PAHs. The percent observation of PAHs were 100 %, except for DahA (94.9 %) given in Table 4.26. As different from the summer samples, BbF and IND had the highest mean values in the particle phase winter samples. The concentrations of the BbF and IND were 25.8 and 23.1 ng m⁻³, respectively. The compounds with high vapor pressure such as ACE and ACY had significantly low concentrations in the particle phase. The gas phase concentrations were considerably higher than the particle phase of the winter season for low molecular weighed-PAHs.

Table 4.26. Statistical evaluation of particle phase PAH concentrations in winter samples (ng m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
ACY	59	100.0	2.62	2.52	2.12	1.73	0.316	11.4	11.1
ACE	59	100.0	2.36	1.83	1.93	1.59	0.170	7.89	7.72
FLU	59	100.0	5.31	4.58	4.21	4.03	0.424	22.6	22.2
PHE	59	100.0	12.8	9.84	9.02	14.8	1.38	108	106
ANT	59	100.0	3.55	2.90	2.64	2.65	0.479	12.0	11.5
FLT	59	100.0	15.2	9.55	9.01	19.5	1.13	127	126
PYR	59	100.0	12.4	6.94	6.96	16.9	0.920	107	106
BaA	59	100.0	11.2	8.82	8.05	9.30	1.27	51.9	50.7
CHR	59	100.0	12.0	9.61	8.73	9.63	1.18	55.6	54.4
BbF	59	100.0	25.8	17.4	16.3	25.2	1.54	125	123
BkF	59	100.0	12.9	10.1	9.12	11.6	1.44	57.4	55.9
BaP	59	100.0	14.8	10.6	10.2	12.6	1.34	66.3	65.0
IND	59	100.0	23.1	13.0	11.8	26.8	0.548	105	105
DahA	56	94.9	3.39	2.01	1.59	3.96	0.0407	16.1	16.0
BghiP	59	100.0	13.0	8.91	8.60	12.6	1.39	68.9	67.5

*Total analyzed sample: 59

**PO: Percent Observation, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Actual Samples

4.2.1.3.1. Seasonal Ratios

A comparison of median values was used for log-normal distributed pollutants in order to evaluate their seasonal differences when the gas and particle phase concentrations were discussed. The median values as well as the other statistical parameters are given in Tables 4.23 to 4.26. The winter PAH concentrations of both phases were generally higher than the summer PAH concentrations. The concentrations of low molecular weight-PAHs were generally higher in the winter than in the summer, while the detection of high molecular weight-PAHs decreased in both seasons. PHE and FLU concentrations were highest in both seasons; however, winter PHE and FLU concentrations were significantly higher than the summer ones when the pyrolysis processes were relatively higher. In addition, ACY, ACE, FLT, IND, and DahA were higher in the gas phase during the summer and in the particle phase during the winter.

When the PAH profiles were analyzed (Figure 4.14) ACY, PHE, FLU, DahA, and IND were the dominant compounds in the winter, while ANT, PYR, BaA, CHR, BbF, BkF, BaP and BghiP were dominant in the summer. The concentrations of PAHs significantly diminished in the summer when the heating requirements in Bolu were about to be finished.

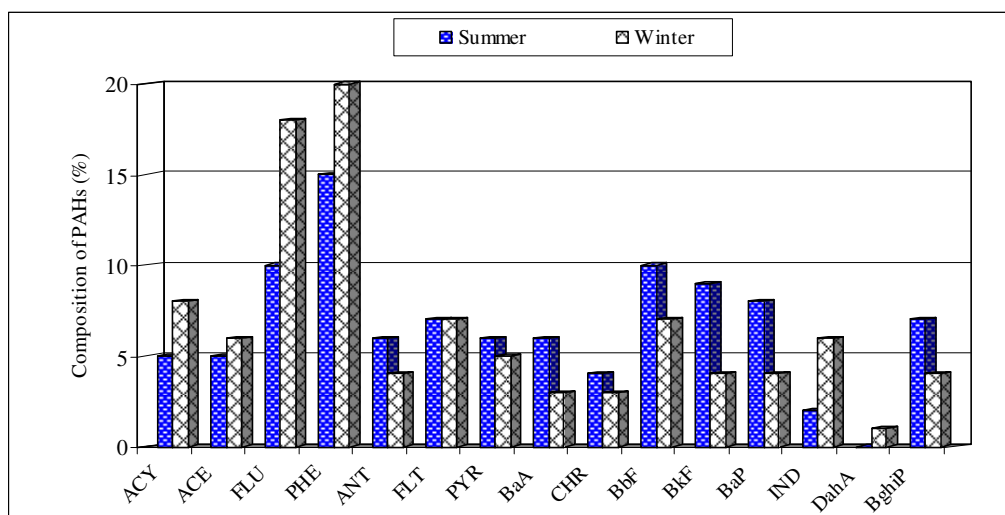


Figure 4.14. PAH profiles for winter and summer seasons

Gas-particle ratio was also used to interpret the seasonality of the PAHs (Figure 4.15). The 3-ring PAH compounds, FLT, PYR, CHR, and BghiP were generally high in the gas phase rather than the particle phase in the summer whereas BbF, BkF, and BaP were significantly ($p < 0.05$) high in the particle phase. In addition, gas phase concentrations of 3-ring PAHs had high concentrations in gas phase whereas 4- and more ring PAHs were significantly ($p < 0.05$) high in particle phase for winter season.

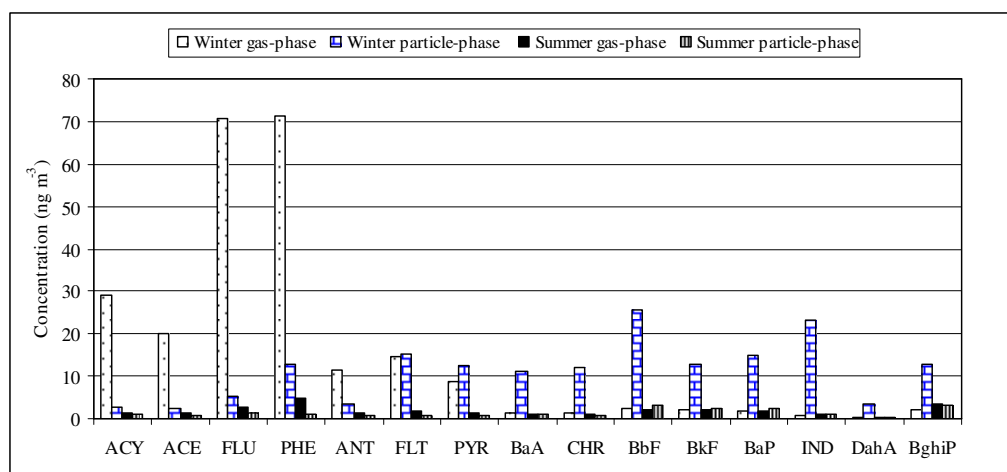


Figure 4.15. Mean concentrations of gas and particle phase PAHs in both seasons

The gas phase PAHs in the winter were, on average, 10 times higher than those in the summer in the study area. The primary component of the seasonal changes in the data was emission strength, which is indirectly related to climate. The main emission sources of the PAHs in the study area were the domestic burning of coal, burning of crop residues, and firewood. Other sources changed with the seasons; however, they are unlikely to be the primary reason for variations in the PAH concentrations. For example, although higher hydroxyl radical concentrations occurred in the summer season, which could cause photo-degradation of the gas phase PAHs, an insignificant diurnal variation in the gas phase PHE and FLU suggested that the gas phase PAHs could not be strongly influenced by photo-degradation near the source region (Li *et al.*, 2006). The seasonality of PAH emissions was the major factor for the gas phase PAHs.

Percent distributions of the total (gas and particle phase) PAHs were given in Figure 4.16 and 4.17 for both seasons. Variations of percent composition of PAHs were detected in both seasons but the most striking change was observed for the FLU

and PHE. Winter contribution of FLU increased from 10 % to 18 % whereas, it was increased from 15% to 20% for PHE. On the other hand for some of the PAHs like BghiP, BaP, BkF, BaA winter time contributions decreased to by an amount of half in winter period. This change in PAH profiles is an indication of source variation for PAHs for both seasons.

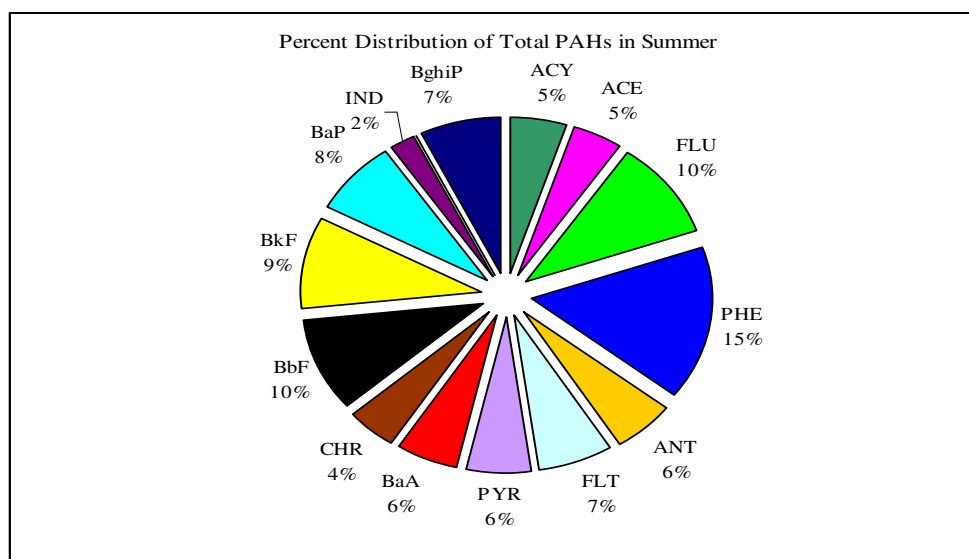


Figure 4.16. Percent distribution of total PAHs in summer

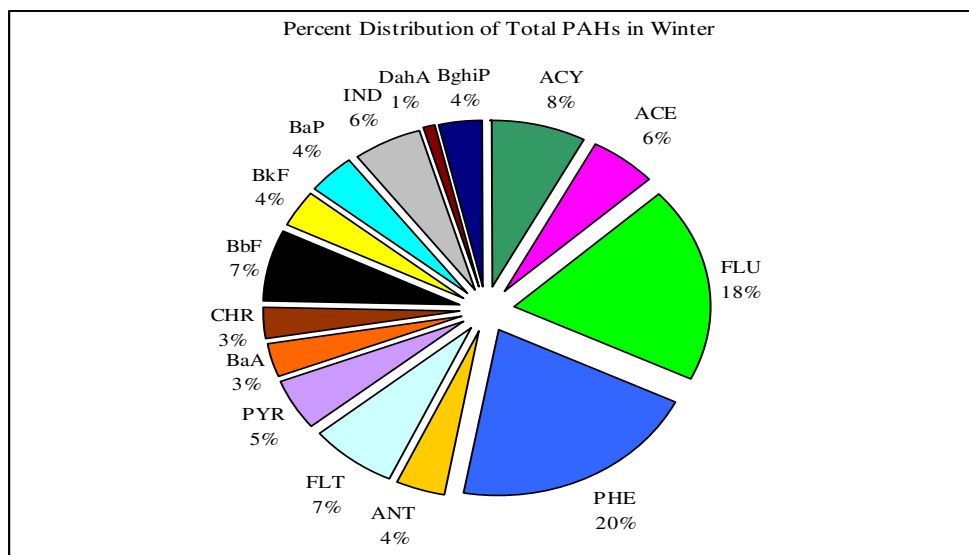


Figure 4.17. Percent distribution of total PAHs in winter

4.2.1.4. A Comparison of PAH Concentrations with Related-Literature Values

In this study, the concentrations of the PAHs were compared for the similar and distinct regions in the related-literature (Table 4.27). Tsapakis and Stephanou (2005) and Bidleman and Cotham (1995) reported significantly lower PAH concentrations than did this study despite the similarity in sampling areas. Esen and Taşdemir's findings (2006) support the observations in this study; however, their study represents the urban region. Results of this study revealed that transportation from the urban areas significantly contributed to the PAHs profiles. Therefore, the average concentration of each PAH observed in the rural areas of Bolu was similar to the urban regions. Eisenreich *et al.* (1998) found lower PAH concentrations in the urban area than did this study. Pankow and Logocki (1989) reported lower PAH concentrations than did this study except for CHR. Bidleman and Cotham (1995) and Polkowska *et al.* (1999) found higher PAH concentrations in the urban areas than this study. According to findings of Arı (2008), PAH concentrations were reported to be higher than this study except for ACE and BkF. When the PAH concentrations in this study are compared to the findings of the study in Bursa (Esen and Taşdemir, 2006), PAH concentrations are higher except for PHE, FLT, PYR and CHR.

Table 4.27. A comparison of PAH concentrations with related-literature mean values (ng m⁻³)

Reference	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IND	DahA	BghiP
This study (Bolu, Turkey), rural, agricultural, total	18.1±33.8	13.2±31.8	43.1.0±85.6	48.2±66.5	9.07±12.2	17.3±24.7	12.4±18.0	7.80±8.80	8.00±9.41	11.4±16.2	17.4±22.5	9.83±10.4	13.7±23.0	3.00±3.86	9.67±11.3
Tsapakis and Stephanou, 2005, (Greece), rural			1.8	7.3	0.9	1.9	1	0.1		0.1	0.1	0.04	0.03	0.002	0.03
Eisenreich <i>et al.</i> , 1998, (Chicago, USA), urban			7.8 ±2.8	21.2 ±10.8	3.2±2.4	12.9±9.6	10.9±8.1	5.2±5.0	6.0±6.1			1.5			1.4
Pankow and Ligocki, 1989, (Portland, USA), urban				1.4±3.5		14±23	12±24	3.5±6.3	14±8.7						
Bidleman and Cotham, 1995, (Green Bay, Amerika), rural			4.1±1.5	9.6±4.7	0.05±0.02	1.0±1.4	0.76±0.61	0.16±0.17				0.12±0.09	0.13±0.13		0.19±0.14
Bidleman ve Cotham, 1995, (Chicago, Amerika), urban.			92±83	159±131	15±17	56±59	36±36	21±21				14±14	13±13		11±11
Polkowska <i>et al.</i> , 1999, (Gdansk, Poland), urban, total		22	60	225	182	679	408	326	478	452	18	76	73	22	49
Ari, 2008, (Eskişehir, Turkey), urban, total	56.7	10.8	85.0	149.0	41	68.3	65.0	25.6	27.5	24.7	14.6	18.0	16.4	8.4	16.8
Esen and Taşdemir, 2006, (Bursa, Turkey), urban	12.5	2.5	22.6	76.2	7.0	47.8	31.1	4.7	10.6	5.8	4.7	3.3	3.9	1.3	5.6

4.2.1.5. Wind Sector Analysis

Wind direction analysis is generally used to explain the transportation of pollutants from local sources as previously explained. Total concentrations of gas and particle phase were analyzed for wind sector analysis (Table 4.28 and Table 4.29). High concentrations are shown in bold in tables. The dominant wind direction in the summer was in the direction of south and west. ACY, ACE, BaA, CHR, IND, BkF, DahA, and BghiP concentrations were high in the SW direction, while FLT had high concentrations in the SSW and NW. In addition, the concentrations of BbF, BkF, BaP, and BghiP were high in the E wind, while ACY, ACE and FLU had significantly ($p < 0.05$) high concentrations in the N winds. High concentrations of PYR and FLT were detected in the NW, SSW, and E directions. ANT was found to be high in the WNW, and PHE in the ESE. As can be seen in Table 4.7, many chemical industries existed towards eastern, northern, and western directions with respect to the sampling point. Moreover, TEM and D- 100 highways are in the northern directions.

The dominant wind directions were the SSE, SSW, WSW, and SE during the winter (Table 4.29). The concentrations of ACY, FLU, PHE, ANT, FLT, PYR, BaA, BaP and CHR were high when the winds has blown from the south and the SE winds also contributed highly to ACE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, BaP and IND. ACE and FLU concentrations were high in the SSW. SSE winds highly affected the BbF, BkF, IND, DahA, and BghiP concentrations. Furthermore, residential and industrial areas were highly concentrated in the SSW, S, SE and SSE directions. Therefore, the high concentrations of these compounds can be said to be mostly come from pyrolysis processes (especially coal) during winter.

Table 4.28. Mean and standard deviations of total summer PAH concentrations with respect to wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	NW	N	NE	ENE	E	SE	ESE
<i>N</i> *	2	2	28	9	4	1	2	3	2	1	1	1
ACY	2.52	3.23	1.92 ± 0.98	1.96 ± 0.75	1.47±0.87	1.63	3.15	1.99 ± 0.38	1.98	0.732	2.36	2.24
ACE	0.990	3.41	1.81 ± 1.28	1.47 ± 1.54	1.79±2.47	0.60	3.18	1.54 ± 0.83	2.51	0.525	1.48	1.39
FLU	2.75	3.57	3.41 ± 2.31	3.60 ± 2.46	4.44±2.81	1.65	7.94	4.68 ± 2.48	4.34	1.88	2.07	4.84
PHE	7.18	4.78	4.87 ± 2.41	5.66 ±2.52	6.39 ±2.06	7.21	6.37	6.44 ± 0.80	5.17	5.94	0.620	10.4
ANT	0.851	2.52	1.29 ± 0.97	1.63 ±1.76	3.22±4.33	0.932	0.860	0.773 ± 0.199	0.757	0.722	0.826	3.71
FLT	3.06	2.26	2.28 ± 0.86	2.62 ± 1.07	2.55 ±0.48	3.03	2.31	2.58 ± 0.60	2.19	2.61	0.544	2.44
PYR	2.58	2.04	1.96 ± 0.67	2.19 ±0.73	2.15 ±0.46	2.90	1.96	2.21 ± 0.73	1.71	2.13	0.544	1.89
BaA	1.90	2.92	2.18 ± 0.88	1.96 ±0.50	1.97 ±1.09	2.02	1.72	1.73 ± 0.46	1.20	1.77	1.03	1.61
CHR	1.70	2.35	1.60 ± 0.63	1.60 ± 0.36	1.49 ±0.76	1.77	1.41	1.39 ± 0.50	1.06	1.57	0.707	1.30
BbF	5.50	5.74	4.28 ± 1.69	3.16 ±2.22	2.70 ±1.51	4.51	3.61	4.14 ± 1.63	2.97	6.73		1.10
BkF	5.19	5.26	3.89 ± 1.49	3.98 ± 1.51	2.59 ± 1.47	4.51	3.48	2.97 ± 0.68	2.71	6.44		1.05
BaP	5.24	3.45	3.62 ±1.84	2.52 ± 1.13	1.80 ±1.04	4.61	1.70	2.14 ± 0.98	2.30	6.59		
IND	0.881	1.95	0.980 ±1.01	0.66 ± 0.53	0.18 ±0.18	1.48	0.697	1.14 ± 0.73	1.63	1.47		
DahA		0.410	0.139 ±0.101	0.097		0.099		0.0970				
BghiP	2.59	4.36	3.51 ± 1.23	2.59 ± 1.16	3.09 ±0.22	5.79	2.05	2.03 ± 1.67	3.26	4.12		

*N**: Number of windy days

Table 4.29. Mean and standard deviations of total winter PAH concentrations with respect to wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
N*	6	7	4	9	1	4	3	3	8	15
ACY	55.4±55.5	28.6±31.1	35.9±53.0	22.9±22.5	12.2	20.7±15.6	16.47±16.4	18.7±15.5	33.1±27.7	36.9±61.0
ACE	20.42±27.0	27.5±52.6	9.00±4.17	8.37±2.32	6.90	7.83±3.74	7.00±2.84	10.3±5.08	73.1±77.8	16.4±23.5
FLU	136.4±138.3	138.2±191.2	41.0±23.7	31.5±13.7	32.7	35.9±16.1	31.5±16.0	39.9±22.7	112.1±134.1	68.8±85.9
PHE	135.0±128.9	103.3±59.8	57.4±36.5	51.2±20.6	53.2	47.8±36.5	51.0±40.9	74.1±53.4	106.4±79.1	89.3±84.1
ANT	20.2±13.2	13.1±12.6	9.87±9.32	4.46±2.92	7.50	9.03±6.54	5.20±2.15	7.94±4.57	27.0±19.9	19.8±13.8
FLT	50.6±66.2	35.3±19.4	24.5±18.1	15.7±5.8	16.2	16.5±15.0	20.9±19.2	22.7±8.89	43.7±29.7	28.0±20.1
PYR	32.3±47.6	24.8±14.0	18.7±16.1	11.3±5.0	10.4	12.1±12.7	16.5±15.4	16.5±5.68	32.9±25.2	19.2±15.1
BaA	19.3±17.0	10.3±8.3	10.2±8.7	3.80±2.13	6.44	7.41±5.26	8.01±5.53	12.1±4.20	20.8±9.6	14.6±7.1
CHR	21.0±17.9	10.9±8.0	9.50±7.42	3.99±1.97	5.89	7.29±5.61	7.51±5.47	12.9±3.90	20.9±8.5	16.6±8.3
BbF	39.0±36.8	16.9±12.4	14.3±11.8	7.34±3.58	9.22	11.6±9.7	12.7±8.2	32.1±11.2	42.7±19.2	43.4±31.1
BkF	19.2±17.7	9.88±5.95	8.68±5.86	5.52±2.27	5.49	7.18±5.01	8.79±4.54	15.6±3.04	21.9±8.6	21.8±14.7
BaP	23.8±22.4	12.1±9.4	11.4±10.3	5.31±2.46	6.43	7.83±5.61	9.60±6.24	18.6±5.96	27.9±11.4	21.3±11.1
IND	29.9±30.2	12.8±13.9	12.0±15.1	3.92±2.34	5.78	6.44±6.28	5.89±4.42	30.7±18.2	38.5±22.4	39.8±35.9
DahA	4.07±3.85	1.97±2.06	1.60±2.41	0.357±0.409	0.826	1.34±1.23	0.920±0.704	4.09±2.27	5.33±2.98	5.73±5.58
BghiP	18.5±14.5	10.5±7.7	9.28±9.72	5.09±2.51	6.09	7.51±5.54	5.66±1.46	14.9±7.22	21.5±9.4	22.5±17.3

N*: Number of windy days

Wind direction analysis was assessed separately for the gas and particle phases. According to the wind directions, the distribution of the gas phase concentrations in the summer is given in Table 4.30. The dominant wind directions come from WSW and W for summer time. However, most PAHs moved from the eastern and southern winds to the sampling point. Particle phase PAHs exhibited the same transportation ways as the gas phase ones. According to wind direction, the particle phase concentrations of PAHs are given in Table 4.31. PAH concentrations were found to be high mainly in the SSW, SW and E sectors. The industrial regions such as asphalt manufacturing plant, wood-pulp industry, and potato plant are present at these sectors.

According to the wind directions, the evaluation of the gas phase PAH concentrations are given in Table 4.32 for the winter season. The gas phase PAHs mainly came from the SSE, SSW, S, and SE sectors that were also the dominant wind sectors in the winter. The SSE winds increased the concentration of BaA, CHR, BbF, BkF, BaP, IND, DahA, and BghiP. The SE contributed highly to ACE and ANT in the gas phase samples. The concentrations of the FLU, FLT and PYR were affected by the SSW winds. In addition, the south winds were effective on PHE, FLT, FLU, and ACY concentrations. The wind direction analysis of the particle phase PAH concentrations are given in Table 4.33. Significantly ($p < 0.05$) high PAH concentrations of particle phase were in the S, SE, and SSE winds, which mean that the air masses were carried by these winds. SW and ESE sectors had also high contribution to the ACE and PHE concentrations. There are residential areas in the southern directions in which coal and other fossil fuels were commonly consumed for heating.

Table 4.30. Mean and standard deviations of the gas phases summer PAH concentrations with respect to wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	NW	N	NE	E	ENE	SE	ESE
<i>N</i> *	2	2	28	9	4	1	2	3	2	1	1	1
ACY	0.959	2.31	1.26±0.81	1.29±0.80	1.27±0.61	0.965	1.78	1.64±0.56	0.732	1.85	2.36	1.61
ACE	0.447	2.95	1.20±0.97	0.978±1.11	1.42±2.00	0.268	2.49	1.38±0.97	0.244	2.44	1.48	1.08
FLU	0.941	2.57	2.22±1.88	2.69±2.26	2.78±1.98	1.07	6.58	4.39±2.75	1.22	4.21	2.07	3.98
PHE	2.95	4.12	4.18±2.51	5.70±1.76	5.61±1.39	6.59	5.88	6.00±0.88	5.48	4.95	0.620	7.74
ANT	0.459	1.99	0.830±0.789	1.07±1.7	2.26±3.62	0.379	0.370	0.452±0.100	0.310	0.581	0.826	0.526
FLT	1.34	1.63	1.68±0.70	2.07±0.86	1.92±0.13	2.19	1.68	2.04±0.27	1.81	1.86	0.544	1.90
PYR	1.13	1.38	1.36±0.50	1.62±0.60	1.52±0.12	2.00	1.29	1.62±0.32	1.33	1.37	0.544	1.45
BaA	1.10	2.03	1.28±0.68	0.865±0.317	0.977±0.28	0.784	0.834	0.986±0.22	0.739	0.785	1.03	0.827
CHR	0.978	1.47	0.974±0.40	0.715±0.217	0.776±0.181	0.705	0.641	0.760±0.085	0.628	0.686	0.707	0.703
BbF	2.00	2.80	2.42±1.26	1.82±0.99	1.91±1.28	1.84	1.72	2.58±0.23	2.76	1.39		1.11
BkF	1.90	2.65	2.32±1.23	2.01±0.81	1.81±1.21	1.84	1.63	2.34±0.15	2.61	1.32		1.05
BaP	1.96		2.33±1.19	1.11±0.59	0.602	1.75			2.61			
IND	0.747		1.45±2.25	0.0640	0.033							
DahA			0.137±0.194									
BghiP	1.27		4.36±1.46			2.23						

*N**: Number of windy days

Table 4.31. Mean and standard deviations of particle phase summer PAH concentrations with respect to wind directions (ng m⁻³)

Sector	SSW	SW	WSW	W	WNW	NW	N	NE	ENE	E	ESE
<i>N</i> *	2	2	28	9	4	1	2	3	2	1	1
ACY	1.56	0.922	1.18±0.73	1.07±0.29	0.807	0.664	2.73	0.510±0.280	0.263		0.628
ACE	0.544	0.4618	0.749±0.506	0.782±0.569	0.745±0.420	0.332	1.36	0.235±0.112	0.132	0.281	0.314
FLU	1.81	1.00	1.42±0.80	1.21±0.76	2.22±0.19	0.581	2.73	0.470±0.225	0.263	0.656	0.863
PHE	4.23	0.655	0.948±1.366	0.600±0.149	1.04±0.71	0.623	0.490	0.651±0.321	0.439	0.464	2.67
ANT	0.391	0.527	0.547±0.267	0.677±0.313	1.27±0.63	0.553	0.490	0.481±0.147	0.351	0.412	3.19
FLT	1.72	0.623	0.850±0.464	0.783±0.171	0.845±0.122	0.841	0.628	0.800±0.235	0.679	0.797	0.534
PYR	1.45	0.665	0.820±0.322	0.758±0.184	0.838±0.135	0.897	0.668	0.878±0.285	0.679	0.797	0.440
BaA	0.798	0.881	1.07±0.32	1.19±0.44	1.33±0.64	1.23	0.884	1.12±0.27	0.822	1.03	0.785
CHR	0.726	0.887	0.861±0.242	0.962±0.284	0.955±0.451	1.06	0.766	0.949±0.266	0.750	0.937	0.597
BbF	3.50	4.35	3.16±0.93	2.42±0.99	2.53±0.28	2.67	1.88	2.33±0.98	3.16	3.98	
BkF	3.28	3.93	2.90±0.99	2.19±1.03	2.46±0.19	2.67	1.84	2.12±0.86	2.78	3.83	
BaP	3.28	3.45	2.92±0.96	2.14±0.91	2.40±0.10	2.87	1.70	2.13±0.98	2.30	3.97	
IND	1.01	1.95	0.885±0.628	0.659±0.540	0.256±0.189	1.48	0.697	1.14±0.73	1.63	1.47	
DahA		0.410	0.0935±0.0530	0.0970		0.0988		0.0975			
BghiP	3.91	4.36	3.34±1.15	2.59±1.16	3.09±0.22	3.56	2.05	2.52±0.99	3.26	4.12	

*N**: Number of windy days

Table 4.32. Mean and standard deviations of gas phase winter PAH concentrations with respect to wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
<i>N</i> *	6	7	4	9	1	4	3	3	8	15
ACY	50.9±52.2	26.5±30.4	33.8±52.6	21.7±22.8	10.2	18.6±15.7	14.5±16.4	17.0±14.8	29.8±26.6	33.8±60.2
ACE	17.5±24.5	25.8±53.2	7.16±3.78	6.62±2.12	5.80	4.98±1.98	5.30±2.61	7.10±3.47	70.8±76.8	13.7±22.4
FLU	128.5±133.5	133.6±192.5	36.6±22.6	28.4±14.1	29.43	30.7±15.0	28.0±16.1	35.5±23.6	105.2±127.8	63.1±82.1
PHE	105.8±90.7	92.5±53.5	47.9±29.4	45.3±22.0	48.86	41.9±32.2	44.7±37.2	66.8±51.5	87.2±72.6	76.5±80.9
ANT	14.6±10.0	10.9±11.7	7.03±7.33	3.58±2.99	4.76	6.76±5.11	3.46±1.72	3.16±2.43	21.9±18.4	15.2±12.8
FLT	19.5±19.8	21.4±11.5	10.7±6.12	11.5±5.8	12.10	9.71±8.78	11.8±11.5	14.4±9.10	15.7±12.0	13.9±12.7
PYR	8.13±7.5	12.5±7.8	6.90±4.50	7.78±4.27	7.6	6.36±6.49	8.11±8.19	9.79±6.19	9.13±7.62	8.50±8.77
BaA	1.15±0.21	1.27±0.23	1.06±0.25	0.984±0.232	1.16	1.14±0.14	1.27±0.26	1.04±0.24	1.27±0.30	2.05±2.80
CHR	1.14±0.25	1.26±0.16	0.847±0.194	0.877±0.189	1.01	1.02±0.23	0.971±0.187	1.01±0.31	1.24±0.42	2.11±3.32
BbF	1.52±0.70	1.70±0.46	1.36±0.36	2.07±1.01	1.43	1.12±0.21	2.24±0.71	2.25±0.72	1.82±0.79	3.93±6.31
BkF	1.44±0.70	1.44±0.30	1.29±0.34	1.95±0.94	1.36	1.08±0.18	2.17±0.71	2.14±0.67	1.64±0.72	2.85±3.34
BaP	1.36±0.62	1.44±0.31	1.26±0.34	1.91±0.95	1.29	1.05±0.18	2.13±0.67	2.11±0.70	1.57±0.71	2.83±3.62
IND	0.138±0.126	0.390±0.60	0.046	0.339±0.181	0.068	0.077±0.032	0.075	0.179	0.403±0.452	1.74±4.50
DahA		0.094						0.090	0.070±0.028	0.845±1.175
BghiP	1.61±0.86	1.80±0.33	1.67±0.50	2.70±1.11	1.63	1.31±0.23	1.81	2.25±0.11	2.12±0.75	2.96±2.72

*N**: Number of windy days

Table 4.33. Mean and standard deviations of particle phase winter PAH concentrations with respect to wind directions (ng m⁻³)

Sector	S	SSW	SW	WSW	NE	ENE	E	ESE	SE	SSE
<i>N</i> *	6	7	4	9	1	4	3	3	8	15
ACY	4.52±3.46	2.16±1.16	2.83±1.47	1.31±0.73	1.975	2.18±0.36	1.96±0.54	1.73±1.34	3.22±1.49	3.10±1.42
ACE	2.89±2.52	1.68±0.95	2.01±0.87	1.97±0.92	1.097	2.85±1.80	1.69±0.29	3.18±2.30	2.33±2.01	2.75±1.67
FLU	7.84±5.04	4.58±2.59	5.01±2.16	3.46±1.75	3.291	5.21±1.89	3.50±0.59	4.32±3.32	6.88±6.72	5.74±4.48
PHE	29.2±38.8	10.8±7.5	21.6±14.9	6.71±5.53	4.388	5.86±4.80	6.36±3.78	7.24±3.52	19.1±11.4	12.8±6.7
ANT	5.63±3.35	2.20±1.02	3.05±1.97	0.997±0.543	2.743	2.27±1.68	1.74±0.51	4.78±3.48	5.08±2.55	4.59±2.66
FLT	31.1±46.9	13.9±13.3	26.3±16.0	4.67±3.12	4.111	6.76±6.77	9.11±7.77	8.34±5.39	28.0±20.6	14.1±10.8
PYR	24.1±40.4	12.3±12.1	22.2±13.4	4.01±3.09	2.781	5.76±6.42	8.42±7.26	6.74±5.66	23.8±19.1	10.7±9.3
BaA	18.2±16.9	9.07±8.13	13.1±5.2	3.17±2.06	5.280	6.27±5.14	6.74±5.29	11.0±4.3	19.5±9.5	12.5±6.0
CHR	19.9±17.8	9.67±7.90	13.8±5.9	3.51±1.84	4.877	6.27±5.42	6.54±5.30	11.9±3.9	19.7±8.4	14.5±7.0
BbF	37.5±36.2	15.2±12.4	25.3±13.3	5.93±3.17	7.791	10.5±9.8	10.5±7.58	29.9±10.8	40.8±19.3	39.5±31.1
BkF	17.8±17.0	8.43±5.87	12.3±6.0	4.02±1.98	4.129	6.09±5.09	6.61±3.97	13.4±2.7	20.2±8.5	18.9±14.5
BaP	22.4±21.8	10.6±9.3	16.1±7.0	3.82±2.23	5.134	6.78±5.62	7.47±5.72	16.5±6.2	26.4±11.4	18.4±10.5
IND	29.7±30.1	12.4±14.1	21.6±9.6	3.71±2.21	5.709	6.40±6.32	5.86±4.46	30.6±18.2	38.2±22.6	38.4±36.2
DahA	4.07±3.85	1.95±2.08	2.99±1.12	0.357±0.409	0.826	1.34±1.23	0.920±0.704	4.06±2.24	5.31±2.99	5.56±5.60
BghiP	17.1±13.7	8.71±7.65	11.8±4.4	3.37±1.85	4.452	6.19±5.64	5.05±1.82	13.4±6.9	19.7±9.8	20.0±17.3

*N**: Number of windy days

4.2.1.7. Correlation Analysis

The correlation coefficients are given in Table 4.34 for PAHs, and correlation coefficients lower than 0.25 are not listed in Table 4.34. Highly correlated compounds are given in bold. A strong correlation was found between ACE and FLU, and the others were also strongly correlated with each other. In general, 5-ring PAH compounds, which includes IND and BghiP, had strong relations with each other as 4-ring and 6-ring PAH compounds. Although some PAH compounds have same ring number, they had no strong correlation coefficients. ACE and ACY had very low correlation, since the correlations lower than < 0.25 , as it was clearly seen in Table 4.34. Also, there was a low correlation between the DahA and IND.

