Air Monitoring of Polychlorinated Biphenyls in Ambient Air of Suburban Area in İzmir, Turkey

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ABSTRACT

Polychlorinated biphenyls (PCBs) are human made toxic chemicals which were first synthesized in 1920s. Because of their inverse effects on environment and human health the usage and production of PCBs were banned in 1970s in United States and all over the Europe. PCBs are prone to long- range atmospheric transport and this makes them ubiquitous in the environment. Due to the importance of long-range transport of PCBs, their concentrations have been measured in many different countries.

In order to determine the atmospheric concentration levels of total (gas+particle) PCBs (ΣPCB) and 41 PCB congeners in İzmir, two sampling programs were designed. 20 successive day and nighttime (called short-term), and 40 a year around representing particle and gas phase samples (called long-term) were collected from May 2003 to March 2004. Effects of temperature, wind speed and direction, and seasonal change on atmospheric concentrations of PCBs were investigated.

In the short-term period, average $\Sigma PCB_{(41)}$ concentration was ~520 pg m^{-3}, while congener base total (gas+particle) polychlorinated biphenyl concentrations ranged from 0.37 ± 0.65 pg m^{-3} (PCB 158) to 305.07 ± 86.01 pg m^{-3} (PCB 33). Similarly, in the long-term analysis average $\Sigma PCB_{(41)}$ concentration was found as 419 pg m^{-3}, while the minimum and maximum concentrations of congener base total (gas+particle) PCB concentrations ranged from 0.11 ± 10.58 pg m^{-3} (PCB 70) to 919.69 ± 281.18 pg m^{-3} (PCB 208). Short-term average total concentration was higher than a year average total concentration. The reason could be the revolatilization of these compounds from the contaminated surfaces due to the increase in temperature in early summer/late spring. Generally, the levels of PCB were within the ranges previously measured at different sites.

The temperature dependence of gas-phase atmospheric concentrations of PCBs was investigated by using Clausius-Clapeyron relationship. The results were statistically significant ($p<0.05$) for 12 PCB congeners (PCB 74, 70, 101, 99, 87, 82/151, 153, 138, 158, and 128). In addition to temperature, the effect of wind speed and direction was investigated using multiple linear regression analysis. Results of the multiple regression analysis indicated that wind speed was a statistically significant

factor for PCB 18 and PCB 17, which have low molecular weights and tendency to be in gas phase.

In the long-term data analysis with respect to Clausius-Clapeyron relationship 13 congeners (PCB 18, 17, 31, 28, 33, 74, 70, 95, 99, 153, 138, 187, and 209) were statistically significant ($p<0.05$) with temperature. Introduction of wind speed and wind direction to the Clausius-Clapeyron equation did not resulted in a better correlation. The statistically significant correlated congeners were attributed as they were originated from short-range transport. The other congeners with lower R^2 values and poor correlations exhibited that their sources were originated from long-range transport.

The only positive slope was obtained for PCB 209 and this could be attributed to the influence of its ongoing source. Since the usage and production of PCBs were banned, the source may be the exchange processes from buildings, indoor air, soils, etc., to overlying atmosphere.

ÖZ

Poliklorlu bifeniller (PCBler), ilk olarak 1920 yılında insanlar tarafından sentezlenmiş toksik bir kimyasal maddedir. İnsan ve çevre sağlığı üzerindeki zaralı etkilerinden dolayı üretimleri ve kullanımları 1970'lerde Amerika'da ve bunu takiben tüm Avrupa ülkelerinde yasaklanmıştır. Uzun mesafeli taşınıma maruz kalmaları nedeniyle çevrede fazlaca yayılmış durumdalardır ve seviyelerinin bilinmesi için çeşitli ülkelerde PCB konsantrasyonları hala ölçülmektedir.

PCB'lerin toplam (gaz+partikül) atmosferik konsantrasyonlarının İzmir'deki ölçümleri için iki ayrı ölçüm programı planlanmıştır. 20 adet gece ve gündüz (kısa dönem), 40 adet de gündüz (uzun dönem) olmak üzere Mayıs 2003 ile Mart 2004 tarihleri arasında yaklaşık bir yıllık örnekler toplanmıştır. Sıcaklığın, rüzgar hızı ve yönünün ve mevsimsel farklılıkların atmosferik konsantrasyonlar üzerindeki etkileri incelenmiştir.

Kısa dönemde, ortalama toplam (41 çeşit PCB için) konsantrasyon 520 pg m^{-3} olarak belirlenmiştir ve, her bir PCB bazında incelendiğinde toplam (gaz+partikül) konsantrasyonlar 0.37 ± 0.65 pg m^{-3} (PCB 158) ile 305.07 ± 86.01 pg m^{-3} (PCB 33) aralığında değiştiği gözlenmiştir. Benzer şekilde uzun dönemde ortalama toplam konsantrasyon 419 pg m^{-3} olarak belirlenmiştir ve minimum ve maksimum toplam (gaz+partikül) konsantrasyon değerleri, her bir PCB için incelendiğinde, 0.11 ± 10.58 pg m^{-3} (PCB 70) ile 919.69 ± 281.18 pg m^{-3} (PCB 208) aralığında değiştiği görülmüştür. Ortalama toplam konsantrasyonlar üzerinden karşılaştırma yapıldığında ölçülen değerlerin farklı bölgelerde daha önce yapılmış çalışmalarda rapor edilen minimum ve maksimum değerler arasında oldukları gözlenmiştir.

PCB'lerin atmosferdeki gaz fazdaki konsantrasyonlarının sıcaklıkla ilişkisi Clausius-Clapeyron eşitliği kullanılarak araştırılmıştır. Araştırma sonuçlarına göre 12 çeşit poliklorlu bifenilin (PCB 74, 70, 101, 99, 87, 82/151, 153, 138, 158, and 128) gaz fazdaki konsantrasyonunun sıcaklıkla ilişkisinin istatistiksel olarak önemli olduğu ($p<0.05$) bulunmuştur. Sıcaklığın gaz konsantrasyonlarındaki etkisine ek olarak, rüzgar yönü ve hızının etkisi de lineer regresyon analizi kullanılarak araştırılmıştır. Regresyon

analizi katsayıları göstermiştir ki rüzgar hızı ölçülen PCB'lerin en hafifleri olan PCB 18 ve PCB 17 için önemli, rüzgar yönü ise sadece PCB 18 için önemli bir faktördür.

Uzun dönem analizlerinde ise Clausius-Clapeyron ilişkisine göre 13 çeşit PCB'nin (PCB 18, 17, 31, 28, 33, 74, 70, 95, 99, 153, 138, 187, ve 209) gaz fazdaki konsantrasyonunun sıcaklıkla ilişkisinin istatistiksel olarak önemli olduğu (p<0.05) bulunmuştur. Rüzgar hızı ve rüzgar yönünün etkileri de incelendiği modele göre önemli bir etki görülmemiştir. Sıcaklıkla önemli bir ilişkide olan PCB'lerin kısa mesafeli taşınımdan kaynaklandıkları söylenebilir. Korelasyon katsayıları daha düşük olan ve sıcaklıkla önemli bir etkileşim göstermeyen PCB'ler için ise uzun mesafeli taşınımın daha baskın olduğu söylenebilir.

Tek pozitif eğim veren PCB 209 için de aktif durumda olan bir kaynak olduğu düşünülebilir. PCB üretimi ve kullanımı yasak olduğundan bu kaynak, binalardan, iç ortam havasından, topraktan, vs. havaya transport prosesleriyle geçişi olarak değerlendirilebilir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Semivolatile organic compounds (SOCs) have been found to be widely distributed in the atmosphere because of their moderate vapor pressure, low solubility and low reactivity. Polychlorinated Biphenyls (PCBs) are one of the group in SOCs and are relatively ubiquitous in the environment due to common usage in the past.

The atmosphere is a major pathway for the transport, deposition, degradation and cycling of past and present SOCs. Because of their chlorine content, PCBs are toxic, persistent in the environment and have the capability of bioaccumulation through the food chain (Breivik et al., 2004). The persistency of these chemicals plays a major role in the transport; especially they are subject to long-range transport. Most of the persistent organic pollutants (POPs) were detected in the remote areas like Arctic (Bidleman et al. 1990) and Antarctica (Montone et al. 2003). Due to their long-range transport potential and harmful effects on man and wildlife, PCBs are subject to international agreements (the 1998 UNECE Protocol on Persistent Organic Pollutants (POPs) signed by 35 governments in Europe and North America and the European Community, Stockholm Convention on Persistent Organic Pollutants signed by 151 governments). Objective of these agreements is to control, reduce or eliminate discharges, and emissions of environmental burdens of POPs.

It has been also shown that the ambient concentrations of SOCs are affected by seasonal temperature variations and long-range transport (Sofuoglu et al., 2001; Lee and Jones, 1999; Cortes et al., 1998; Hoff et al., 1998; Honrath et al., 1997; Hillery et al., 1997; Wania et al., 1998). As the temperature rises, air concentrations increase as a result of (re)volatilization from previously contaminated surfaces such as soil, atmospheric particles, water, and vegetation. Short-term studies have indicated that SOCs also respond to short-term temperature changes, hence resulting in rapid movement between environmental compartments (i.e. diurnal cycling) (Lee et al., 1998, 2000). Advection and ongoing sources are other important factors affecting the variation of ambient SOCs.

Because of the short and long range transport and cycling behavior of these compounds, PCB levels have been widely measured around the world. However, there is no available study on atmospheric concentrations of these compounds in Turkey. The motivation of this research is to obtain knowledge and to begin creating a database on the levels of these compounds in the suburban atmosphere.

İzmir metropolitan city is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. İzmir is situated in a basin surrounded by mountain series of approximately 1000-1500 m height with only the west end open to the Aegean Sea. The climate in the area is dominantly Mediterranean with warm and rainy winters, hot and dry summers. The major air movements over the area are mainly from northerly directions. The city with the 2.7 million population has sizeable economic, industrial, and agricultural activities emitting high quantities of air pollutants. The use and production of polychlorinated biphenyls (PCBs) was banned/restricted in Turkey as in many countries due to persistent contamination of the environment.

The objective of this study is to obtain the concentration profiles of polychlorinated biphenyls in the ambient air of İzmir. Specifically the objectives of this research are:

- To determine atmospheric gas and particle phase concentrations of PCBs in the ambient air of İzmir.

- To determine day/night and seasonal variation.

- To determine the dominating transport mechanism (short or long-range) based on the temperature dependency point of view.

This thesis is divided into five different chapters. The first chapter is an overview and objectives of the study. The second chapter reviews concepts and previous studies in the literature. The third chapter presents site description and sampling program, sample preparation and analysis, and quality assurance/quality control applications.

Results and discussions are presented in the fourth chapter. In the fifth chapter includes the conclusions drawn from this research and recommendations for possible future work are given.

CHAPTER 2

LITERATURE REVIEW

This chapter introduces the sources, ambient concentrations, phase distribution and environmental fate of polychlorinated biphenyls (PCBs) as they are reported in the literature.

2.1. Chemical Structure and Properties of PCBs

PCBs are a group of synthetic organic chemicals consisting of two aromatic rings of carbon atoms binded with carbon-carbon bonds. The general chemical formula for PCBs is:

$$C_{12}H_{10-n}Cl_n$$

with n indicating the number of chlorine substitutions. PCBs can have 1 to 10 chlorine atoms substituting for hydrogen atoms on the biphenyl rings (Figure 2.1). According to the number and position of the chlorine atoms on the biphenyl ring, PCBs can have 209 possible chemical structures designated as congeners. For instance, if a biphenyl ring has two chlorine atoms at 2 and 4' position, the name becomes 2, 4'-dichlorobiphenyl based on the number of chlorine atoms per biphenyl molecule. PCBs are subdivided into groups such as thrichlorobiphenyls which have exactly three chlorines in the structure while tetrachlorobiphenyls have four chlorines. According to the International Union of Pure and Applied Chemistry (IUPAC) system of nomenclature, the 209 PCB congeners are arranged in ascending numerical order (e.g. PCB 1, PCB 2, etc.).

Between 1930 and 1977, they were used widely and marketed under the name of Aroclors. Each Aroclor has a code number (e.g., Aroclor 1242, Aroclor 1248, etc.), in which the first two digits indicate that the parent molecule is biphenyl and the last two digits refer to the chlorine content by weight percent in the mixture (LaMP 2000). For example Aroclor 1242 is 42 % chlorine by weight. The other trade-names of PCBs depending upon the manufacturer are; Apirolio, Ascarele, Clophen, Delor, Fenclor, Inerteen, Kanechlor, Phenoclor, Pyralene, Pyranol, Pyroclor, Sovtol and etc.

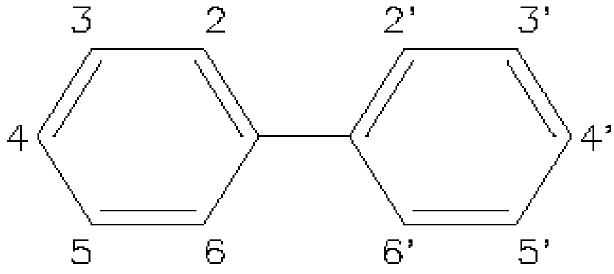

Figure 2.1. General Structure of the Biphenyl Ring System

The superior chemical properties of PCBs made them desirable in use until their environmental effects were noticed. For example, PCBs are nonflammable, chemically and thermally stable chemicals. They also are miscible with organic compounds, and have high dielectric constants and high absorption capacity. These properties can vary for every individual congener due to the chlorine content. As the degree of chlorination increases, PCBs become less soluble, less volatile, less biodegradable (more persistent) and more toxic. In contrast to these properties, their hydrophobicity and sorption tendency increases with the degree of chlorination (Vallack et al. 1998, Jones and Voogt 1999, LaMP 2000). Examples of some PCB structure, important physical and chemical properties are given in Table 2.1. The examples are given to represent each chlorine group and all values are given at 20-25 °C temperature range.

The most important property of PCBs is their persistency in air, water, and soil. PCBs have low water solubility and low vapor pressures that allow them to partition among water, soil, and the atmosphere. They have a high potential for bioaccumulation and when released to the environment they are sorbed strongly on the organic matter. They are hydrophobic and lipophilic in nature, so they can accumulate on the fatty tissues, and enter the food chain. PCBs are very resistant and do not degrade easily. The high thermodynamic stability of PCBs makes the degradation difficult (Erickson 1997). However, under certain conditions, PCBs may be destroyed by chemical, thermal, and biological processes (Erickson 1997). With intentional degradation, PCBs can be generally degraded or destroyed by high temperature or by catalytic degradation. The unintentional degradation, on the other hand, may be proceeded by the environment. Chemical degradation occurs by photolysis with hydroxyl radicals

(Anderson et al. 1996, Wania et al. 2002) while microbial degradation occurs anaerobically or aerobically (Totten et al. 2002). However, microbial degradation is quite slow and does not have a significant role in the degradation of PCBs. Therefore, PCBs are considered as one of several truly global environmental pollutants, including mercury, lead, and many pesticides (Erickson 1997). In fact, atmosphere is the primary mode of global distribution of PCBs. For instance, Eisenreich et al. (1981) estimated that the atmospheric pathway was responsible for 60-90% of PCB input into the Great Lakes region.