Table 4.34. Pearson's correlation matrix of PAHs

Compound	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IND	DahA	BghiP
ACY	1		0.49	0.84	0.54	0.70	0.65	0.67	0.68	0.66	0.65	0.71	0.69	0.62	0.67
ACE		1	0.68	0.48	0.55	0.45	0.46	0.50	0.45	0.35	0.35	0.44	0.26		0.26
FLU			1	0.77	0.48	0.77	0.99	0.61	0.59	0.48	0.49	0.56	0.42	0.47	0.45
PHE				1	0.64	0.91	0.86	0.81	0.84	0.79	0.78	0.83	0.75	0.75	0.77
ANT					1	0.62	0.59	0.79	0.76	0.70	0.68	0.77	0.68	0.60	0.64
FLT						1	0.75	0.88	0.89	0.75	0.76	0.85	0.66	0.67	0.72
PYR							1	0.87	0.87	0.72	0.73	0.83	0.62	0.62	0.69
BaA								1	0.97	0.83	0.83	0.96	0.77	0.69	0.77
CHR									1	0.91	0.91	0.97	0.84	0.78	0.87
BbF										1	0.99	0.93	0.95	0.93	0.96
BkF											1	0.93	0.94	0.93	0.96
BaP												1	0.89	0.85	0.89
IND													1		0.96
DahA														1	0.95
BghiP															1

p < 0.05

4.2.1.8. Diagnostic PAH ratios

The diagnostic PAH ratios are used for determination of their sources in the related literature. Various types of the diagnostic ratio have been given in the literature. However, FLT/FLT+PYR, BaP/BghiP, BaA/BaA+CHR, BaA/CHR, IND/IND+BghiP and IND/BghiP ratios are commonly used. Table 4.35 summarizes the PAH ratios and source types (Yunker *et al.*, 2002; Gaga, 2004; Ari, 2008). FLT/FLT+PYR, BaP/BghiP, BaA/BaA+CHR and BaA/CHR ratios indicated the combustion processes for coal and the other fossil fuels, while IND/IND+BghiP ratio points to the mixed combustion processes at the sampling area.

Table 4.35. Diagnostic ratios of PAHs and source types

Source	FLT/ FLT+PYR	BaP/BghiP	BaA/CHR	IND/BghiP	IND/ IND+BghiP
Traffic		0.3-0.78 ^{a,b}	0.63 ^b		
Gasoline Exhaust	0.44 ^h	0.3-0.4 ^d	0.28-1.2 ^{c,d}	0.4 ^e	0.09-0.22 ^h
Coal	>0.5 ^h	0.9-6.6 ^a	1-1.2 ^{c,f}		0.57 ^h
Diesel	0.39 ^h	0.46-0.8 ^f	0.17-0.36 ^{d,g}	1 ^e	0.35 ^h
Bolu summer	0.54 ± 0.03	1.25 ± 0.83	1.29 ± 0.32	0.34 ± 0.28	0.23 ± 0.13
Bolu winter	0.59 ± 0.04	1.20 ± 0.34	0.94 ± 0.14	1.35 ± 0.58	0.53 ± 0.14

^a Daisey *et al.*, 1979;

^b Harrison and Smith., 1996

^c Gschwend and Hites, 1981

^d Rogge *et al.*, 1993

^e Caricchia *et al.*, 1999

^f Masclet *et al.*, 1987

^g Khalili *et al.*, 1995

^h Yunker *et al.*, 2002

When the FLT/FLT+PYR ratios were evaluated, it was seen that for both seasons it was close to 0.5 (0.54 in winter, 0.59 in summer) indicating coal combustion. On the other hand, BaP/BghiP ratios show great variation having higher

standard deviation in summer time. For that reason, it was not suitable to use that ratio for summer period. Having smaller standard deviation for the BaP/ BghiP in winter, again coal combustion looks like a source. Likewise, BaA/CHR ratio deviated less in winter time indicating coal as a source. The ratio for the IND/BghiP shows variation for both seasons having very close to 0.4 in summer time indicating traffic emissions. According to comparison of the literature values, IND/IND+BghiP ratio indicates coal as a source for winter and traffic for the summer time.

4.2.1.9. Factor Analysis (FA)

The purpose of the analysis was to obtain a relatively small number of factors which would account for the most of variability. The principles of the factor analysis were explained in the previous section (Section 1.5). Applying the factor analysis to the total PAHs enabled sources, and which wind directions contributed to the PAHs to be determined. Factor analysis was applied separately for summer and winter samples. Summer samples FA results were shown in Table 4.36. Factor analysis explains 80 % of the total variance in two factors. Most of the variance was explained in the first factor. Low molecular weight PAH compounds contribute to the first factor. It looks like that combustion activities were still in operation in summer months. Sampling location is close to the agricultural areas and wheat is in the second place after potato being produced on those agricultural activities. Burning of agricultural residues is a common practice in the rural and agricultural areas. Low temperature conditions during the burning of agricultural residues may lead to incomplete combustion and dominance of low molecular weight PAHs. On the other hand, there is an asphalt manufacturing plant near to the sampling location and it

might be a potential source for the PAHs especially in summer months. Sampling location receives some northerly winds and industrial cities (Adapazarı and Düzce) located on those directions. Long range transport may take place also but this point needs to be investigated more in detail. The second factor accounted for 9.29 % of the total variance and loaded with BbF, BkF, IND, BghiP, which are indicators of traffic activities. These PAH compounds are the marker elements according to the source types in this case mainly traffic.

Table 4.36. Factor analysis results (summer)

Compound	Factor 1	Factor 2
ACE	0.73	0.26
ACY	0.59	0.36
FLU	0.88	0.29
PHE	0.89	0.23
FLT	0.92	0.28
PYR	0.92	0.28
BaA	0.72	0.56
CHR	0.84	0.49
BbF	0.36	0.77
BkF	0.66	0.67
BaP	0.72	0.42
IND		0.88
BghiP	0.43	0.82
% Variance	70.3	9.3
Source	Mixed Combustion	Traffic

Factor analysis applied to winter samples explains 90 % of the total variation in three factors (Table 4.37). In the first factor, 65 % of the variance explained and this factor loaded with high molecular weight PAHs; BaA, BbF, BkF, BaP, IND, DahA and BghiP. Those PAHs have known to be emitted as a result of combustion processes. For this reason it is assigned as coal and wood combustion. This factor also loaded with IND, CHR and BghiP which are known to be traffic markers. Since combustion of fossil fuel is a dominant source and PAHs were emitted from wide variety of sources it is not easy to discriminate the sources. The second factor loaded

with low molecular weight PAHs; ACE, FLU, PHE, ANT, FLT and PYR. The marker compounds of the unburnt fossil fuels, PHE, PYR and FLT (Kavouras *et al.*, 2001) appears on the second factor which is assigned as petrogenic factor. Third factor loaded with ACY, FLU, ANT and PHE explains the 7 % of the total variance. Since these compounds are the more volatile ones and mostly exist in gas phase, they represent more local source of origin because of their high photochemical activity. In the literature, especially ACE, ANT and ACY were not included in most of the factor analysis statistics. The only information about these compounds were found in the literature regarding their emissions is the study undertaken by Ravindra *et al.*, 2008. In this work, indicatory PAHs of the cement factory were reported as ACY, ACE and ANT. Third factor might be related to the emissions of cement factory in the study region.

Table 4.37. Factor analysis (winter)

Compound	Factor 1	Factor 2	Factor 3
ACE		0.76	
ACY			0.90
FLU		0.54	0.81
PHE		0.65	0.70
ANT	0.39	0.69	0.39
PYR	0.48	0.81	
BaA	0.45	0.81	
CHR	0.85	0.46	
BbF	0.87	0.42	
BkF	0.95		
BaP	0.95	0.26	
IND	0.93	0.31	
PYR	0.94		0.27
DahA	0.93		0.30
BghiP	0.94		
% Variance	65.0	18.7	7.1
Source	Coal and Traffic	Petrogenic Unburnt fossil fuel	Current factory (Cement)

3.2.2. PAHs in Soils

PAHs of the particle phase inevitably deposits on the soil surfaces by the meteorological factors since most of the PAHs are emitted from the combustion processes and get suspended in the air. In this study, the 29 soil samples were collected in the air sampling region and correlated with the air concentrations.

4.2.2.1. Statistical Evaluation of PAHs

A statistical assessment of the 15 individual PAHs, sum of the 15 PAHs in the soil samples close to the air sampling areas is shown in Table 4.38. The total concentrations of individual PAHs in the rural area of Bolu were in the range of 11.1 ng g⁻¹ to 1549 ng g⁻¹, with a mean of 540.7 ng g⁻¹. The 15 PAHs targeted were detected in all the soil samples except for DahA, BghiP, and IND. The higher PAH concentrations were detected for PHE and FLU (53.4 and 38.5 ng g⁻¹, respectively) in the soil samples. The lower concentrations were observed for IND and DahA (3.21 and 1.39 ng g⁻¹, respectively) in the soil samples.

The frequency diagrams are drawn in Figure 4.18 for all the PAHs that generally showed a log-normal distribution except for BkF, BaP, and BghiP. Mean, geometric mean and median values in Table 4.38 also indicated a log-normal distribution for the most of the PAHs in soil, as well. Median and geometric mean are very close to each other. Standard deviations of the PAHs were generally higher than the mean, which means that the concentrations were affected from the chemical and physical transformations as well as meteorological parameter. As a result, various types of sources caused abrupt changes in the PAH concentrations.

Table 4.38. Statistical evaluation of soil samples taken in summer and winter (ng g^{-1})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
ACY	29	100	19.1	12.8	13.1	22.3	1.68	108.0	106.3	554
ACE	28	97	7.06	5.54	5.15	6.26	0.793	30.5	29.7	198
FLU	29	100	38.5	15.4	17.5	67.4	1.88	333.5	331.7	1118
PHE	29	100	53.4	17.3	23.4	100.8	5.74	499.2	493.4	1549
ANT	29	100	10.9	7.28	7.13	14.1	2.33	63.7	61.4	316
FLT	29	100	25.1	14.6	15.7	38.9	5.22	212.6	207.4	729
PYR	29	100	19.0	12.4	12.3	29.9	4.67	165.8	161.2	552
BaA	29	100	15.0	11.9	12.6	11.5	5.87	62.9	57.0	436
CHR	29	100	11.8	8.35	9.63	9.50	4.37	50.7	46.4	343
BbF	29	100	20.8	18.2	18.4	9.92	4.42	47.6	43.2	604
BkF	29	100	18.5	17.1	16.6	7.77	4.04	36.1	32.1	535
BaP	29	100	18.3	17.1	16.7	7.26	3.86	32.7	28.8	530
IND	22	76	3.21	1.36	1.54	5.95	0.290	28.1	27.8	70.6
DahA	8	28	1.39	1.20	1.21	0.872	0.454	3.39	2.94	11.1
BghiP	28	97	20.1	18.9	17.6	9.44	4.64	38.1	33.4	564

*Total analyzed sample: 29

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Actual Samples

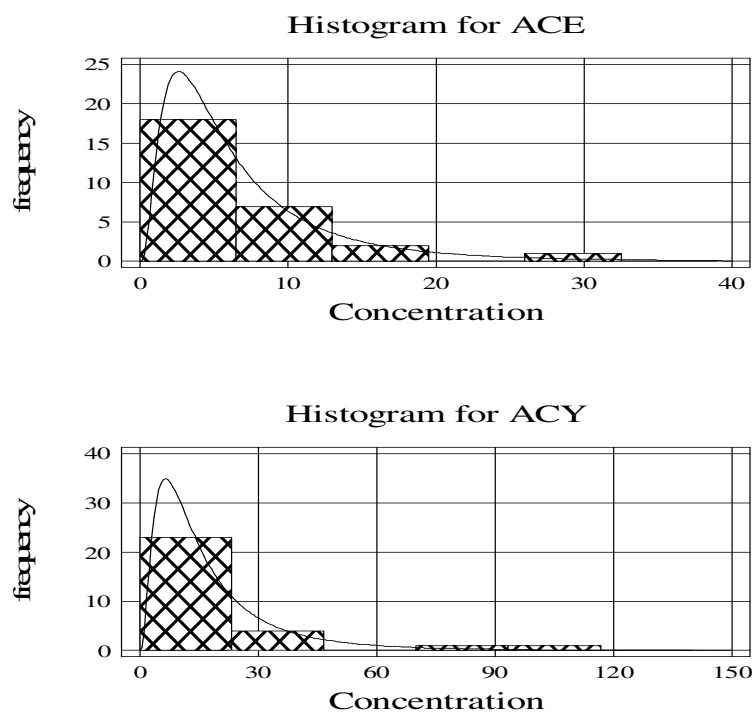


Figure 4.18. Statistical distribution of PAH concentrations in soil (ng m^{-3})

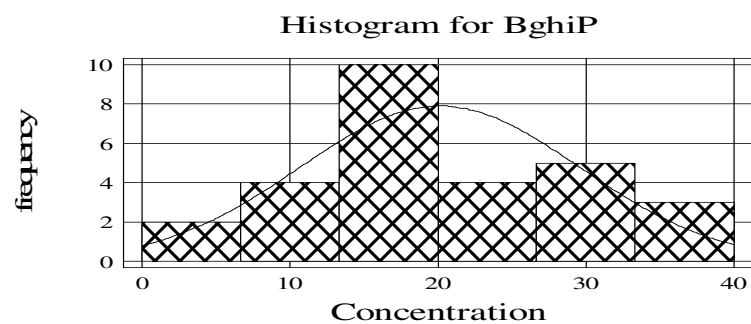
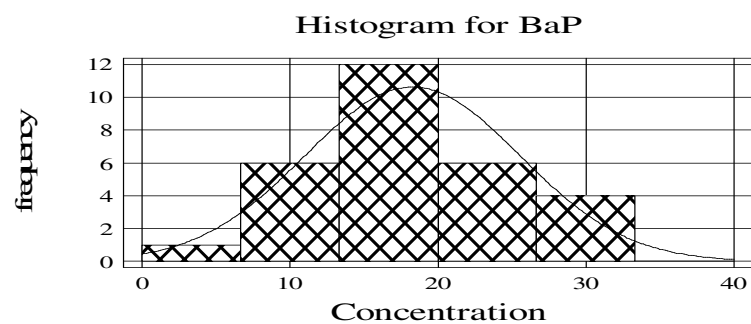
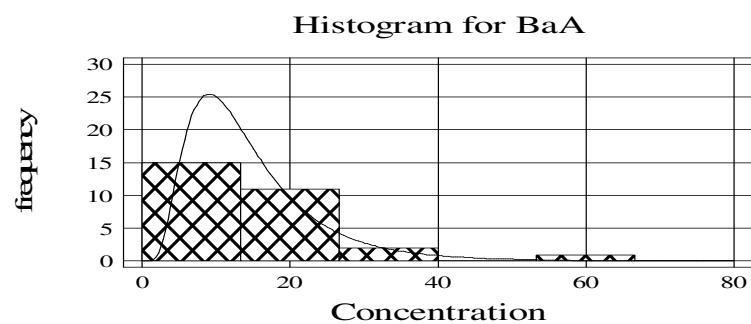
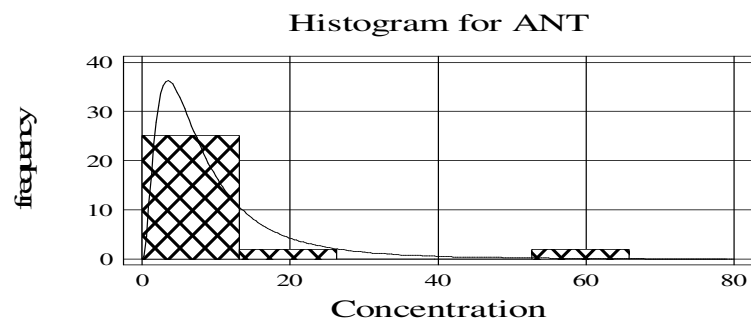


Figure 4.18. Statistical distribution of PAH concentrations in soil (ng m^{-3})
(Continued)

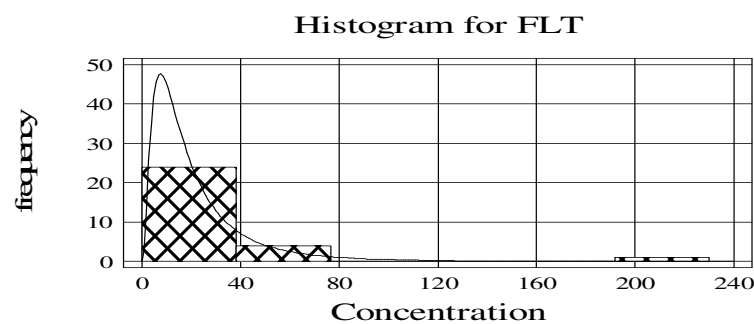
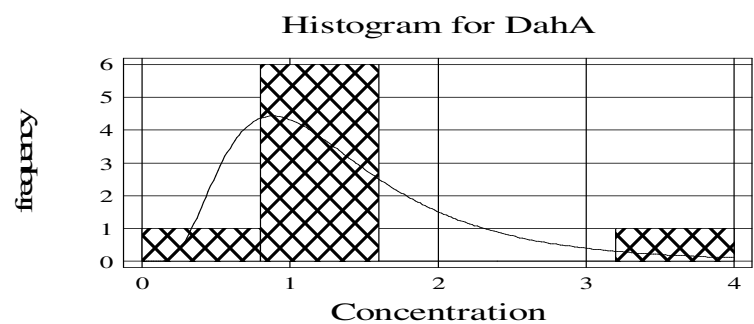
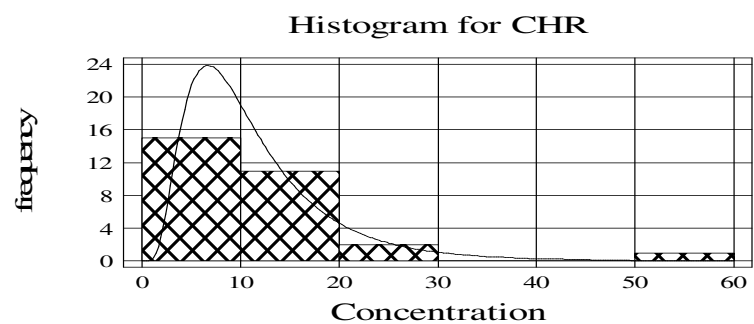
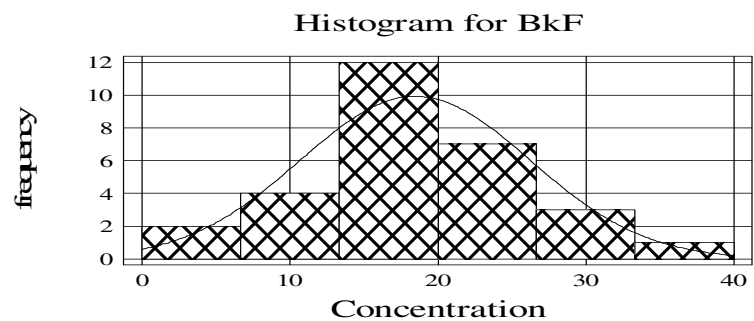


Figure 4.18. Statistical distribution of PAH concentrations in soil (ng m^{-3})
(Continued)

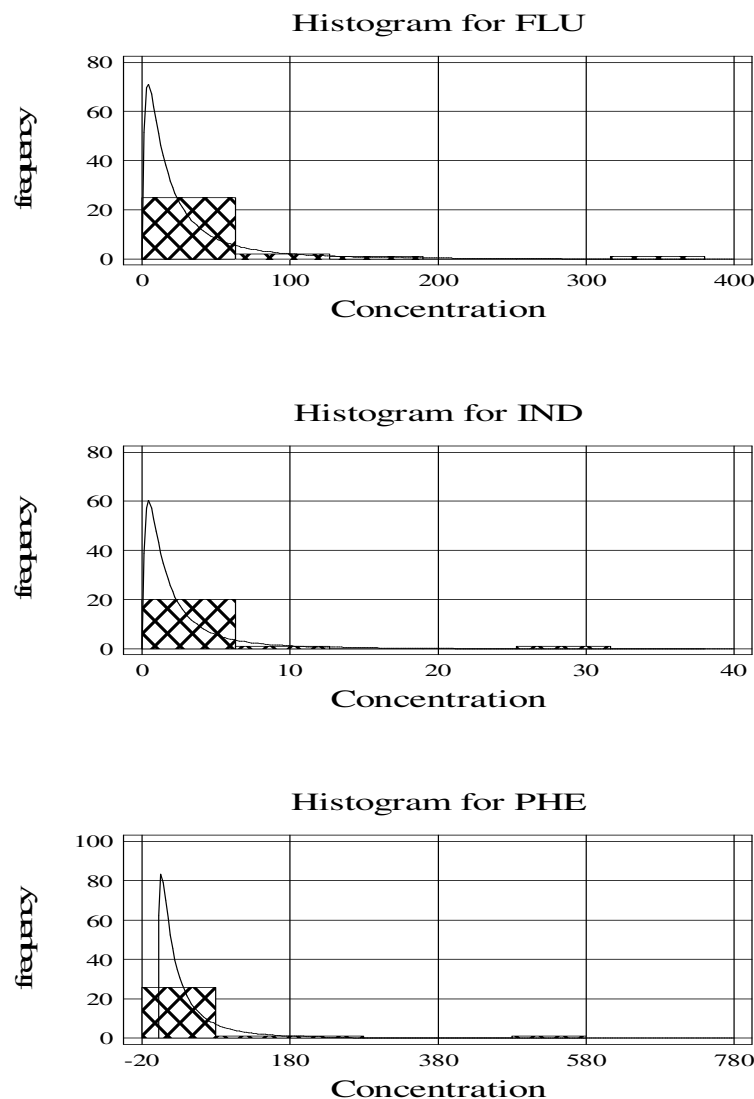


Figure 4.18. Statistical distribution of PAH concentrations in soil (ng m^{-3}) (Continued)

4.2.2.2. Seasonal Differences in PAHs

The PAHs measured had a high percent observation in the winter (Table 4.39). However, DahA had a very low percent observation. The highest average concentrations of PHE, FLU, and FLT were 60.9 , 45.1 , and 27.1 ng g^{-1} , respectively, which were the highest mean values. IND and DahA had the lowest concentrations in

the winter (2.06 and 0.943 ng g⁻¹, respectively). In the soil, low molecular weight-PAHs were observed to be higher in the winter, which was the result of the direct exposure by the local sources. The main sources of these compounds are the combustion processes principally derived from the diesel motors. The individual average PAH concentrations decreased in the following order: PHE > FLU > FLT > PYR > ACY > BbF > BghiP > BkF > BaP > BaA > ANT > ACE > IND > DahA.

Table 4.39. Statistical evaluation of soil samples taken in winter (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
ACY	19	100	19.8	11.4	11.6	27.2	1.67	108	106	376
ACE	18	95	7.01	3.17	4.45	7.63	0.793	30.5	29.7	126
FLU	19	100	45.1	12.5	16.9	81.8	1.88	333	332	858
PHE	19	100	60.9	14.4	22.9	120.5	5.74	499	493	1157
ANT	19	100	9.96	3.96	6.08	14.3	2.33	63.7	61.4	189
FLT	19	100	27.1	10.5	14.3	47.3	5.22	213	207	515
PYR	19	100	21.1	8.81	11.5	36.8	4.67	166	161	402
BaA	19	100	13.5	8.22	10.5	13.8	5.87	62.9	57.0	257
CHR	19	100	10.7	6.18	8.10	11.2	4.37	50.7	46.4	203
BbF	19	100	17.4	17.1	15.2	9.59	4.42	47.6	43.2	331
BkF	19	100	15.2	14.3	13.7	7.02	4.04	36.1	32.1	290
BaP	19	100	14.7	13.9	13.6	5.66	3.86	30.8	26.9	280
IND	15	79	2.06	1.27	1.25	2.49	0.290	9.14	8.85	31.0
DahA	3	16	0.943	1.04	0.857	0.448	0.454	1.33	0.879	2.83
BghiP	18	95	15.3	16.2	14.3	5.14	4.76	23.4	18.6	276

*Total analyzed sample: 19

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Actual Samples

The most of PAHs were observed at a high percent (100 %) in the soil for the summer samples except for IND and DahA. Although IND and DahA had a low percentage of observation, they are still over 50 % (Table 4.40). A statistical assessment of PAH concentrations (ng g⁻¹) in the soil is given in Table 4.40. Average concentrations of PHE, BghiP and BbF were higher than the other PAHs, while IND and DahA had the lowest mean concentrations as well as the lowest percent observation. The highest concentrations in the soil belonged to PHE, BghiP, BbF and FLU which were 39.1, 28.7, 27.3 and 26.0, respectively. Unlike the winter soil

samples, BghiP and BbF showed high concentrations in the summer since the deposition on the surface increased after the heavy heating and combustion season. The other high molecular weight-PAHs were also higher than the summer due to the similar reasons such as pyrolysis processes. Figure 4.19 summarizes the comparison of seasonal mean PAH concentrations in the soil.

Table 4.40. Statistical evaluation of soil samples taken in summer (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
ACY	10	100	17.8	15.0	16.5	7.86	9.28	36.3	27.0	178
ACE	10	100	7.16	6.10	6.68	2.80	3.71	11.6	7.87	71.6
FLU	10	100	26.0	17.3	18.7	21.7	6.02	65.8	59.8	260
PHE	10	100	39.1	18.5	24.4	47.3	6.89	164	157	391
ANT	10	100	12.7	8.00	9.66	14.3	4.84	53.1	48.2	127
FLT	10	100	21.5	17.7	18.5	14.1	8.03	55.8	47.8	215
PYR	10	100	15.1	13.7	14.1	6.70	7.11	32.9	25.8	151
BaA	10	100	17.9	17.4	17.5	4.16	11.9	26.9	15.0	179
CHR	10	100	14.0	13.0	13.4	4.77	8.35	25.1	16.7	140
BbF	10	100	27.3	25.8	26.4	7.20	15.5	40.9	25.3	273
BkF	10	100	24.6	24.5	24.1	5.08	14.6	32.0	17.4	246
BaP	10	100	25.0	25.9	24.5	4.80	14.7	32.7	17.9	250
IND	7	70	5.68	2.67	2.37	9.95	0.387	28.1	27.7	39.7
DahA	5	50	1.66	1.33	1.48	0.995	0.970	3.39	2.42	8.29
BghiP	10	100	28.7	30.3	25.7	9.43	4.64	38.1	33.5	287

*Total analyzed sample: 10

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Actual Samples

The predominance of low molecular weight-PAHs in the agricultural soil reflects the presence of significant combustion products from low temperature pyrolytic processes such as biomass burning and/or petrogenic sources (Agarval *et al.*, 2009). Moreover, it points to recent soil pollution since the lighter PAHs are more biodegradable and less lipophilic and are not expected to persist or to be sorbed as strongly as heavier PAHs. Burning of agricultural residues is a common practice in the rural and agricultural areas. Low temperature conditions during the burning of agricultural residues may lead to incomplete combustion and dominance of low molecular weight-PAHs.

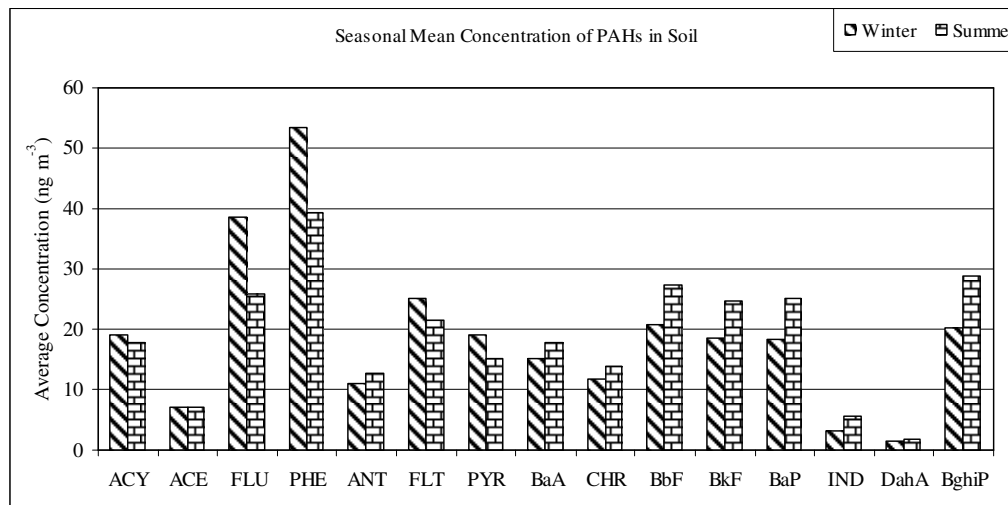


Figure 4.19. A comparison of seasonal PAH concentrations in soil

4.2.2.3. A Comparison of PAH Concentrations with Related-Literature Values

Total average PAH concentrations were compared separately with other studies for similar and different regions in the related literature (Table 4.41). Nam *et al.* (2003) reported lower ACY, ACE, FLU, PHE, ANT, BkF, BaP, and BghiP concentrations and higher concentrations of the remaining PAHs than did this study. The soil samples were influenced from the recent heating events, and therefore, low molecular weight-PAHs were dominant when compared to a rural region with limited combustion processes. In the rural region, Wang *et al.* (2007) found ACE, FLU, PYR, BaA, CHR, BkF, BaP, and BghiP concentrations to be lower and the concentrations of other PAHs to be higher than this study. Bozlaker *et al.* (2008), and Jiang *et al.* (2009) found the most of PAHs in the urban areas, especially the heavy ones, to be higher than this study. The PAH concentrations in this study were mainly affected from the seasonal events such as low temperature heating processes.

Table 4.41. A comparison of the soil concentration (mean) of PAHs with related-literature (ng g⁻¹)

Reference	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IND	DahA	BghiP
This study (Bolu, Turkey), rural, agricultural	19.1±22.3	7.06±6.26	38.5±67.4	53.4±100	10.9±14.1	25.1±38.9	19.0±29.9	15.0±11.5	11.8±9.50	20.8±9.92	18.5±7.8	18.3±7.3	3.21±5.9	1.39±0.87	20.1±9.4
Nam <i>et al.</i> , 2003 (South Korea). Rural, agricultural	2.1	1.5	3.6	20.5	7.5	33.7	26.0	18.6	14.6	31.8	7.7	16.3	12.2	3.2	12.4
Bozlaker <i>et al.</i> , 2008 (Turkey), urban.		2.5±1.0	3.7±0.7	29.9±6.9	4.3±1.1	34.0±9.5	32.1±9.7	22.3±8.0	54.2±20.4	31.4±10.3	19.1±5.0	18.6±5.5	22.3±6.9	23.4±13.3	43.0±19.8
Wang <i>et al.</i> 2007 (China), rural		2	18	90	5	30	18	6	5	29	4	6	5	2	6
Agarwal <i>et al.</i> , 2008 (India), agricultural	183±96	282±140	77±35	76±54	48±31	191±153	124±87	121±156	58±43	87±56	53±21	49±19	79±109	134±96	97±77
Jiang <i>et al.</i> , 2009 (China), urban.	4.98	15.3	9.12	83.4	16.4	199	180	92.1	123	171	69.4	93.2	80.6	16.8	86.1

4.2.2.4. Correlation Analysis of PAHs

Binary correlation (pearson's) among the PAH compounds is generally used for environmental studies so as to determine their sources, pathways and fate according to the sampling point as was expressed in section 4.1.1.7. Highly correlated compounds are given in bold for the soil samples. The 3-ring compounds were highly correlated with each other and 4-ring PAHs in soil. 5-ring and 6-ring PAH compounds had strong relations with each other in soil samples, as well (Table 4.42).

Table 4.42. Pearson's correlation matrix of PAHs

Compound	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IND	DahA	BghiP
ACY	1	0.89	0.96	0.92	0.66	0.79	0.77	0.57	0.56	0.43	0.39	0.30			
ACE		1	0.93	0.87	0.72	0.76	0.70	0.55	0.53	0.55	0.52	0.44			
FLU			1	0.97	0.76	0.87	0.83	0.61	0.60	0.43	0.38	0.28		0.80	
PHE				1	0.86	0.92	0.86	0.67	0.66	0.44	0.38	0.28			
ANT					1	0.85	0.75	0.72	0.68	0.45	0.42	0.36			
FLT						1	0.98	0.87		0.55	0.86	0.35	0.31		0.46
PYR							1	0.91	0.90	0.53	0.42	0.32	0.33	0.97	
BaA								1	0.99	0.59	0.50	0.32	0.42	0.77	
CHR									1	0.62		0.44		0.73	0.51
BbF										1	0.97	0.92	0.67	0.75	0.73
BkF											1	0.95	0.57	0.66	0.84
BaP												1	0.63	0.73	0.88
IND													1	0.93	0.42
DahA														1	0.56
BghiP															1

$p < 0.05$

4.2.2.5. Factor Analysis (FA)

The factor analysis is commonly used for source determination. When FA was applied to all soil samples (Table 4.43), ACY, ACE, FLU, PHE, ANT, FLT and PYR were clustered in the first factor, while BbF, BkF, BaP and BghiP were gathered in the second factor. The third factor represented only BaA and CHR. The

contribution to IND was shared by the first and second factors. First factor indicates incineration and wood combustion sources, while second factor pointed to emission from the traffic and high temperature combustion processes. The third factor denotes the mixed combustion processes.

Table 4.43. Results of factor analysis applied to PAH concentrations

Compound	Factor 1	Factor 2	Factor 3	Communality
ACY	0.95			0.95
ACE	0.92	0.30		0.95
FLU	0.97			0.98
PHE	0.95		0.25	0.98
ANT	0.85		0.49	0.97
FLT	0.80		0.55	0.97
PYR	0.77		0.60	0.97
BaA	0.55		0.78	0.95
CHR	0.51		0.81	0.97
BbF	0.32	0.86	0.33	0.96
BkF	0.31	0.91		0.97
BaP		0.94		0.97
IND		0.60	0.57	0.69
BghiP		0.94		0.90
% Variance	65.0	21.5	7.7	
Source	(Wood combustion and incineration)	(Traffic and high temperature pyrolysis)	(Wood and tire dust)	

4.2.3. Exchanges of PAHs

The fate of PAHs in environment has various kind of transformation by chemical or physical processes. They can be in equilibrium at all types of exchanges or they can be found higher in a phase.

4.2.3.1. Application of Clausius-Clapeyron Equation to Gas Phase PAHs

The temperature dependency of the gas phase PAHs is determined by the Clausius-Clapeyron equation whose principles were given in the previous section

(Section 4.1.3.1). Graphs of the $\ln P$ vs $1/T$ are drawn to determine m and b values (Figure 4.20) in comparison to the related literature. The high slope value ($m = -\Delta H/R$) indicates the closeness of sources and volatilization. The slope of the total PAHs was found to be positive (7016), as well. In the literature, positive slopes were also determined by Sofuoğlu *et al.* (2001), Esen (2006) and Arı (2008). However, there existed many studies determining the negative slopes. Mainly, positive results reveal the short range transportations from the local sources and the dominance of condensation (Esen *et al.*, 2008). This application also clearly explained the temperature dependence of the PAHs and vaporization for instance the high slopes indicated the evaporation.

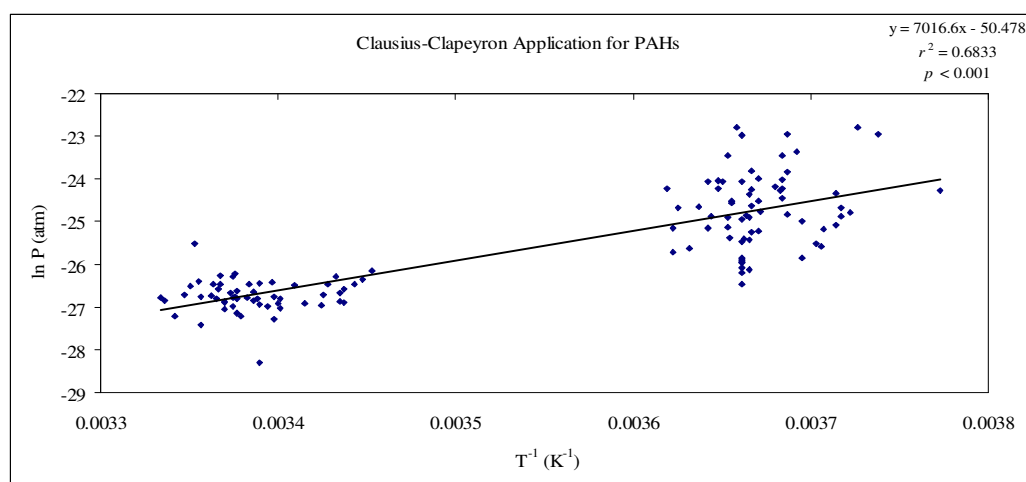


Figure 4.20. Temperature relationship with partial pressure of gaseous PAHs

4.2.3.2 Gas to Particle Exchange

Gas-particle distribution of the PAHs explains the behavior that they exhibit either in the gas phase or in the particle phase (Figures 4.21 and 4.22). As can be seen in Figure 4.21, the particle phase of the heavy PAHs was dominant in the

winter, while the low molecular weight-PAHs were significantly ($p = 0.05$) high in the gas phase. The incineration of wood, coal, and the other fossil fuels increases in the winters, and hence, the low molecular weight-PAHs are constituted by wood combustion, whereas high ones derived from the coal and other fossil fuel combustion as sorbed to the particles.

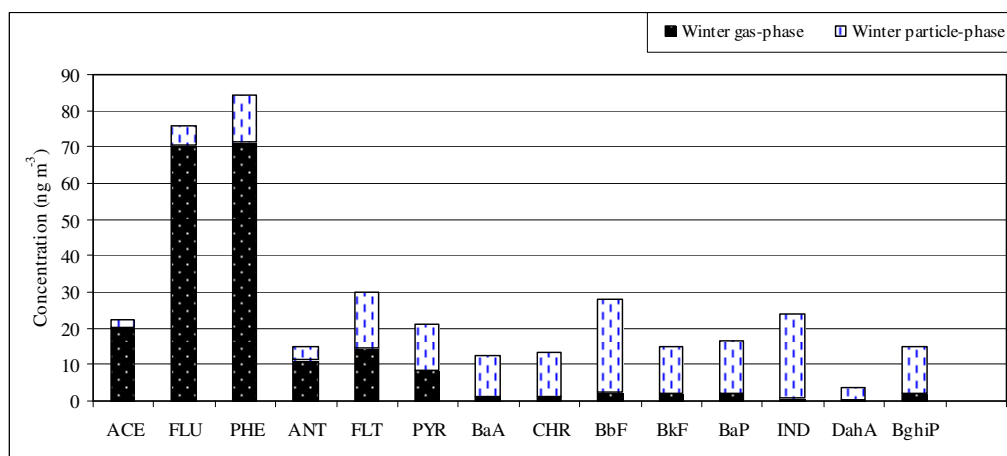


Figure 4.21. Gas and particle distribution of PAHs in winter

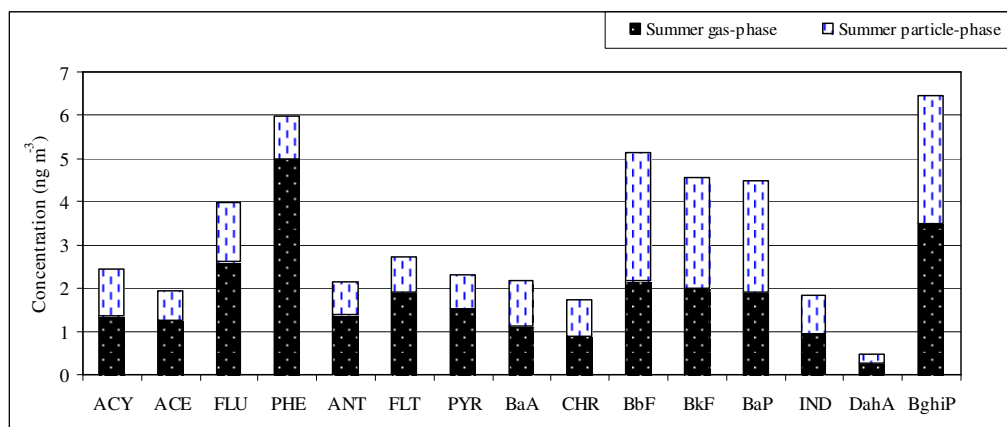


Figure 4.22. Gas and particle distribution of PAHs in summer

4.2.3.2.1. Junge-Pankow Model

Junge and Pankow (Junge, 1977 and Pankow, 1987) applied an adsorption model to determine the sorption of POPs to aerosols. The model equation is ϕ

$=c\theta/(P_L^0+c\theta)$; where ϕ , is the fraction of chemical adsorbed to particle, P_L^0 is the saturation liquid-phase vapor pressure of the adsorbing substance (Pa), θ is the aerosol surface area per unit volume of air ($\text{cm}^2 \text{ cm}^{-3} \text{ air}$) and the parameter c is related to the heat of desorption from the particle surface, the heat of vaporization of the compound and the moles of adsorption sites on the aerosol. Typical values for θ are determined as 4.2×10^{-7} (continental air), 3.5×10^{-6} (rural air) and 1.1×10^{-5} (urban air) (Bidleman, 1999). The value of c is usually taken as 17.2 Pa cm (Harner and Bidleman, 1998). Experimental results were used to calculate adsorption of POPs onto aerosols with an equation of $\phi = C_p/(C_p+C_g)$; where, C_p is the concentrations of the pollutants in particle phase and C_g is the concentrations of the pollutants in gas phase.

The Junge-Pankow model explained well the distribution of gas and particle phase PAHs (FLU, PHE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, and BaP) which were adsorbed to the aerosols at the sampling point in this study. The following figures (Figure 4.23) show the relation of the modelled ϕ and experimental ϕ . The modelled and experimental ϕ were statistically significant for summer and winter terms ($r^2 = 0.46-0.95$ and $p < 0.05$, $r^2 = 0.69-0.96$ and $p < 0.05$, respectively). The ratios of the measured ϕ with the modelled ϕ were lower than one for low molecular weight PAHs whereas they were found to be higher than one for high molecular weight PAHs. The particle phase concentrations were underestimated for low molecular weight PAHs whereas they were overestimated for high molecular weight PAHs. Therefore high molecular weight PAHs adsorbed to the aerosols rather than low molecular weight ones. The modelled ϕ indicated the approximately similar values therefore, Junge-Pankow model come across with the experimental values under the adsorption approach.

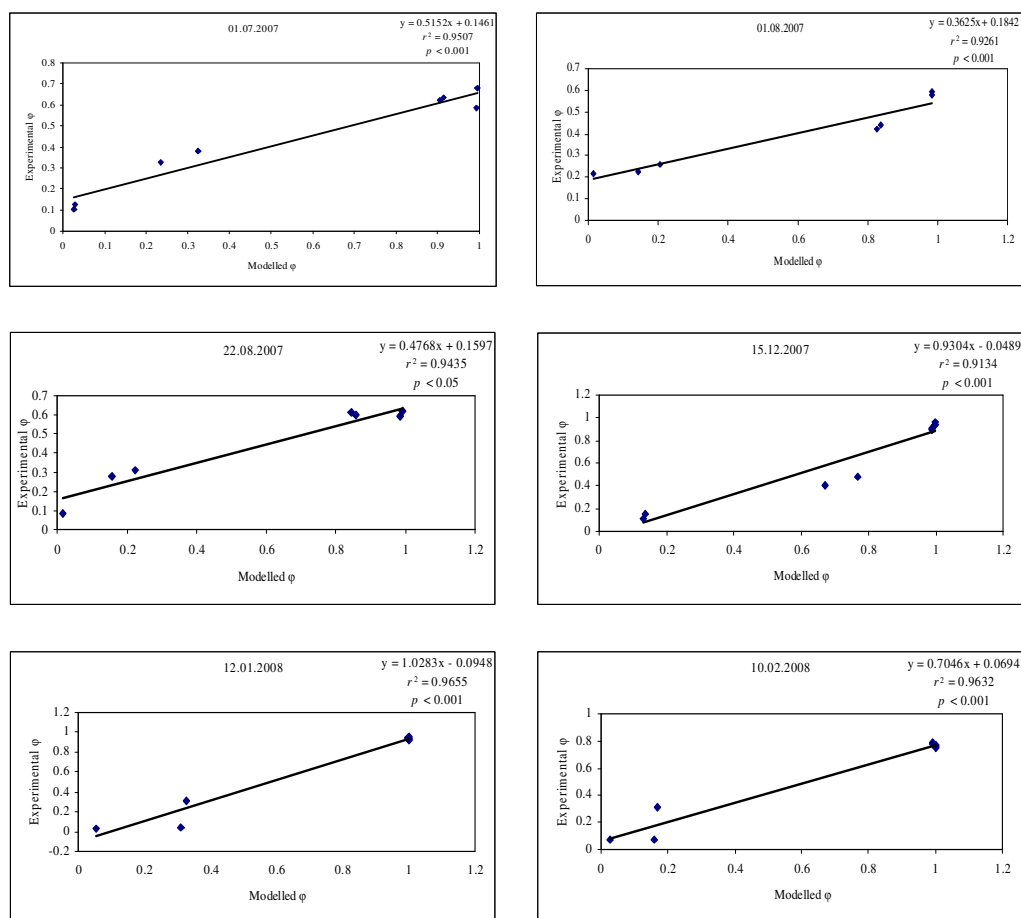


Figure 4.23. Relationship between experimental and modelled ϕ values for winter and summer

4.2.3.2.2. Log K_p and Log P_L^0

Log K_p and log P_L^0 were successfully applied in order to determine the sorption on the particles in a time interval (Simcik *et al.*, 1998; Mandalakis *et al.*, 2002; Cindoruk *et al.*, 2007). $\log K_p = m_r \log P_L^0 + b_r$, where, K_p is experimentally determined partition coefficient, P_L^0 is sub-cooled vapour pressure. m_r is the slope of the relation, b_r is the intercept of the line. It has been suggested in literature that at equilibrium, the slope for either adsorption or absorption should be close to the -1 (Pankow, 1994). However, field measurements, mainly indicates the deviation from the -1.

The m_r values are approaches to one when the following assumptions are considered:

1- the difference between desorption and H_{vap} and the properties of regions that are suitable for the absorption must be constant for adsorption.

2- activity coefficients must be constant for one group of compounds for the absorption.

3- the difference between the desorption and the H_{vap} must be constant for one class of the compounds. P_L^0 can be calculated by the known slope and intercept in the following equation (Falconer *et al.*, 1995), $\log P_L^0 = m_L/T + b_L$. The slope m_L and b_L values can be found anywhere in literature for PAHs.

The slope and the intercepts determined for summer and winter seasons and compared with the related literature (Table 4.44). The slopes of statistically significant $\log K_p$ versus $\log P_L^0$ plots ranged for PAHs from -0.10 to -0.52 in summer and from -0.16 to -0.63 in winter. In addition, the intercepts b_r of the same plots ranged from -2.60 to -5.63 in summer and from -2.54 to -6.97 in winter. Regression coefficients of $\log K_p$ versus $\log P_L^0$ plots were highly significant for summer and winter samples, ($r^2=0.58-0.99$; $0.65-0.97$, $p < 0.01$ respectively).

Table 4.44. Regression values in the related-literature for $\log K_p$ versus $\log P_L^0$ graph of PAHs

Country	Sampling Region	m_r	b_r	r^2	Reference
Atina	Urban	-0.47	-4.52	0.74	Manolis <i>et al.</i> , 2002
Prato	Industrial	-0.81	-6.91	0.97	Cincinelli <i>et al.</i> , 2007
Heraklion	Urban	-0.89	-6.93	-	Tsapakis and Stephanou, 2005
Denver	Urban	-0.76	-6.71	-	Foreman and Bidleman, 1990
Oregon	Rural	-0.98	-7.16	-	Ligocki and Pankow, 1989
Bursa	Industrial	-0.87	-7.2	0.93	Esen <i>et al.</i> , 2008
Bursa	Urban	-0.98	-7.5	0.95	Esen <i>et al.</i> , 2008
Eskişehir	Urban -winter	-0.50	-6.20	0.85	Ari, 2008
Eskişehir	Urban -summer	-0.34	-4.92	0.75	Ari, 2008
Bolu	Rural-winter	-0.40	-4.61	0.86	This Study
Bolu	Rural-summer	-0.36	-4.46	0.87	This Study

In this study, the $\log K_p$ versus $\log P_L^o$ graphs were drawn for determination of sorption of PAH compounds in individually both seasons. The average slopes of $\log K_p$ versus $\log P_L^o$, which were shallow, were found to be -0.39 and -0.36, for winter and summer seasons, respectively. Some of the $\log K_p$ versus $\log P_L^o$ graphs is given in Figure 4.24 and Figure 4.25. The more shallow slopes were determined in summer season which is the result of the temperature increase in summer.

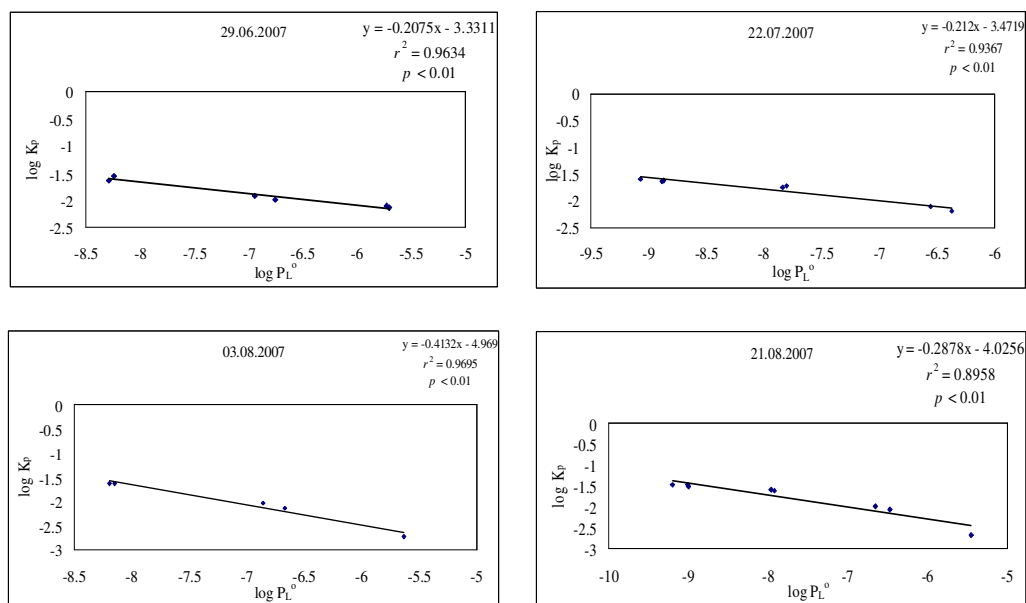


Figure 4.24. $\log K_p$ - $\log P_L^o$ applications for summer

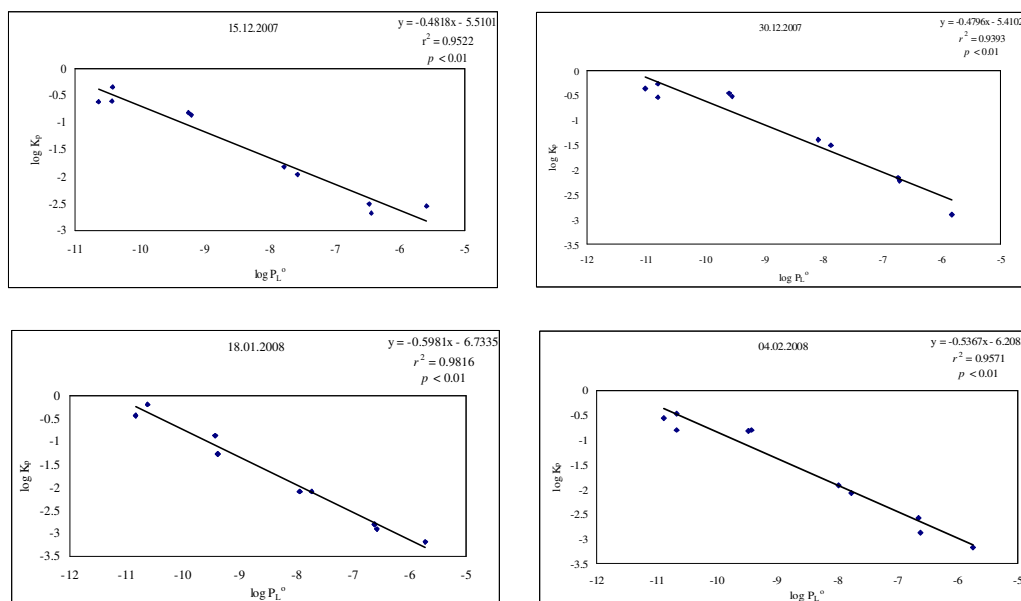


Figure 4.25. Log K_p -log P_L^o applications for winter

Pankow and Bidleman (1992) among other reasons for shallow slopes of log K_p versus log P_L^o curves have suggested: (a) the presence of non-exchangeable compounds on or in the particles, (b) differences in the “excess” heat of desorption (heat of desorption minus heat of volatilization) of the various compounds, (c) slow adsorption kinetic when relatively clean particles enter a contaminated atmosphere, (d) slow desorption kinetic when relatively contaminated particles are either emitted to a relatively clean atmosphere or diluted by less contaminated air, (e) sampling artifacts (gas sorption to GFF filters), and (f) nonequilibrium. In addition, Goss and Schwarzenbach (1998) and Simcik *et al.* (1998) proposed that slopes m_r can easily deviate from -1 even in the case when equilibrium sorption processes occur and sampling artifacts are negligible. The slopes determined from the log K_p versus log P_L^o had high deviation from the -1, therefore it would be suggested that absorption or adsorption had the important effect on the behaviour of PAH compounds in the Bolu atmosphere.

4.2.3.3 Air-to-Soil Exchange of PAHs

The equilibrium partitioning of a chemical between air and soil is described by the dimensionless soil–air partition coefficient, whose principals were explained in the 4.1.3.2 section. Fugacity ratios are used for estimation of air to soil exchange of PAHs. If the fugacity ratio was higher than one, the volatilization process is a common transfer process which indicates the air as a sink.

In this study, the fugacity ratios and K_{SA} values were calculated at the air sampling site using the 109 air samples and 29 soil samples concentrations for PAH compounds. Each season discussed individually to obtain seasonal difference (Table 4.45 and 4.46). The average organic matter content of soil samples was 10.8 % (in dry sample). The density of soil solids was experimentally determined as 2.01 g cm^{-3} . The PAH compounds had the similar K_{SA} values in related literature (Hippelin and Mclachlan, 1998). Soil is again sink for PAH compounds.

Table 4.45. Calculated soil-air exchange parameters for winter

Compound	K_{SA}	Log K_{SA}	f_S/f_A	Log f_S/f_A
ACY	1.37E+06	6.14	8.09E-07	-6.09
ACE	7.00E+05	5.85	6.05E-04	-3.22
FLU	1.28E+06	6.11	4.17E-04	-3.38
PHE	1.72E+06	6.23	8.35E-05	-4.08
ANT	1.77E+06	6.25	1.98E-03	-2.70
FLT	3.72E+06	6.57	7.09E-06	-5.15
PYR	4.89E+06	6.69	1.73E-05	-4.76
BaA	1.98E+07	7.30	2.33E-10	-9.63
CHR	1.62E+07	7.21	1.01E-11	-11.00
BbF	1.52E+07	7.18	3.09E-07	-6.51
BkF	1.59E+07	7.20	4.90E-08	-7.31
BaP	1.56E+07	7.19	8.16E-08	-7.09
IND	5.79E+06	6.76	2.15E-08	-7.67
DahA	4.64E+06	6.67	2.38E-08	-7.62
BghiP	1.39E+07	7.14	1.45E-08	-7.84

Table 4.46. Calculated soil-air exchange parameters for summer

Compound	K_{SA}	Log K_{SA}	f_s/f_A	Log f_s/f_A
ACY	5.08E+05	5.71	2.77E-07	-6.56
ACE	2.13E+05	5.33	1.70E-04	-3.77
FLU	3.54E+05	5.55	1.06E-04	-3.97
PHE	2.82E+05	5.45	1.26E-05	-4.90
ANT	3.25E+05	5.51	3.36E-04	-3.47
FLT	4.15E+05	5.62	7.28E-07	-6.14
PYR	3.64E+05	5.56	1.19E-06	-5.93
BaA	5.75E+05	5.76	6.24E-12	-11.20
CHR	5.97E+05	5.78	3.42E-13	-12.47
BbF	6.82E+05	5.83	1.28E-08	-7.89
BkF	6.15E+05	5.79	1.75E-09	-8.76
BaP	1.21E+06	6.08	5.81E-09	-8.24
IND	1.71E+06	6.23	5.86E-09	-8.23
DahA	1.21E+07	7.08	5.73E-08	-7.24
BghiP	2.76E+06	6.44	2.65E-09	-8.58

4.3. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are the compounds produced for the dielectric fluids and adhesive in motor oils and do not have natural origins but have anthropogenic sources in the environment (Kim and Masunaga 2005). The production of the PCBs is restricted in some countries, while being entirely banned in most countries. However, the use of PCBs in the past has caused important pollution loadings on the environment (Stevens *et al.*, 2001). When these compounds released into the environment, they can persist there or decompose into dangerous compounds by chemical transformations (Guerzoni *et al.*, 2005; Cindoruk *et al.*, 2007).

4.3.1. PCBs in air

The atmosphere behaves as a sink for PCBs as well as other volatile and semi-volatile compounds. Main sources of the PCBs include direct emissions from the plants and vaporization from the dump sites (Biterna and Voutsas, 2005; Taşdemir and Holsen, 2005).

4.3.1.1. Statistical Interpretation of Data

Gas and particle phases of 15 PCBs in the field were measured from June to August of 2007 and from December of 2007 to February of 2008. The sampling point was selected from rural-agricultural region of Bolu. Even though the 15 PCBs were targeted, 14 PCBs were determined in the samples except for 2,2',3,4,4',5'-Hexachlorobiphenyl (PCB-138) which was not detected in samples. The concentrations of the 2,4,4'-Trichlorobiphenyl (PCB-28) and 2,4',5-Trichlorobiphenyl (PCB-31) were given as the sum of both compounds due to the separation difficulties by the instrument. The other PCBs determined in this study are 2,2',5-Trichlorobiphenyl (PCB-18), 2,3,3'-Trichlorobiphenyl (PCB-20), 2,4',5-Trichlorobiphenyl, 2,4',5-Trichlorobiphenyl (PCB-52), 2,2',4,5,5'-Pentachlorobiphenyl (PCB-101), 2,3,3',4,4'-Pentachlorobiphenyl (PCB-105), 2,3,3',4,5'-Pentachlorobiphenyl (PCB-108), 2,2',3,4',5',6-Hexachlorobiphenyl (PCB-149), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB-153), 2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB-170), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB-180), and 2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB-194).

The observed percentage for the total (gas and particle phase) PCBs ranged from 3 % to 91 %, with the least observed one being PCB-44 and the most observed ones being PCBs-28 and 31. In addition, PCBs-158 and PCB-20 had also a relatively high percentage of observation. However, the remaining PCBs had a relatively low percentage of observations.

As far as PCB concentrations are concerned, PCB-52, PCBs-28 and -31, and PCB-194 were 38.7, 23.4 and 20.6 pg m^{-3} , respectively. The lowest mean PCB concentration belonged to PCB 170 of 2.93 pg m^{-3} (Table 4.47). The PCBs as well as PAHs and OCPs in air exhibit a log normal distribution of data. The closeness of a geometric mean to median shows that log-transformed data follows a normal (Gaussian) distribution. The frequency plots given in Figure 4.26 reveal the log normal distributions of PCBs, as well.