Table 2.1. Chemical and physical properties of some PCBs

Congener name	**Chlorine place in the structure**	**Molecular Weight (g/gmole)**	**Subcooled liquid solubility (g m^{-3})**	**Subcooled liquid vapor pressure (Pa)**	**Henry's Constant (m^3Pa/mole)**
PCB 1	2	188.66	5.5	2.5	70.1
PCB 14	3,5	223.11	NA	0.12	NA
PCB 18	2,2',5	257.56	0.4	0.22	92.21
PCB 52	2,2',5,5'	292.01	0.03	0.002	47.59
PCB 87	2,2',3,4,5'	326.46	0.004	0.0023	24.81
PCB 128	2,2',3,3',4,4'	360.91	0.0006	0.00034	11.91
PCB 171	2,2',3,3',4,4',6	395.36	0.002	0.00025	5.4
PCB 202	2,2',3,3',5,5',6,6'	429.81	0.0003	0.0006	38.08
PCB 206	2,2',3,3',4,4',5,5',6	464.26	0.00011	0.000012	82.2
PCB 209	2,2',3,3',4,4',5,5',6,6'	498.71	0.000001	0.00003	20.84

NA: not available

The vapor pressures of PCBs indicate that they generally exist in the vapor phase in the atmosphere. It is reported that 87-100% of PCBs are found in the gas phase (LaMP 2000; Axelman and Broman 2001; Mandalakis et al. 2002; Yeo et al. 2003a). Their melting temperatures and boiling temperatures range between 98-181°C and 275-450°C, respectively. Additionally, they are semivolatile and toxic chemicals.

According to Environmental Protection Agency (EPA) they are classified as probable human carcinogens (group B).

2.2. Sources of Polychlorinated biphenyls (PCBs)

PCBs were first synthesized in the late 1920s. The industrial production started in 1929 and reached at maximum level in 70's. Due to their physical and chemical properties, PCBs were used widely in many industrial processes. They had been used as dielectric fluids, coolants, and lubricants in transformers and large capacitors, as insulating fluids in electrical equipment and surface coatings. In addition, they were used as pesticide extenders, plasticisers in sealant, as heat exchange fluids, cutting oils, flame retardant, dedusting agents, laminating and impregnating agents, waxes, additives in cement and plaster, and in plastics, paints, inks, fluorescent lights, adhesives and carbonless copy paper, and old immersion oils.

As a result, sources for PCBs can be (a) continued use and disposal of PCB-containing products (such as transformers etc., that were manufactured before 1977), (b) recycling of PCB-contaminated products (such as carbonless copy paper), (c) combustion of PCB-containing materials, (d) release of PCBs from waste storage and disposal. Old consumer goods and household waste might also contain PCBs and their use and disposal are unregulated, (e) spill of PCBs during handling or transport, and (f) minor quantities emitted from various combustion processes (Vallack et al. 1998, Jones and Voogt 1999, Axelman and Broman 2001, EPA, Farrington et al. 2001, Breivik et al. 2004). The contaminated aquatic media can also act as sources of persistent pollutants (POPs) in the atmosphere. For example, it has been shown that such compounds were readily volatilized from water, as shown in the Great Lakes in North America (Achman et al. 1994, Hornbuckle et al. 1993) and Lake Baikal in Russia (Iwata et al. 1995), and also from contaminated soil in United Kingdom (Harrad et al. 1994).

Although the usage and manufacturing of PCBs were banned in many countries, they are reported to be manufactured in Russia and might also be manufactured in North Korea (Farrington et al. 2001). It is estimated that 2 million tones of PCBs have been produced world-wide since 1930s (Tanabe 1988, WHO 1993, Breivik et al. 2004).

2.3. Health Effects of PCBs

Even though PCBs are no longer manufactured, people can still be exposed to them due to the volatilization from the old contaminated areas. Many older transformers and capacitors containing PCBs can be in use for 30 years or more. Old fluorescent lighting fixtures and old electrical devices and appliances, such as television sets and refrigerators may contain PCBs if they were made before PCB use was banned. The devices that contain PCBs could leak with age and cause also a source of skin exposure to PCBs.

Exposure to PCBs can be in three ways; inhaling the contaminated air, ingesting the contaminated food, and dermal contact to contaminated surfaces. Health effects of PCBs on human beings was obtained from the studies of people exposed in their workplace by the consumption of contaminated food (the *Yusho* incident, 1968, and the *Yu-Cheng* incident, 1979) (Agency for toxic substances and disease registry(ATSDR) 2000). They have revealed that PCBs contributed adverse health effects on humans, but which congeners could have caused the effects could not be determined. The most commonly observed health effects on people exposed to large amounts of PCB are skin problems such as acne and rashes. PCBs may also cause irritation of the nose and lungs, depression and fatigue, liver, thyroid dermal and ocular changes, immunological alterations, neurodevelopment changes, reduced birth weight, reproductive toxicity, and cancer. The US Department of Health and Human Services (DHHS) has concluded that PCBs may reasonably be anticipated to be carcinogens. In addition, the EPA and the International Agency for Research and Cancer (IARC) have determined that PCBs are probably carcinogenic to humans (ATSDR 2000).

Similarly, animal studies showed that they had mild liver damage with some observed deaths and developing anemia, acne-like skin conditions, and liver, stomach, and thyroid gland injuries, changes in immune system, behavioral alterations, and impaired reproduction after consumption of PCB contaminated food. Rats that ate food containing high levels of PCBs for two years developed liver cancer (ATSDR 2000).

2.4. Ambient Concentrations of Polychlorinated Biphenyls (PCBs)

Last two decades, the development in analytical techniques of PCB isolation and measurement made it possible to detect very low levels of concentrations. Then increased attention was given to the local concentration measurements of these compounds due to the fact that they have been detected in remote areas.

Ambient air concentrations of PCBs were measured in urban (Granier and Chevreuil 1997, Mandalakis et al. 2002, Totten et al. 2002), suburban and rural (Mandalakis et al. 2002, Yeo et al. 2003a) areas throughout the world.

The concentrations in remote areas like Arctic and Antarctic have always been concerned. The presence of PCBs in the Arctic atmosphere was taught to be the result of a combination of processes. These include long-range transport, revolatilization from previously contaminated surfaces (snow, ice and water bodies) (Hung et al. 2001). The five year concentration trend of Canadian Arctic was studied and seen that PCB concentrations have not declined significantly over the period of 1993-1997 (Hung et al. 2001). They worked with 102 PCB congeners and measured the concentrations both in the gas and particulate phases. It was noted that the lower chlorinated congeners (PCB 28, 31, and 52) declined in the five-year period of investigation. The reason of this trend is taught to be the dominating effect of long-range transport, whereby levels in the Arctic would simply reflect the falling levels encountered in the source regions, and the fast OH depletion rates (which is the most important degradation mechanism of PCBs) during the Arctic summer. A significant decreasing trend was seen for PCB 180 (heptachlorinated) while no clear trend was apparent for the penta- and hexachlorinated congeners. Nevertheless, the lack of declining trend may be the result of slow biotic and abiotic degradation because of the lower temperatures in Arctic, coupled with winter darkness. Lastly it was implied that the Arctic is still acting as a sink for PCBs transported from the south.

Mostly, the total (gas+particulate phase) concentrations are reported in previous studies. In Table 2.2 the total concentrations of PCBs are listed for several countries.

The other study related to a remote area was conducted by Montone et al. (2003) in the other polar region, Antarctica. They searched for 10 PCB congeners (PCB 18, 44, 52, 101, 118, 128, 138, 153, 180 and 187) and found a total mean concentration of 37 pg m^{-3}. The lower chlorinated congeners predominated in the samples and represented 66.7% of the total PCB concentrations. On the other hand, the results of a previous study (Kallenborn et al. 1998) where the similarities and differences between the PCB concentrations in Arctic atmosphere were discussed exhibited there were no big difference between two polar regions. While the minimum and maximum values for PCB 28, 31 and 52 were approximately the same, those of the higher chlorinated PCBs (PCB 101 and higher) were approximately two to three times lower in Antarctica.

Table 2.2. Ambient air concentrations of PCBs

LOCATION	**Concentration (ng/m^3)**	**Reference**
Antarctic Coast	0.06-0.2	Tannabe et al.,1983
Arctic	0.002-0.013	Bidleman et al.,1990
Canadian Arctic	0.1-0.3	Bidleman et al.,1990
Bombay,Goa,Bangalore, Calcutta,India	0.5-4.5	Iwata et al.,1994
Chicago,USA	1.3	Cotham and Bidleman,1995
London,Manchester, Cardiff,UK	0.2-3.5	Halsall et al.,1995
Tainan City,Taiwan	2.6-7.1	Lee et al.,1996
Paris,France	2.0-6.0	Granier and Chevreuil,1997
Gardsjön,Sweden	0.298	Brorström and Löfgren, 1998
Galveston Bay, Texas	1.18	Park et al., 2001
Athens,Greece	0.35	Mandalakis et al., 2002
Madrid, Spain	1,155	Garcia-Alonso et al., 2002
Kyonggi-do,Korea	0.066	Yeo et al., 2003
Antarctica	0.037	Montone et al., 2003
Birmingham, UK	0.252	Harrad and Mao, 2004

In Korea, the concentration distribution and temperature dependency of PCBs in air were studied in rural areas (Yeo et al. 2003a). In this study, a total of 22 types of PCB congeners [tri-(PCB 18, 27, 28, 33, 38), tetra-(PCB 47, 49, 52, 60, 61/74, 66), penta-(PCB 87, 101, 118, 126), hepta-(PCB 170, 180/193, 183, 187), deca-CB (PCB 209)] were detected and the average concentration of total PCB was 19.9 pg m^{-3}. The highest concentrations were belong to tri-CBs followed by tetra-CBs, penta-CBs, hepta-CBs, hexa-CBs, and deca-CBs. There seemed a tendency for the concentration of PCBs in the atmosphere to decrease with increasing number of Cl. Therefore, tri-CBs were found to be the most abundant homologs in air in the rural area of Korea. From the correlation analysis of PCB homologs with temperature it was reported that, except deca-CBs, PCBs were significantly temperature dependent. The amount of PCBs in the gas phase was 90% and they observed that particle-bound fractions of higher molecular PCB congeners with low vapor pressure were considerably higher than those of lower molecular PCB congeners (Yeo et al. 2003a).

For representing a recent study and to be the nearest country, the atmospheric concentrations of PCBs measured in Athens, Greece is an important study for comparison while long-range transport is one of the transport mechanisms of an atmospheric contamination. Mandalakis et al. (2002) have worked with 38 PCB congeners (6, 8, 5, 18, 17, 16, 32, 31, 28, 33, 20, 22, 52, 49, 47, 48, 44, 41, 46, 74, 70, 66, 95, 101, 90, 136, 110, 123, 149, 118, 153, 132, 105, 138, 163, 164, 158, and 160). They measured the atmospheric concentrations at three sites representing the urban, coastal and rural sites. The total mean PCB concentrations of the urban site, which is 348.6 pg m $^{-3}$ and has the highest concentrations among the other two sites, is given here to be comparable with the results in this study. The tri- and tetra-chlorinated biphenyls (PCB congener 18 to PCB congener 66) were reported to be the most abundant homolog groups and 99% of the total concentration was in the gas phase in the urban air of Athens. In the other study by Kouimtzis et al. (2002) only particulate phase concentrations of six PCB congeners (PCB 28, 52, 101, 138, 153, 180) were measured in urban and subrural (suburban) atmosphere of Thessaloniki area and found total mean concentrations of 9.8 and 3.0 pg m^{-3} . These concentrations are comparable with those obtained in Athens, however they are much lower than the other reported concentrations.

In the urban air of Madrid, Σ PCB (gas+particulate) concentrations were determined to be 1154.6 pg m^{-3} where 72% of it represented gas phase PCBs. They selected 31 congeners to analyze and 20 of them were determined in gas phase (PCB 7, 8, 18, 28+31, 44, 52, 66, 70, 77, 97, 101, 105, 118, 138, 151, 153, 170, 180, 194, 195, 207) and particulate phase (PCB 8, 18, 28+31, 44, 52, 66, 70, 77, 97, 101, 105, 118, 138, 151, 153, 170, 180, 187, 195, 194) samples.

Granier and Chevreuil (1997) made a five-year study to determine the trend in the total concentration of PCBs (15 congeners; PCB 28, 31, 33, 22, 101, 110, 149, 118, 108, 153, 138, 196, 201, 189 and 206) in the urban atmosphere of Paris. They observed approximately twofold drop (from 12 ng m^{-3} to 5.2 ng m^{-3}) in the level of PCBs between 1986-1990, and concluded that this would be the result of a greater control by the authorities and a greater awareness of the public. In this investigation PCBs did not exhibit a clear seasonal cycle and this was explained by the presence of a variety of low intensity sources still emitting PCBs in the Paris atmosphere. The distribution between the vapor phase and the particle phase was 79 and 21%, respectively. The percent of particle-bound PCB components increased, in general, with their degree of chlorination as a consequence of their decreasing vapor pressure from light to heavy component.

In Galveston Bay, Texas the total mean air concentration of PCBs (97 congeners) was 1.18 ng m^{-3} and 96% of it was in the gas phase (Park et al. 2001). It was observed that highly chlorinated PCBs were found in the particulate phase while lower molecular weight congeners were found in the gas phase. There was no apparent seasonal trend, however the highest concentration of total PCBs was reached in the warmest weather of the sampling period and specific wind directions and speeds effected the trend. High temperature accompanied by wind from urban and industrialized areas (S, SW, W, and NW) and relatively slower wind speed resulted in elevated PCB concentrations in air samples. The higher atmospheric concentrations in USA is probably due to the fact that much larger amounts of PCB commercial mixtures were produced and consumed in this country.

The recent study representing an urban site in UK (Harrad and Mao 2004) searched for atmospheric concentrations and seasonal trends of 41 PCB congeners. They got lower values for an urban site (total gas and particulate phase PCBs (ΣPCBs) 252 pg m^{-3}). PCB congeners influenced by a combination of reciprocal temperature, wind direction, and wind speed. However, when samples for which the wind speed <4.4 m s^{-1} were analysed; only temperature and relative humidity were influential for most congeners. They concluded that the long-range transport rather than local sources exerts the greatest influence on PCB concentrations at Birmingham.

In the literature, similar sampling methods were used for the measurement of atmospheric concentrations of PCBs. High volume samplers were used with glass fiber filters (GFF) for collecting particulate matter and polyurethane foam plugs (PUF) for collecting the gas phase PCBs and other organochlorine compounds (Granier and Chevreuil 1997, Brorström and Löfgren 1998, Mandalakis et al. 2002, Montone et al. 2003, Yeo et al. 2003b, Harrad and Mao 2004).

2.5. Fate of PCBs in the Environment

As discussed before, persistent organic pollutants (POPs) are resistant to photolytic, biological and chemical degradation so that they are capable of long-range transport. As a result of this phenomenon they have become ubiquitous. They were detected even in the Arctic in 1960s and 1970s where they have never been used or manufactured (Vallack et al. 1998). Atmosphere is the major pathway for the transport and deposition of POPs to ecosystems both far and near source areas. Due to their lipophilic property they are able to accumulate in the ecosystem, and they can also be released back to the atmosphere by some environmental processes which will be discussed later (Wania and Mackay 1996, Brorström and Löfgren 1998).

POPs have tendency to migrate from warmer regions and deposit in polar regions. This is explained with their moderate volatility and ambient temperature, meaning that POPs tend to volatilize from tropical and temperate regions of the globe, and condense, and then tend to remain in colder regions. For example, PCB congeners having one chlorine can move world-wide being deposited, whereas congeners with 8-9 chlorines tend to be deposited closer to the source. The concentration of volatile compounds is thus low in tropical areas, and higher in temperate or Polar Regions (Wania and Mackay 1996). In Figure 2.2 the schematic view of migration process is summarized.

It has been suggested that POPs migrate to higher latitudes in a series of short jumps, called as “grasshopper effect”, whereby they migrate, remain in the atmosphere and migrate again with seasonal temperature changes at mid-latitudes. Another suggestion is, more highly volatile POPs will tend to remain airborne and migrate faster and further towards the Polar Regions than the less volatile ones. While the cooler conditions favor greater adsorption onto atmospheric particulate matter and promote enhanced adsorption from the vapor phase onto environmental surfaces (e.g. vegetation, water, soil, snow and ice), deposition is the dominating mechanism over evaporation in polar regions and it is opposite in low latitudes (Vallack et al. 1998, Jones and Voogt 1999).

2.5.1 Temperature Dependency of PCBs

It has been known that the air concentrations of PCBs have a strong relationship with ambient air temperature (Halsall et al. 1995, Hillery et al. 1997, Lee et al. 1998, Sofuoglu et al. 2001). The processes of volatilization, deposition, transport and transformation for these atmospheric chemicals respond to variations in ambient temperature. This is an important factor for understanding the distribution and movement of POPs far from areas where they are discharged (Gouin et al. 2002). At high temperatures, the air gas phase concentrations increase indicating that volatilization from the Earth's surface (e.g. vegetation, soil, water, etc.). Temperature dependence of air concentrations appears to be most pronounced for the more chlorinated congeners. This is caused by the energy required to effect the phase transition from the environmental surface to the atmosphere. Therefore, the temperature dependency generally increases with the degree of chlorination. In other words, less volatile PCBs show the strongest temperature dependence (Breivik et al. 2004). The temperature dependence of a phase transition has been expressed by the Clausius-

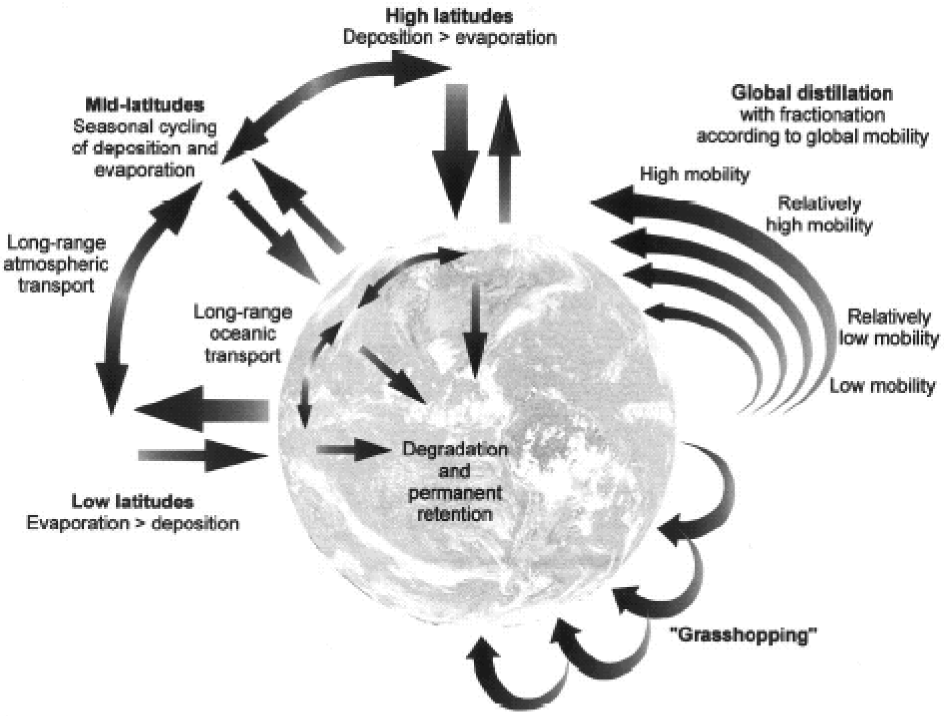

Figure 2.2. Global POP Migration Process *(Vallack et al. 1998)*

Clapeyron equation when the system is at equilibrium (Burgoyne and Hites 1993, Hornbuckle and Eisenreich 1996, Honrath et al. 1997, Hoff 1998):

$$\ln P = (-\Delta H_v / R)(1/T) + \text{constant} \tag{2.1}$$

where P is the gas-phase semivolatile organic compound (SOC) partial pressure (atm), ΔH_v is the enthalpy of vaporization (kJ mol^{-1}), R is the gas constant (K atm mol kJ^{-1}), and T is the average atmospheric temperature (K) during the sampling period. ΔH_v is the heat required for phase change of a pure compound. It has been suggested that the slopes of Clausius Clapeyron equation could be interpreted as a parameter that implies the source of the chemicals of concern (Hung et al. 2001, Harrad and Mao 2004). For a more moderately volatile chemical, long-range transport becomes less important and the overall slope becomes steeper. For a chemical that is more strongly bound to surfaces, long-range transport is going to be a very small contributor to the local variation in partial pressure and the slope will assume a shape that is strongly dependent on the ratio of concentrations in local surface sources. In other words a steep slope indicates that compound concentrations in air are controlled by revolatilization from surfaces in the local surroundings of the sampling site, and when the slopes begin to flatten out, it can be assumed that long-range transport is becoming dominant in the contribution to the air concentration (Hoff 1998, Sofuoglu et al. 2001, Gauin et al. 2002, Yeo et al. 2003a). By considering the source of the contaminants it can be dealt that contaminant on a continental or global basis. This information would be necessary for the international agreements on persistent organic pollutants.

When the number of chlorine atom increases in the form of PCBs, their atmospheric concentrations seemed to decrease. The log K_{OA} (octanol-air partition coefficient), vapor pressure, solubility and the physical and chemical characteristics of PCBs, may explain this. As the number of chlorine increases, log K_{OA} also increases Eventually, PCB homologs, having higher chlorine atoms than penta-CBs, settle more easily on surfaces and evaporate less to the atmosphere because of having lower vapor pressure than the tri- and tetra-CBs. Due to their lower K_{OA} values these lighter homologs mainly exist in the gas phase in air (LaMP 2000, Axelman and Broman 2001, Mandalakis et al. 2002, Yeo et al. 2003a).

PCBs can be found either in the gas phase or particle phase in the atmosphere. Therefore, they reach a partitioning equilibrium between these two phases according to the temperature dependences and the vapor pressure of the chemicals. The partitioning of semivolatile organic compounds in the atmosphere is an important factor in their transformation and transport (Mandalakis et al. 2002). The atmospheric transport is the main pathway for the spread of PCBs in the environment (Gevao et al. 1998, Harner and Bidleman 1998, Yeo et al. 2003a). SOCs are present in the gas phase and in the condensed form in the atmosphere, sorbed to a particulate matter (Gevao et al. 1998, Sanusi et al. 1999). Their distribution between these phases influences the atmospheric transport and removal of chemicals via deposition or degradation. This partitioning phenomenon is controlled by factors such as the vapor pressure of the compound, the ambient temperature and the nature, size distribution and total suspended particle (TSP) concentration. PCBs are removed from the atmosphere by wet deposition (by dissolving in a rain/ snow droplet), dry deposition (by adsorption on effective surfaces) and vapor absorption at the air-water interface (Finizio et al. 1997, Gevao et al. 1998, Sanusi et al. 1999, Mandalakis et al. 2002, Yeo et al. 2003b). The removal mechanism could be manifested by Henry's law constant (H) for the gas phase compounds, having longer atmospheric residence times. For example, having low H values shows that the compound is more effectively washed out by rain, while the high H values demonstrate the long atmospheric residence time since they are removed by neither precipitation nor particle deposition. The dominating removal mechanism for gaseous compounds is the vapor deposition on a suitable surface in environment or atmospheric chemical or photochemical reactions (Sanusi et al. 1999).

CHAPTER 3

MATERIALS AND METHODS

Sampling techniques and experimental procedures, quality control and assurance for the measurement of ambient air concentrations of PCBs and calculations will be given in this chapter.

3.1. Sampling Program

Samples were collected at the Dokuz Eylül University, Tınaztepe campus (Figure 3.1) where a 4 m-high platform is located on 38 degrees 22 minutes 08 seconds North latitude and 27 degrees 12 minutes 43 seconds East longitude. The sampling site was located in a suburban area, approximately 10 km southeast of Izmir city center. The campus is relatively far from any settlement zone and industrial facilities. For example, there are residential areas located approximately 3 km southwest and a highway 0.5 km south of the sampling site. Land cover in the immediate area is a young coniferous forest. There are steel plants, a petroleum refinery and a petrochemical industry located 45 km to the northwest. The nearest industrial facility is a cement work about 10 km at the north and an open road gravel storage site nearly 3 km at the east. Annual windrose for Izmir points to prevalence of northerly winds.

In this investigation, 20 short-term (daytime and nighttime), and 40 long-term (daytime) ambient air samples were collected both for PCBs and total suspended particulates (TSP), between May-2003 and May-2004. All samples were collected when there is no rain and also long-term samples were collected once in every six days in order to see if any fluctuation occurs throughout a week.

Meteorological data was obtained from a 10 m high tower located on top of the same platform where sampling instruments were located. However, during blackout periods and the malfunctionin of instruments, meteorological data was obtained from the İzmir Menderes Airport’s meteorological unit. A summary of meteorological, TSP

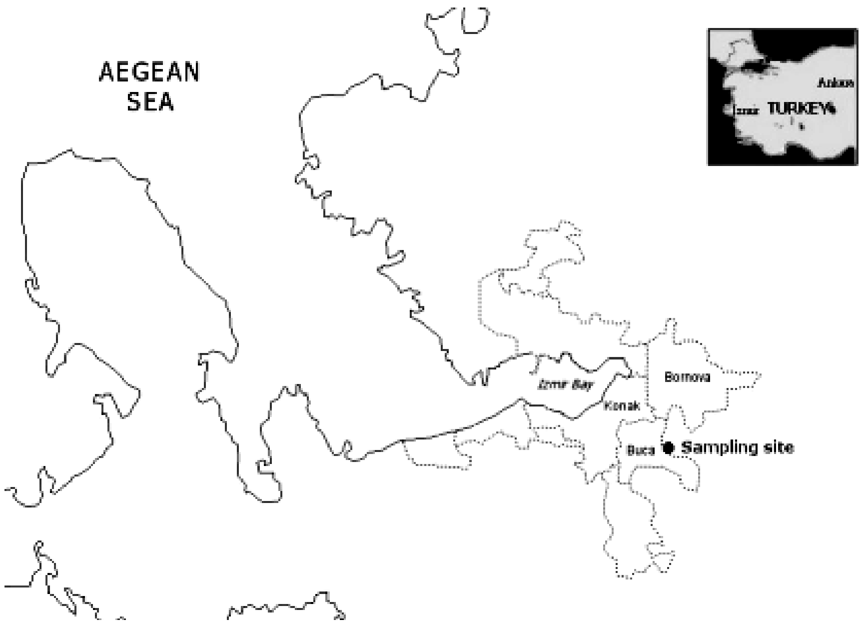

Figure.3.1. Area of study and location of the sampling site.

and organic matter (OM) data is shown in Table 3.1 and Table 3.2 for daytime and nighttime sampling period, respectively. Long-term sampling information is given in Table 3.3. The average sampling volumes were 223 ±8 and 41 ± 4 m^3 for PCB and TSP samples, respectively.

Table 3.1. Summary of Sampling Information for the short-term daytime sampling

Date (2003)	Sample Number	T (°C)	Relative Humidity (%)	Wind Speed (m/s)	Wind Direction	TSP (µg m^{-3})	OM (µg m^{-3})	OM (%)
14.05	1	23.50	53.17	2.76	WNW	72.44	59	81
15.05	2	25.04	46.75	2.16	WNW	84.47	44	52
16.05	3	26.38	43.08	3.38	WNW	127.4	54	43
17.05	4	25.66	45.05	3.50	WNW	94.63	59	62
18.05	5	23.19	58.22	4.99	WNW	108.97	57	52
19.05	6	21.90	63.92	5.08	NW	108.25	59	55
20.05	7	22.49	55.90	5.54	N	68.79	47	44
21.05	8	24.16	53.26	3.10	ESE	93.4	55	59
22.05	9	22.63	50.79	6.03	ESE	72.6	34	47
23.05	10	21.50	50.47	3.78	SE	42.94	25	58
Average			52.06	4.03		87.39	49.30	55
SD			1.91	0.72		20.86	24.04	16

Table 3.2. Summary of Sampling Information for the short-term nighttime sampling

Date (2003)	**Sample Number**	**T (°C)**	**Relative Humidity (%)**	**Wind Speed (m/s)**	**Wind Direction**	**TSP (µg m^{-3})**	**OM (µg m^{-3})**	**OM (%)**
14.05	1	18.24	68.86	1.43	ESE	72.78	45	62
15.05	2	20.08	64.11	0.76	N	101.42	52	51
16.05	3	20.77	62.74	0.90	N	95.31	39	41
17.05	4	20.04	67.98	1.19	N	88.65	18	20
18.05	5	17.98	78.57	1.74	NW	89.51	35	39
19.05	6	17.21	74.08	4.28	WNW	77.37	37	48
20.05	7	18.47	72.40	1.00	NW	84.39	87	69
21.05	8	16.94	71.71	2.41	WNW	48.20	27	57
22.05	9	17.25	71.59	3.82	SSE	25.01	14	55
23.05	10	15.71	82.64	2.15	SE	39.88	24	73
Average			71.47	1.97		72.25	37.8	52
SD			9.74	0.51		23.26	14.85	8

3.2. Sampling Method

Air samples were collected using a high-volume sampler modified Model GPS-11 (Thermo-Andersen Inc.). The PUF sampler (Figure 3.2) is designed to collect suspended airborne particulate matter on a filter and vapor phase compounds on a backup sorbent. Particles were collected on 10.5 cm diameter glass fiber filters. The gas phase compounds were collected in a modified cartridge containing XAD-2 resin placed between two sections of polyurethane foam (PUF) plug (Figure 3.3).

The PUF is 2-inch thick sheet stock polyurethane type (density 0.022 g cm^{-3}). The PUF cylinders (plugs) were slightly larger in diameter than the internal diameter of the cartridge.

Table 3.3. Summary of Sampling Information for Long-term Sampling

Sample Number	**Date**	**T (°C)**	**Relative Humidity (%)**	**Wind Speed (m/s)**	**Wind Direction**	**TSP (µg m^{-3})**	**OM (µg m^{-3})**	**OM (%)**
1	14.05.2003	23.50	53.17	2.76	WNW	72.44	59	81
2	17.05.2003	25.66	45.05	3.50	WNW	94.63	59	62
3	23.05.2003	21.50	50.47	3.78	SE	42.94	25	58
4	29.05.2003	20.98	60.11	6.14	N	51.0	7.3	14
5	23.06.2003	31.70	28.62	5.22	N	163.1	64.8	40
6	27.06.2003	29.50	34.26	5.77	WNW	103.1	59.8	58
7	29.06.2003	30.25	25.64	5.03	WNW	73.3	50.3	69
8	05.07.2003	34.61	25.35	4.28	WNW	71.0	22.3	31
9	17.07.2003	30.01	32.14	6.93	S	52.2	25.1	48
10	23.07.2003	29.89	29.53	7.12	N	24.6	12.3	50
11	29.07.2003	29.56	30.48	7.03	N	39.1	30.9	79
12	04.08.2003	30.36	41.59	8.31	N	73.3	12.2	17
13	10.08.2003	27.43	47.90	6.73	WNW	44.3	23.2	52
14	16.08.2003	30.75	29.15	3.91	WNW	84.57	45.14	53
15	28.08.2003	28.44	45.48	3.36	WNW	40.64	28.45	70
16	03.09.2003	27.87	51.69	4.87	WNW	87.48	27.22	31
17	08.09.2003	22.78	36.69	4.05	WNW	51.12	16.27	32
18	15.09.2003	21.33	57.97	5.74	WNW	104.35	53.97	52
19	21.09.2003	24.54	30.62	7.81	N	57.16	43.97	77
20	27.09.2003	22.68	55.67	5.24	N	76.24	30.03	39
21	03.10.2003	21.52	53.67	4.21	WNW	70.76	30.66	43
22	10.10.2003	16.55	55.00	4.63	NNW	28.40	26.03	92
23	15.10.2003	19.41	47.40	4.67	N	84.66	44.68	53
24	22.10.2003	25.33	41.96	4.86	SSE	38.72	13.67	35
25	05.11.2003	18.16	67.08	9.17	N	84.57	45.14	53
26	10.11.2003	9.07	62.94	8.44	N	32.10	23.33	73
27	16.11.2003	13.70	57.57	1.58	WNW	86.15	80.76	94
28	22.11.2003	17.06	56.04	2.35	SSE	18.42	42.98	79
29	05.12.2003	8.97	61.62	5.92	N	35.71	6.49	18
30	18.12.2003	1.85	60.00	7.95	N	84.57	45.14	53
31	27.12.2003	6.85	72.87	7.29	N	78.51	75.49	96
32	07.01.2004	-1.20	54.42	4.65	N	44.77	11.94	27
33	14.01.2004	9.50	81.50	0.15	N	17.4	10.20	58
34	30.01.2004	2.60	82.50	1.70	SSE	476.29	235.09	49
35	05.02.2004	5.75	67.00	4.25	NW	91.44	22.86	25
36	11.02.2004	3.80	43.50	4.05	N	84.61	45.14	53
37	19.02.2004	4.85	65.50	2.00	WNW	80.74	53.82	67
38	26.02.2004	13.90	70.50	7.60	SE	44.03	12.58	29
39	05.03.2004	4.00	59.50	9.40	N	48.48	10.77	22
40	11.03.2004	7.85	62.00	4.00	N	45.57	22.79	50
Average			50.85	5.16		74.56	38.90	52.
SD			15.22	2.18		71.20	37.30	22