Table 4.47. Statistical assessment of total (gas and particle phase) concentrations of PCBs (pg m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
PCB-18	39	41	13.1	11.4	9.02	10.2	0.665	44.4	43.8
PCB-31+28	87	91	23.4	15.8	13.8	27.6	0.440	161	160
PCB-20	72	75	50.8	23.4	25.3	53.6	0.693	203	202
PCB-52	22	23	38.7	22.4	20.4	46.0	1.91	184	183
PCB-44	3.1	3	10.3	10.0	9.87	3.52	6.88	13.9	7.03
PCB-101	57	59	5.34	3.81	3.06	5.77	0.0674	31.1	31.0
PCB-149	55	57	4.92	3.67	3.24	4.26	0.117	21.6	21.4
PCB-118	42	44	4.57	3.10	2.73	4.39	0.121	20.0	19.9
PCB-153	75	78	6.25	4.26	3.67	5.60	0.111	26.5	26.4
PCB-105	20	21	10.7	8.33	5.97	9.96	0.671	34.4	33.7
PCB-180	27	28	17.9	19.6	15.2	8.92	2.51	38.9	36.3
PCB-170	28	29	2.94	2.14	1.65	4.00	0.229	20.1	19.8
PCB-194	18	19	20.6	4.67	5.23	35.8	0.0620	120	120

*Total samples analyzed: 96

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

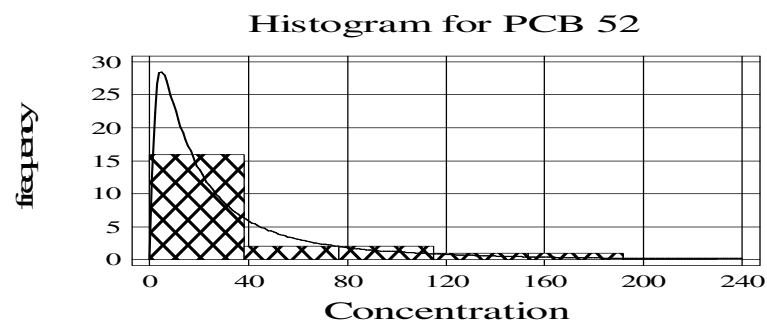
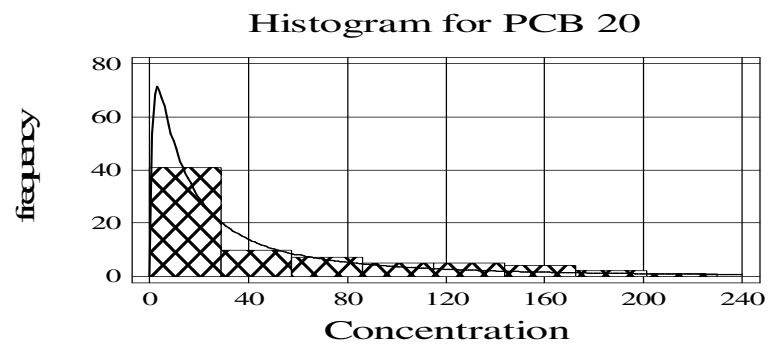
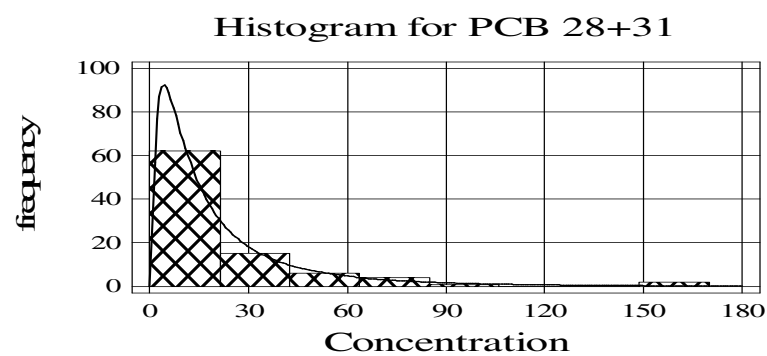
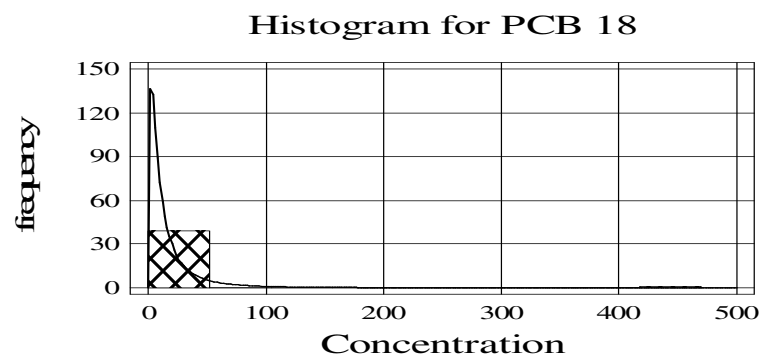


Figure 4.26. Statistical distribution of PCB concentrations (pg m^{-3})

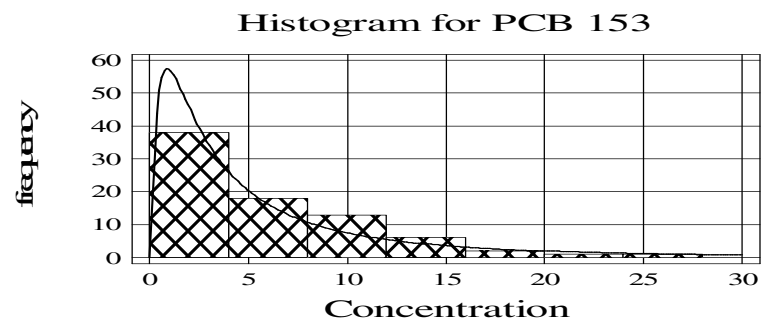
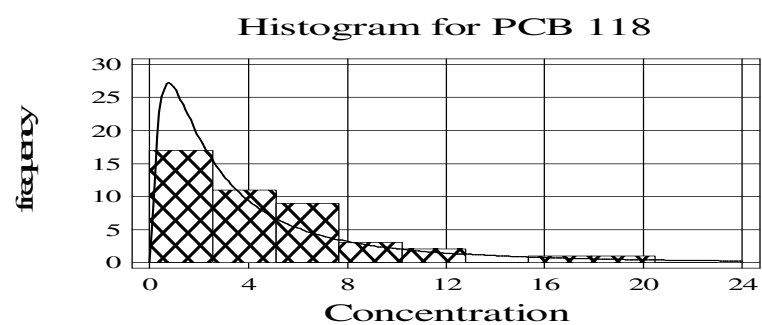
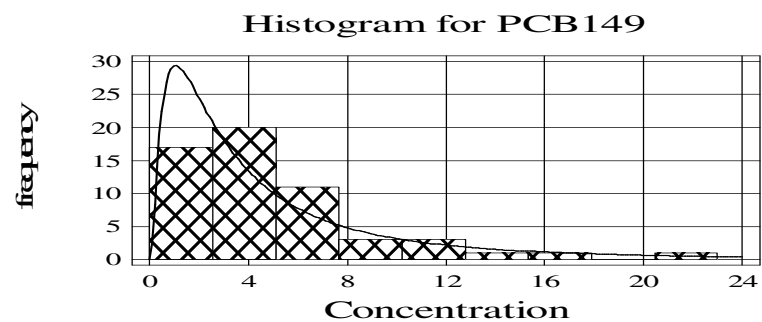
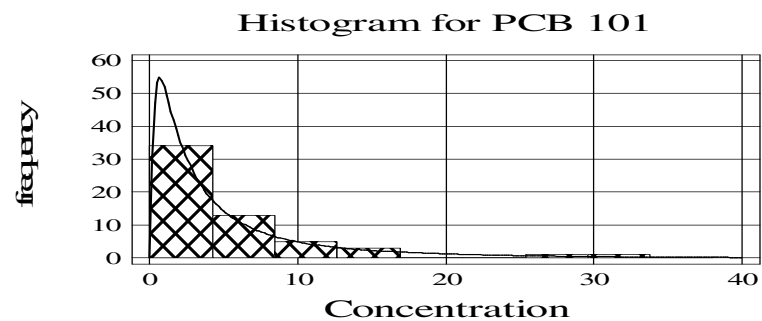


Figure 4.26. Statistical distribution of PCB concentrations (pg m^{-3}) (Continued)

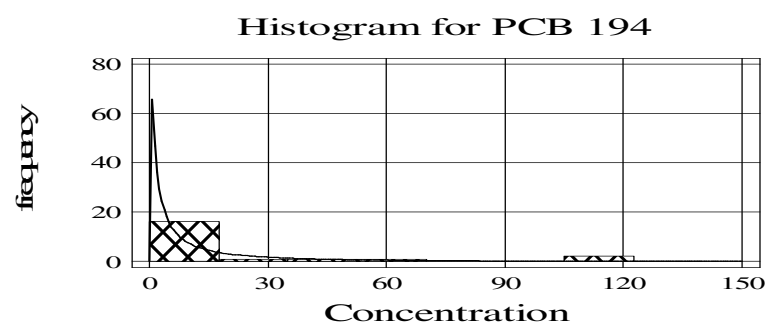
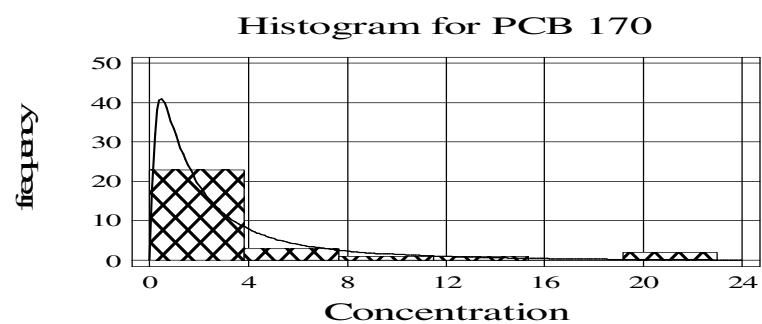
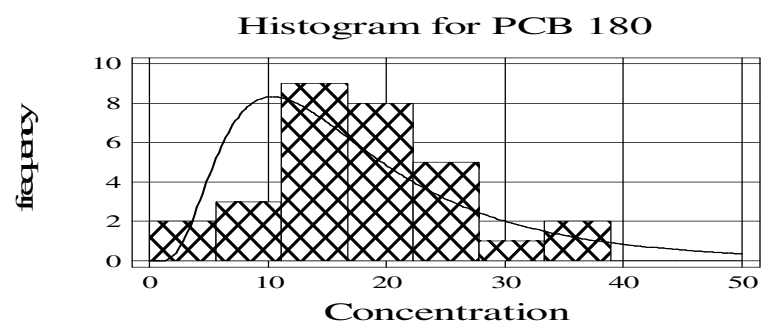
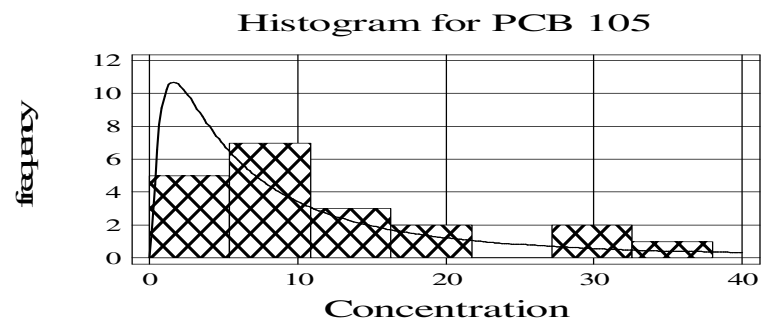


Figure 4.26. Statistical distribution of PCB concentrations (pg m^{-3}) (Continued)

4.3.1.2. Diurnal Distribution of PCBs

Total (gas and particle phase) concentrations of the PCB congeners obtained in this study are summarized in Figures 4.27 to 4.29 representing the homolog groups of the PCBs. It is clear that 3- and 4-chlorinated biphenyls had the highest concentrations, which had higher vapor pressure than 5 and more-chlorinated biphenyls. For instance, PCB-20 showed significantly high concentrations (50.8 pg m^{-3}) in the entire PCBs, whereas PCB-170 (hepta-chlorinated biphenyl) had the lowest one. The compositional PCB profiles showed that 3- and 4-chlorinated compounds were abundant. The concentration of total PCBs (ΣPCB , sum of 12 PCB congeners) in the ambient air (vapor plus particle-phase) of the rural area of Bolu ranged from 1.02 to 562 pg m^{-3} , with an average value of 99.7 pg m^{-3} . This value is similar to the total PCB concentrations of 110 pg m^{-3} in the rural area of Germany as shown in the study by Mandalakis and Stephanou (2007). The concentrations of the PCBs were generally increasing in winter months.

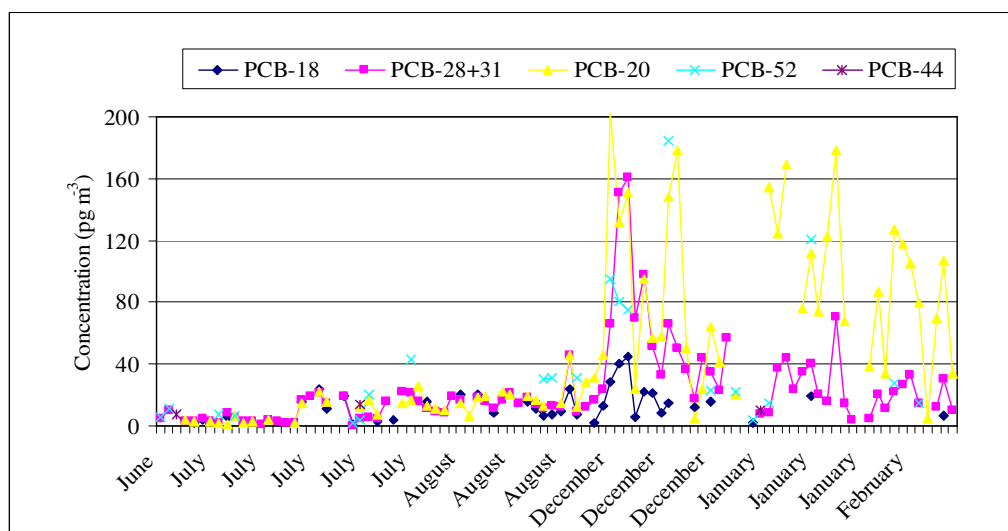


Figure 4.27. Daily concentrations of PCBs (3- and 4-chlorinated)

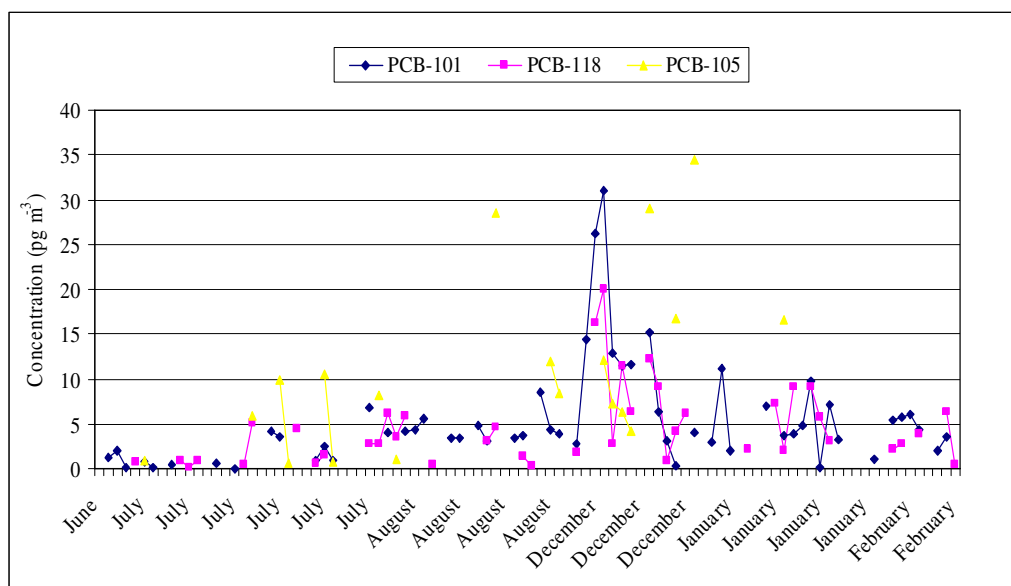


Figure 4.28. Daily concentrations of PCBs (5-chlorinated)

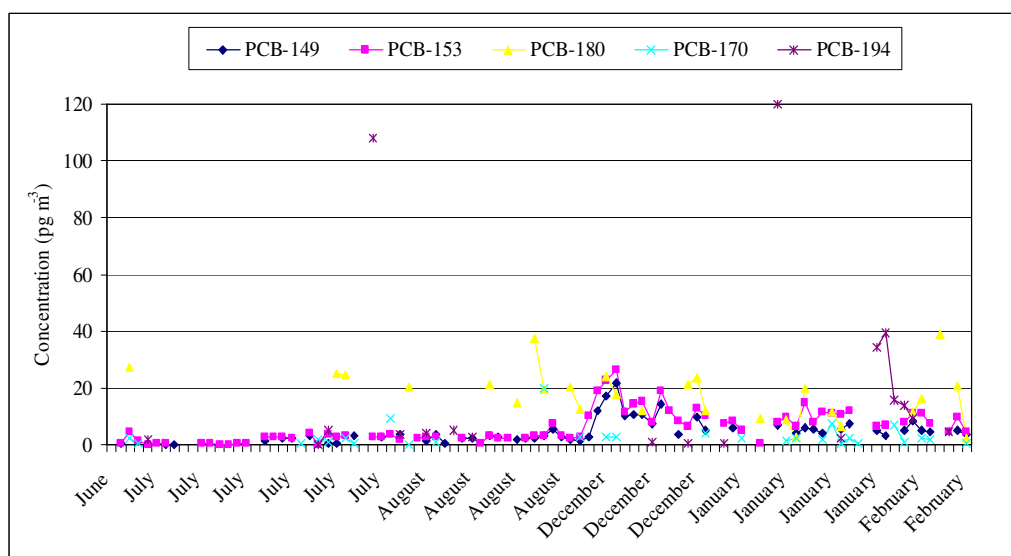


Figure 4.29. Daily concentrations of PCBs (6- and more chlorinated)

4.3.1.3. Seasonal Changes in PCBs

The concentrations of 15 PCBs were evaluated to find out their seasonal variations in the air in both of gas and particle phases. PCB-138 was not detected in the summer samples of gas phase as it was explained in the previous sections. In Table 4.48, PCB-28+31, PCB-153 and PCB-20 had the highest observation percentage, whereas PCB-44, PCB-170, and PCB-180 had the lowest observation percentage in the summer. Although, the highest mean values belong to PCB-180 and PCB-194, we will not consider them due to their low observation percentage. Meanwhile, PCB-153 and PCB-149 had the lowest mean concentrations with a moderate observation percentage. Mean concentration of the PCBs for the gas phase summer samples varied between 2.31 pg m^{-3} and 38.3 pg m^{-3} . The order from higher to lower concentrations is as follows: PCB-52 > PCB-20 > PCB-28+31 > PCB-18 > PCB-105.

Table 4.48. Statistical evaluation of gas phase PCB concentrations for summer samples (pg m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
PCB-18	23	43	10.5	8.00	7.60	7.45	0.665	23.9	23.3
PCB-28+31	49	91	10.7	10.7	7.34	8.38	0.441	46.1	45.6
PCB-20	34	63	13.4	13.6	10.0	9.31	1.79	45.2	43.5
PCB-52	9	17	20.5	19.8	16.0	13.6	5.77	42.6	36.8
PCB-44	2	4	10.4	10.4	9.79	4.97	6.88	13.9	7.03
PCB-101	28	52	2.95	3.35	1.87	2.12	0.0674	8.50	8.43
PCB-149	24	44	2.33	2.45	1.75	1.27	0.117	5.61	5.49
PCB-118	16	30	2.77	2.71	2.02	1.98	0.466	6.27	5.80
PCB-153	35	65	2.31	2.39	1.73	1.47	0.222	7.39	7.17
PCB-105	8	15	9.18	9.12	7.05	4.93	0.671	17.9	17.2
PCB-180	4	7	22.5	22.6	22.2	4.58	17.3	27.5	10.3
PCB-170	3	6	3.87	2.23	1.86	4.60	0.316	9.07	8.75
PCB-194	3	6	38.3	4.22	10.6	60.4	2.62	108	106

*Total analyzed samples: 54

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Statistical evaluation of the summer samples of particle phase is given in Table 4.49. The percent observations of 12 PCBs ranged from 4 % to 27 % among the 56 samples. PCB-153 and PCB-28+31 had the highest percent observation, and PCB-52 and PCB-149 had the lowest percent observation. The mean concentrations of the PCBs varied between 0.28 and 60.1 pg m^{-3} . The highest mean concentration was determined for PCB-180, and the lowest one for PCB-149. Although PCB-44 was determined in the PCBs of gas phase, it was not detected in the summer samples of particle phase. The range of the particle phase concentrations for summer season as follows: PCB-105 > PCB-18 > PCB-20 > PCB-194 > PCB-170 > PCB-52 > PCB-28+31 > PCB-118 > PCB-153.

Table 4.49. Statistical evaluation of PCB concentrations of particle phase for summer samples (pg m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
PCB-18	3	5	6.36	2.31	3.18	8.29	0.88	15.90	15.0
PCB-28+31	15	27	2.31	0.805	1.02	4.56	0.269	18.4	18.1
PCB-20	5	9	4.74	1.29	1.68	7.94	0.309	18.9	18.6
PCB-52	2	4	2.60	2.60	2.50	0.974	1.91	3.29	1.38
PCB-149	3	5	0.286	0.237	0.248	0.183	0.131	0.488	0.357
PCB-118	7	13	0.922	0.275	0.408	1.62	0.121	4.58	4.46
PCB-153	15	27	0.455	0.258	0.319	0.556	0.111	2.36	2.24
PCB-105	5	9	6.39	0.912	1.71	12.4	0.690	28.5	27.8
PCB-180	6	11	20.2	20.4	19.9	3.11	14.8	24.4	9.62
PCB-170	10	18	2.81	0.781	1.00	6.09	0.229	20.1	19.8
PCB 194	6	11	3.14	3.29	1.80	1.93	0.0620	5.19	5.13

*Total analyzed samples: 56

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

The data given in Table 4.50 represent the statistical calculations for the PCBs of gas phase in the winter. Percent observation range varied between 11 % and 85 %. The lowest percent observation belonged to the PCB 105, while the highest ones were PCB-28+31 and PCB-153. As for the mean values, the highest mean value

was obtained for PCB-20, and the lowest one for PCB-170. The mean concentrations of the remaining PCBs are in the following order of PCB-52 > PCB-28+31 > PCB-194 > PCB-18 > PCB-180 > PCB-153 > PCB-101 > PCB-149 > PCB-118 > PCB-105.

Table 4.50. Statistical evaluation of PCB concentrations of gas phase in winter samples (pg m^{-3})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
PCB-18	13	28	15.4	13.6	11.9	10.9	1.46	40.42	39.0
PCB-28+31	40	85	30.1	23.8	22.9	26.7	3.83	144	140
PCB-20	37	79	81.2	69.0	65.4	44.7	2.07	178	176
PCB-52	9	19	47.8	27.5	36.3	37.3	14.3	121	107
PCB-101	30	64	6.39	4.97	5.18	5.33	1.94	26.2	24.2
PCB-149	31	66	6.21	5.50	5.62	3.16	1.61	17.2	15.6
PCB-118	17	36	5.80	3.87	4.68	4.12	1.81	16.3	14.5
PCB-153	40	85	7.24	6.66	5.56	3.56	0.00576	19.9	19.9
PCB-105	5	11	3.78	2.23	3.12	2.55	1.48	6.69	5.21
PCB-180	15	32	12.0	11.7	9.88	6.57	2.51	23.4	20.9
PCB-170	8	17	2.50	2.33	1.90	2.11	0.491	7.35	6.86
PCB-194	11	23	24.3	13.7	8.44	34.5	0.305	120	120

*Total analyzed samples: 47

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

Statistical calculations were performed for the PCB concentrations of particle phase in the winter season as given in Table 4.51. Eleven compounds were also observed for the winter samples and the percent observation varied between 7 % and 60 %. The most of PCBs had percent observations lower than 30 % except for the PCB-153, PCB-28+31 and PCB-20. As different from the winter samples of the gas phase, PCB-194 was not detected in the samples. PCB-170 had the lowest mean concentration (1.96 pg m^{-3}), whereas PCB-52 had the highest concentration (61.8 pg m^{-3}). PCB-20, PCB-180, PCB-28+31 and PCB-105 had the highest mean concentrations (27.1 , 16.9 , 16.0 and 15.7 pg m^{-3}), respectively.

Table 4.51. Statistical evaluation of PCB concentrations of particle phase for winter samples ($\mu\text{g m}^{-3}$)

Compound	<i>N</i>	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range
PCB-18	10	18	7.55	5.70	5.86	5.10	1.64	16.0	14.4
PCB-28+31	30	55	16.0	9.60	11.1	15.2	2.31	64.1	61.8
PCB-20	23	42	27.1	21.7	19.1	23.9	2.07	92.3	90.2
PCB-52	4	7	61.8	29.3	26.4	83.4	3.89	184	181
PCB-101	14	25	5.00	4.63	2.95	3.71	0.144	10.5	10.4
PCB-149	11	20	4.34	4.91	3.77	2.30	1.57	8.88	7.31
PCB-118	15	27	4.79	3.56	3.29	4.11	0.415	16.4	15.9
PCB-153	33	60	4.49	3.33	3.76	2.91	1.23	13.9	12.8
PCB-105	7	13	15.7	15.2	9.62	11.9	0.637	34.4	33.8
PCB-180	7	13	16.9	19.4	16.0	5.61	9.37	24.2	14.8
PCB-170	12	22	1.96	2.00	1.44	1.53	0.287	6.03	5.74

*Total analyzed samples: 55

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, *N*: Number of Observed Samples

4.3.1.3.1. Seasonal Ratios

Seasonal variations of particle and gas phase PCBs are noted in the following section. The seasonal contributions (%) of the PCB congeners during the sampling periods are shown in Figure 4.30. The seasonal mean contributions of the PCB congeners for total particle and gas phase PCBs were calculated in order to make a direct comparison of the PCB congeners' distribution between the seasons (Figure 4.31). The contributions of the PCB congeners were 68 % for tri-CBs, 9 % for tetra-CBs, 7 % for penta-CBs, 8 % for hexa-CBs, 5 % for hepta-CBs, and 3 % for octa-PCBs in the winter. However, the contributions of the PCB congeners in the summer months were as follows: 55 % for tri-CBs, 10 % for tetra-CBs, 10 % for penta-CBs, 7 % for hexa-CBs, 12 % for hepta-CBs, and 6 % for octa-PCBs.

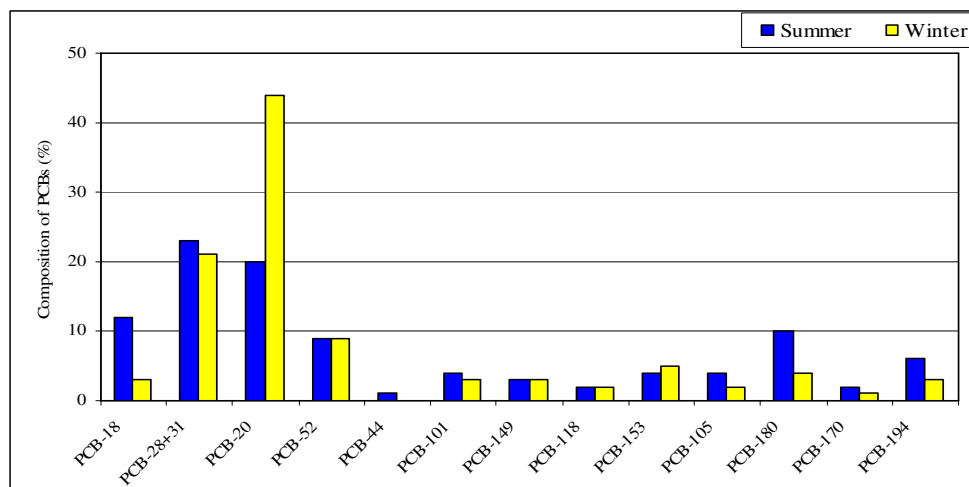


Figure 4.30. PCB profiles for winter and summer seasons

Most PCB congeners showed a maximum contribution in the winter and a minimum in the summer (Figure 4.31) which would be the result of the production as a byproduct. Grenier and Chevreuil (1997) reported a clear augmentation of particle phase PCBs in the winter which can be linked both to a drop of temperature and an increase in suspended particles. In other words, particle matter is enriched in the PCBs under the colder weather conditions. This could be an explanation for a greater incorporation of condensed gas phase material at a low temperature.

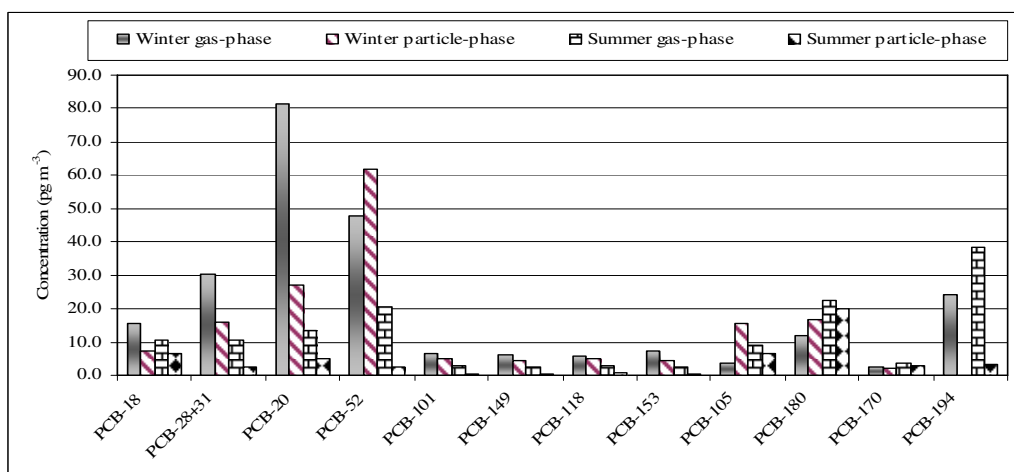


Figure 4.31. Mean concentrations of gas and particle phase PCBs

In Figure 4.32, the gas phase PCB concentrations showed significantly high values in the winter, while particle phase PCBs had relatively low values in both seasons. However, the total gas phase PCBs were in very low quantity in the summer. The PCBs were in gas phase rather than the particle phase due to the diurnal effects. When the chlorination number increased, the observation and mean concentrations decreased because of physicochemical properties.