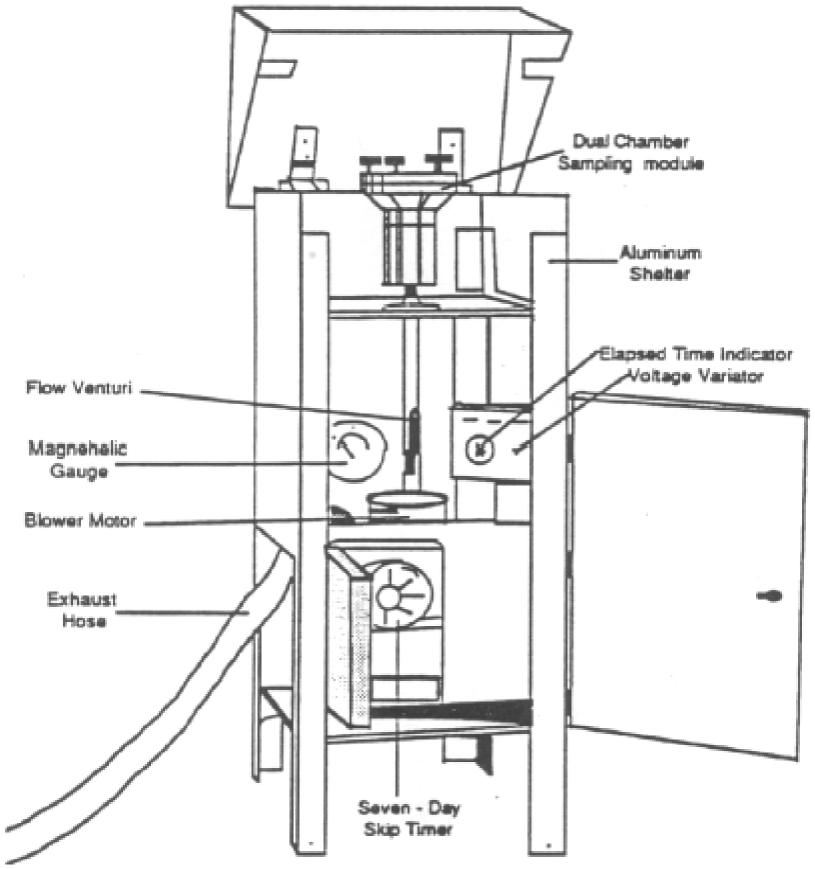

Figure.3.2. Schematic of PUF sampler (Bunckland et. al. 1999)

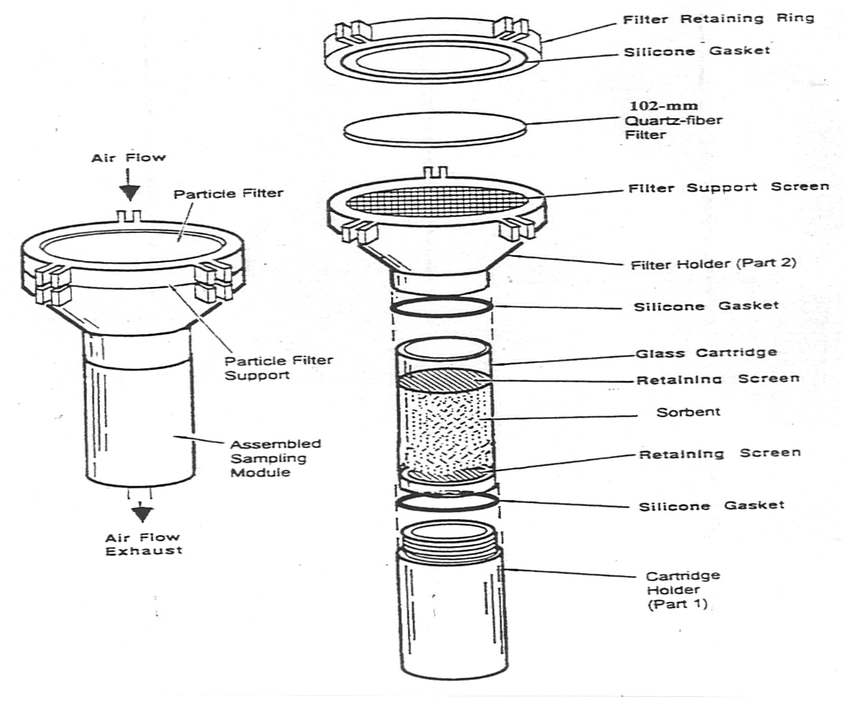

Figure.3.3. Schematic of sorbent cartridge and filter holder (Bunckland et. al. 1999)

Particulate samples were collected on 11-cm diameter quartz filters using another high volume sampler to determine total suspended particulate matter (TSP) and its organic matter (OM) content. The high-volume design causes the TSP to be deposited uniformly across the surface of a filter located downstream of the sampler inlet. The high volume sampler is a compact unit consisting of a protective housing; an electric motor driven; a high-speed. high-volume blower; a filter holder capable of supporting a filter.

3.3. Sample Preparation

Glassware: All glassware used in the sampling and analysis processes were washed with tap water and detergent, and rinsed for a number of times with tap water and then distilled water. Subsequently the glassware was rinsed with a series of polar and non-polar solvents (acetone. hexane) and dried in an oven at 110 °C for 4 hours. The openings of the glassware were covered with aluminum foil as soon as they were removed from the oven. Glassware was rinsed prior to use with dichloromethane.

Glass Fiber Filters (GFFs) and Quartz Filters: Glass fiber filters used in PUF sampler and quartz filters used in high volume air sampler were wrapped loosely with aluminum foil and baked in a muffle furnace at 450 °C for 2 hours to remove any organic residues. Then they were stoppered and allowed to cool to room temperature in a desiccator.

PUF Cartridges and XAD-2 Resin: PUF cartridges and XAD-2 resin used in PUF sampler were cleaned by Soxhlet extraction using a series of solvents (deionized water (DI) 1:1 acetone: hexane mixture) for 24 hours. After extraction cartridges, including polyurethane foam (PUF) and XAD-2 resin, were wrapped loosely with aluminum foil and dried in an oven at 70 °C. Cleaned cartridges were stored in glass jars with Teflon-Lined lids.

3.4. Sample Handling

Cleaned and prepared glass fiber filters, quartz filters, and PUF cartridges were transported to the field in air-tight containers, in order not to allow any exposure to air prior to sampling. After sampling, glass fiber filters were wrapped with aluminum foil, quartz filters were placed in a box of comparable size and then both of them transferred into storage bags. PUF cartridges were wrapped with foil and transferred into glass jars. Then samples were brought back to laboratory and stored in the dark at -20 °C until they were analyzed.

3.5. Sample Extraction and Clean-up

PCB congeners were adsorbed onto a matrix from the ambient air and removed from the matrix by extraction. Then the samples were purified and concentrated prior to analysis. The procedure used in this thesis was a combination of methods developed by University of Minesota and Atmospheric Environment Service in Canada.

3.5.1. Extraction: Gas phase and particulate phase samples (including GFFs and sorbent cartridges) were spiked with PCB surrogate standards prior to extraction in order to determine analytical recovery efficiency. Then they were Soxhlet extracted with a mixture of dichloromethane (DCM): petroleum ether (PE) (20:80) for 12 hours. After extraction, solvents with the extracted samples were stored in dark colored glass bottles with Teflon lined caps at -20 °C.

3.5.2. Concentration: All sample extracts were concentrated using a rotary evaporator. They were evaporated to approximately 5 mL, then solvent exchanged into hexane by the addition of 15 mL and 10 mL hexane in two steps, respectively and again the volume was reduced to 5 mL. The temperature of the water bath was maintained at ~30 °C during sample concentration and solvent exchange. The 5 mL sample was transferred to a 40 mL vial. The sample flasks used for evaporation were rinsed with 5 mL of hexane and this also added into the same vial. The total volume of 10 mL was concentrated down to 2 mL by gently blowing a high purity stream of nitrogen on the surface at a flow rate of 150-200 mL/min.

3.5.3. Sample Clean-up and Fractionation: All concentrated samples were cleaned and fractionated on alumina-silicic acid column (Figure 3.4) to enhance the PCB phase and to get rid of any other organic contamination (Sofuoğlu et al. 2001). Silicic acid was prepared by oven drying at ~100 °C for several hours in a flask loosely covered with aluminum foil to remove moisture and then cooled in a desiccator. Three grams of silicic acid was deactivated by adding 100 µL of deionized (DI) water and shaking the mixture (silicic acid- 3 % water). The mixture sat at room temperature for 1 hour before use and was used within 12 hours.

Alumina was prepared by oven drying at 450 °C for several hours. After cooling to room temperature, two grams of alumina was deactivated by addition of 120 µL DI water (alumina-6% water). Na_2SO_4 placed in beakers and baked in a muffle furnace at 450 °C for several hours, then cooled to room temperature in a desiccator. The column was pre-washed with 20 mL DCM followed by 20 mL PE. The sample in 2 mL hexane was added into the column with a 2 mL rinse of PE and eluent was collected in a vial at a rate of two drops per second. After letting the sample pass through the column, 20 mL PE was added and eluent collected in the same vial. This fraction (Fraction 1) contained PCBs. The vial used for eluent collection was changed, 20 mL DCM was added into the column and eluent containing organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) (Fraction 2), collected at the same rate.

For both fractions the solvent was exchanged into hexane, and the final sample volume was adjusted to 1 ml by nitrogen blow-down and then the samples were taken into 2 mL vials and get ready for the analysis in gas chromatography.

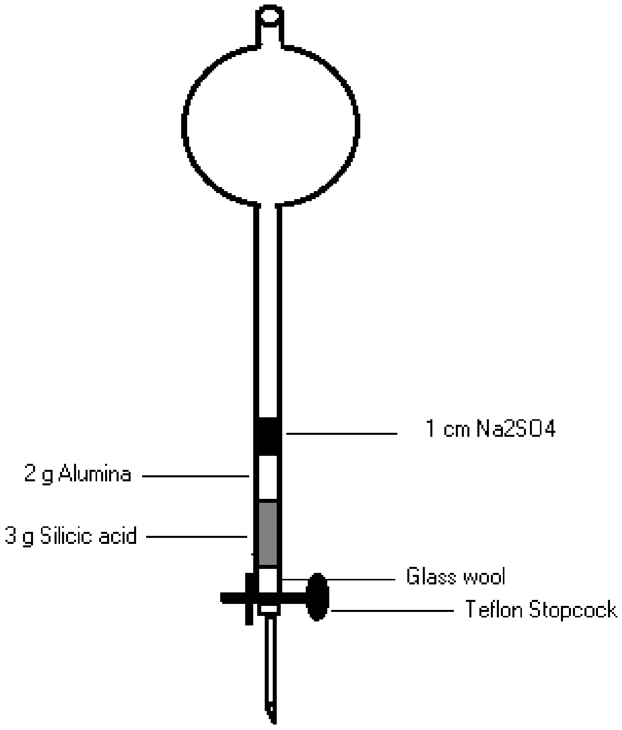

Figure 3.4. Clean-up and fractionation column

3.6. Determination of TSP and Organic Matter Content

Glass fiber filters were wrapped loosely with aluminum foil and they were baked overnight at 450 ºC in a muffle furnace to remove any organic residues. They were then allowed to cool to room temperature in a desiccator and were weighed using a micro balance capable of weighing 0.1 mg. After sample collection filters were kept in a desiccator overnight and they were reweighed. TSP was determined by subtracting the initial weight from the final weight. To determine the organic matter content of the particles, filters were then baked for 1 h at 450 ºC in a furnace, allowed to cool to room temperature in a desiccator, and weighed. Organic matter was determined by subtracting the final weight (after baking) from the initial weight (before baking). It is possible that the determination of OM content by this method may be interfered by the weight loss of glass fiber filters at high temperatures. The hourly weight loss of filters at 450 ºC with time was monitored for 12 hours. It was observed that the maximum weight loss (3 mg) occurs within a 2 h period and the weight loss decreases to 0.3 mg h^{-1} and becomes stable for the remaining period. To minimize the interference from weight loss of filters at high temperatures in OM determination, concurrent blank filters were run for each sample. Determined OM contents were corrected using the weight loss in blank filters during baking. The average weight loss of blank filters (0.3 mg) was significantly lower than the average weight loss of the samples (2.4mg) indicating that the interference was not significant in OM determination.

3.7. PCB Analysis

Samples were analyzed for PCBs using an Agilent 6890N gas chromatography (GC) equipped with a micro-electron capture detector (μ-ECD). A capillary column (HP-5, 30 m, 0.25 mm, 0.25 μm) was used. Instrument operating conditions for PCB analysis are given in Table 3.4.

The software Chemstation was used to acquire and quantify the data. Concentrations of the congeners and compounds were calculated using the internal standard method, where the calculation of the corrected concentration ratio of a compound in an unknown sample occurs in four steps (Cakan. 1999).

Table 3.4. GC/ ECD Operating Conditions

Gas Chromatography	
Column	HP-5. 30 m. 0.25 mm. 0.25 µm
Carrier gas	Helium at 35 cm s^{-1} linear velocity
Detector make-up gas	Nitrogen
Injection mode	Splitless
Injection temperature	250 ºC
Injection volume	1 µl
Purge time	0.6 min
Temperature program for PCBs	Initial oven temperature 50 ºC for 1 min. Raised to 100 ºC at 25 ºC min^{-1}. 100 ºC to 300 ºC at 5 ºC min^{-1}. hold time 7 min. Detector temperature 320 ºC.

1. The calibration points are constructed by calculating a concentration ratio and a response ratio for each level of a calibration for a particular compound,

$$\text{Concentration ratio} = C_{xc}/C_{ic} \tag{3.1}$$

$$\text{Response ratio} = A_{xc}/A_{ic} \tag{3.2}$$

where C_{xc} is the concentration of the compound, C_{ic} the concentration of the internal standard, A_{xc} is the response of the compound, and A_{ic} is the response of the internal standard at this calibration level.

2. A line is fitted through the calibration points using linear regression:

$$Y = mx+b \tag{3.3}$$

where y is the response ratio, x is the concentration ratio, m is the slope of the line, and b is the intercept of y,

3. The response ratio for the unknown is calculated using the response of the compound in the sample (A_{xs}) and response of the internal standard in the sample (A_{is}),

$$\text{Response ratio for unknown} = A_{xs}/A_{is} \tag{3.4}$$

4. A corrected concentration of the compound in the sample (C_{xs}) is calculated as follows:

$$C_{xs} = \text{Corrected concentration ratio x } C_{is} \tag{3.5}$$

Procedural recovery efficiencies were calculated by spike recovery:

$$\text{Recovery Efficiency (\%)} = 100\text{x}(C_f /C_i) \tag{3.6}$$

where C_f is the concentration of the spiked sample processed as a regular sample and Ci is the initial concentration in the spike solution.