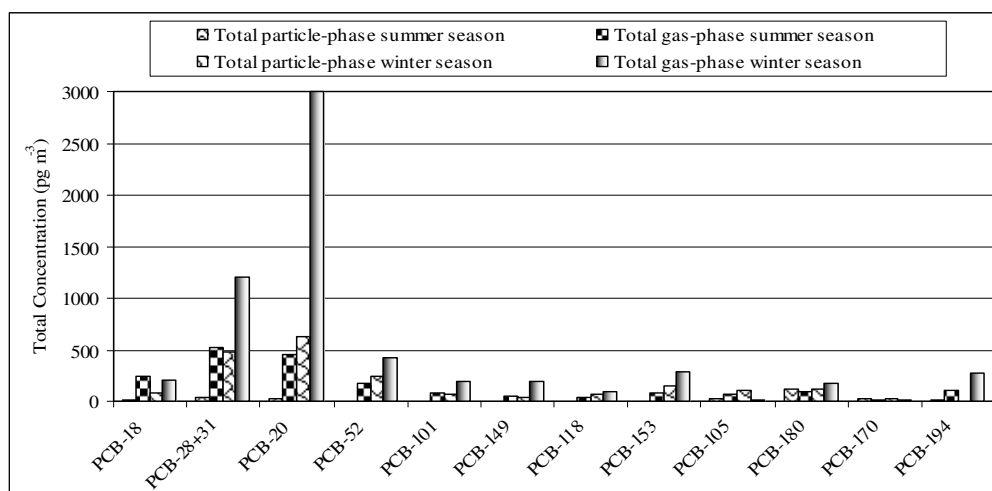


Figure 4.32. ΣPCB concentrations for winter and summer seasons

The higher concentration fraction of the PCB congeners with a low molecular weight observed at the sampling area showed that this site is most likely to be considerably influenced by long-range transport, which involves mainly less chlorinated congeners (Oehme *et al.*, 1996; Wania and Mackay, 1996). A similar result was obtained by Yeo *et al.* (2004) in that the concentration fraction of the low molecular-mass PCB congeners (tri-CBs) was found to contribute more in the rural rather than in the urban areas. Thus, Yeo *et al.* (2004) reasoned that the concentrations of the PCBs may be affected more by long-range transport in the rural areas than in the urban areas.

4.3.1.4. A Comparison of PCB Concentrations with Related-Literature Values

The concentrations of the PCBs in the related-literature were compared for similar and different regions in order to determine PCB loadings in Bolu (Table 4.52). Although the use of these compounds have been banned in Turkey since 1980s, the determined concentrations showed that PCBs persist in the environment as a result of extremely high application rates in the past. The PCB concentrations in the industrial and urban areas as reported in the study by Çetin *et al.* (2007) were significantly higher than those in this study except for the urban region in summer. Çetin *et al.* (2007) found the lower concentrations than this study for the high molecular weighed PCBs such as PCB-170, PCB-180, and PCB 194. Mandalakis and Stephanou (2007) and Yeo *et al.* (2004) found the PCB concentrations in a rural area lower than this study. Panshin and Hites (1994) estimated PCB-18, PCB-44 and PCB-101 concentrations in a rural area were higher than that of this study, and the other PCBs were lower than that of this study.

Table 4.52. A comparison of PCB concentrations with related-literature mean values (pg m⁻³)

Reference	PCB-18	PCB-28+31	PCB-20	PCB-52	PCB-44	PCB-101	PCB-149	PCB-118	PCB-153	PCB-105	PCB-180	PCB-170	PCB-194
This study (Bolu, Turkey), rural, agricultural, particle	7.21±5.32	10.1±12.2	23.1±23.5	47.3±78.6		4.01±3.45	3.30 ±2.26	2.97±2.77	2.80±2.62	11.8±12.5	18.9 ± 4.52	2.42±4.25	3.21±2.14
This study (Bolu, Turkey), rural, agricultural, gas	12.5 ± 9.0	19.4± 1.6	48.7±47.3	34.2±30.6	10.3 ± 3.52	4.82±4.57	4.57±3.23	4.32±3.62	4.95±3.78	6.58±3.77	15.06±7.40	3.13±2.80	27.31±40.53
This study (Bolu, Turkey), rural, agricultural, total	13.1 ±10.2	23.4±27.6	50.8±53.6	30.3±33.2	10.3 ±3.52	5.34±5.77	4.92±4.26	4.57±4.39	6.25±5.60	10.7±9.96	17.90±8.92	2.93±4.00	20.62±35.83
Yeo <i>et al.</i> , 2004 (Korea), rural, total				2		4.37		0.8	0.55		0.19		
Mandalakis and Stephanou, 2007 (Germany), rural, total				8		3			2		1		
Cotham and Bidleman, 1995, (Chicago, USA), urban, total	188±196	158±152		123±143	58±55	100±147		46±69	96±175	16±22	75±167	63±112	
Panshin and Hites, 1994 (Bermuda) rural, total	16.7±11.6			17.6±11.4	21.7±13.8	10.2±6	1.8±1.8				0.5±0.6		0.1±0.1
Cindoruk and Taşdemir, 2007 (Bursa, Turkey), urban, particle	9.86±7.23	17.06±6.64		8.74±6.35		0.6±1.23	0.38±1	0.89±1.51	1.49±1.9				
Cindoruk and Taşdemir, 2007 (Bursa, Turkey), urban, gas	60.65±25.16	105.82±44.06		33.39±16.39	13.18±13.39	7.12±4.46	5.56±3.3	6.89±6.49	7.63±4.37	0.06±0.27	0.68±1.21		0.3±1.25
Çetin <i>et al.</i> , 2007 (İzmir, Turkey), Industrial, winter	212.3±105.9	260.3±84.7		96.2±44.5	64.8±26.6	44.3±22.8		27.4±14.0	29.5±16.8	11.1±6.5	11.8±5.9	5.2±5.0	
Çetin <i>et al.</i> , 2007 (İzmir, Turkey), Industrial, summer	520.1±200.3	615±150		222.2±53.2	137.3±27.4	97.6±22.5		55.6±13.0	67.3±22.5	24.9±6.2	22.0±9.1	12.4±6.0	1.5±2.7
Çetin <i>et al.</i> , 2007 (İzmir, Turkey), urban, winter	92.7±107.4	155.8±103.6		63.3±44.7	38.3±29.7	26.3±11.9		17.8±7.8	19.9±2.2	7.1±3.5	8.6±1.4	4.6±1.7	1.1±2.7
Çetin <i>et al.</i> , 2007 (İzmir, Turkey), urban, summer	31.0±12.9	45.3±14.7		20.9±9.4	13.4±5.5	11.0±4.5		7.6±2.8	11.9±4.8	3.3±0.8	6.7±4.4	2.7±2.1	0.9±2.3

In the urban region, Cindoruk and Taşdemir (2007) had similar PCB concentrations as far as gas and particle phase concentrations are concerned. Cindoruk and Taşdemir (2007) found that the gas phase PCB concentrations were higher than the particle phase ones as with this study. Particle phase PCB concentrations in the study by Cindoruk and Taşdemir (2007) were lower than this study except for PCB-18, whereas gas phase PCB concentrations in the region were higher than this study except for the higher chlorinated and higher molecular weighed-PCBs such as PCB-105, PCB-180 and PCB-194. Another study for the urban region published by Cotham and Bidleman (1995) indicated the higher PCB concentrations than this study.

4.3.1.5. Wind Sector Analysis

The wind directions were determined in order to identify the sources of PCBs. The total, gas and particle concentrations are given with respect to the wind directions in Tables 4.53 to 4.54. High concentrations are shown in bold in tables. The predominant wind direction in the summer is in the south and west directions. Hence, SSW and SW had the greatest contributions to the PCBs. In addition, high mean concentrations of PCB-118, PCB-180, and PCB-194 were observed in N, E and WSW directions, respectively. In the winter, the prevailing wind direction was from the east and the south. The ESE and WSW winds had a high effect on the concentrations of the PCBs. Also, the SE and SSE winds significantly affected PCB-105, PCB-118, PCB-170, PCB-180, and PCB-194 concentrations. As can be seen in Table 4.7, there are not common industrial regions except for wood-pulp plant. Therefore, the contribution of these directions may be due to long-range transport.

Table 4.53. Mean and standard deviations of total concentrations of PCBs in summer with respect to wind directions (pg m⁻³)

Sector	SSW	SW	WSW	W	WNW	N	NE	ENE	E	SE
N*	2	2	25	8	4	2	2	2	1	1
PCB-18	15.4		10.3±7.14	9.11±8.74	4.03±2.13	15.5	10.6	23.9	7.63	
PCB-28+31	27.7	18.1	10.7±7.01	7.71±6.51	7.94±5.43	17.8	13.5	11.7	12.9	1.18
PCB-20	28.7	20.8	12.1±5.76	7.44±7.11	9.86±9.25	14.7	21.6	12.0		
PCB-52	31.2	42.6	10.5±13.3	6.94	19.8				30.6	
PCB-101	6.40	6.80	2.88±1.99	1.54±1.37	1.61±1.54		3.73	4.13	3.76	
PCB-149	4.27	2.65	2.24±1.34	1.64±1.44	1.25±1.25	1.58	2.23	2.31	2.45	
PCB-118		2.82	2.78±2.39	1.30±1.56	1.48	5.15		0.540	1.39	
PCB-153	5.28	3.25	1.95±1.33	1.51±1.45	2.06±0.74	2.65	2.28	2.74	3.06	0.111
PCB-105	12.0	8.29	6.38±12.37	0.726	10.51	5.90	9.12			
PCB-180			20.4±0.8	19.6±6.80	24.9		20.4		37.7	
PCB-170		9.07	3.50±7.32	2.22	0.621					
PCB-194			20.7±42.9	3.49±2.00						

N*: Number of windy days

Table 4.54. Mean and standard deviations of total concentrations of PCBs in winter with respect to wind directions (pg m⁻³)

Sector	S	SSW	SW	WSW	ENE	E	ESE	SE	SSE
N*	3	3	3	8	3	2	3	5	13
PCB-18		13.1	22.1	16.1±17.4	15.1±19.1	11.6	23.2±24.3	15.9	17.1±3.06
PCB-28+31	19.7±4.32	26.0±17.1	52.2±42.4	63.6±59.5	51.0±29.7	11.2	62.6±76.8	37.5±17.2	28.1±15.7
PCB-20	98.4±34.5	82.9±74.9	61.9±36.0	61.8±52.9	137.5±92.8	21.8	119.0±17.2	96.6±54.3	91.0±46.6
PCB-52				33.6±36.7	95.3		80.7	22.6	72.4±76.9
PCB-101	4.55±4.87	2.71	7.41±5.80	13.7±10.6	10.7±5.20	0.316	14.9±15.9	3.84±1.61	5.86±3.92
PCB-149	4.31±0.01	3.18±0.69	9.23±1.97	11.2±6.13	6.33±5.32	4.88	11.2±8.44	5.52±0.80	6.43±3.38
PCB-118	5.65±3.57	3.17±3.64	8.84±3.75	9.75±9.05	3.14	4.11	8.32±7.23	9.15±0.01	4.41±4.53
PCB-153	9.79±2.72	8.25±3.07	13.1±1.1	12.4±7.74	10.8±8.05	6.50	10.9±11.2	9.77±4.02	9.77±3.87
PCB-105	16.6		6.43	7.88±3.96		16.7		34.4	28.9
PCB-180	7.35±6.22	5.58±4.35	23.4	14.8±3.71	9.48±4.16	21.1	18.2±7.82	15.9±5.5	22.3±14.5
PCB-170	3.86±3.03	0.949±0.937	2.44	1.82±1.28	1.63±1.39		2.56	4.00	3.08±2.60
PCB-194					2.36	17.2		2.50±2.76	39.7±46.5

N*: Number of windy days

The gas phase and particle phase concentrations were separately evaluated with respect to the wind direction analysis. Wind direction and the distribution of the gas phase concentration in the summer are given in Table 4.55. The prevalent wind directions were the SSW and the SW for the gas phase PCBs. Gas phase concentrations were affected from the local sources. Particle phase PCBs were high in the WSW and W directions. The south directions had also contribution to the gas phase PCB compounds. These concentrations mainly transported from the highly industrial regions, such as; Kocaeli, Sakarya, and Düzce. According to wind directions, the particle phase concentrations of the PCBs are given in Table 4.56. In general, PCB concentrations were found to be high in the WSW, SW, SSW, and W wind directions in the summer. Eskişehir, Kocaeli, Düzce are on these directions.

For the winter, the evaluation of the concentrations of gas phase PCBs with respect to the wind directions is given in Table 4.57. The ESE direction had high effects on the concentration of most PCBs, while the S, SW, SE, SSE, and WSW directions had a high contribution to PCB-170, PCB-153, PCB-180, PCB-194, PCB-20, and PCB-118, for the gas phase samples. The local sources contribute at these directions. The wind direction analysis of the particle phase samples is given in Table 4.58. High concentrations of the particle phase PCB-18 and PCB-28+31 were present in the SW and WSW directions, while the SE and E directions had a high effect on the concentrations of PCB-105 and PCB-180, respectively. Although dominant wind direction was SSE, the concentrations of only PCB-52 and PCB-170 were affected by that direction. The ENE direction had the greatest effect on PCB-20 and PCB-101, while the S direction affected PCB-118, PCB-149, and PCB-153. The industrial cities appear at these directions such as Eskişehir and Ankara.

Table 4.55. Mean and standard deviations of the gas phase summer concentrations of PCBs with respect to wind directions (pg m⁻³)

Sector	WSW	W	WNW	N	NE	ENE	E	SSW	SW	SE
N*	25	9	4	2	3	2	1	2	2	1
PCB-18	9.78±7.25	9.55±8.32	4.03±2.13	15.5	10.6	23.9	7.62	15.4		
PCB-28+31	10.0±6.92	7.39±6.24	7.46±5.51	17.2	14.6±2.26	11.8	12.9	27.7	18.1	0.706
PCB-20	11.4±5.67	7.44±7.10	12.9±8.50	14.7	22.2±6.52	12.0		28.7	20.8	
PCB-52	18.3±16.9	6.94	19.8				30.6	31.2	42.6	
PCB-101	2.84±2.03	1.67±1.15	1.61±1.54		3.73±0.31	4.13	3.76	6.40	6.81	
PCB-149	2.62±1.12	1.64±1.44	1.24±1.25	1.57	2.23±0.32	2.31	2.45	4.26	2.65	
PCB-118	3.16±2.44	1.66±1.34	1.48	5.14	4.61	0.540	1.39		2.82	
PCB-153	2.05±1.28	1.35±1.24	1.82±1.16	2.52	2.03±0.17	2.39	3.06	5.28	3.25	
PCB-105	0.671		10.5	5.90	12.0±5.11			12.0	8.29	
PCB-180			24.9		20.4		17.3			
PCB-170		0.316							9.07	
PCB-194	38.3±60.4									

N*: Number of windy days

Table 4.56. Mean and standard deviations of particle phase summer concentrations of PCBs with respect to wind directions (pg m⁻³)

Sector	WSW	W	WNW	N	NE	ENE	E	ESE	SE
N*	27	8	4	2	2	2	1	1	1
PCB-18	118.7±145.3	2.31						0.8773	
PCB-28+31	5.13±7.54	0.480±0.231	0.964±0.841	1.25				0.8783	0.478
PCB-20	7.24±10.1		0.69					1.29	
PCB-52	2.60±0.97								
PCB-101	0.389								
PCB-149	0.363±0.177							0.1315	
PCB-118	1.42±2.12	0.287±0.236						0.2054	
PCB-153	0.551±0.740	0.608	0.728	0.266	0.175	0.350			0.111
PCB-105	7.80±13.80	0.726							
PCB-180	20.4±0.76	19.6±6.80					20.4		
PCB-170	3.50±7.32	2.22	0.621					0.7806	
PCB-194	3.03±2.66	3.49±2.00						2.7671	

N*: Number of windy days

Table 4.57. Mean and standard deviations of gas phase winter concentrations of PCBs with respect to wind directions (pg m⁻³)

Sector	S	SSW	SW	WSW	ENE	E	ESE	SE	SSE
N*	3	5	3	8	3	2	3	6	13
PCB-18		8.96	16.7	13.7±14.3	13.6	11.60	23.2±24.3	14.3	17.1±3.06
PCB-28+31	16.4±6.8	21.3±11.2	37.6±27.7	40.8±40.3	35.2	11.2	60.4±72.9	29.5±15.0	24.12±8.59
PCB-20	80.8±36.8	66.1±53.0	67.8±0.30	57.8±34.1	105.9±76.2	38.7	112.5±26.4	109.4±54.8	78.3±39.1
PCB-52				48.5±37.0	52.5		80.7	22.5	44.3±51.47
PCB-101	4.43±1.02	3.25±1.39	7.41±5.80	9.67±7.58	7.06		14.9±15.9	4.04±1.52	5.22±1.19
PCB-149	4.31±0.01	2.99±1.08	7.48±0.10	8.39±4.01	6.15	4.88	11.2±8.44	5.51±0.56	5.71±1.77
PCB-118	3.59±1.94	4.55±3.89	7.07±1.24	13.1	3.14	3.19	9.72±9.32	9.16	4.15±2.56
PCB-153	6.12±.56	4.95±1.06	9.78±0.59	9.13±4.65	5.84	5.72	8.95±9.96	6.51±1.42	7.48±1.72
PCB-105		2.09	6.43	6.69		1.48			2.23
PCB-180	7.35±6.22	4.84±3.33	23.4	14.8±3.71	6.54		21.1	11.42±0.81	15.8±3.87
PCB-170	4.82±3.59	1.61	2.44	1.54±1.48				2.38	0.841
PCB-194					2.36	17.2		10.7±14.3	39.6±46.5

N*: Number of windy days

Table 4.58. Mean and standard deviations of particle phase winter concentrations of PCBs with respect to wind directions (pg m⁻³)

Sector	S	SSW	SW	WSW	ENE	E	ESE	SE	SSE
N*	6	4	4	9	4	3	3	6	15
PCB-18		4.10	10.7±7.52	8.69±2.47	8.34±9.48			3.61±2.74	
PCB-28+31	8.27±2.36	8.97±0.41	35.9±25.7	28.5±20.2	15.8±15.8	6.88	6.72	13.6±8.80	10.7±10.2
PCB-20	17.6±2.37	21.3±3.24	34.9±17.3	26.0±20.9	47.4±60.2	7.9	13.0	25.8±16.2	31.4±31.4
PCB-52	15.9			3.89	42.8				184.5
PCB-101	4.92±4.92		10.5	6.73±2.60	7.36	0.316		4.64	3.05±3.38
PCB-149	8.87		2.62	4.61±1.69	3.35±2.53			4.98	4.07±3.37
PCB-118	11.3±7.21	0.415	5.02	5.37±2.19		0.923	2.76±0.75	5.44	2.71±2.46
PCB-153	7.07±4.70	4.57	4.51	4.98±3.11	5.00±3.88	1.97	3.02±0.21	4.93	3.29±2.48
PCB-105	16.6			5.65±5.86		15.2		34.4	26.7
PCB-180					12.4	21.1	16.8±10.5	19.8	15.6±5.39
PCB-170	1.95	0.287		1.20±1.20	1.63±1.39		2.56	1.62	2.87±2.19

N*: Number of windy days

4.3.1.6. Back Trajectories

The three day backward trajectory drawings give important information about the sources of pollutants, where the air mass starts its journey from the source, where it passes through until it reaches to the sampling station as expressed in the section 4.1.1.6. The trajectories were drawn for the days of the high concentration are shown in Figure 4.33. As it is seen in the wind sector analysis, the dominant wind directions were the south, the east and the west. Although sampling point had low northern windy days, they had the greater contribution to the concentrations. These air masses indicated usually remote sources. The long-range transportation from the north directions derived from the Karabük where, there are blast furnaces and steel plants and Gerede where, there are leather factories (textile dying). The drawn back trajectories distinctly signaled to the transportation from the industrial regions such as Adapazarı and Düzce from west; Eskişehir from the SW; and Ankara from the SE. Other than sources exist in Turkey, there may be effect of the European countries and Russia on the sampling site.

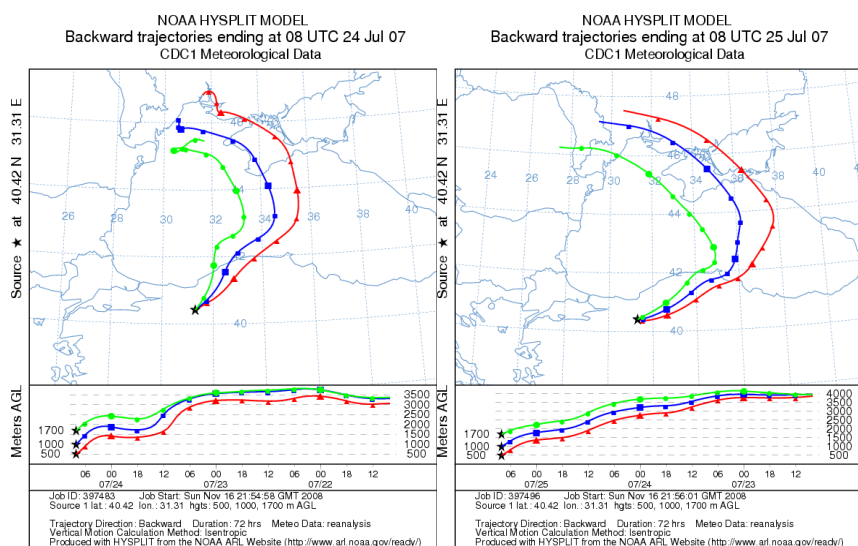


Figure 4.33. Back trajectory models for PCBs

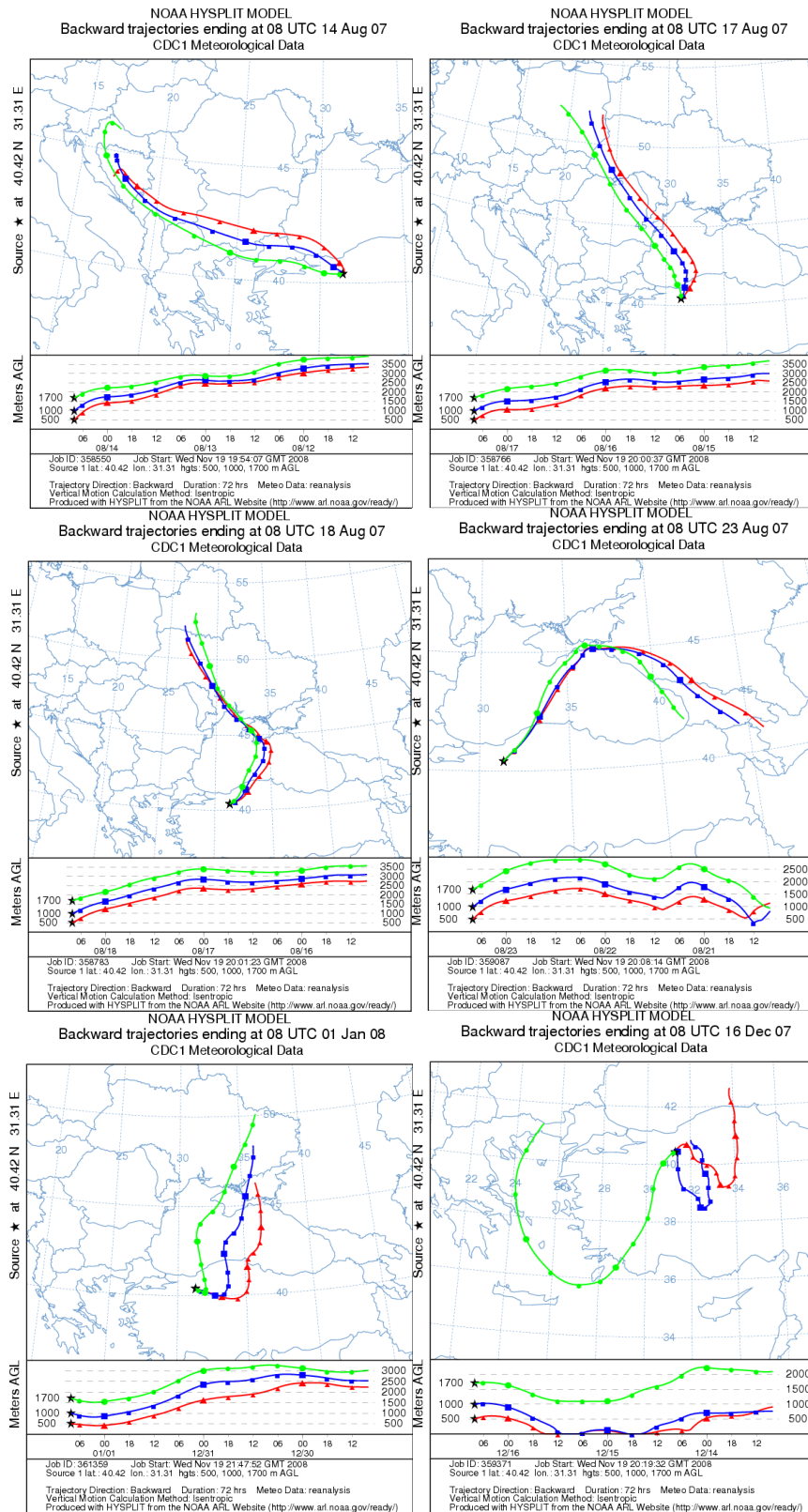


Figure 4.33. Back trajectory models PCBs (continued)

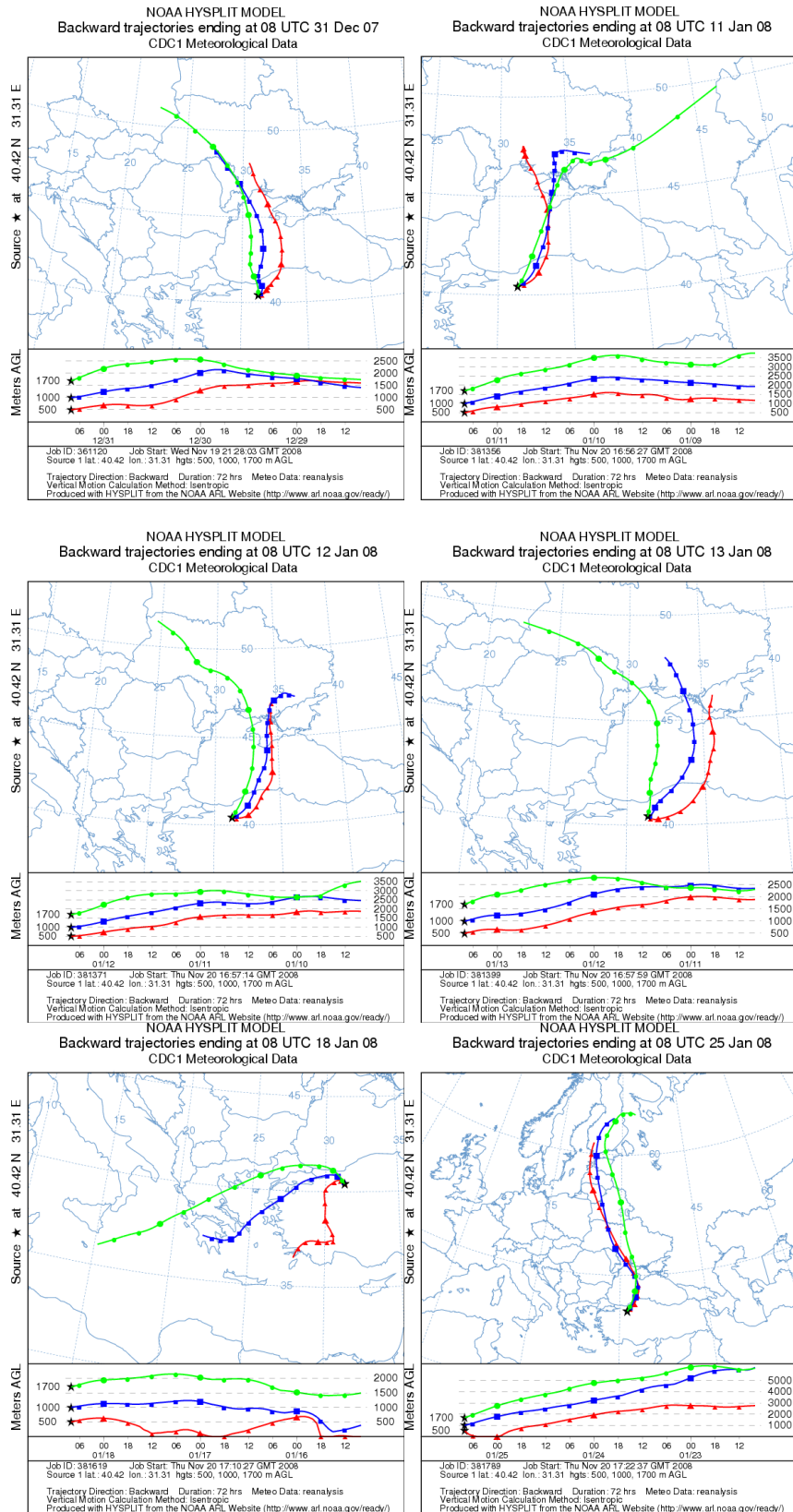


Figure 4.33. Back trajectory models PCBs (continued)

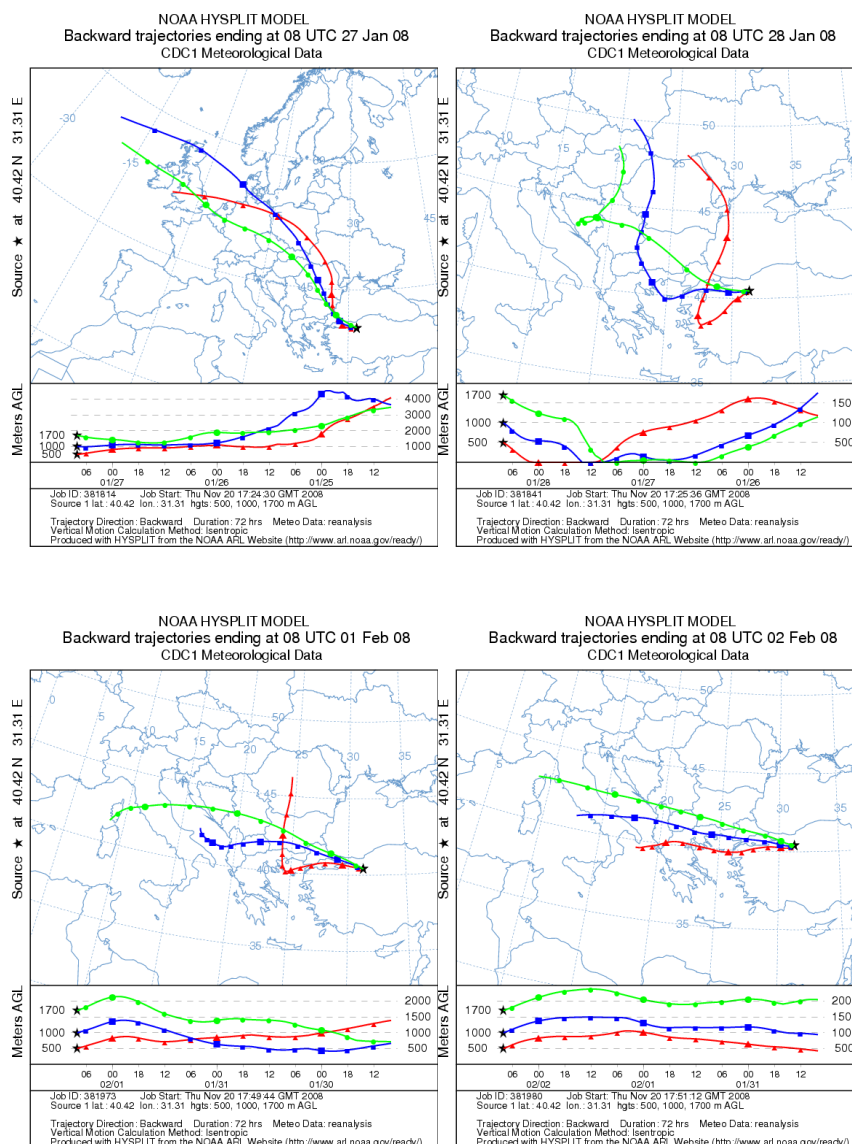


Figure 4.33. Back trajectory models PCBs (continued)

4.3.1.7. Correlation Analysis

Binary correlation was determined from the total (gas and particle phase) concentrations of the PCBs, based on the identification of sources. The correlation coefficients are given in Table 4.59. For the PCBs and correlation coefficients lower than 0.25 are not listed in table. A high correlation between two compounds shows that the compounds are most likely to result from the same source and are exposed to

similar atmospheric processes. Bold values are highly correlated compounds. In Table 4.59, the strong relation was found between PCB-18 and PCB-101; PCB-20 and PCB-153; PCB-28+31 and PCB-101, PCB-149 PCB-153, PCB-118; PCB-101 and PCB-118, PCB-149, PCB-153; and PCB-118 and PCB-149, PCB-153. The strong relation between 6-chlorinated biphenyls observed at the PCB-149 and PCB-153 and 3-chlorinated biphenyls showed strong relation with the 5- and 6-chlorinated biphenyls. PCB-101 and PCB-118, which are 5-chlorinated biphenyls, exhibit high relation. However, the other PCBs did not exhibit strong relation between each other in the approach of chlorination number.

Table 4.59. Pearson's correlation matrix of PCBs

Compound	PCB-18	PCB-20	PCB-28+31	PCB-52	PCB-101	PCB-118	PCB-149	PCB-153	PCB-170	PCB-180
PCB-18	1.00	0.64			0.84				0.65	-0.29
PCB-20		1.00	0.61	0.62	0.51	0.62	0.68	0.75		-0.47
PCB-28+31			1.00	0.59	0.91	0.82	0.89	0.84		
PCB-52				1.00	0.52	0.68	0.67	0.66	0.38	
PCB-101					1.00	0.83	0.92	0.81		
PCB-118						1.00	0.85	0.82		
PCB-149							1.00	0.93		
PCB-153								1.00		
PCB-170									1.00	
PCB-180										1.00

$p < 0.05$

4.3.2. PCBs in Soils

The particle and gas phase PCB compounds are deposited on the soil surfaces by the meteorological events. As a result, their deposition on the surface is inevitable. In this study, the 29 soil samples were collected at locations where the air sampling was carried out.

4.3.2.1. Statistical Evaluation of PCBs

The statistical assessment of nine individual PCBs and sum of PCB-28 and PCB-31 in the soil samples at the locations of air sampling is shown in Table 4.60. PCB-52, PCB-44, PCB-138 and PCB-149 were not determined in the soil samples. The total concentrations (sum of the concentrations of the entire data) of the PCBs were in the range of 0.22 pg g^{-1} to 16.8 pg g^{-1} , with a mean of 3.00 pg g^{-1} in Bolu. The higher concentrations of the PCBs were detected for PCB-18 and PCB-180 (0.80 and 0.19 pg g^{-1} , respectively) in the soil samples. The lower concentrations were observed for PCB-118 and PCB-101 (0.034 and 0.036 pg g^{-1} , respectively) in the soil samples. Percent observation of the PCBs varied between 28 % and 100 %, while the lowest and highest percent observations belonged to the PCB-194 and PCB-180, respectively.

When the frequency diagrams were drawn for PCB compounds (Figure 4.34), they showed normal distributions except for PCB-18, PCB-20 and PCB-170. Medians and geometric means are very close to each other and similar to arithmetic means. The mean, geometric mean and median values in Table 4.60 also indicate normal distribution, as well. Standard deviations of the PCBs are generally lower than the arithmetic mean, which means that the concentrations are not affected from the chemical and physical transformations and from different sources. However, the concentrations of PCB-18, PCB-20 and PCB-170 were affected from the distinct sources.

Table 4.60. Statistical evaluation of PCB compound in soil samples (pg g^{-1})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
PCB-18	21	72	0.798	0.354	0.341	0.991	0.0344	3.34	3.31	16.8
PCB-28+31	18	62	0.0433	0.0340	0.0384	0.0275	0.0216	0.135	0.113	0.779
PCB-20	26	90	0.0862	0.0557	0.0702	0.0715	0.0348	0.293	0.258	2.24
PCB-101	6	21	0.0364	0.0373	0.0363	0.0031	0.0308	0.0396	0.0088	0.218
PCB-118	23	79	0.0345	0.0325	0.0333	0.0089	0.0138	0.0586	0.0448	0.793
PCB-153	13	45	0.0376	0.0370	0.0360	0.0117	0.0235	0.0614	0.0379	0.489
PCB-105	28	97	0.0509	0.0470	0.0478	0.0224	0.0298	0.141	0.111	1.42
PCB-180	29	100	0.194	0.195	0.193	0.0160	0.167	0.219	0.0518	5.62
PCB-170	24	83	0.0473	0.0324	0.0391	0.0344	0.0188	0.146	0.127	1.13
PCB-194	8	28	0.0623	0.0575	0.0594	0.0219	0.0416	0.107	0.066	0.498

*Total analyzed samples: 29

**PO: Percent Observation, Art: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

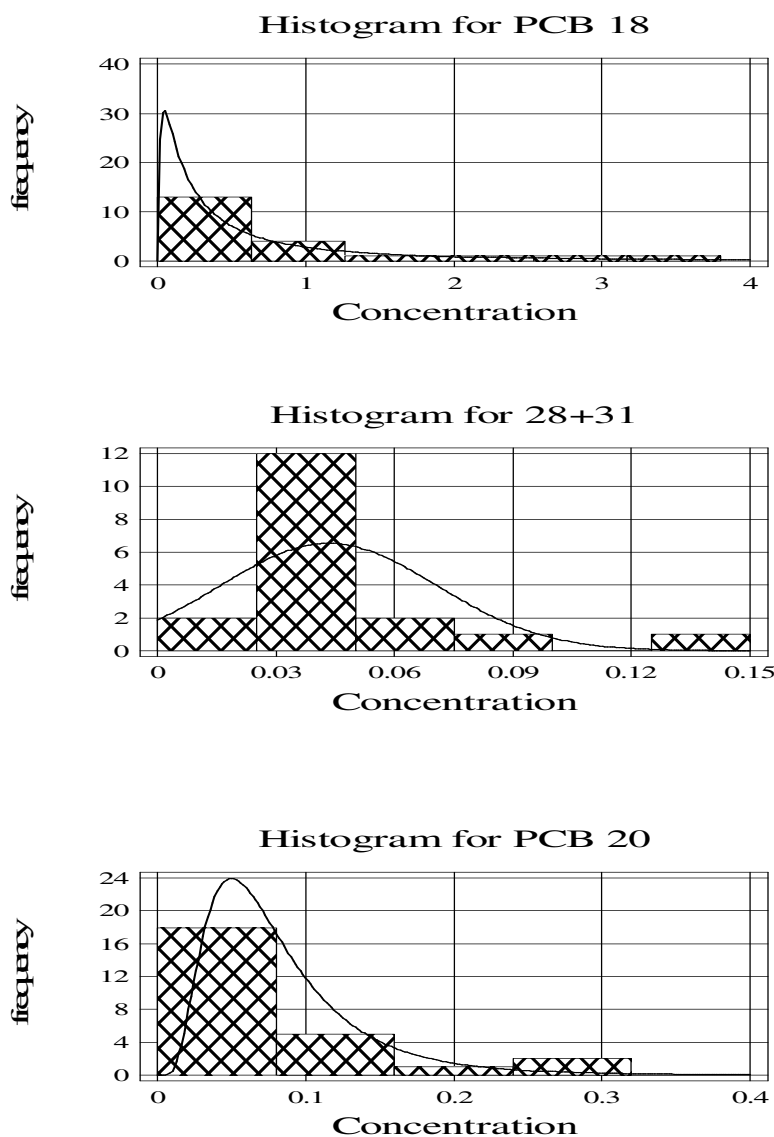


Figure 4.34. Statistical distribution of PCB concentrations (pg g^{-1})

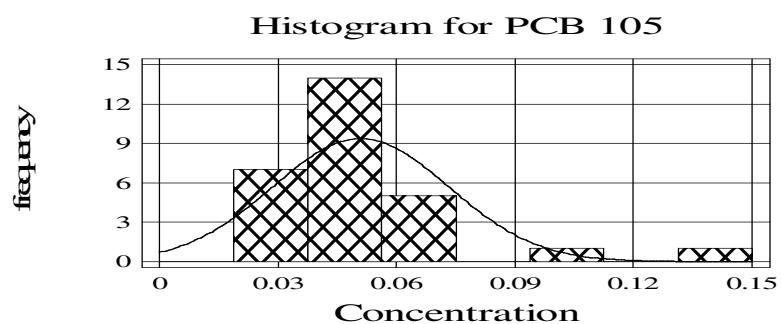
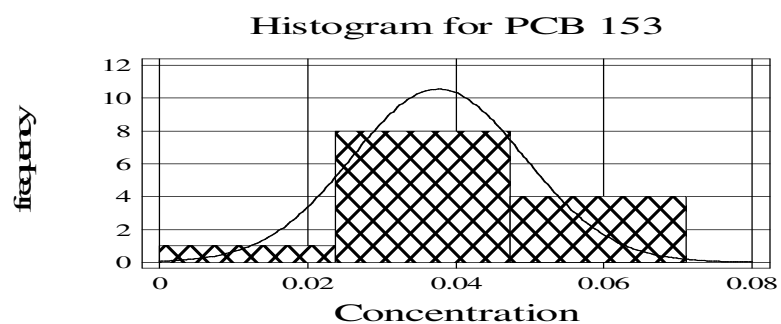
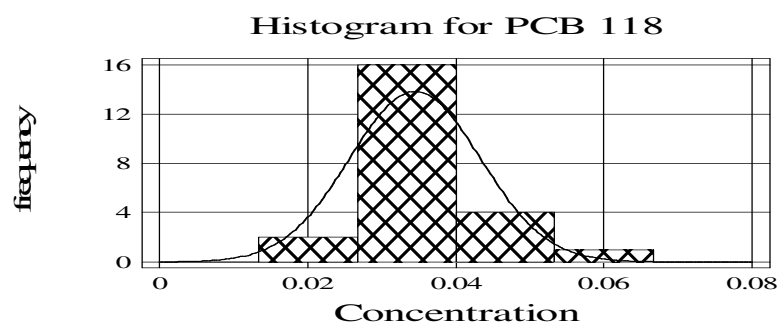
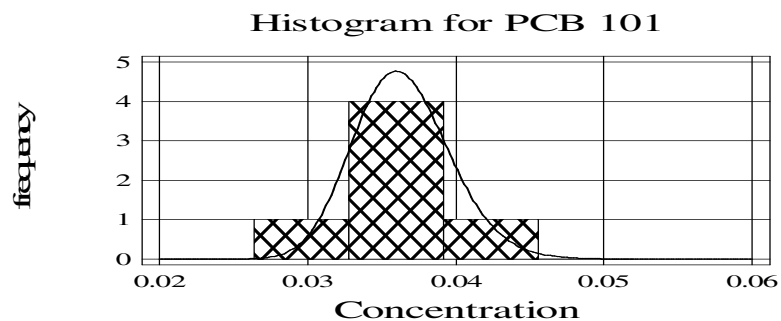


Figure 4.34. Statistical distribution of PCB concentrations (pg g^{-1}) (Continued)

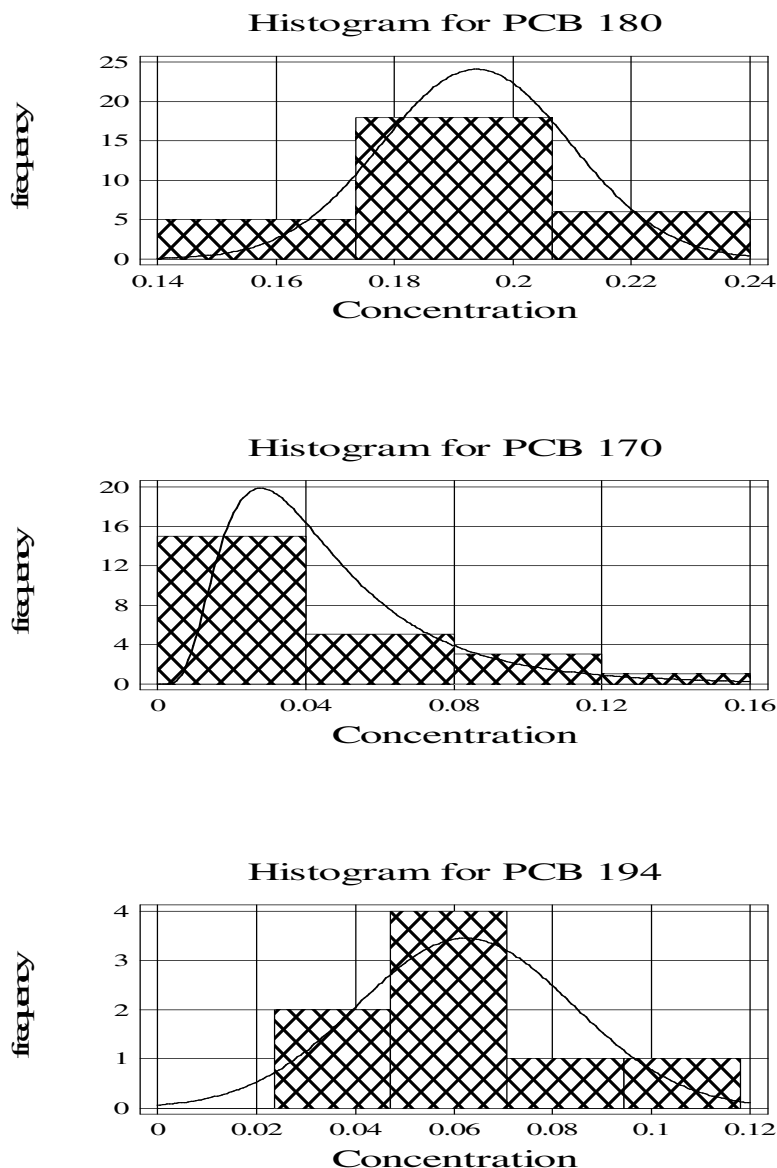


Figure 4.34. Statistical distribution of PCB concentrations (pg g⁻¹) (Continued)

4.3.2.2. Seasonal Differences in PCBs

The percent observations of the PCBs varied between 11 % and 100 % in the winter (Table 4.61). However, tetra-chlorinated PCBs, PCB-149, and PCB-138 were not observed in all the samples including the soil samples. PCB-101 had a very low

percent observation. The highest mean values were observed for the concentrations of PCB-18 and PCB-180 (1.01 and 0.195 pg g^{-1}), whereas the lowest mean values belonged to the PCB-118 and PCB-153 (0.033 pg g^{-1}). In the soil samples, low molecular weighed-PCBs were observed to be high in the winter. The main sources of these compounds were the deposition from the air. The individual average PCB concentrations were in the decreasing order as follows: PCB-18 > PCB-180 > PCB-20 > PCB-194 > PCB-28+31 > PCB-105 > PCB-101 > PCB-170 > PCB-153 > PCB-118.

Table 4.61. Statistical evaluation of PCBs in soil samples in winter (pg g^{-1})

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
PCB-18	13	68	1.01	0.499	0.434	1.18	0.0591	3.34	3.28	13.1
PCB-28+31	12	63	0.0437	0.0325	0.0379	0.0311	0.0216	0.135	0.114	0.524
PCB-20	16	84	0.0876	0.0539	0.0706	0.0736	0.0348	0.293	0.258	1.40
PCB-101	2	11	0.0366	0.0366	0.0366	0.0020	0.0352	0.0381	0.0028	0.0733
PCB-118	14	74	0.0332	0.0325	0.0328	0.0054	0.0257	0.0431	0.0174	0.464
PCB-153	9	47	0.0339	0.0285	0.0328	0.0096	0.0235	0.0484	0.0249	0.305
PCB-105	18	95	0.0427	0.0432	0.0418	0.0089	0.0298	0.0636	0.0338	0.768
PCB-180	19	100	0.195	0.195	0.194	0.0162	0.1708	0.217	0.0465	3.69
PCB-170	16	84	0.0341	0.0283	0.0302	0.0234	0.0188	0.116	0.0976	0.545
PCB-194	4	21	0.0559	0.0575	0.0550	0.0107	0.0416	0.0667	0.0251	0.223

*Total analyzed sample: 19

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

The soil samples in the summer contained the same compounds as did those in the winter. Unlike the winter samples, the summer samples had a high observation percentage. PCB-20, PCB-105 and PCB-180 were determined in all the PCB samples, while PCB-101, PCB-153 and PCB-194 were determined in 40 % of the samples (Table 4.62). The highest average concentrations of the PCBs belonged to the PCB-18 and PCB-180, whereas the lowest concentrations were observed in PCB-101 and PCB-118. The decreasing order of the average concentrations were as follows: PCB-18 > PCB-180 > PCB-20 > PCB-170 > PCB-194 > PCB-105 > PCB-153 > PCB-28+31 > PCB-101 ~ PCB-118.

Table 4.62. Statistical evaluation of PCBs in soil samples in summer (ng g⁻¹)

Compound	N	PO (%)	Art M	Median	Geo M	SD	Min	Max	Range	Total
PCB-18	8	80	0.458	0.308	0.231	0.446	0.0344	1.14	1.11	3.66
PCB-28-31	6	60	0.0424	0.0349	0.0394	0.0209	0.0307	0.0848	0.0541	0.254
PCB-20	10	100	0.0841	0.0591	0.0695	0.0718	0.0417	0.281	0.240	0.841
PCB-101	4	40	0.0362	0.0373	0.0361	0.0038	0.0308	0.0396	0.0088	0.145
PCB-118	9	90	0.0365	0.0337	0.0342	0.0127	0.0138	0.0586	0.0448	0.328
PCB-153	4	40	0.0459	0.0454	0.0445	0.0128	0.0314	0.0614	0.0299	0.183
PCB-105	10	100	0.0656	0.0579	0.0608	0.0312	0.0402	0.141	0.101	0.656
PCB-180	10	100	0.192	0.188	0.191	0.0164	0.168	0.219	0.0518	1.92
PCB-170	8	80	0.0736	0.0548	0.0658	0.0390	0.0354	0.146	0.111	0.589
PCB-194	4	40	0.0687	0.0623	0.0641	0.0298	0.0425	0.108	0.0653	0.275

*Total analyzed sample: 10

**PO: Percent Observation, Art M: Arithmetic Mean, Geo M: Geometric Mean, SD: Standard Deviation, Min: Minimum, Max: Maximum, N: Number of Observed Samples

The average concentrations of the summer and winter samples exhibited the same fluctuations except for PCB-18 which had higher average concentrations in the winter than in the summer (Figure 4.35). Concentrations of heavier PCBs were high in the summer due to the ease of their transportation from the sources relative to the winter. The heavier PCBs adsorbed on the particles were deposited on the soil surface close to the source point in winter time, whereas, the lighter PCBs were remained in the gas phase and travel longer distances than the heavier ones.

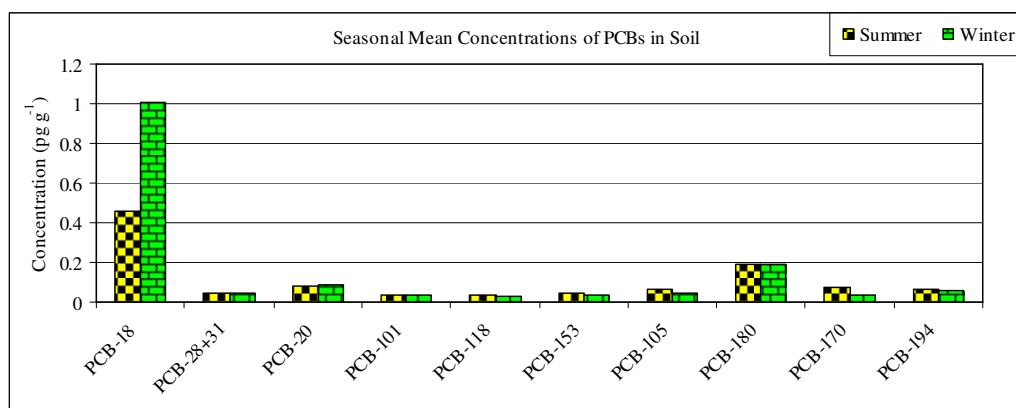


Figure 4.35. A comparison of seasonal concentrations of PCBs in soil

4.3.2.3. A Comparison of PCB Concentrations with Related-Literature Values

Data on soil concentrations of the PCBs reported in the related-literature are given in Table 4.63. Average concentrations of the PCBs are compared for similar and different regions in order to determine the PCB loadings in the soil samples. Heywood *et al.* (2006) and Alcock *et al.* (1993) found higher concentrations of the PCBs in UK soils of rural regions than that of this study. However Wong *et al.* (2009) determined the PCBs concentrations to be lower than this study except for PCB-153. Motelay-Massei *et al.* (2004) determined PCBs concentrations in the rural region and found that the concentrations for the detected compounds were higher than this study.

Table 4.63. A comparison of the soil concentration (mean) of PCBs with related-literature (ng g⁻¹)

Reference	PCB-18	PCB-28+31	PCB-20	PCB-28	PCB-101	PCB-118	PCB-153	PCB-105	PCB-180	PCB-170	PCB-194
This study (Bolu, Turkey), rural, agricultural	0.798 ±0.991	0.043 ±0.027	0.086 ±0.07		0.0364 ±0.003	0.0345 ±0.0089	0.038 ±0.012	0.051 ±0.022	0.194 ±0.016	0.047 ±0.034	0.062 ±0.032
Heywood <i>et al.</i> , 2006, (UK), rural	0.43 ±1.07			0.44 ±1.30	0.18 ±0.44	0.27 ±0.79	0.45 ±1.02	0.12 ±0.30	0.30 ±0.86	0.13 ±0.31	0.09 ±0.25
Alcock <i>et al.</i> , 1993, (UK), rural, total	4			3	10	<1	4	<1	3	1	
Wong <i>et al.</i> , 2009 (Canada and UK), rural				<0.03	<0.03	<0.03	0.19		0.13		
Motelay-Massei <i>et al.</i> , 2004, (France), rural,	n.d.			1.57	0.40	n.d	0.42	n.d.	7.95	n.d.	

n.d. not detected.

4.3.3. Exchanges of PCBs

4.3.3.1. Application of Clausius-Clapeyron Equation for Gas Phase

The temperature dependency of the gas phase PCBs are determined by the Clausius-Clapeyron equation whose principles of calculation were given in the previous section (Section 4.1.3.1). Graphs of the $\ln P$ vs $1/T$ were drawn to determine m and b values (Figure 4.36) that are compared to the literature. The slope of total PCBs was found to be positive (4322). In the literature, low slopes depend on the transportation by meteorological agents, while high slopes were correlated with evaporation from the polluted regions (Sofuoğlu *et al.*, 2001, Esen, 2006 and Ari, 2008). Most researches have estimated negative slopes. Positive results corresponds to the short range transportations from the local sources (Esen *et al.*, 2008). In the literature, positive slopes also existed for the low molecular weighed-PCBs (Agrell *et al.*, 1999).

Low slope is an indication that advection of air masses from areas experiencing no or little effect of temperature is the driving force behind a given atmospheric concentration. Steep slopes at a sampling location indicate that the concentration in air is largely determined by diffusive exchange with contaminated air subjected to wind sectors (Agrell *et al.*, 1999). The gas phase PCBs derived from the short range transport from the local sources, in this study.

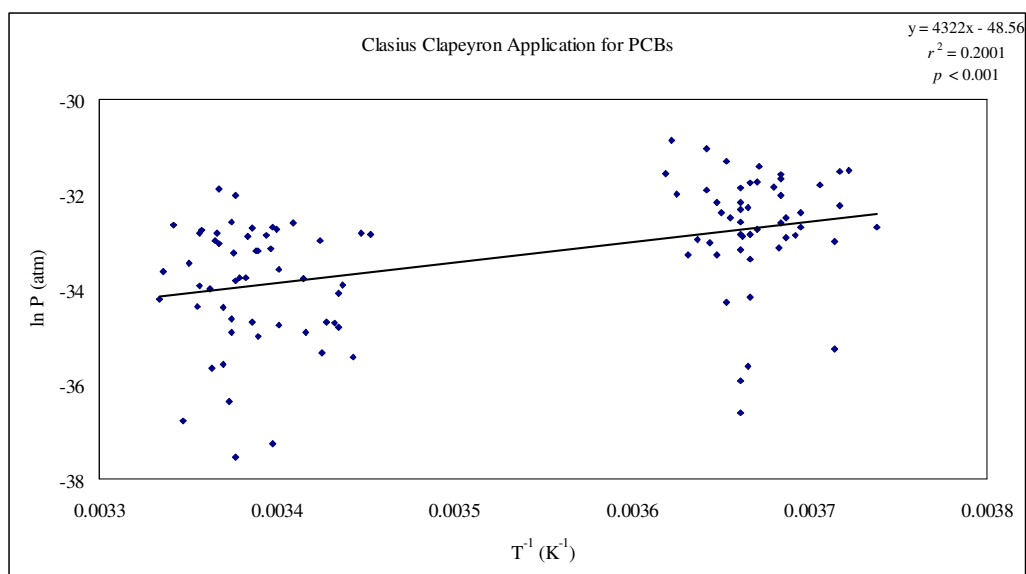


Figure 4.36. Temperature relationship with partial pressure of gas phase PCBs

4.3.3.2. Gas to Particle Exchange

Partitioning between particle and gas phases of the PCBs evaluated for determination of which phase had the greater contribution to total PCBs. Since, they are used for source identification. Also, the fate of PCBs in environment can be estimated by gas-particle partitioning coefficient (K_p , $m^3 \mu g^{-1}$). In this study the concentrations gas and particle phases given in Figures 4.37 and 4.38. The particle phase concentrations of the PCBs were significantly high in winter, while the gas phase concentrations were higher than the particle phase concentrations in summer.

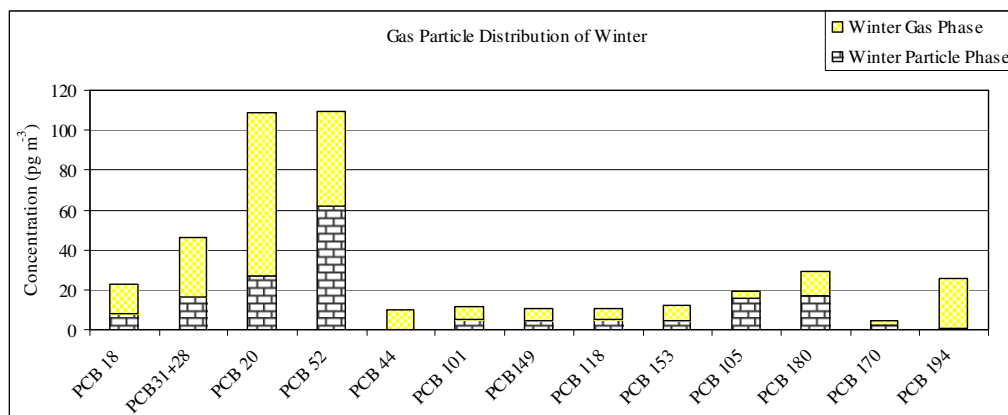


Figure 4.37. Gas-particle distribution of the PCBs in winter

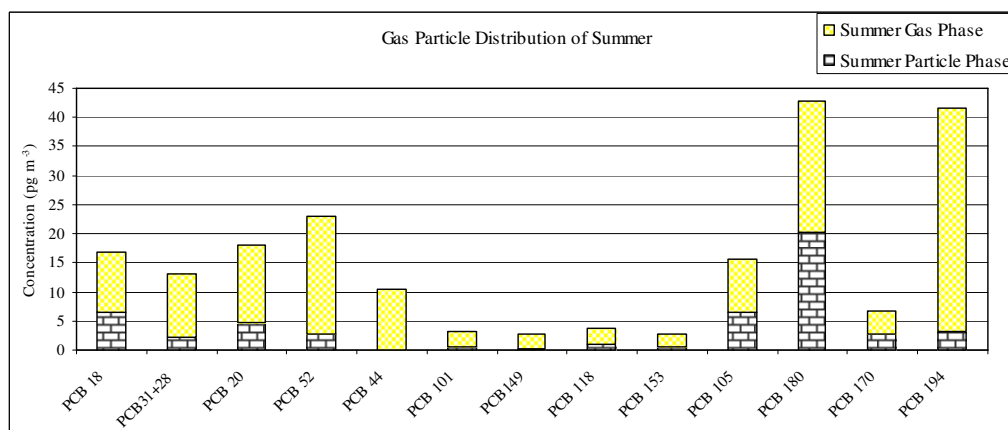


Figure 4.38. Gas-Particle distribution of the PCBs in summer

Gas-particle partitioning was generally explained as a function of sorption processes. In this study, it is not possible to determine the partitioning constants due to low set of both gas and particle phase concentrations. Therefore, the partitioning models did not applied to PCB compounds as well as OCPs. Nevertheless, experimentally obtained $\log K_p$ values of the PCBs in the range of -0.66 to -3.40 with an average value -2.07.

4.3.3.2. Air-to-Soil Exchange

The exchange of the air to soil is one of the explanation methods for determination of the behaviour of the PCBs in environment. The air to soil exchange of the PCBs was obtained by calculation of the partition coefficients such as K_{SA} which is dependent the nature of the compound in air and soil. The K_{SA} is temperature dependent on value when the K_{OW} is used for calculation of fugacity. Fugacity greater than one points out that the soil is a source with gas volatilization to air, and a value less than one indicates that the soil is a sink with gas deposition from air.

In this study, the fugacity ratios were calculated at the air sampling site using the mean air ($N = 120$) and mean soil PCB concentrations ($N = 29$) for summer and winter season. The average organic matter content of soil samples was 10.8 % (in dry sample). The density of soil solids was experimentally determined as 2.01 g cm^{-3} . The result of the fugacity calculations and experimentally determined K_{SA} values are given in Tables 4.64 and 4.65, for winter and summer seasons, respectively. In literature the K_{SA} of some of the PCB compounds has been given by Cousins *et al.*, (1998), Hippelein and McLachlan, (1998) Hippelein and McLachlan, (2000), Salihoğlu and Taşdemir (2009). However, the K_{SA} values found by fugacimeter (Cousins *et al.*, 1998; Hippelein and McLachlan, 1998; Hippelein and McLachlan, 2000) were approximately 1000 fold higher than this study. According to the fugacity calculations, soil is a sink for PCB compounds.