3.8. Quality Assurance / Quality Control

3.8.1 Sample Collection Efficiency

Sample collection efficiency can be evaluated using the important parameters for the samplers used in this study. These parameters are adsorption on the filters, volatilization and breakthrough for SOC sampling with polyurethane foam (PUF). Polyurethane foam has been used by other researchers for SOC sampling with volumes ranging from 300 to 600 m^3. The most volatile compound in a previous study was found in the back plug in an amount less than 11% of the front plug (average for all compound was 4%). It has been determined by many researchers that with these samplers using PUF breakthrough is not a problem at reasonable flow rates and sample volumes (Cakan, 1999). In this study, the sample volume used ~230 m^3 was significantly lower than the volumes used in other studies. In addition, XAD-2 resin was used between two PUF plugs, XAD-2 resin has a higher collection and retention efficiency than PUF for relatively volatile organics. This combination increases adsorption capacity and minimizes post-volatilization problems (Cakan, 1999). Therefore breakthrough was not considered as a problem in this study.

Sampling artifacts associated with the glass fiber filter (GFF) and polyurethane foam (PUF) can affect the apparent gas-particle distributions of PCBs. The glass fiber filter may exhibit two such artifacts with counteracting effects on the distribution. The more volatile compounds maybe stripped from the filter by continuing gas flow if the gas-phase concentration decreases, the temperature increases during the sampling periods, or if there are gas-phase reactions on the filter. Another possible artifact is the adsorption of gas phase compounds by the filter. The extent of gas adsorption is often estimated using a tandem back-up filter. In a recent study, a backup filter was used on five samples collected in Ansung City (Yeo et al. 2003a). The percent mass on the back-up filter was either below 5% or not detected at all for PCBs. Therefore, the mass from the filter was neither subtracted from the particle phase concentration nor added to the gas-phase concentration. Also, volatilization from the filter for PCBs has the opposite effect and its impact is usually less than or equal to 10% (Yeo et al. 2003a). Since the impact of volatilization and adsorption artifacts is generally less than 5%, they were considered as insignificant and were not determined in this study.

3.8.2 Calibration Standards

The calibration standard solution contained 41 PCBs (AccuStandard. Inc., Quebec Ministry of Environment Congener Mix) and PCB 14, 65, and 166 as the internal standard. Five levels of calibration standards (1, 2.5, 10, 15, and 25 ng ml^{-1} for PCB 17 and 158; 2, 5, 20, 30, and 50 ng ml^{-1} for PCB 95; 3, 7.5, 30, 45, 75 ng ml^{-1} for PCB 31, 132/105, 199-201; 4, 10, 40, 60, and 100 ng ml^{-1} for 30 PCBs; 5, 12.5, 50, 75, and 125 ng ml^{-1} for PCB 82/151; 8, 20, 80, 120, and 200 ng ml^{-1} for PCB 171/156, and PCB 14, 65, and 166 at a fixed concentration of 26.25 ng ml^{-1}) were used to prepare the calibration curves. For all compounds the linear fit was good (R^2>0.99).

3.8.3 GC Performance

A mid-range calibration standard was analyzed for every twelve-hour period to confirm GC-ECD performance (i.e., peak area, and retention time). If the percent difference of a response factor of any compound was greater than 20%, the initial calibration was asssumed to be invalid, and the system was recalibrated. Samples were analyzed occasionally as duplicates. Differences in duplicate samples were less than 5%.

3.8.4 Procedural Recovery

Hi-vol PUFs (n=3) and Hi-vol filters (n=3) were spiked with a mid-range PCB calibration standard (10-40 ng ml^{-1}) prior to extraction and clean-up to determine the analytical recoveries. Table 3.5 shows the average recovery efficiencies for each internal standart.

Procedural recoveries of PCBs ranged from 58.7±32.9% (PCB 132/105) to 130.9±16.3% (PCB 49). Thirty seven of the PCBs had recoveries greater than 70%. Since the recoveries were generally high, sample amounts were not corrected for procedural recoveries.

On the other hand, all samples were spiked with internal standarts prior to extraction to determine the recovery efficiencies of PCB internal standarts. The average recovery efficiencies were 107.26 ±35.26% for PCB 14, 122.68 ± 32.60% for PCB 65, and 71.48 ±10.60% for PCB 166. Each samples were checked for the internal recovery efficiencies if they were in the range of 50-120%. The PCBs that should be integrated for that internal standart were not integrated if the recovery efficiency of the standart was out of the range.

Table 3.5. Summary of Recovery Efficiencies (%) of Internal Standarts

	Hi-Vol PUF		**Hi-Vol Filter**		**(Filter+PUF)**	
PCBs	**AVG**	**SD**[a]	**AVG**	**SD**[a]	**AVG**	**SD**[a]
PCB-14	117.6	46.65	96.91	10.72	107.3	35.26
PCB-65	123.7	24.99	121.7	38.96	122.7	32.6
PCB-166	74.65	11.82	68.3	8.154	71.48	10.6

[a] Standart Deviations of the recovery efficiencies

3.8.5 Blanks

Field blanks were analyzed to assess possible contamination through the sample collection and analysis process. The PCB amounts found in field blanks are presented in Table 3.6.

Table 3.6. PCB Amounts in Field Blanks

PCBs	PUF		Filter	
	AVG	SD	AVG	SD
	(ng)		(ng)	
PCB 18	1.6	0.2	1.4	0.1
PCB 17	1.0	0.2	0.8	0.1
PCB 31	-	-	-	-
PCB 28	1.7	0.3	1.2	0.4
PCB 33	1.7	0.4	1.0	0.2
PCB 52	6.6	3.4	-	-
PCB 49	-	-	-	-
PCB 44	4.1	0.5	-	-
PCB 74	-	-	-	-
PCB 70	0.2	0.2	0.2	0.3
PCB 95	0.9	0.4	1.0	1.1
PCB 101	0.5	0.2	1.1	1.2
PCB 99	-	-	0.2	0.2
PCB 87	0.4	0.4	0.8	0.4
PCB 110	1.0	0.9	1.7	0.7
PCB 82/151	-	-	-	-
PCB 149	-	-	-	-
PCB 118	-	-	-	-
PCB 153	-	-	-	-
PCB 132/105	-	-	-	-
PCB 138	-	-	0.8	1.2
PCB 158	-	-	-	-
PCB 187	-	-	-	-
PCB 183	1.2	1.1	-	-
PCB 128	-	-	-	-
PCB 177	-	-	-	-
PCB 171/156	-	-	-	-
PCB 180	-	-	2.2	1.9
PCB 191	-	-	-	-
PCB 169	-	-	-	-
PCB 170	2.1	1.9	1.2	1.0
PCB 199-201	-	-	-	-
PCB 208	-	-	-	-
PCB 195	-	-	-	-
PCB 194	-	-	-	-
PCB 205	-	-	-	-
PCB 206	-	-	-	-
PCB 209	-	-	-	-

3.8.6 Detection Limits

Limit of detection (LOD) has been used to determine the analytical quality of the data. The lower limit of quantification is based on the sensitivity of the analytical equipment. Quantifiable amounts of pesticides were determined from sequential injections of diluted standard solutions to the GC, using a signal to noise ratio of ten. The quantifiable amounts of PCBs ranged from 11.72 (PCB 199-201) to 62.5 fg (PCB 18, 17, 33, 52, 208+195) for 1 µl injection volume.

The limit of detection (LOD) is defined as average blank mass plus three standard deviations (mean + 3σ). Instrumental detection limits were used for compounds that were not detected in blanks. LODs for PCBs ranged from 4 pg (PCB 199-201) to 17 ng (PCB 52) for PUFs and from 8 pg (PCB 31) to 8 ng (PCB 180) for filters (Table 3.7). Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

3.8.7 Compound Identification

ChemStation software was used for the identification of PCBs in the samples. Identification of individual PCBs was based on their retention times (within±0.05 minutes of the retention time of calibration standard).

Table 3.7. LODs for Individual PCBs

PCBs	**PUF LOD (ng)**	**Filter LOD (ng)**	**Instrumental LOD (ng)**	**PUF LOD (blank+instr.)**	**Filter LOD (blank+instr.)**
18	2.1	1.7	0.063	2.168	1.723
17	1.7	1.2	0.063	1.786	1.271
31	-	-	0.023	0.008	0.008
28	2.6	2.2	0.031	2.651	2.273
33	2.9	1.5	0.063	2.932	1.585
52	16.9	-	0.063	16.958	0.063
49	-	-	0.031	0.031	0.031
44	5.5	-	0.031	5.547	0.031
74	-	-	0.031	0.031	0.031
70	0.7	1.2	0.031	0.715	1.199
95	2.1	4.2	0.031	2.128	4.197
101	1.2	4.8	0.031	1.271	4.816
99	-	0.7	0.031	0.031	0.757
87	1.5	1.9	0.016	1.506	1.937
110	3.7	3.9	0.031	3.696	3.978
82/151	-	-	0.020	0.020	0.020
149	-	-	0.016	0.016	0.016
118	-	-	0.016	0.016	0.016
153	-	-	0.016	0.016	0.016
132/105	-	-	0.047	0.047	0.047
138	-	4.3	0.016	0.016	4.316
158	-	-	0.016	0.016	0.016
187	-	-	0.016	0.016	0.016
183	4.5	-	0.016	4.511	0.016
128	-	-	0.016	0.016	0.016
177	-	-	0.016	0.016	0.016
171/156	-	-	0.031	0.031	0.031
180	-	7.9	0.016	0.016	7.942
191	-	-	0.016	0.016	0.016
169	-	-	0.016	0.016	0.016
170	7.6	4.2	0.016	7.646	4.181
199-201	-	-	0.012	0.004	0.012
208+195	-	-	0.063	0.063	0.063
194	-	-	0.016	0.016	0.016
205	-	-	0.016	0.016	0.016
206	-	-	0.016	0.016	0.016
209	-	-	0.016	0.016	0.016

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents and discusses the results of 20 day and night time samples (short-term), and 40 a year around daytime (long term) samples for ambient air concentration measurements of polychlorinated biphenyls (PCBs). The atmospheric concentrations of samples were given as total PCB (ΣPCB), gas and particle phase concentrations based on congeners and their variations with temperature, wind speed and direction, seasonal change were also investigated.

4.1. Ambient PCB Concentrations

4.1.1 Short-term Sampling Period

Twenty successive daytime and nightime air samples were collected between 14–23 May 2003. The results of gas and particle phase PCB concentrations (pg m^{-3}) measured in this study is presented in Table 4.1. Congener base total (gas+particle) polychlorinated biphenyl concentrations ranged from 0.37 ± 0.65 pg m^{-3} (PCB 158) to 305.07 ± 86.01 pg m^{-3} (PCB 33), average of total concentration for each congener and their deviation over the sampling duration is given in Figure 4.1. PCB 169, which has a dioxin-like toxicity, was not detected either in daytime or in nighttime samples. PCB 49 had the highest average total concentration and was followed by PCB 33, 44, and 18 which are among the tri- and tetra-chlorinated PCB homologs. Average gas phase and particle phase PCB concentrations were 418.21 and 101.02 pg m^{-3}, respectively. The most similar study was conducted by Harrad and Mao (2004) in England. Their total concentrations were obtained from 38 PCB congeners most of which are similar to those investigated at this thesis and was held for approximately a year time. Average total PCB concentration was 252 pg m^{-3} which was lower than what was detected in this thesis.

Table 4.1. Summary of Gas (C_g) and Particle Phase (C_p) PCB Concentrations (pg m^{-3})

	C_g					C_p				
PCBs	**n**	**min**	**max**	**average**	**SD**	**n**	**min**	**max**	**average**	**SD**
18	16	4	119	51	36	8	2	24	13	8
17	15	5	60	24	15	6	3	10	7	3
31	10	18	73	41	17	6	5	27	15	9
28	16	4	66	34	20	8	5	24	15	7
33	14	11	277	73	82	11	3	28	11	9
52	4	47	72	58	11	20	23	62	33	10
49	7	91	150	118	21	0	nd	nd	nd	-
44	16	7	88	41	24	13	8	22	13	5
74	19	2	21	11	5	17	1	5	3	1
70	19	3	35	19	9	19	0	10	3	3
95	19	7	60	29	14	0	nd	nd	nd	-
101	16	7	53	20	13	1	3	3	3	-
99	19	3	23	10	5	7	2	4	3	1
87	15	5	20	10	4	0	nd	nd	nd	-
110	11	13	36	22	6	0	nd	nd	nd	-
82/151	14	6	35	13	8	8	3	8	6	2
149	9	31	64	47	12	1	31	31	31	-
118	1	45	45	45	-	0	nd	nd	nd	-
153	19	3	17	9	4	16	2	9	3	2
132/105	0	nd	nd	nd	-	8	1	86	19	35
138	19	3	19	10	4	0	nd	nd	nd	-
158	14	0	2	1	1	4	0	1	0	0
187	15	1	5	3	1	3	1	3	2	1
183	0	nd	nd	nd	-	7	1	4	2	1
128	16	1	6	3	1	5	1	3	2	1
177	8	4	11	8	3	2	3	8	5	4
171/156	10	1	12	5	3	5	2	3	3	1
180	13	5	22	12	6	11	0	12	7	3
191	0	nd	nd	nd	-	1	10	10	10	-
169	0	nd	nd	nd	-	0	nd	nd	nd	-
170	0	nd	nd	nd	-	2	1	2	1	1
199-201	4	3	12	8	4	2	3	3	3	0
208	2	4	6	5	1	3	1	3	2	1
195	2	4	5	4	0	0	nd	nd	nd	-
194	0	nd	nd	nd	-	2	1	2	2	0
205	0	nd	nd	nd	-	1	3	3	3	-
206	5	4	10	8	2	17	4	11	8	2
209	4	2	10	6	4	0	nd	nd	nd	-
Σ PCBs				418					101	

n: Number of the samples above the detection limit
nd: Not Detected

On the other study held by Mandalakis et al. (2002) in Greece, was similar to short-term results of this thesis. They reported average of 4 samples from the urban atmosphere and analysed for 38 congeners. The average ΣPCB concentration was 344.9 pg m^{-3} which was comparable to the results found in this thesis. Mandalakis et al. (2002) also reported that 400 transformers and 15,000 capacitors containing PCBs were used in 1993. Since the determined mean ΣPCB concentration in İzmir were higher than the results of Mandalakis et al. (2002), it can be speculated that the usage of PCB containing material could be higher than Greece.

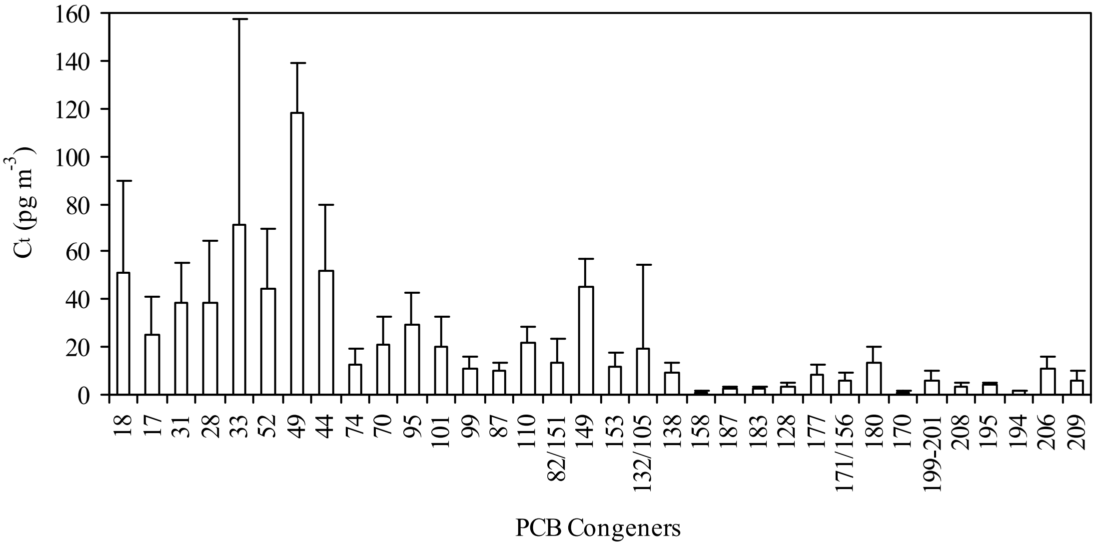

Figure 4.1. Average total air concentrations of each PCB congener. Error bars represent the standart deviation.