Table 4.64. Calculated soil-air exchange parameters for winter

Compound	K_{SA}	Log K_{SA}	f_s/f_A	Log f_s/f_A
PCB 18	1.31E+05	5.12	1.10E-02	-1.96
PCB31+28	2.92E+03	3.47	2.32E-04	-3.63
PCB 20	2.17E+03	3.34		
PCB 101	1.15E+04	4.06	8.59E-05	-4.07
PCB 118	1.15E+04	4.06	5.39E-05	-4.27
PCB 153	9.42E+03	3.97	4.05E-06	-5.39
PCB 105	2.27E+04	4.36	5.03E-05	-4.30
PCB 180	3.26E+04	4.51	3.30E-06	-5.48
PCB 170	2.74E+04	4.44	2.19E-07	-6.66
PCB 194	4.62E+03	3.66	2.92E-09	-8.53

Table 4.65. Calculated soil-air exchange parameters for summer

Compound	K_{SA}	Log K_{SA}	f_s/f_A	Log f_s/f_A
PCB-18	8.75E+04	4.94	2.43E-02	-1.61
PCB-28+31	7.94E+03	3.90	2.16E-03	-2.67
PCB-20	1.26E+04	4.10		
PCB-101	2.47E+04	4.39	5.63E-04	-3.25
PCB-118	2.65E+04	4.42	3.45E-04	-3.46
PCB-153	4.00E+04	4.60	9.52E-05	-4.02
PCB-105	1.44E+04	4.16	3.09E-04	-3.51
PCB-180	1.71E+04	4.23	2.34E-05	-4.63
PCB-170	3.82E+04	4.58	4.26E-05	-4.37
PCB-194	3.60E+03	3.56	6.39E-07	-6.19

CHAPTER 5

CONCLUSIONS

A comprehensive study was performed to investigate the air and soil deposition of PAHs, PCBs, and OCPs in Bolu. It was possible to determine the concentrations of 15 PAHs, 15 PCBs, and 11 OCPs in both air and soil samples. Soxhlet extraction (SE) and ultrasonic extraction (UE) techniques were used for the extraction of compounds from samples. Petroleum ether and DCM were used as a solvent for extraction process. Different solvents were tried to improve the recovery of fractional separation of PCBs, PAHs and OCPs. Hexane and hexane ethyl acetate mixture resulted in higher recoveries. Surrogate standards were used to calculate the recoveries of PAHs and internal standard correction was done for OCPs and PCBs. Gas Chromatography-Mass Spectrometry used in Selected Ion Monitoring Mode (SIM) provided high analytical capacity for the analysis of samples. Quantitative analysis of PAHs and PCBs were performed by monitoring target and qualifier ions. OCPs in air and soil samples were analyzed by GC-ECD.

The usage of the most OCP compounds generally was banned in Turkey, however, some of them are still in use or illegally used. Although the use of most of the OCPs ceased in all over the world as well as in Turkey, these chemicals have

been still observed in the atmosphere even now. In this study, both the air and soil samples were analyzed in order to determine the source of the pollutants and exchange relationships between them. OCP compounds are intentionally used compounds for medication to avoid some harmful insect, however OCPs persists in environment resulting any harm to other organisms. At the sampling period, 60 summer and 60 winter samples were collected in both gas and particle phase by PUF plugs and GFFs, respectively. It was possible to determine 11 OCPs in samples although 18 OCP compounds were validated and used in optimization process.

The percent observation of compounds was in the range of 31 % and 73 %. Heptachloroepoxide had the lowest observation percentage in samples and endrin and endosulfan sulfate was the highest ones in the air samples. In this study, the relative atmospheric level of the various OCPs was as follows: beta BHC > endrin > methoxychlor > endosulfan.

Endrin and beta-BHC showed the highest concentrations at sampling point with values typically ranging from 10s to 1000s of pg m^{-3} , while the others show values ranging from 1s to 100s of pg m^{-3} . Endosulfan is one of the OCPs registered in Bolu to be used for controlling wide spectrum of insect pests on fruits and vegetables, and commonly used pesticide in agricultural applications in Bolu. Determination of 4,4'-DDD and 4,4'-DDE in samples, which are the oxidation and reduction product of DDT, indicates the former usage and persistence of DDT. According to the daily concentrations of the OCPs, the winter season showed significant increase except for beta BHC.

Seasonal variations can be explained better when the gas-particle ratios were discussed. According to the median values of the summer and winter seasons gas phase concentrations, the summer concentrations of the OCPs were higher than the winter except for 4,4'-DDE, endrin and methoxychlor. When the particle phase concentrations of winter were compared to summer season, all OCP compounds under discussion were high in winter except for beta BHC. Since beta BHC is not only more stable but also is a by-product of lindane and PVC production, the high gas phase concentration of the beta BHC mainly derived from the near pollution source.

The gas-particle ratio was investigated in both seasons in order to determine the fractional distribution in either particle or gas phase. Gas phase concentrations of the all compounds were high in summer as it is expected from the effect of the rise in temperature. On the contrary, all compounds except for Beta BHC, 4,4'-DDE and heptachloroepoxide were significantly high in particle phase in winter.

Generally, maximum values were obtained in summer at the gas phase and at the particle phase in winter. Although beta BHC had low observation percentage, the concentration had high values in both seasons in gas phase. This could be explained by instantaneous spreading of this compound from the local sources.

The data for similar regions in the literature was compared with this study. The data collected in İzmir has significant importance because of similar beta BHC concentrations whereas other studies have 100 fold lower. Although the usage of this compound was banned in Turkey in 1985, the high concentrations show that beta

BHC is still in use or used at extremely high application rate in the past. Endrin concentration was 30-50 fold higher than literature values. Although the usage of that compound was banned in 1979, it was found at high levels in the atmosphere and observed nearly in all samples.

The dominant wind directions were in the direction of the south, south east and the west. It was compatible with most of the compounds, which had high concentrations in this direction. There are highly agricultural regions such as Mudurnu, Seben and Kırısıcık and villages that are close to the sampling point also have similar agricultural lands on these directions.

In the factor analysis, 84.2 % of total variance was explained by selected two factors. The first factor that explained the 70.7 % of the total variation, identified as representing the south east directions to the sampling point. The OCP compounds that had high loadings under this factor were endosulfan II, endosulfan I, endrin, endrin aldehyde, methoxychlor. When the wind sector analysis was reviewed, the compounds under factor 1 had the highest concentration values at the south east directions (ESE, SE, and SSE). The second factor affecting the concentration of samples was identified as in the south, the west and the south west directions. The loadings of 4,4'-DDE, endosulfan sulfate, endrin aldehyde under that factor were high. These compounds had high concentrations at the WSW (generally in summer) when the wind sector analysis was reviewed. This factor explained the 13.5 % of the total variance. The regions close to the sampling point have intensive agricultural applications. These applications occur in Mudurnu in the south west, Seben in the south and south east, Dörtdivan in the east and Kırısıcık in the south directions.

The major groups of OCPs in the soil belonged to the endosulfan sulfate, metoxychlor, endrin, and beta BHC. The total (sum of concentrations of each compound in the all samples) concentrations of endosulfan I, endosulfan II, and endosulfan sulfate were 0.71, 6.80 and 12.7 ng g⁻¹, respectively, and endrin ketone, endrin aldehyde, and endrin were 2.09, 2.73 and 11.2 ng g⁻¹, respectively. Although the use of some OCPs has been banned in Turkey, the results disclosed in this study show that residues still persist in the soils at considerable concentrations.

The beta BHC content was the second highest in soil samples. The endosulfan sulfate was derived from the last transformation product of the endosulfan family. Therefore, the concentration percentage had comparable values with the other parents. For instance, endosulfan I had very low observation percentage and the lowest concentration among its parents and whole OCPs. The usage of endosulfan parents is not completely restricted and most medication is done by the endosulfan I. As it was found in air samples, observation percentage of the endrin in soil samples denoted that it is still in use or persistence after a long time application in the past at the agricultural medications.

In this study, total soil concentration of the 4,4'-DDE was higher than 4,4'-DDE, since the surface soil directly exposed to the air. The presence of the 4,4'-DDE and 4,4'-DDD indicated the former usage of DDT. There is also exceptional usage of the DDT, endrin and BHC for beet seed medications in Turkey. As expressed before, the beet seed growing has application at the agricultural areas in Bolu.

The temperature dependency of the gas phase OCPs are determined by the Clausius-Clapeyron equation. Graphs of the $\ln P$ vs $1/T$ are drawn to determine the slope and intercept. The OCP compounds, which were determined at the sampling area, indicate the transportation from the near sources that are highly agricultural regions and most of them are not away far from the sampling area.

Gas-particle partition of the OCPs explains the behavior which they are either in gaseous or in particulate form in air. Particulate forms of OCPs were dominant in winter, while the gaseous form of the OCPs were high in summer as a function of rise in temperature.

In this study, the fugacity ratios were calculated at the air sampling site using the air and soil OCP concentrations. From these ratios it was found out that soil was a sink for OCP compounds.

In this study, gas and particle phase concentrations of 15 PAHs were measured in a rural and agricultural site in Bolu. Fluorene (FLU), phenanthrene, anthracene, fluoranthene, pyrene, Benz[a]anthracene (BaA), and chrysene (CHR) were observed in either gas or particle phase or both, while observation percentage of dibenz (a,h) anthracene (DahA) had the lowest in the samples. Fluorene (FLU) and phenanthrene (PHE) contribute more to the total PAH concentrations with high average concentrations of 43.1 ng m^{-3} and 48.2 ng m^{-3} , respectively. Dibenz (a,h) anthracene (DahA) had the lowest concentration (3.00 ng m^{-3}) in all samples. The relative concentrations of the other PAHs were as follows: Acenaphthylene (ACY) > benzo(b) fluoranthene (BbF) > flouranthene (FLT) > indeno (1,2,3-cd) pyrene (IND)

> acenaphthene (ACE) > pyrene(PYR) > benzo(a)pyrene (BaP) > benzo(k)fluoranthene (BkF) > benzo(g,h,i)perylene (BghiP) > anthracene (ANT) > chrysene (CRY) > benz(a)anthracene (BaA).

PHE and FLU had the highest concentrations under the daily measurements, with instantaneous high concentrations. However, the dibenz (a,h) anthracene had the lowest percent observation with a low daily contribution to the total concentrations of the PAHs. The compositional profiles of PAHs at the sampling point designated that 3-ring and 4-ring PAHs were abundant.

Gas and particle phase concentrations were determined separately for summer and winter time to examine seasonal variation and contributing sources. PHE and FLU had the highest concentrations with high percent observation, while CHY and IND had the lowest gas concentrations in the summer. The highest mean concentrations observed for BghiP and BbF, and the lowest one to DahA in particulate summer samples. FLU and PHE had the highest mean concentrations, whereas IND and DahA had the lowest ones in gaseous winter samples. Different from the summer samples, BbF and IND had the highest mean values in the particle phase winter samples. The compounds with high vapor pressure such as ACE and ACY had a significantly ($p < 0.01$) low concentration in the particle phase in winter.

The winter PAH concentrations of both phases were generally higher than the summer. The concentrations of low molecular weight-PAHs were generally higher in the winter than in the summer, while the detection of high molecular weight-PAHs decreased in both seasons. PHE and FLU concentrations were highest in both

seasons; however, winter PHE and FLU concentrations were comparably higher than the summer ones when the pyrolysis processes were relatively higher. In addition, ACY, ACE, FLT, IND, and DahA were higher in the gas phase during the summer and in the particle phase during the winter. PAH profiles indicates that ACY, PHE, FLU, DahA, and IND were the dominant compounds in the winter, while ANT, PYR, BaA, CHR, BbF, BkF, BaP, and BghiP were dominant in the summer. The concentrations of PAHs significantly decreased in the summer when the heating requirements in Bolu were about to be finished.

Seasonality of the PAHs was determined by gas to particle distribution. The 3-ring PAH compounds, FLT and BghiP were generally in the gas phase rather than the particle phase in the summer whereas PYR, BaA, CHR, BbF, BkF, BaP, IND, DahA, and BghiP were in the particle phase. Moreover, PAHs had similar trends in the winter except for BghiP whose gas phase concentration is high in the summer in contrast to the winter as an indication of near pollution source.

In the winter, the gas phase PAHs were, on average, 10 times higher than those in the summer in the study area. The seasonal changes in the data come from emission strength, which is indirectly related to climate. The main emission sources of the PAHs were the domestic burning of coal, crop residues, and firewood in the study area. Other sources changed with the seasons; however, they are not dominant the primary reason for variations in the PAH concentrations. The seasonality of PAH emissions was the major factor for the gas phase PAHs.

Variations of percent composition of PAHs were determined in both seasons but the most important change was observed for the FLU and PHE. On the other hand, for some of the PAHs like BghiP, BaP, BkF, BaA winter time contributions lessened to by an amount of half in winter period. This change in PAH profiles is an indication of variety of sources for both seasons.

The concentrations of the PAHs were compared with the similar and distinct regions in the related-literature. The similar sampling areas (rural) in literature reported significantly lower PAH concentrations than this study. However, the studies represented the urban regions support the observations in this study. Results of this study revealed that transportation from the urban areas significantly contributed to the PAHs profiles. Therefore, the average concentration of each PAH observed in the rural areas of Bolu was similar to the urban regions.

Diurnal concentrations of gas and particle phase were used to determine the contribution of the each wind sector. The dominant wind direction in the summer was southern and western directions. The low molecular weight PAHs were high at the SW and N directions where there are the TEM and D-are 100 highways and industrialized cities. The dominant wind directions were the SSE, SSW, WSW, and SE during the winter. The concentrations of most of PAHs were high when the winds has blown from the N the SE winds. ACE and FLU concentrations were high in the SSW. SSE winds affected high molecular weight PAHs. Furthermore, residential and industrial areas are highly concentrated in the SSW, S, SE, and SSE directions. Therefore, the high concentrations of these compounds can be said to be mostly come from pyrolysis processes during winter.

Wind sector analysis was assessed separately for the gas and particle phases. The dominant wind directions come from WSW and W for summer time. However, the most PAHs moved from the eastern and southern winds to the sampling point. Particle phase PAHs exhibited the same transportation ways as the gas phase ones. PAH concentrations were found to be high mainly in the SSW, SW and E sectors. The industrial regions such as asphalt manufacturing plant, wood-pulp industry, and potato plant are present at these sectors.

The gas phase PAHs mainly transported from the SSE and SSW directions that were also the dominant wind sectors in the winter. The SSE winds had greater contribution to the concentration of BaA, CHR, BbF, BkF, BaP, IND, DahA, and BghiP. The SE winds increased the concentration of ACE and ANT in the gas phase samples. In addition, the SSW winds affected the concentrations of the FLU, FLT and PYR. Significantly, high PAH concentrations of particle phase were determined in the S, SE, and SSE winds which means that the air masses were carried by these winds, as with PAHs. There are residential areas in the southern directions in which coal and other fossil fuels were generally consumed for heating.

Several ratios are generally used in the literature for source identification. FLT/FLT+PYR, BaP/BghiP, BaA/BaA+CHR and BaA/CHR ratios denoted the combustion processes for coal and the other fossil fuels, while IND/IND+BghiP ratio points to the mixed combustion processes at the sampling area.

Factor analysis was applied separately for summer and winter PAH samples to identify the season-dependent sources. Low molecular weight PAH compounds

collected in the first factor. It indicated that combustion activities were still in operation in summer months such as; burning of agricultural residues. Incomplete combustion and dominance of low molecular weight PAHs were the result of the low temperature conditions during the burning of agricultural residues. In addition, there is an asphalt manufacturing plant close to sampling location and it might be a potential source for the PAHs especially in summer months. Sampling location receives southern and western winds and industrial cities (Adapazarı, Düzce and Ankara) located on those directions. Long range transport may carry the PAHs, but this point must be investigated more in detail. Second factor accounted for 9.29 % of the total variance and loaded with BbF, BkF, IND, and BghiP which are indicators of traffic activities.

In winter, factor analysis applied to samples explained 90 % of the total variation in three factors. The first factor explained 65 % of the variance and this factor was loaded with high molecular weight PAHs that are emitted by combustion processes. Therefore, it was assigned as coal and wood combustion. This factor was also loaded with traffic marker PAHs. Low molecular weight PAHs were collected in the second factor. Unburnt fossil fuels (PHE, PYR, and FLT) appeared on the second factor that is known as petrogenic factor. Third factor loaded with ACY, FLU, ANT, and PHE explained the 7 % of the total variance. These compounds have more volatility and mostly existed in gas phase. Therefore, they represent local source origin because of their high photochemical activity. In this work, ACE, ACY, and ANT were indicator PAHs of the cement factory. Third factor might be related to the emissions of cement factory in the study region.

Meteorological factors cause the deposition of the particle phase PAHs on the soil surface since most of the PAHs are emitted from the combustion processes and get suspended in the air.

The total concentrations of PAHs were determined in the rural area of Bolu which were in the range of 11.1 ng g⁻¹ to 1549 ng g⁻¹, with a mean of 540.7 ng g⁻¹ in soil. Apart from the DahA, BghiP, and IND, 12 PAHs were detected in the soil samples. PHE and FLU had the highest mean concentrations in the soil as well as in air whereas IND and DahA had the lowest concentrations.

The PAHs measured had a high percent observation in the winter. In the soil, low molecular weight-PAHs were determined higher in the winter. The combustion processes primarily affected the concentrations of these compounds, which were mainly derived from the diesel motors. The highest concentrations in the soil belonged to PHE, BghiP, BbF, and FLU in summer. After the heavy heating and combustion season, BghiP and BbF showed higher concentrations in the summer than in the winter since the deposition on the surface increased onto the summer soil samples. However, the other high molecular weight-PAHs were high in the winter due to pyrolysis processes. Thus, various types of sources caused abrupt changes in the PAH concentrations in soil.

The high concentration of low molecular weight-PAHs in the agricultural soil indicated the combustion products from pyrolytic processes such as biomass burning and/or petrogenic sources. Moreover, it designated recent soil pollution since the lighter PAHs are easily break down than the heavy ones and are not expected to

persist or to be sorbed as strongly as heavier PAHs. Low temperature conditions during the burning of agricultural residues may point to incomplete combustion and dominance of low molecular weight-PAHs in soil.

Average PAH concentrations were compared separately with other studies for similar and different regions in the related literature. PAH concentrations were found higher than the other rural areas whereas they were lower than the urban soils. The soil samples were influenced from the recent heating events, and therefore, low molecular weight-PAHs were dominant when compared to a rural region with limited combustion processes.

FA was applied to the total soil samples and ACY, ACE, FLU, PHE, ANT, FLT, and PYR were loaded in first factor, while BbF, BkF, BaP, and BghiP were gathered in second factor. The third factor that denoted the mixed combustion processes represented only BaA and CHR. The contribution to IND was shared by first and second factors. First factor indicated the PAHs released from incineration and wood combustion sources, while second factor points to the emission from the traffic and high temperature combustion processes.

The slope of Clausius-Clapeyron graph of the total PAHs was found positive (7016), result of the closeness of sources and volatilization as well. Mainly, positive results supported the short range transportations from the local sources and the dominance of condensation for gas phase PAHs. There would be also contribution of the long-range transportation however; it was not effective as local transportation

Gas-particle distribution of the PAHs is applied to explain the behavior of PAHs in environment. The particle phase of the heavy PAHs was dominant in the winter, while the low molecular weight-PAHs were significantly high in the gas phase. The combustion of wood, coal, and the other fossil fuels rises in the winters, and hence, the low molecular weight-PAHs were comprised by wood combustion, whereas high ones derived from the coal and other fossil fuel combustion as sorbed to the particles.

The distribution of gas and particle phase PAHs were explained well by the Junge-Pankow model. The ratios of the measured ϕ with the modelled ϕ were higher than one for low molecular weight PAHs while they were found lower than one for high molecular weight PAHs indicating the adsorption. The particle phase concentrations were determined lower for low molecular weight PAHs whereas they were determined higher for high molecular weight PAHs.

$\log K_p$ and $\log P_L^\circ$ were applied in order to determine the sorption on the particles for PAHs besides the Junge-Pankow model. The slope of the K_p versus P_L° plot for either adsorption or absorption should be close to the -1 at equilibrium in literature. The slope and the intercepts determined for both seasons in this study. The adsorption and the absorption for PAH compounds were predominant according to the slopes of statistically significant $\log K_p$ versus $\log P_L^\circ$ plots. The average slopes which were shallow, were found -0.39 and -0.36, for winter and summer seasons. In summer season, more shallow slopes were founded which was the result of the temperature increase in summer.

The dimensionless soil–air partition coefficient described the equilibrium partitioning of a chemical between air and soil and fugacity ratios were common method for estimation of air to soil exchange of PAHs. In this study, the fugacity ratios and K_{SA} values of PAH compounds were calculated at the air sampling site. The PAH compounds measured in this study had the approximately similar K_{SA} values in literature and the deposition from the air is dominant. Therefore the soil indicated as a sink for PAH compounds as well as OCPs.

PCBs are the third group of POPs determined in this study. Gas and particle phases of 15 PCBs in the field were determined except for PCB-138 due to below detection limit values. The observed percentage for the total (gas and particle phase) PCBs ranged from 3 % to 91 %, with the least observed one being PCB-44 and the most observed ones being PCBs-28 and 31. In addition, PCBs-158 and 20 had also relatively high percentage of observation. However, the remaining PCBs had a relatively low percentage of observations. When the total (gas and particle phase) concentrations of the PCB congeners obtained, 3- and 4-chlorinated biphenyls had the highest concentrations, which had higher vapor pressure than 5 and more-chlorinated biphenyls.

The seasonal mean contributions of the PCB congeners for total particle and gas phase PCBs were calculated to compare the PCB congeners' distribution between the seasons. The contributions of the PCB congeners were found 68 % for tri-CBs, 9 % for tetra-CBs, 7 % for penta-CBs, 8 % for hexa-CBs, 5 % for hepta-CBs, and 3 % for octa-PCBs in the winter. In addition, the contributions of the PCB congeners in the summer month were as follows: 55 % for tri-CBs, 10 % for tetra-

CBs, 10 % for penta-CBs, 7 % for hexa-CBs, 12 % for hepta-CBs, and 6 % for octa-PCBs.

In the winter, most PCB congeners showed a maximum contribution and while they had a minimum contribution in the summer. Particle matter is enriched in the PCBs under the colder weather conditions which could be due to a greater incorporation of condensed gas phase material at a low temperature.

The gas phase PCB concentrations showed high values in the winter, while particle phase PCBs had relatively low values in both seasons. However, the total gas phase PCBs were in very low quantity in the summer. Because of diurnal effects, the PCBs are in gas phase rather than the particle phase. The observation and mean concentrations decreased because of physicochemical properties by increase in the chlorination number.

The higher concentration low molecular weight PCB congeners showed that this site is most likely to be considerably influenced by long-range transport at the sampling area which involves mainly less chlorinated congeners. The low molecular-mass PCB congeners (tri-CBs) was found to contribute more in the rural rather than in the urban areas.

The PCB loadings (Bolu) were determined by the comparison of mean concentrations with similar and different regions in the related-literature. Although the use and production of PCBs compounds have been banned in Turkey since 1980s, the determined concentrations showed that PCBs persist in the environment

as a result of extremely high application rates in the past or dispersed as a byproduct. The higher chlorinated and higher molecular weighed-PCBs such as PCB-105, PCB-180 and PCB-194 were higher than the literature values. The urban areas had significantly high PCB concentrations while they were comparable values in the rural areas.

The sources of PCBs were identified by wind sector analysis. The predominant wind direction in the summer is in the south and west directions. SSW and SW had the greatest contributions to the PCBs in summer. Furthermore, high mean concentrations of PCB-118, PCB-180, and PCB-194 were observed in N, E and WSW directions, respectively. The prevailing wind direction was from the east and the south in the winter. The concentrations of the PCBs were highly affected the ESE and WSW winds. In addition, the SE and SSE winds significantly affected PCB-105, PCB-118, PCB-170, PCB-180, and PCB-194 concentrations. There are not common industrial regions at these directions except for wood-pulp plant. Therefore, long-range transport may increase the contribution of these directions.

In general, PCB concentrations were determined higher in the WSW, SW, SSW, and W wind directions in the summer. Eskişehir, Kocaeli, Düzce are on these directions. These concentrations mainly derived from the highly industrial regions, such as; Kocaeli, Sakarya, and Düzce. For the winter, the concentration of most PCBs were affected from the ESE winds, while the S, SW, SE, SSE, and WSW directions had a high contribution to PCB-170, PCB-153, PCB-180, PCB-194, PCB-20, and PCB-118, for the gas phase samples which points to local sources at these directions. High concentrations of the particle phase PCB-18 and PCB-28+31 were

determined in the SW and WSW direction, while the SE, SSE, and E directions had a high effect on the concentrations of PCB-105, PCB-170, and PCB-180, respectively in particle phase. These sectors signalled to the industrial regions. In addition, the industrial cities appear at these directions such as Eskişehir and Ankara.

The trajectories were drawn for the days of the high concentration. The dominant wind directions were the south, east, and west when the wind sector analysis is reviewed. The numbers of northern windy days were low however; they had the greater contribution to the concentrations. These air masses usually transported from remote sources. The long-range transportation came from Karabük and Gerede from the north directions. The drawn back trajectories distinctly signaled to the transportation from the Karabük where there are blast furnaces and steel plants. In addition, the industrial regions had contribution to the PCB concentrations at the west directions.

The PCB compounds were also determined in soil. The soil samples in the summer exhibit similar trend in approach of compound types as in the winter. The summer samples had a high observation percentage whereas the winter samples comparable low observation percentage. Some of the PCBs such as PCB-20, PCB-105, and PCB-180 were detected in all soil samples. The average concentrations of the summer and winter samples showed the same oscillation except for PCB-18 which had higher average concentrations in the winter than in the summer. In the soil samples, low molecular weighed-PCBs were determined to be high in the winter. Concentrations of heavier PCBs were determined higher in the summer than in the winter due to the ease of their transportation from the sources relative to the winter.

Unlike the lighter PCBs, the heavier PCBs adsorbed on the particles were deposited on the soil surface close to the source point in winter time. The lighter PCBs were remained in the gas phase and transports longer distances than the heavier ones. The main sources of these compounds depended upon the deposition from the air.

Average concentrations of the PCBs were compared with similar and different regions so as to determine the PCB loadings in the soil samples. The rural regions in the world had the higher PCB concentration in soil than this study.

Partitioning of the PCBs in the gas and particle phase evaluated for determination of which phase had the greater contribution total PCBs. Since, they indirectly were used for source apportionment. Gas-particle partitioning coefficient is also effective estimation method for fate of the PCBs in environment. In winter, the particle phase concentrations of the PCBs were high, while the gas phase concentrations were higher than the particle phase in summer. In this study, it was not possible to determine the partitioning constants due to low set of concentrations. Therefore, the partitioning models could not work for PCB compounds as well as OCPs.

Calculation of the partition coefficients provided the air to soil exchange of the PCBs. K_{SA} which is dependent temperature and the nature of the compound in air and soil was determined to associate the soil pollution with its sources. Fugacity is also used for partitioning of PCBs which greater than 1 points out that the soil is a source with gas volatilization to air, and a value less than 1 indicates that the soil is a sink with gas deposition from air.

In this study, the fugacity ratios were calculated at the air sampling site for summer and winter season. In literature the K_{SA} of some of the PCB compounds has been given, however, the K_{SA} values found by fugacimeter were approximately 1000 fold higher than this study. There was net deposition from the air to the soil that one can identify the soil as a sink for PCBs.

To sum up, the three group POP compounds (PAH, PCB, OCP) were determined in air and soil samples. Therefore, this study has great importance for literature and research at the ng and pg level analysis. Several researches were published related to the POPs in urban areas in Turkey however; there was no research of POPs in the rural regions. This study fills the gap in literature. Bolu has been known as a clean atmosphere, however this study found out that there is a common pollution in air and soil by either local or the long range transport.

CHAPTER 6

RECOMMENDATIONS

Pollution is the main problem in the world nowadays. This study tried to determine the concentrations of the pollutants in the air and soil at the rural area and to explain and identify the sources of pollutants.

Further researches can be performed to support this study. The deposition of organic and inorganic compounds can be determined at the surface layer and under the surface soils. The complete characterization of the sources can be performed by doing multi-sampling point around the Bolu. The sample stations should be placed at city center to interpret the urban pollution and to correlate with this study.

Dry deposition and wet deposition of the organic pollutants can be studied in order to determine the exchanges of the pollutants. Pesticide fluxes can be calculated. In addition, such a study may supply definite exchange profiles for organic pollutants. Deposition rate and meteorological parameters can be used for the determination of sink of the pollutants.

The metal determination in size fractionated ($PM_{2.5}$ and PM_{10}) samples will support this study and source characterization may be more meaningful with metal data. Long range transport can be clearly determined with the metal concentrations. Particularly, the major constituents (i.e., organic carbon, elemental carbon, SO_4^{2-} and NO_3^-) should be measured. The complete characterization of the sources can be performed. The source profiles may be employed in future source apportionment studies quantitatively by using chemical mass balance. Since some sources (i.e., soil, coal, and traffic) may differ significantly with respect to locations, such sources should be characterized locally.

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APPENDICES

Appendix I. IUPAC name, abbreviation, and chemical structure of OCPs.

Common Name	IUPAC Name	Chemical Structure
Alfa HCH	Alfa 1,2,3,4,5,6-hexachlorocyclohexane	
Beta HCH	Beta 1,2,3,4,5,6-hexachloro-cyclohexane	
Gamma HCH (Lindane)	Gamma 1,2,3,4,5,6-hexachlorocyclohexane	
Delta HCH	Delta 1,2,3,4,5,6-hexachlorocyclohexane	
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	
Aldrin	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-endo-1,4-exo-5,8-dimethano-naphthalene	
Heptachlor- endo-epoxide	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan	
Alpha- Endosulfan	(3α,5αβ,6α,9α,9αβ)-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide	
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a,octahydro-1,4-endo-,exo- 5,8-dimethanonaphthalene	

Appendix I. IUPAC name, abbreviation, and chemical structure of OCPs (continued)

Common Name	IUPAC Name	Chemical Structure
4,4'-DDE	1,1-bis-(4-chlorophenyl)-2,2-dichloroethene	
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a,octahydro-1,4-endo-,endo- 5,8-dimethanonaphthalene	
Beta-Endosulfan	1,4,5,6,7,7,-hexachloro-8,9,10-triorborn-5-en-2,3-ylenebismethylene sulfite	
Endrin aldehyde	1,2,4-Methenocyclopenta(cd)-pentalene-5-carboxaldehyde,2,2a,3,3,4,7-hexachlorodecahydro-(1α,2β,2aβ,4β,4aβ,5β,6aβ,6bβ,7R)	
4,4'-DDD	1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene	
Endosulfan sulfate	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-,6,9-methano-2,4,3-benzodioxathiepin-3,3-dioxide	
4,4'-DDT	1,1-bis-(4-chlorophenyl)-2,2,2-trichloroethane	
Endrin ketone	2,5,7-Metheno-3H-cyclo-penta(a)pentalen-3-one,3b,4,5,6,6a-hexachlorodecahydro(2α,3aβ,3bβ,4β,5β,6aβ,7α,7aβ,8R)	
Methoxychlor	1,1,1-Trichloro-2,2-bis(4-methoxyphenyl)ethane	

Appendix II. Chemical and Physical Properties of OCPs (<http://www.atsdr.cdc.gov/toxprofiles/>, 2008)

Common Name	Formula	CAS Number	Molecular Weight	Color	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure	Solubility 25°C in water (mg L ⁻¹)	Henry Constant 25°C (atm m ³ mol ⁻¹)	Log K _{ow}	Log K _{oc}
Alfa HCH	C ₆ H ₆ Cl ₆	319-84-6	290.83	white	159–160	288	4.5x10 ⁻⁵ mmHg at 25°C	10	6.86x10 ⁻⁶	3.8	3.57
Beta HCH	C ₆ H ₆ Cl ₆	319-85-7	290.83	white	314–315	60 at 0.5 mmHg	3.6x10 ⁻⁷ mmHg at 20°C	5	4.5x10 ⁻⁷	3.78	3.57
Gamma HCH (lindane)	C ₆ H ₆ Cl ₆	58-89-9	290.83	NI	112.5	323.4	4.2x10 ⁻⁵ mmHg at 25°C	17	3.5x10 ⁻⁶	3.72	3.57
Delta HCH	C ₆ H ₆ Cl ₆	319-86-8	290.83	NI	141–142	60 at 0.36 mmHg	3.5x10 ⁻⁵ mmHg at 25°C	10	2.1x10 ⁻⁷	4.14	3.8
Heptachlor	C ₁₀ H ₅ Cl ₇	76-44-8	373.32	white	95-96	145	3x10 ⁻⁴ mmHg at 20°C	0.05	2.94x10 ⁻⁴	6.1	4.34
Aldrin	C ₁₂ H ₈ Cl ₆	309-00-2	364.91	white	104–105.5	Decomposes	7.5x10 ⁻⁵ mmHg at 20°C	0.011	4.9x10 ⁻⁵	6.5	7.67
Heptachlor-endo-epoxide	C ₁₀ H ₅ Cl ₇ O	1024-57-3	389.40	white	160-161.5	ND	1.95x10 ⁻⁵ mmHg at 30°C	0.275	3.2x10 ⁻⁵	5.4	4.37
Dieldrin	C ₁₂ H ₈ Cl ₆ O	60-57-1	380.91	white	176–177	Decomposes	3.1x10 ⁻⁶ mmHg at 20°C	0.11	5.2x10 ⁻⁶	6.2	6.67
Endosulfan sulfate	C ₉ H ₆ Cl ₆ O ₄ S	1031-07-8	422.9	Brown	181	No data	1x10 ⁻⁵ mmHg at 25°C	0.117	2.61x10 ⁻⁵	3.66	No data
Alpha-Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	959-98-8	406.93	Colorless	108–110	ND	1x10 ⁻⁵ mmHg at 25°C	0.53	1x10 ⁻⁵	3.83	3.55
Beta-Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	33213-65-9	406.93	Cream	208–210	No data	1x10 ⁻⁵ mmHg at 25°C	0.28	1.91x10 ⁻⁵	3.52	No data

Appendix II. Chemical and Physical Properties of OCPs (<http://www.atsdr.cdc.gov/toxprofiles/>, 2008) (continued)

Common Name	Formula	CAS Number	Molecular Weight	Color	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure	Solubility 25°C in water (mg L ⁻¹)	Henry Constant 25°C (atm m ³ mol ⁻¹)	Log K _{ow}	Log K _{oc}
Endrin	C ₁₂ H ₈ Cl ₆ O	72-20-8	380.9	White	235	decomposes	2.0x10 ⁻⁷ mmHg at 25 °C	0.25-0.26	4.0x10 ⁻⁷	5.34	4.53
Endrin aldehyde	C ₁₂ H ₈ Cl ₆ O	7421-93-4	380.9	No data	145-149	No data	2.0x10 ⁻⁷ mmHg at 25 °C	0.2	2.0x10 ⁻⁹	5.6	4.80
Endrin ketone	C ₁₂ H ₈ Cl ₆ O	53494-70-5	380.9	No data	No data	No data	No data	No data	2.02x10 ⁻⁸	4.99	No data
Methoxychlor	C ₁₆ H ₁₅ Cl ₃ O ₂	72-43-5	345.65	Pale yellow	89	No data	1.4x10 ⁻⁶ mmHg at 25 °C	0.045	1.6x10 ⁻⁵	4.68–5.08	4.9
4,4' -DDT	C ₁₄ H ₉ Cl ₅	50-29-3	354.49	Colorless crystals	109	decomposes	1.60x10 ⁻⁷ at 20 °C	0.025	8.3x10 ⁻⁶	6.91	5.18
4,4' -DDE	C ₁₄ H ₈ Cl ₄	72-55-9	318.03	White	89	336	6.0x10 ⁻⁶ at 25 °C	0.12	2.1x10 ⁻⁵	6.51	4.70
4,4' -DDE	C ₁₄ H ₁₀ Cl ₄	72-54-8	320.05	Colorless crystals	109	350	1.35x10 ⁻⁶ at 25 °C	0.090	4.0x10 ⁻⁶	6.02	5.18

Appendix III. Chemical and physical properties of PAHs (<http://www.atsdr.cdc.gov/toxprofiles/>. 2008)

Compound	CAS-Numbers	Formula	Molecular Weight	Color	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure Pa (25°C)	Density (g cm ⁻³)	Solubility 25°C in water (µg L ⁻¹)	Henry Constant 25°C(kPa)	Log K _{ow}	Log K _{oc}
Naphthalene	91-20-3	C ₁₀ H ₈	128.19	White	80.5	218	0.087 mmHg	1.145 g/mL	31.7x10 ³	4.6x10 ⁻⁴ atm-m ³ /mol	3.29	2.97
Acenaphthylene (Acy)	208-96-8	C ₁₂ H ₈	152.2	-	92-93	265-275	2.9x10 ⁻² mm-Hg(20°C)	-	3.93x10 ³	1.45x10 ⁻³ (atm-m ³ mol ⁻¹)	4.07	1.40
Acenaphthene (Ace)	83-32-9	C ₁₂ H ₁₀	154.2	White	95	279	2.9x10 ⁻¹	1.024	3.93x10 ³	1.48x10 ⁻²	3.92	3.66
Fluorene (Flu)	86-73-7	C ₁₃ H ₁₀	166.2	White	115-116	295	8x10 ⁻²	1.203	1.98x10 ³	1.01x10 ⁻²	4.18	3.86
Anthracene (Ant)	120-12-7	C ₁₄ H ₁₀	178.2	Colorless	216.4	342	8x10 ⁻⁴	1.283	73	7.3x10 ⁻²	4.5	4.15
Phenanthrene (Phe)	85-01-8	C ₁₄ H ₁₀	178.2	Colorless	100.5	340	1.6x10 ⁻²	0.98	1.29x10 ³	3.98x10 ⁻³	4.6	4.15
Fluoranthene (Flt)	206-44-0	C ₁₆ H ₁₀	202.3	Yellow	108.8	375	1.2x10 ⁻³	1.252	260	6.5x10 ⁻⁴ (20°C)	5.22	4.58
Pyrene (Pyr)	129-00-0	C ₁₆ H ₁₀	202.3	Colorless	150.4	393	6x10 ⁻⁴	1.271	135	1.1x10 ⁻³	5.18	4.58
Chrysene (Chr)	218-01-9	C ₁₈ H ₁₂	228.3	Colorless	253.8	448	8.4x10 ⁻⁵ (20°C)	1.274	2	1.05x10 ⁻⁶ (atm m ³ mol ⁻¹)	5.91	5.30
Benzo[a]anthracene (BaA)	56-55-3	C ₁₈ H ₁₂	228.3	Colorless	160.7	400	2.8x10 ⁻⁵	1.226	14	1.0x10 ⁻⁶ (atm m ³ mol ⁻¹)	5.61	5.30
Benzo[b]fluoranthene (BbF)	205-99-2	C ₂₀ H ₁₂	252.3	Colorless	168.3	481	6.7x10 ⁻⁵ (20°C)	-	1.2 (20°C)	5.1x10 ⁻⁵	6.12	5.74
Benzo[k]fluoranthene (BkF)	207-08-9	C ₂₀ H ₁₂	252.3	Yellow	215.7	480	1.3x10 ⁻⁸ (20°C)	-	0.76	4.4x10 ⁻⁵ (20°C)	6.84	5.74
Benzo[a]pyrene (BaP)	50-32-8	C ₂₀ H ₁₂	252.3	Yellowish	178.1	496	7.3x10 ⁻⁷	1.351	3.8	3.4x10 ⁻⁵	6.50	6.74
Benzo[g,h,i]perylene (BghiP)	191-24-2	C ₂₂ H ₁₂	276.3	Yellow-Green	278.3	545	1.4x10 ⁻⁸	1.329	0.26	2.7x10 ⁻⁵ (20°C)	7.1	6.20
Dibenzo[a,h]anthracene(DahA)	53-70-3	C ₂₂ H ₁₄	278.4	Colorless	262	524	1x10 ⁻¹⁰ mm-Hg (20°C)	1.282	0.5	7.3x10 ⁻⁸ (atm m ³ mol ⁻¹)	6.84	6.52
Indeno[1,2,3-c,d]pyrene (Ind)	193-39-5	C ₂₂ H ₁₂	276.3	Yellow	163.6	536	1.3x10 ⁻⁸	-	62	2.9x10 ⁻⁵	6.58	6.20

Appendix IV. IUPAC name, CAS number, abbreviation, and chemical structure of PCBs.

Abbreviation	CAS- Number	IUPAC name	Chemical structure
PCB 18	37680-65-2	2,2',5-trichlorobiphenyl	
PCB 20	38444-84-7	2,3,3'-trichlorobiphenyl	
PCB 28	7012-37-5	2,4,4'-trichlorobiphenyl	
PCB 31	16606-02-3	2,4',5-trichlorobiphenyl	
PCB 44	41464-39-5	2,2',3,5'-tetrachlorobiphenyl	
PCB 52	35693-99-3	2,2',5,5'-tetrachlorobiphenyl	
PCB 101	37680-73-2	2,2',4,5,5'-pentachlorobiphenyl	
PCB 105	32598-14-4	2,3,3',4,4'-pentachlorobiphenyl	
PCB 118	70362-41-3	2,3',4,4',5-pentachlorobiphenyl	
PCB 138	35065-28-2	2,2',3,4,4',5'-hexachlorobiphenyl	
PCB 149	38380-04-0	2,2',3,4',5',6-hexachlorobiphenyl	
PCB 153	35065-27-1	2,2',4,4',5,5'-hexachlorobiphenyl	
PCB 170	35065-30-6	2,2',3,3',4,4',5-heptachlorobiphenyl	
PCB 180	35065-29-3	2,2',3,4,4',5,5'-heptachlorobiphenyl	
PCB 194	35694-08-7	2,2',3,3',4,4',5,5'-octachlorobiphenyl	

Appendix V. Chemical and physical properties of PCBs (<http://www.atsdr.cdc.gov/toxprofiles/>, 2008; Erickson, 1997)

Number of Chlorine Substituents	Number of Isomers	Formula	Molecular Weight	Mean Melting Point (°C)	Mean Boiling Point (°C)	Vapor Pressure Pa (25°C)	Solubility 25°C in water (g m ⁻³)	Henry Constant 25°C (atm·m ³ mol ⁻¹)	Log K _{ow}
0	0	C ₁₂ H ₁₀	154.1	71	259	4.9	9.4		4.3
1	3	C ₁₂ H ₉ Cl	188.7	45.6	285	1.1	4.0	6.2x10 ⁻⁴	4.7
2	12	C ₁₂ H ₈ Cl ₂	223.0	52.8	312	0.24	1.6	3.5x10 ⁻⁴	5.1
3	24	C ₁₂ H ₇ Cl ₃	257.5	59.8	337	0.054	0.65	5.2x10 ⁻⁴	5.5
4	42	C ₁₂ H ₆ Cl ₄	292.0	107.6	360	0.012	0.26	2.2x10 ⁻⁴	5.9
5	46	C ₁₂ H ₅ Cl ₅	326.4	97.2	381	2.6x10 ⁻³	0.099	7.0x10 ⁻⁴	6.3
6	42	C ₁₂ H ₄ Cl ₆	360.9	101.1	400	5.8x10 ⁻⁴	0.038	2.9x10 ⁻³	6.7
7	24	C ₁₂ H ₃ Cl ₇	395.3	135.7	417	1.3x10 ⁻⁴	0.014	5.3x10 ⁻⁵	7.1
8	12	C ₁₂ H ₂ Cl ₈	429.8	160.5	432	2.8x10 ⁻⁵	5.5x10 ⁻³	3.8x10 ⁻⁴	7.5
9	3	C ₁₂ HCl ₉	464.2	194.4	445	6.3x10 ⁻⁶	2.0x10 ⁻³	NA	7.9
10	1	C ₁₂ Cl ₁₀	498.7	305.9	456	1.4x10 ⁻⁶	7.6x10 ⁻⁴	2.1x10 ⁻⁴	8.3

Appendix V. Chemical and physical properties of PCBs (continued)

PCB No	m _L ¹	b _L ²	ΔH_h^3 (kJ mol ⁻¹)	ΔS_h^4 (kJ mol ⁻¹ K ⁻¹)	K _{ow} ⁵	S _w ⁶ (mg L ⁻¹)	Mw (g mol ⁻¹)	MH ⁷ (cm ³ mol ⁻¹)	K _{oc} ⁸
18	-3935	12.09	34.9	0.079	354813.39	0.40000	257.5	247.3	4.79
17	-3935	12.05	39	0.1	301995.17		257.5	247.3	4.81
31	-4058	12.15	41	0.1	489778.82	0.14300	257.5	247.3	4.96
28	-4075	12.2	32.5	0.074	416869.38	0.27000	257.5	247.3	4.98
33	-4075	12.09	42	0.11	741310.24	0.11500	257.5	247.3	5.08
52	-4220	12.2	30.5	0.066	1230268.77	0.01530	292.0	268.2	5.10
49	-4229	12.41	25	0.05	1659586.91	0.03200	292.0	268.2	5.09
44	-4229	12.29	25.8	0.049	645654.23	0.03800	292.0	268.2	5.10
74	-4382	12.56	25	0.05	4677351.41	0.00496	292.0	268.2	5.39
70	-4431	12.6	29	0.06	1698243.65		292.0	268.2	5.26
95	-4399	12.48	21	0.04	3548133.89	0.01350	326.4	289.1	5.62
101	-4514	12.67	29.7	0.066	6309573.44	0.01540	326.4	289.1	5.78
99	-4533	12.68	16	0.02	16218100.97	0.00366	326.4	289.1	5.66
87	-4562	12.66	32.5	0.074	7079457.84	0.00698	326.4	289.1	5.82
110	-4522	12.43	43	0.11	1659586.91	0.00730	326.4	289.1	5.80
82	-4522	12.63	42	0.11	6606934.48	0.00665	326.4	289.1	5.86
151	-4681	12.95	37	0.1	14454397.7		360.9	310.0	6.02
149	-4689	12.78	46	0.12	19054607.18	0.00424	360.9	310.0	6.05
118	-4664	12.72	49.8	0.132	13182567.39	0.00389	326.4	289.1	5.99
153	-4775	12.85	66.1	0.19	56234132.52	0.00100	360.9	310.0	6.19
132	-4681	12.58	20	0.03	10964781.96		360.9	310.0	6.06
105	-4758	12.9	75.6	0.218	8709635.90	0.00340	326.4	289.1	6.07
138	-4800	12.81	87.1	0.259	27542287.03		360.9	310.0	6.20
158	-4816	12.94	80	0.24	23442288.15		360.9	310.0	6.20
187	-4911	12.96	96.3	0.293	61659500.19	0.00065	395.3	330.9	6.28
183	-4962	13.19	100	0.3	72443596.01		395.3	330.9	6.32
128	-4881	12.91	118	0.36	22908676.53	0.00035	360.9	310.0	6.32
177	-4962	13.04	112	0.34	61659500.19		395.3	330.9	6.35
171	-5008	13.07	101	0.31	67608297.54	0.00217	395.3	330.9	6.43
156	-4949	12.94	112	0.34	28183829.31	0.00102	360.9	310.0	6.10
180	-5042	13.03	143.6	0.447	83176377.11	0.00037	395.3	330.9	6.37
191	-5109	13.15	149	0.46	85113803.82		395.3	330.9	6.56
169	-5313	13.64	162	0.51	31622776.6	0.00051	360.9	310.0	6.23
170	-5139	13.17	164	0.51	87096358.99		395.3	330.9	6.66
199	-5244	13.36	167	0.52	194984460	0.00034	429.8	351.8	6.57
208	-5127	12.68	145	0.46	851138038.2	0.00002	464.2	372.7	6.86
195	-5244	13.24	167	0.518	223872113.9		429.8	351.8	6.86
194	-5402	13.43	169	0.52	263026799.2	0.00020	429.8	351.8	6.96
205	-5402	13.51	169	0.52	295120922.7	0.00009	429.8	351.8	6.99
206	-5526	13.57	167	0.52	1174897555	0.00003	462.2	372.7	7.13
209	-5402	13.27	145	0.46	15135612480	0.00001	498.7	393.6	7.27

1, 2: Falconer and Bidleman 1994. 3, 4: Bamford *et al.*, 2000, Bamford *et al.*, 2002. 5: Mackay *et al.*, 1992, 6: <http://www.tomasoberg.com/qspr/paper.html>. 7: Taşdemir 1997, www.es.lanacs.ac.uk/ecerg/kcjgroup/1.html. 8: Hansen *et al.*, 1999.

Appendix VI. Average recoveries compounds and surrogates

Compound	AR (%) $\pm$ SD ¹	AR (%) $\pm$ SD ²	AR (%) $\pm$ SD ³	AR (%) $\pm$ SD ⁴
β -BHC	91 $\pm$ 13.0	n. d.	61 $\pm$ 13	93 $\pm$ 5.3
Heptachloroepoxide	93 $\pm$ 13.3	20 $\pm$ 0.7	57 $\pm$ 13	78 $\pm$ 6.0
Endosulfan I	86 $\pm$ 15.2	80 $\pm$ 3.5	53 $\pm$ 12	92 $\pm$ 4.5
4,4 DDE	82 $\pm$ 16.8	77 $\pm$ 3.9	67 $\pm$ 15	94 $\pm$ 5.6
Endin	76 $\pm$ 17.9	75 $\pm$ 6.6	65 $\pm$ 15	101 $\pm$ 5.5
Endosulfan II	11 $\pm$ 4.9	95 $\pm$ 2.8	67 $\pm$ 16	101 $\pm$ 4.0
4,4 DDD	70 $\pm$ 14.1	2 $\pm$ 0.1	53 $\pm$ 14	75 $\pm$ 10
Endrin aldehyde	15 $\pm$ 5.7	70 $\pm$ 1.4	62 $\pm$ 17	90 $\pm$ 4.2
Endosulfan sulfate	23 $\pm$ 3.5	25 $\pm$ 0	72 $\pm$ 23	128 $\pm$ 10.1
Endrin ketone	32 $\pm$ 9.8	80 $\pm$ 0.6	69 $\pm$ 19	98 $\pm$ 6.2
Methoxychlor	73 $\pm$ 18.2	83 $\pm$ 1.9	93 $\pm$ 30	114 $\pm$ 6.0
Dibutyl chloredate(Surr)	26 $\pm$ 45.6	76 $\pm$ 2.0	78 $\pm$ 19	103 $\pm$ 5.8
PCB-14(Surr)	88 $\pm$ 4.5	40 $\pm$ 22	26 $\pm$ 5.9	88 $\pm$ 2.1
PCB-18	86 $\pm$ 4.1	79 $\pm$ 3.1	77 $\pm$ 8.5	85 $\pm$ 2.4
PCB-20	91 $\pm$ 4.3	123 $\pm$ 74	55 $\pm$ 6.4	90 $\pm$ 3.9
PCB-28	87 $\pm$ 2.2	80 $\pm$ 0.7	85 $\pm$ 10	90 $\pm$ 3.9
PCB-31	90 $\pm$ 2.8	74 $\pm$ 6.4	51 $\pm$ 9.4	92 $\pm$ 4.2
PCB-44	97 $\pm$ 3.9	91 $\pm$ 4.6	99 $\pm$ 11	92 $\pm$ 4.7
PCB-65(Surr)	94 $\pm$ 2.4	89 $\pm$ 4.0	77 $\pm$ 11	92 $\pm$ 4.6
PCB-52	95 $\pm$ 3.3	87 $\pm$ 3.5	85 $\pm$ 10	93 $\pm$ 4.5
PCB-101	109 $\pm$ 3.5	83 $\pm$ 5.2	91 $\pm$ 9.3	92 $\pm$ 5.5
PCB-105	106 $\pm$ 2.4	83 $\pm$ 4.0	91 $\pm$ 10	90 $\pm$ 4.5
PCB-108	95 $\pm$ 0.5	70 $\pm$ 6.2	84 $\pm$ 7.3	93 $\pm$ 5.6
PCB-138	102 $\pm$ 0.6	80 $\pm$ 5.5	90 $\pm$ 9.3	93 $\pm$ 6.1
PCB-149	88 $\pm$ 1.2	65 $\pm$ 6.0	53 $\pm$ 6.3	92 $\pm$ 5.8
PCB-153	102 $\pm$ 0.	75 $\pm$ 3.9	85 $\pm$ 8.8	94 $\pm$ 5.7
PCB-166(Surr)	101 $\pm$ 0.5	74 $\pm$ 6.1	88 $\pm$ 8.5	93 $\pm$ 4.8
PCB-170	102 $\pm$ 1.1	71 $\pm$ 6.1	89 $\pm$ 8.8	94 $\pm$ 5.7
PCB-180	96 $\pm$ 0.8	68 $\pm$ 10	84 $\pm$ 6.9	91 $\pm$ 6.1
PCB-194	106 $\pm$ 1.0	69 $\pm$ 7.9	88 $\pm$ 10	99 $\pm$ 7.3
Acy	28 $\pm$ 3.0	70 $\pm$ 19	46 $\pm$ 5.0	66 $\pm$ 14
Ace d10(Surr)	27 $\pm$ 4.6	66 $\pm$ 16	41 $\pm$ 4.5	60 $\pm$ 9.1
Ace	25 $\pm$ 4.0	65 $\pm$ 15	40 $\pm$ 4.4	56 $\pm$ 9.1
Flu	69 $\pm$ 4.7	94 $\pm$ 11	58 $\pm$ 3.7	81 $\pm$ 8.8
Phe d10(Surr)	86 $\pm$ 8.9	105 $\pm$ 5.7	67 $\pm$ 6.4	86 $\pm$ 6.2
Phe	79 $\pm$ 8.9	108 $\pm$ 5.1	73 $\pm$ 6.8	86 $\pm$ 6.4
Ant	85 $\pm$ 9.8	106 $\pm$ 6.1	71 $\pm$ 6.3	90 $\pm$ 5.4
Flt	97 $\pm$ 12.1	111 $\pm$ 4.7	80 $\pm$ 8.5	107 $\pm$ 3.7
Pyr	92 $\pm$ 11.9	109 $\pm$ 5.1	70 $\pm$ 7.7	99 $\pm$ 5.8
BaA	88 $\pm$ 9.3	122 $\pm$ 12	99 $\pm$ 10	108 $\pm$ 4.5
Chr d12(Surr)	87 $\pm$ 9.5	99 $\pm$ 7.2	83 $\pm$ 7.6	107 $\pm$ 4.5
Chr	91 $\pm$ 10.9	104 $\pm$ 6.9	116 $\pm$ 10	112 $\pm$ 7.9
BbF	87 $\pm$ 4.4	191 $\pm$ 28	103 $\pm$ 10	118 $\pm$ 8.5
BkF	90 $\pm$ 5.3	127 $\pm$ 14	96 $\pm$ 9.0	115 $\pm$ 4.7
BaP	88 $\pm$ 5.5	201 $\pm$ 31	96 $\pm$ 6.3	102 $\pm$ 4.0
Per d12(Surr)	60 $\pm$ 1.2	119 $\pm$ 14	74 $\pm$ 2.9	105 $\pm$ 5.7
Ind	101 $\pm$ 4.2	176 $\pm$ 47	93 $\pm$ 3.2	109 $\pm$ 5.2
DahA	101 $\pm$ 14.4	139 $\pm$ 41	88 $\pm$ 6.5	114 $\pm$ 7.4
BghiP	94 $\pm$ 0	145 $\pm$ 32	93 $\pm$ 7.1	113 $\pm$ 6.3

AR: Average Recovery, SD: Standard Deviation, Surr: Surrogate, n. d.: not detected

1. Two fractions: fraction I hexane, fraction II, hexane-ethyl acetate 1:1 mixture, 1 g florisil and sodium sulfate

2. Two fractions: fraction I hexane, fraction II, cyclohexane ethyl acetate 1:1 mixture, 1 g florisil sodium sulfate and alumina.

3. Two fractions: fraction I hexane, fraction II, hexane ethyl acetate 1:1 mixture, 2 g florisil sodium sulfate and alumina.

4. Two fractions: fraction I hexane, fraction II, hexane ethyl acetate 1:1 mixture, 1 g florisil sodium sulfate and alumina.

Appendix VII. Meteorological parameters of sampling period

Date	Average Temperature (C°)	Average Moisture (%)	Average Velocity of Wind (m s ⁻¹)	Wind Direction	Daily Total Fall (mm)
25.06.2007	22.2	55	1.49	MD	0.2
26.06.2007	24.8	53	1.29	MD	n.d.
27.06.2007	25.1	51	1.29	MD	n.d.
28.06.2007	25.3	54	1.95	MD	n.d.
29.06.2007	18.2	79	1.13	WNW	n.d.
30.06.2007	17.8	66	1.59	ESE	6.2
01.07.2007	18.0	62	1.39	W	n.d.
02.07.2007	18.6	63	1.44	WSW	n.d.
03.07.2007	20.9	59	1.34	WSW	n.d.
04.07.2007	23.2	59	1.34	W	n.d.
05.07.2007	24.9	50	1.49	WNW	n.d.
06.07.2007	18.0	74	1.75	WSW	n.d.
07.07.2007	17.3	60	1.8	W	0.2
08.07.2007	19.6	51	1.39	WSW	0.2
09.07.2007	21.2	49	1.34	SE	n.d.
10.07.2007	23.2	48	1.29	W	n.d.
11.07.2007	24.2	48	1.39	WSW	n.d.
12.07.2007	23.3	60	1.8	WSW	n.d.
13.07.2007	18.8	73	1.85	ENE	n.d.
14.07.2007	16.5	73	1.23	N	n.d.
15.07.2007	16.9	67	1.54	NE	n.d.
16.07.2007	17.8	65	1.54	N	n.d.
17.07.2007	20.2	59	1.65	ENE	n.d.
18.07.2007	22.4	50	1.8	NE	n.d.
19.07.2007	23.0	55	1.44	WSW	n.d.
20.07.2007	23.1	62	1.59	WSW	n.d.
21.07.2007	23.8	69	1.54	WSW	n.d.
22.07.2007	25.6	63	1.49	WSW	n.d.
23.07.2007	26.6	59	1.29	WSW	n.d.
24.07.2007	26.1	49	1.49	WNW	n.d.
25.07.2007	26.8	39	1.34	W	n.d.
26.07.2007	24.3	55	1.49	WSW	n.d.
27.07.2007	23.6	72	1.54	WSW	n.d.
28.07.2007	23.6	70	1.8	WSW	n.d.
29.07.2007	23.1	68	1.7	WSW	n.d.
30.07.2007	23.8	71	1.59	SW	n.d.
31.07.2007	23.9	67	1.59	SW	n.d.
01.08.2007	23.2	72	1.65	WSW	n.d.
02.08.2007	18.9	79	1.8	WSW	8.6
03.08.2007	19.7	73	1.54	WSW	0.2
04.08.2007	20.9	75	1.7	WSW	n.d.
05.08.2007	23.0	72	1.65	WSW	n.d.
06.08.2007	24.7	62	1.75	WSW	n.d.
07.08.2007	21.9	66	1.65	WSW	n.d.
08.08.2007	21.5	61	1.54	W	n.d.
09.08.2007	22.0	60	1.44	WNW	n.d.
10.08.2007	22.5	57	1.44	WSW	n.d.
11.08.2007	24.8	53	1.13	WSW	n.d.

Appendix VII. Meteorological parameters of sampling period (continued)

Date	Average Temperature (C°)	Average Moisture (%)	Average Velocity of Wind (m s ⁻¹)	Wind Direction	Daily Total Fall (mm)
12.08.2007	24.0	61	1.8	WSW	n.d.
13.08.2007	22.8	65	1.7	W	n.d.
14.08.2007	21.9	63	1.54	WSW	n.d.
15.08.2007	21.3	63	1.59	W	n.d.
16.08.2007	21.0	67	1.7	WSW	n.d.
17.08.2007	21.2	63	1.44	E	n.d.
18.08.2007	21.9	67	1.44	WSW	n.d.
19.08.2007	23.0	64	1.13	SSW	n.d.
20.08.2007	23.2	65	1.54	SSW	2.6
21.08.2007	23.6	57	1.44	W	n.d.
22.08.2007	22.2	51	1.59	NW	n.d.
23.08.2007	22.2	58	1.75	NE	n.d.
13.12.2007	2.2	98	4.2	ENE	12.7
14.12.2007	1.8	92	3.0	SSW	7.4
15.12.2007	3.2	84	4.0	ENE	0.8
16.12.2007	2.9	88	3.1	ESE	n.d.
17.12.2007	1.4	91	7.2	WSW	n.d.
18.12.2007	-0.7	81	6.0	WSW	0.3
19.12.2007	-0.7	83	3.4	SW	0.1
20.12.2007	-0.4	82	3.1	SW	n.d.
21.12.2007	-0.3	81	3.7	WSW	n.d.
22.12.2007	0.8	76	4.2	WSW	n.d.
23.12.2007	-0.3	80	2.3	SE	n.d.
24.12.2007	-0.7	85	2.3	SSE	n.d.
25.12.2007	-1.7	86	2.0	SE	n.d.
26.12.2007	-1.9	83	2.3	SSE	n.d.
27.12.2007	-0.4	81	3.9	E	n.d.
28.12.2007	0.6	71	6.8	E	n.d.
29.12.2007	-0.4	77	2.9	SW	n.d.
30.12.2007	-1.7	76	2.5	SE	n.d.
31.12.2007	-2.3	73	3.0	SSE	n.d.
01.01.2008	-1.9	68	2.4	SE	n.d.
02.01.2008	0.2	77	4.1	SSW	n.d.
03.01.2008	-0.1	93	7.9	WSW	1.2
04.01.2008	-3.1	88	6.7	WSW	6.0
05.01.2008	-3.9	87	6.8	WSW	1.7
06.01.2008	-4.8	84	2.6	S	0.2
07.01.2008	-1.6	89	5.9	SSW	n.d.
08.01.2008	0.0	90	6.6	WSW	3.9
09.01.2008	-0.4	86	3.3	ESE	1.0
10.01.2008	-0.3	82	6.3	SSE	0.7
11.01.2008	-4.5	78	3.5	SE	0.2
12.01.2008	-5.6	76	2.6	SSE	n.d.
13.01.2008	-4.1	75	2.1	SSE	n.d.
14.01.2008	-3.4	75	2.7	SSE	n.d.
15.01.2008	-1.7	79	6.3	SSW	n.d.
16.01.2008	1.0	89	3.2	S	1.6
17.01.2008	0.0	83	3.0	SE	n.d.

Appendix VII. Meteorological parameters of sampling period (continued)

Date	Average Temperature (C°)	Average Moisture (%)	Average Velocity of Wind (m s ⁻¹)	Wind Direction	Daily Total Fall (mm)
18.01.2008	0.6	84	2.7	SSE	n.d.
19.01.2008	-1.9	96	2.8	S	n.d.
20.01.2008	-1.7	86	2.8	S	n.d.
21.01.2008	1.0	70	5.2	SSW	n.d.
22.01.2008	2.7	69	5.1	S	n.d.
23.01.2008	2.9	73	5.4	SSW	n.d.
24.01.2008	0.5	92	6.2	ENE	0.5
25.01.2008	-0.8	68	6.3	ENE	3.0
26.01.2008	-2.5	80	3.6	SW	n.d.
27.01.2008	-0.3	77	14.3	WSW	n.d.
28.01.2008	-0.2	90	5.9	NE	27.2
29.01.2008	-2.5	92	4.6	E	3.1
30.01.2008	-4.1	84	6.4	SSE	8.4
31.01.2008	-8.1	83	2.8	S	0.9
01.02.2008	-3.9	77	3.1	SSE	n.d.
02.02.2008	-3.3	84	2.3	SSE	n.d.
03.02.2008	-1.4	81	2.4	SSE	n.d.
04.02.2008	0.0	88	2.1	SSE	n.d.
05.02.2008	0.0	82	2.7	SSE	n.d.
06.02.2008	0.4	80	2.5	SE	n.d.
07.02.2008	0.6	84	2.8	SSE	n.d.
08.02.2008	0.4	87	2.5	SE	n.d.
09.02.2008	1.4	78	4.7	ESE	n.d.
10.02.2008	1.3	88	3.2	SSW	n.d.

n.d.: Not detected