The contribution of homolog groups on to $\Sigma PCB_{(41)}$ was also investigated. The dominancy of the homolog groups could give an idea about what kind of commercial mixtures were used in PCB containing materials (capacitors, transformers, etc.). The dominating homolog groups on ΣPCB concentrations were in the order of tetra>tri>penta>hexa>hepta>octa>nona>deca chlorobiphenyls (CBs). These results were also comparable with the other studies in the literature. For example, Simcik et al. (1997) reported that the concentrations of PCB 28+31, 44, 52+43, 49, and 74, which are tri-and tetra-chlorinated, were dominant than the other congeners in Chicago area where the detected ΣPCB concentration was one of the highest level compared to the other areas in the world (270-14000 pg m^{-3}).

In this investigation, about 81% (average) of the total PCBs (gas + particle) resided in the gas phase, which was in good agreement with the previous studies (Mandalakis et al. 2002, Montone et al. 2003, Yeo et al. 2003a). Distribution of gas and particle phase percentages are given in Figure 4.2. for congeners detected in both phases.

Gas phase concentrations were dominated with the lower chlorinated PCBs while the particle phase PCB concentrations increased for the heavier congeners (Yeo et al. 2003a).

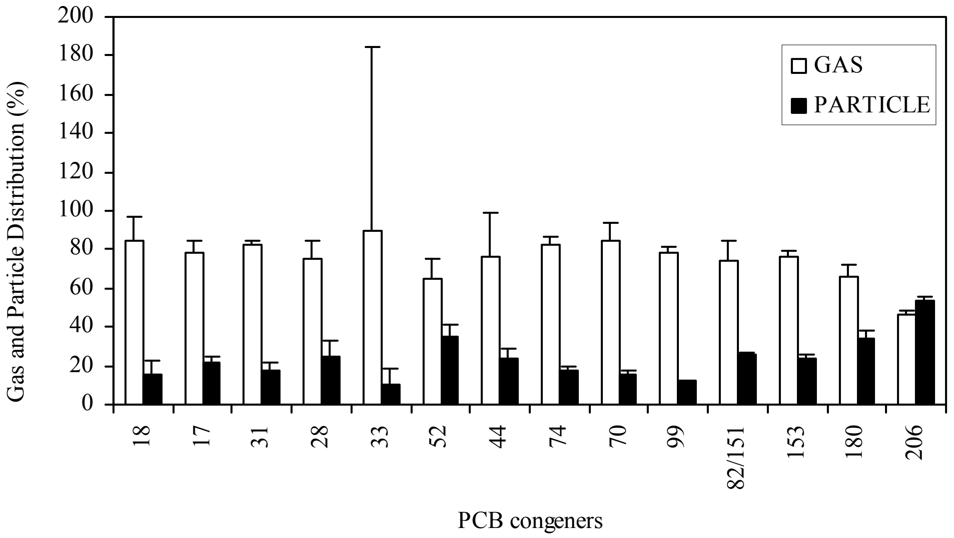

Fig. 4.2. Average Particle/Gas Phase Distribution of Individual PCB congeners. Error Bars Represent the Standart Deviation.

4.1.2. Long-term Sampling Period

PCB congener concentrations of gas and particle phases were measured in suburban atmosphere from May 2003 to March 2004. The mean total concentration of 41 PCB congeners were 319.46 pg m^{-3} in gas phase and 102.24 pg m^{-3} in particle phase, respectively (Table 4.2). Backe et al. (2000) measured 51 congener concentrations at 11 rural and urban sites in Sweden. There was no detail about specific congener names, but the sampling duration was a year. The values detected in the two urban sites showed a wide range in concentration 22-983 and 9-211 pg m^{-3}, respectively. Due to the variation of the total number of investigated PCB congeners with each study in the literature, it was not possible to compare total air concentrations of the results of this study with others. Therefore, the comparison was done based on the similarities in congener numbers and names.

Table 4.2. Summary of Gas (C_g) and Particle Phase (C_p) PCB Concentrations (pg m^{-3})

	C_g (pg m^{-3})					C_p (pg m^{-3})				
PCBs	**n**	**min**	**max**	**average**	**SD**	**n**	**min**	**max**	**average**	**SD**
18	32	4	434	47	74	29	3	50	19	13
17	28	6	180	25	33	20	5	19	11	4
31	27	9	381	40	70	16	6	27	15	5
28	25	9	278	34	53	11	6	24	10	5
33	26	5	302	56	81	22	4	28	9	5
52	3	8	187	80	-	16	22	62	44	12
49	4	7	215	119	91	1	93	93	93	-
44	11	5	88	28	26	4	11	17	14	3
74	22	1	35	9	8	19	1	4	2	1
70	22	5	40	14	8	27	0	9	4	3
95	19	8	60	22	14	2	2	2	2	0
101	17	4	60	16	15	0	nd	nd	nd	-
99	21	2	34	9	7	2	3	3	3	0
87	11	5	23	11	6	0	nd	nd	nd	-
110	6	1	41	22	13	0	nd	nd	nd	-
82/151	12	6	41	15	10	2	3	8	5	3
149	8	19	130	64	31	1	31	31	31	-
118	2	72	73	72	-	0	nd	nd	nd	-
153	21	2	32	10	7	16	1	9	3	2
132/105	2	6	25	16	14	6	1	3	2	1
138	20	1	33	10	8	0	nd	nd	nd	-
158	17	0	27	3	6	1	1	1	1	-
187	27	1	19	4	4	4	1	5	3	2
183	2	1	39	20	27	5	1	4	2	1
128	24	1	39	6	8	3	1	2	2	0
177	10	3	25	11	7	1	3	3	3	-
171/156	10	2	19	9	6	5	2	11	5	3
180	12	8	53	27	16	4	5	16	9	5
191	0	nd	nd	nd	-	0	nd	nd	nd	-
169	0	nd	nd	nd	-	0	nd	nd	nd	-
170	0	nd	nd	nd	-	1	2	2	2	-
199-201	5	3	61	28	21	4	2	8	5	3
208	9	18	429	137	137	9	1	490	113	158
195	1	21	21	21	-	0	nd	nd	nd	
194	3	7	21	12	7	2	6	6	6	0
205	1	11	11	11	-	0	nd	nd	nd	-
206	19	5	31	15	6	23	6	21	13	4
209	9	1	13	4	4	7	1	6	3	2
Σ PCBs				319					102	

n: Number of the samples above the detection limit
nd: Not Detected

In this thesis, the measured PCB 18, 28, 101 were lower, but PCB 180 was relatively higher than those measured in the urban atmosphere of Baltimore (UK) and suburban atmosphere of New Brunswick (USA) (Brunciak et al., 2001a, Brunciak et al., 2001b). As it was mentioned in chapter 2 (2.4), generally the total mean concentrations of PCBs were reported, and the total mean concentration observed in this study (~422 pg m^{-3}) was in the range of the other studies (Table 2.2).

Congener base total (gas+particulate) polychlorinated biphenyl concentrations ranged from 0.11 ± 10.58 pg m^{-3} (PCB 70) to 919.69 ± 281.18 pg m^{-3} (PCB 208), average of total concentration for each congener is given in Figure 4.3. PCB 169 was also not detected in long-term samples.

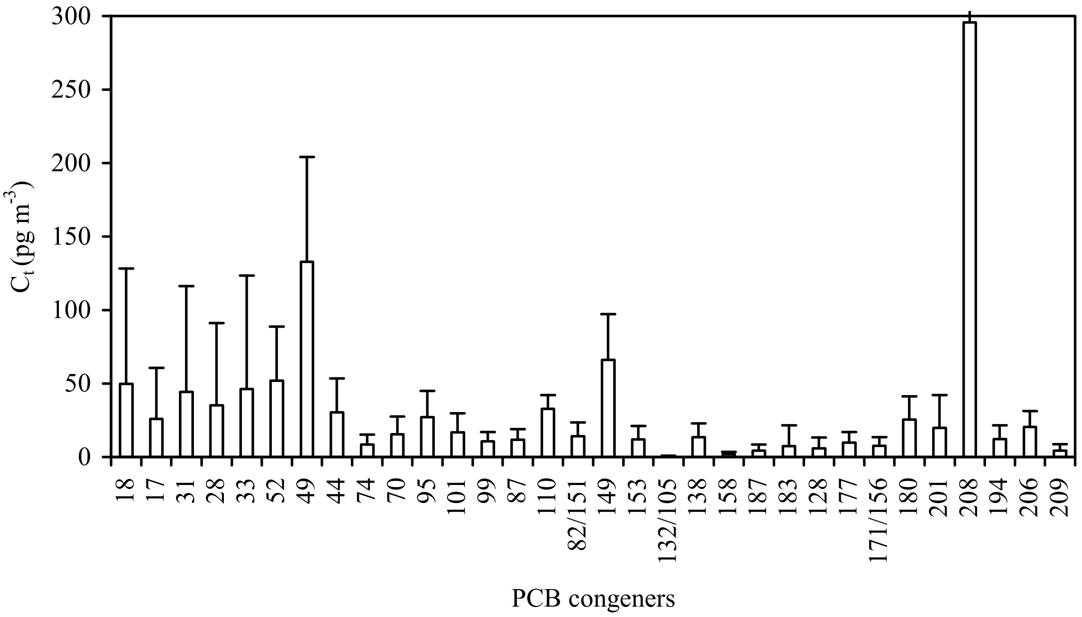

Figure 4.3. Average total air concentrations of each PCB congener. Error bars represent the standart deviation.

Homolog contribution order was also computed to see if there were any change in the order by comparing long term results to short term results. Unfortunately, due to unexpected increase in the PCB 208 concentration in the long term sampling duration for the last five samples affected the order of homolog contribution.

The sudden increase of concentration reasons could be the effect of long-range transport on that sampling period which needs further investigation such as back trajectory analysis. Therefore, this compound was excluded in the homolog contribution calculation and the order became similar to the short term results (Figure 4.4).

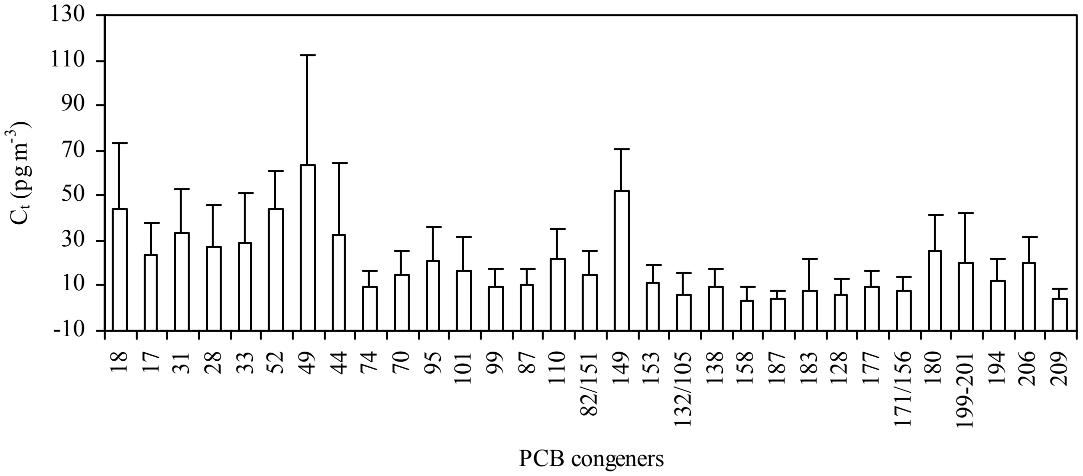

Figure 4.4. Average total air concentrations of each PCB congener without PCB 208.

The ΣPCB (gas+particulate) concentration pattern shows the highest level for tetra-chlorinated biphenyls (CBs) (222.37 pg m^{-3}), followed by tri-CBs (221.94 pg m^{-3}), penta-CBs (167.59 pg m^{-3}), hexa-CBs (104.19 pg m^{-3}), octa-CBs (64.13 pg m^{-3}), hepta-CBs (48.43 pg m^{-3}), nona-CBs (20.42 pg m^{-3}) and deca-CBs (4.28 pg m^{-3}), in that order. In other words, there was a decreasing tendency in the concentrations of PCB in the atmosphere with increasing number of chlorine, as expected.

In the long-term period, about 76% (average) of the total PCBs (gas + particle) resided in the gas phase (Figure 4.5), consistent with short-term sampling results. These values were comparable with the two studies conducted in European countries Spain (Garcia-Alonso et al. 2002) and France (Granier and Chevreuil 1997) with the percentages 72 and 79, respectively.

The analysis of the seasonal or temporal variation results showed that highest mean concentration for ΣPCBs (41 congeners) was observed in autumn (493 pg m^{-3}). This could be the result of highest concentration presence in the beginning of September. In the literature it was mentioned that higher temperature in early summer results in higher PCB concentration in air (Backe et al. 2000).

Moreover, some research results showed that the peak concentration in SOCs could occure between May and September (Halsall et al. 1999). This seasonal average was followed by spring (446 pg m^{-3}, n=6) which has also second highest concentration presence, summer (419 pg m^{-3}, n=11), and winter (291 pg m^{-3}, n=10).

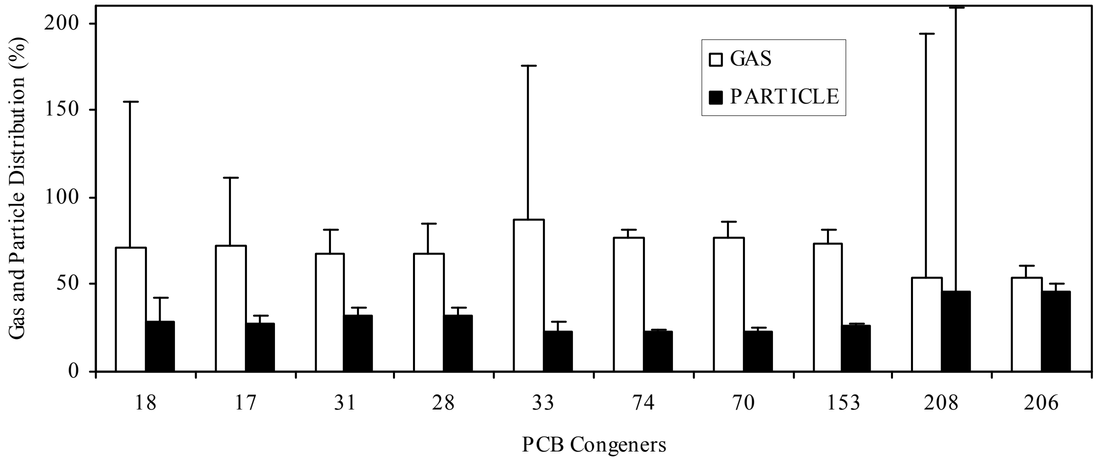

Figure 4.5. Average Particle/Gas Phase Distribution of Individual PCB Congeners for Long-term Sampling. Error Bars Represent the Standart Deviation.

Figure 4.6 describes the seasonal contribution of PCB homologs relative to the ΣPCBs. Maximum concentrations were achieved in summer for tetra (206.93 pg m^{-3}), penta (106.1 pg m^{-3}), hexa (82.07 pg m^{-3}) and hepta-CBs (67.7 pg m^{-3}). Tri-CBs highly detected in fall (755.79 pg m^{-3}). Highest concentrations for all tri-CBs (PCB 18-484.62 pg m^{-3}, 17-196.09 pg m^{-3}, 31-380.60 pg m^{-3}, 28-278.32 pg m^{-3}, and 33-313.28 pg m^{-3}, while the average concentrations in this season for each congener were 64.74, 29.67, 43.83, 24.40, 30.95 pg m^{-3}, respectively) were observed in the first sample in autumn. Octa-CBs were detected in only 1 sampling day in spring, 5 days in summer, and 2 days both in autumn and winter. Thus, the percentages were very small but they had the highest concentrations in fall (21.19 pg m^{-3}, 2%) and minimum in spring (2.89 pg m^{-3}, 0.4%). Because of the unusual increased concentrations of PCB 208, nona-CBs were at the highest concentration in winter (70%) when PCB 208 was detected at highest levels and minimum (4%) in summer.

Deca-CB (PCB 209) was not detected in every sampling day for each season, the minimum concentration was 0.69 pg m^{-3} (spring, 0.03%), the maximum was 39.56 pg m^{-3} (in fall, 0.6%), and was not detected in winter. As seen in the Figure 4.5 the highest seasonal contribution was attributed to nona-CBs in winter time while all the other compounds contributed to every season varies. In the study conducted by Yeo et al. (2003) showed similar behavior on the deca-CB.

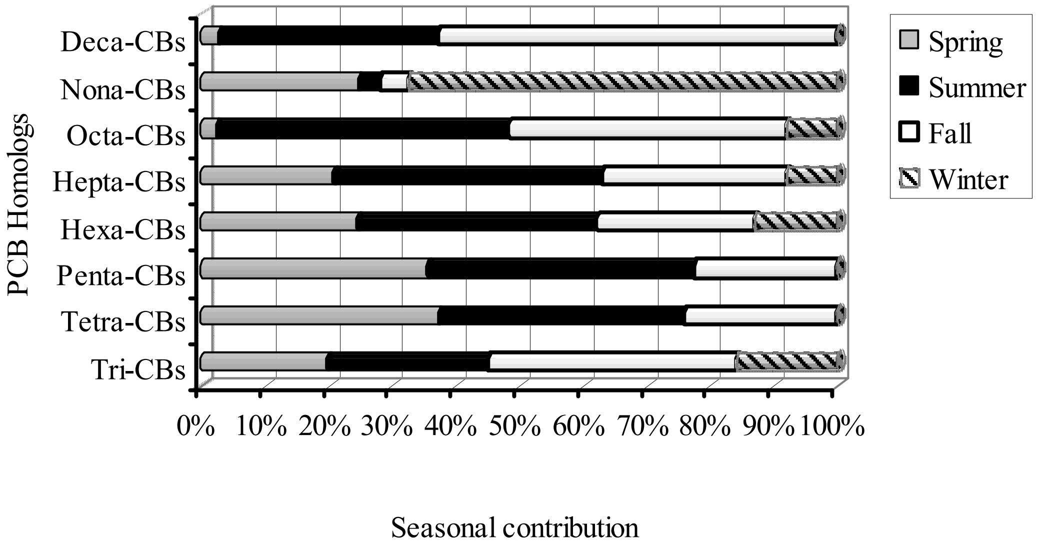

Figure 4.6. Seasonal contribution (%) of PCB homologs (May 2003-March 2004)

4.2. Effect of Temperature

Semivolatile organic compounds such as PCBs have an ability to revolatilize from the secondary source compartment which can be referred as soil, vegetation, water and atmospheric particles. Since PCBs were banned, their primary sources such as manufacture and specific use of PCBs, have been largely reduced. Therefore, these secondary sources becomes more important for the condensation and volatilization process which controls the cycling nature of SOCs between air and other surfaces (Halsall et al. 1999). It has also been shown that the air concentrations of semivolatile organic compounds (SOCs) have a strong relationship to ambient temperature (Lee and Jones 1999; Cortes et al. 1998; Hoff et al. 1998; Honrath et al. 1997, Hillery et al. 1997).

4.2.1. Short-term Sampling Period

In order to see the temperature effect, the study was designed in two different sampling program. Shortterm sampling programme was designed to see sharp temperature changes between night and daytime, and to see the concentration variation. The long-term sampling was designed to see seasonal temperature effect on PCB concentrations.

The average day and night temperature and mean $\Sigma PCB_{(41)}$ concentration variations were given in Figure 4.7. There was not any significant diurnal variation in concentrations for short-term sampling periods, however nighttime concentrations were lower than daytime concentrations as a result of the decreasing temperature at night (Tables 3.1 and 3.2).

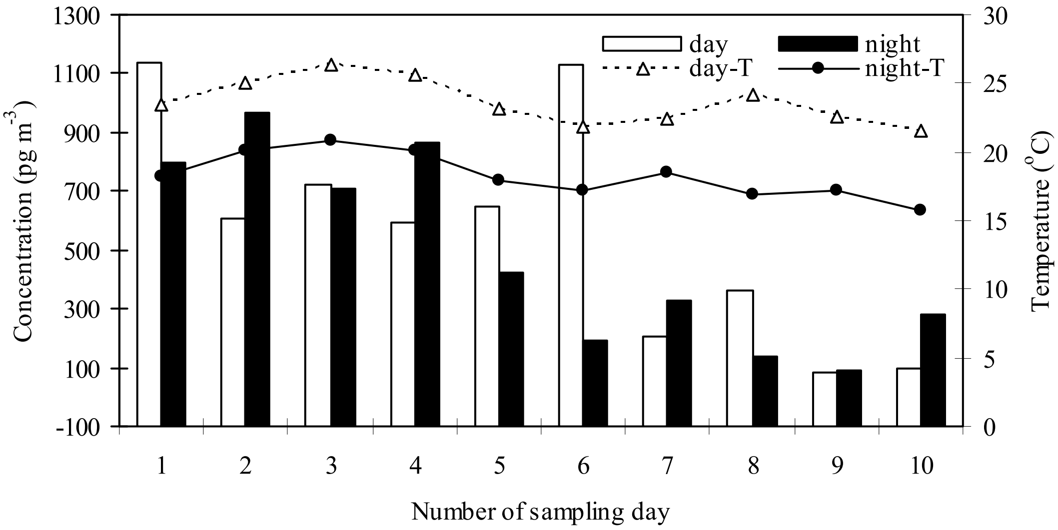

Figure. 4.7. Total concentration of PCBs for each day and nighttime sampling days

SOCs are reported to follow clear diurnal cycles (Lee et al. 1998; 2000). Two homolog groups of PCBs (tri-and penta-CBs)showed diurnal cycling of in some sampling days for the short-term sampling duration are given in Figures 4.8 and 4.9. Diurnal cycling was observed for only a few days and they can not be interpreted as strong cycles.

The diurnal variations of SOCs are explained by sorption processes. Strong variations are mostly dominated by surface adsorption processes, because adsorption response times to changes in temperature are relatively fast while absorption response times are slow (Hornbuckle and Eisenreich 1996). Gouin et al. (2002) explained this mechanism by comparing molar volumes of two groups of SOCs. When the molar volume is small there is more tendency to absorb into the organic matrix than to adsorp on to surfaces.

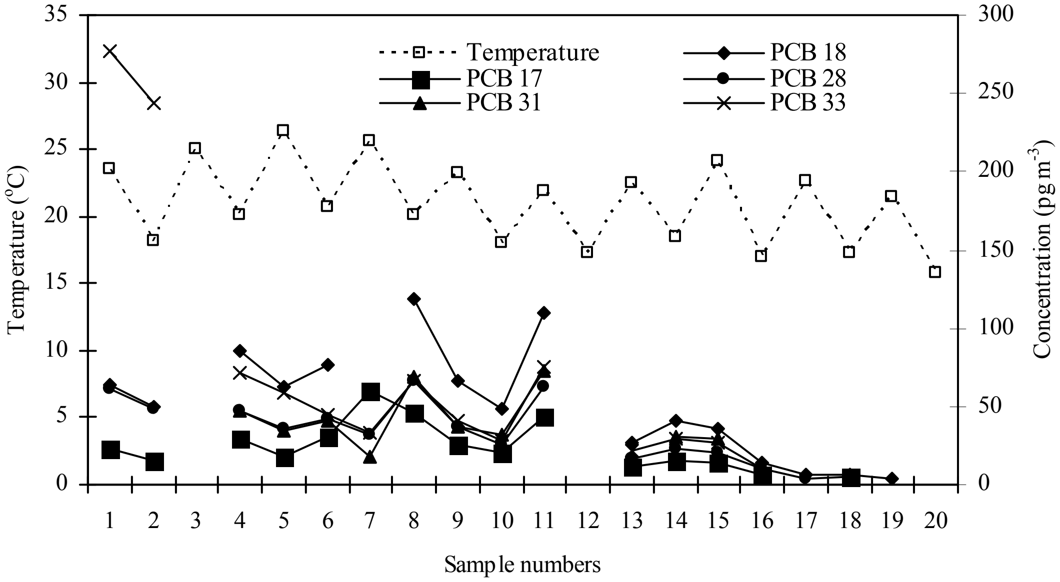

Figure 4.8. Diurnal variation of tri-chlorinated biphenyls and temperature

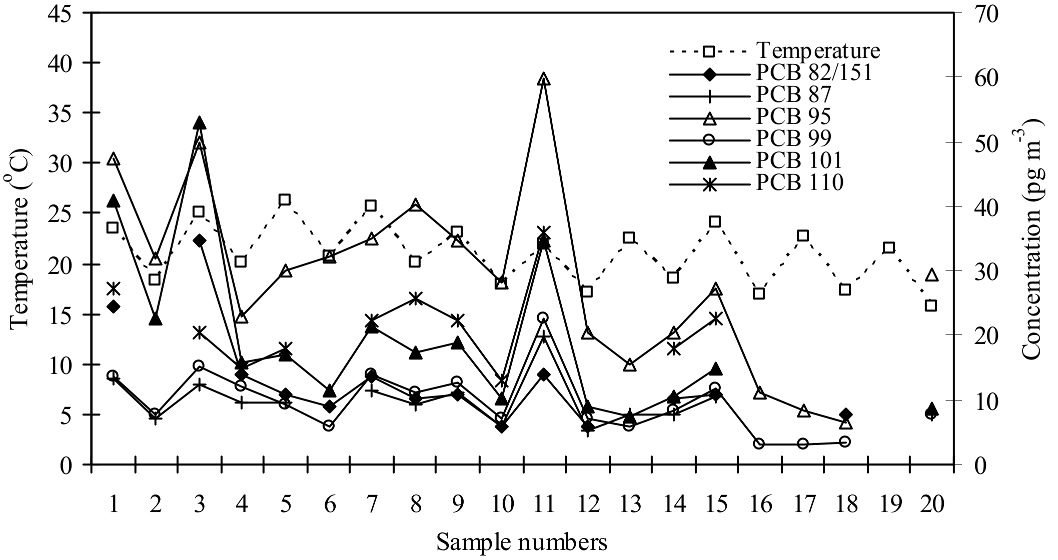

Figure 4.9. Diurnal variation of penta-chlorinated biphenyls and temperature

As referred before, the Clausius-Clapeyron equation was used to interpret the temperature dependency of gas phase PCB congeners and total gas phase concentration for a detailed information about cycling and transport behavior of PCBs. The partial pressures (atm) of individual compounds were calculated for each sample using gas-phase concentrations and the ideal gas law. Natural logarithms of calculated partial pressures were plotted against reciprocal mean temperature for each sampling day. The mean temperature was obtained by averaging the temperatures measured in 1-minute intervals over the each sampling period and ranged from 15.7 to 26.4°C during the short-term sampling program.

$\Sigma PCB_{(41)}$ gas concentration was plotted ln P of versus 1/T (Figure 4.10) and a steeper (-11200) slope was obtained with a very low correlation coefficient. The statistical analysis showed that $\Sigma PCB_{(41)}$ gas phase was significantly (<0.05) correlated with temperature which was reported in the literature (Hoff et al. 1998; Halsall et al.. 1999). It is better to analyse the congener based temperature dependency to get detailed information.

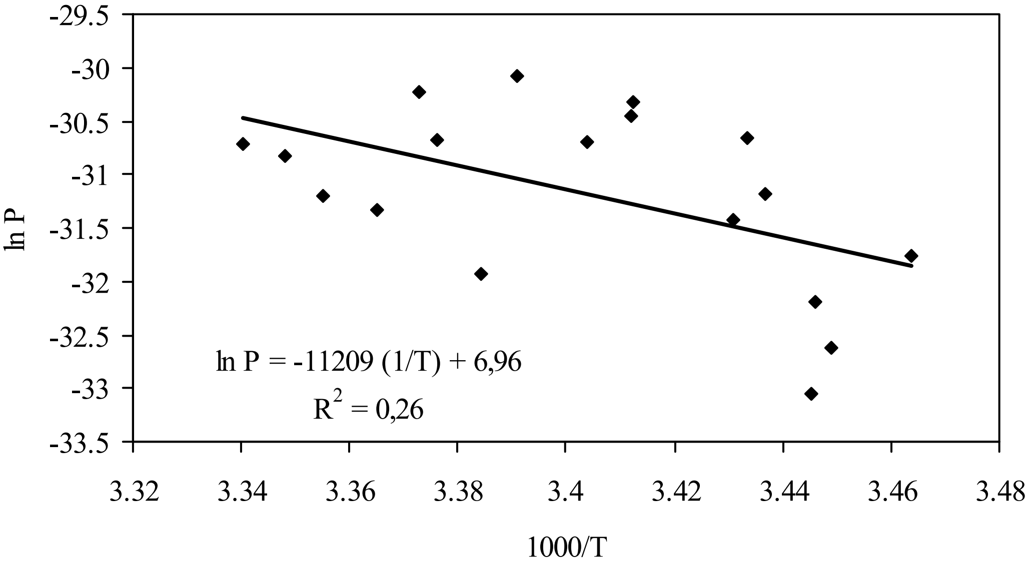

Figure 4.10. Temperature dependence of atmospheric gas phase PCB concentrations

The results of congener based temperature dependency analysis were presented in Table 4.3. The statistical results showed that the partial pressures of 12 PCB congeners were significantly correlated with the inverse temperature ($p<0.05$). For all PCBs, except PCB 49, slope was negative indicating that their concentrations increased with increasing temperature. The slopes belong to statistically significant congeners were relatively steep and varied between -5845.43 and -10088.8. These steeper values suggests that their ambient concentrations were influenced by short-range transport or regional volatilization. The sudden temperature change between day and night time showed the change more clear, but still was not enough to make a conclusion becuse of the low correlation value implying the other factors, like wind speed, could effect the concentration variation. Scattering in the data interpreted as wind speed causing advection in the area and masking the temperature effects on gas phase concentrations.

For the PCBs that did not have significant correlation with the temperature, other meteorological conditions such as wind speed and wind direction might have been effective factors for gas phase PCBs. In order to investigate the effect of these meteorological parameters, the following model including wind speed and direction as factors was applied (Hillery et al. 1997. Harrad and Mao 2004):

Table 4.3. Summary of regression parameters for Clasius-Clapeyron equation

PCBs	m	*p*	b	r^2	n
18	-6952		-9.7	0.04	16
17	-10234		0.9	0.26	15
28	-6182		-13	0.06	16
33	-3824		-20	0.02	14
49	4201		-46	0.41	7
44	-2857		-24	0.02	16
74	-8878	<0.05	-4.6	0.31	19
70	-7607	<0.05	-8.4	0.22	19
95	-6355		-12	0.16	19
101	-8880	<0.05	-4.2	0.33	16
99	-7493	<0.05	-9.5	0.25	19
87	-5845	<0.01	-15	0.43	15
110	-3151		-23	0.13	11
82/151	-8947	<0.01	-4.4	0.44	14
149	-2516		-25	0.10	9
153	-6841	<0.05	-12	0.31	19
138	-6744	<0.05	-12	0.26	19
158	-10089	<0.05	-3	0.31	14
187	-3060		-26	0.09	15
128	-8281	<0.01	-7.9	0.54	16
177	-1839		-29	0.04	8
171/156	-1880		-29	0.01	10
180	-2454		-27	0.02	13
Σ PCBs	-11209	<0.05	7	0.26	18

$$\ln P = m_1 (1/T) + m_2 U + m_3 \cos WD + b \qquad (4.1)$$

where U is the wind speed (m s^{-1}), WD is the predominant wind direction during the sampling period (degrees), m_1, m_2, m_3, and b are the regression parameters. The results of multiple linear regression analysis are presented in Table 4.4. The correlation was statistically significant for 14 PCB congeners ($p<0.01$ to $p<0.05$). For all PCBs m_1 was negative indicating that their concentrations increased with increasing temperature. This approves that the model including wind speed and wind direction reveals the effect of those factors on tri-and tetra-chlorinated biphenyls. When effect of advection (opposite correlation of gas phase concentrations with high wind speeds) was considered by this model. Temperature effect happened to be significant yielding higher slopes on the forementioned congeners.

The gas phase PCBs and the the total gas phase PCB that were significantly correlated to temperature were already significant in the previous model, which implies the consistency of the two models. Besides, regression coefficients were improved by introduction of new factors. Hence, it could be possible to discuss the source and behavior of the PCBs considering the meteorological conditions.

The PCBs with significant correlations by wind direction were PCB 18, and 171/156 with relatively high positive correlation factors, PCB 49 exhibited an exceptional characteristics with very low dependence on temperature and high correlation with wind direction. When the wind directions at the intervals at time PCB 49 appeared were looked up, it was obvious that northerly winds were dominating. Remarking the unexpected positive slope yielded by the single factor model which correlated the lnP values according to 1/T, it is concluded that the second model fits well for the specific case for this congener. Besides, it can be speculated that those PCBs that correlated well with wind direction may have an ongoing source.

Some of the PCBs showed low correlation factors for all of the parameters considered and considerably high constant values that were significant. These results showed that gas phase concentrations of those PCBs, namely PCB110, 149, 187, 177 and 180, were almost constant at various levels with very shallow slopes when correlated to temperature.

Table 4.4. Summary of regression parameters for eq. (4.1)

PCBs	m_1	m_2	m_3	b	r^2	n
18	-20088[b]	-0.34[b]	0.90[b]	35.63	0.62[a]	16
17	-15588 [b]	-0.20	0.42	19.39	0.47	15
28	-14960[b]	-0.31[b]	0.38	17.95	0.48[b]	16
33	-8307	-0.20	-0.37	-4.08	0.15	14
49	-2865	0.06	0.90	-23.35	0.76	7
44	-7582	-0.20	-0.57	-6.97	0.37	16
74	-11446[a]	-0.17[b]	-0.09	4.70	0.51[a]	19
70	-10277 [a]	-0.18[b]	-0.12	1.30	0.42[b]	19
95	-8876 [b]	-0.17[b]	-0.10	-3.17	0.36	19
101	-10562 [b]	-0.08	-0.14	1.84	0.38	16
99	-9068 [b]	-0.11	0.00	-3.84	0.35	19
87	-5711 [b]	0.01	-0.01	-15.53	0.44	15
110	-1221	0.12	0.13	-30.33	0.38	11
82/151	-10681 [b]	-0.05	0.22	1.53	0.50	14
149	-2293	0.00	-0.06	-25.60	0.10	9
153	-8225[a]	-0.10	0.02	-6.85	0.42[b]	19
138	-8225[a]	-0.11	0.06	-6.82	0.38	19
158	-14138.[a]	-0.08	0.59	10.75	0.52	14
187	-4946	-0.09	-0.05	-19.29	0.23	15
128	-8938[a]	-0.05	0.09	-5.47	0.61[a]	16
177	-4077	-0.14	0.01	-21.08	0.37	8
171/156	-10910	-0.15	0.87	2.07	0.52	10
180	-482	0.14	-0.24	-33.66	0.38	13
Σ PCBs	-12987[b]	-0.32[b]	0.63	13.51	0.46[b]	20

[a] $p<0.01$

[b] $p<0.05$

4.2.2. Long-term Sampling Period

The variation of PCB concentrations were researched for long-term sampling results. In Figure 4.11, the variation of total gas phase concentrations of 41 PCB congeners, with the temperature of the sampling days is given. Similarly with the short-term investigation, it can be drawn out that PCBs did not exhibited strong variation for each sampling day.

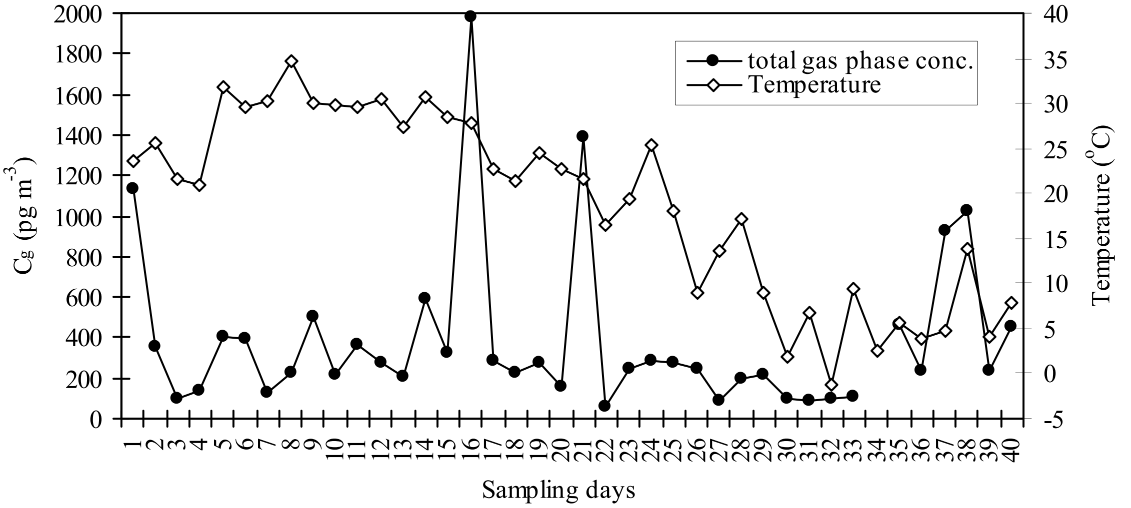

Figure 4.11. Variation of total gas phase concentrations with temperature

Since the temperature variation of total gas phase PCB concentration was not clear, variation of gas phase PCB homologs were investigated separately. Variations with the temperature are given in Figure 4.12 and 4.13 for tri-and penta-CBs.

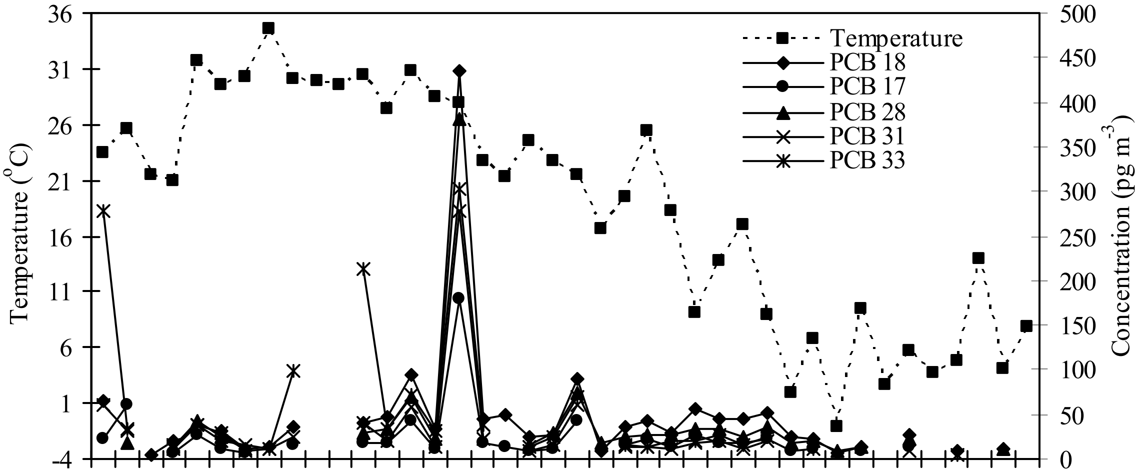

Figure 4.12. Variation of tri-CBs and temperature.

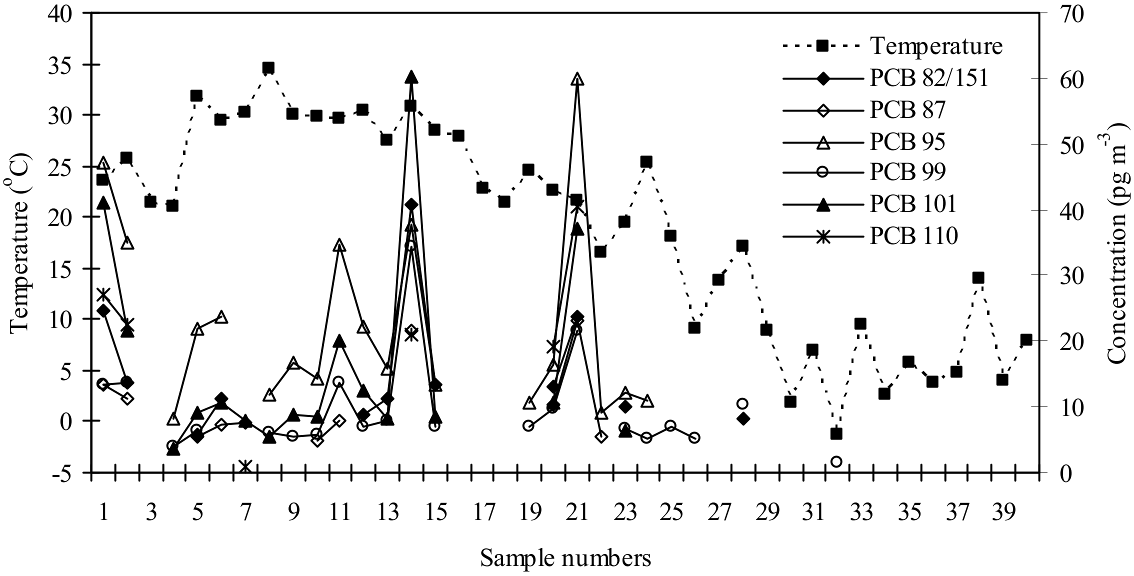

Figure 4.13. Variation of penta-CBs and temperature.

The variation with temperature in two homolog groups was similar to short-term results. No clear daytime variation with the temperature observed for gas phase PCB homologs in long-term results. The reason could be long sampling times andchange in meteorological conditions, advection effect due to wind direction and speed, and also their chemical properties which could drect different sorption processes for each compound and result in inhibition of volatilization.

Same procedure was followed for long-term results to have a detailed conclusion about temperature dependency. Table 4.5 presents the results of regression analysis including the slope and intercept values with the degree of correlation. The congeners with less than 8 number of observations were not taken into account in the regression analysis because fewer observations displayed inconsistent correlations when applied to different models.

ΣPCB gas concentration was plotted ln P of versus 1/T and a steep slope was -4197.6 (Figure 4.14) was obtained. The statistical analysis showed that ΣPCB gas phase was significantly (<0.01) correlated with temperature. The slope was shallower (-4197) than the slope of the short-term plot (-12987), but the correlation coefficient was better. To see the individual temperature variation congener based temperature dependencies were investigated for long-term period.

Table 4.5. Summary of regression parameters for Clasius-Clapeyron equation

PCBs	**m_1**	**b**	**r^2**	**n**
18	-28134[b]	-23.8824	0.13	32
17	-2509[b]	-25.406	0.15	26
31	-2858[b]	-23.8504	0.21	27
28	-3797[b]	-20.92	0.18	24
33	-4814[b]	-17.1963	0.19	26
44	-2682	-26.651	0.01	9
74	-4257[a]	-20.7142	0.34	22
70	-3691[b]	-22.074	0.22	21
95	-4798[b]	-18.311	0.29	17
101	-1561	-29.373	0.01	16
99	-3386[b]	-23.667	0.26	21
87	-1705	-29.231	0.04	9
82/151	-2589	-25.835	0.07	11
153	-3827[a]	-22.2034	0.36	21
138	-5643[a]	-16.2259	0.46	20
158	-8709	-7.729	0.21	15
187	-2905[b]	-26.4219	0.19	27
128	-1507	-30.6222	0.02	24
171/156	-1131	-31.259	0.09	8
180	-2063	-27.376	0.03	11
206	-1266	-30.624	0.06	17
209	10840[b]	-72.7903	0.47	9
Σ PCBs	-4198[a]	-17.3	0.34	**36**

[a] $p<0.01$

[b] $p<0.05$

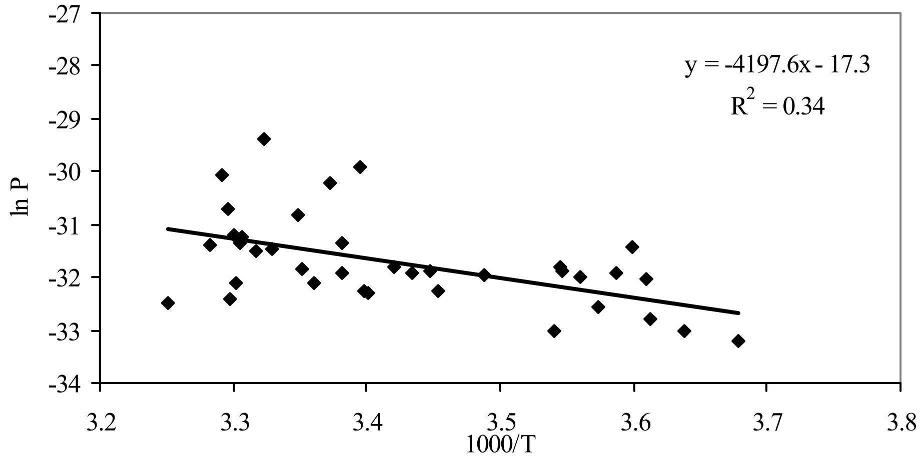

Figure 4.14. Temperature dependence of atmospheric gas phase PCB concentrations in the long-term

The partial pressures of 13 PCB congeners were significantly correlated with the inverse temperature (<0.001 to <0.05), and negative slopes varied between -2508.9 and -5643 as coefficients of 1/T. In both of the short and long-term analysis almost the same congeners were significantly correlated with temperature. The significant m_1 coefficients of the long-term sampling were lower than those in short-term due to gradual seasonal variation in temperature. Hence, more shallow slopes in the long-term sampling were reasonable due to scattering in the data. The reasons for the scattering of the data may be the changes in the meteorological conditions during the sampling time. Increase in the wind speed causes the dilution of the atmospheric concentration even though the temperature increases. Brunciak et al. (2001) mentioned that on a warm summer days due to the convective mixing, the occurrence of turbulence caused by warm "bubbles" of air rising from the ground yielding a faster dilution.

The Clausius-Clapeyron equation was applied to each seasonal data and were compared with variation of ln P versus 1/T obtained from the complete long-term data. It was observed that the slopes decreased as the temperature variation range increased. Considering this effect, short and long-term results confirm each other with comparable significant values in terms of temperature dependance. In this case, except the heavier congeners (PCB 171/156, 180, and 206) the source of these PCBs with significant correlation with 1/T were attributed to short-range transport. The others with lower r^2 values and poor correlations exhibited that their sources were originated from long-range transport.

However, the positive slope obtained for PCB 209 can be attributed to the influence of its ongoing source. The source may be the exchange processes from buildings, indoor air, soils, urban dust etc... to overlying atmosphere. For instance, Halsall et al. (1995) identified building air as one of the primary PCB sources of gas phase PCB 52 to the urban atmosphere of Manchester. As the heaviest PCB with ten chlorine PCB 209 has a tendency to deposit on surfaces. The temperature was above 20 °C (especially 29-30 °C) when this congener was detected and the concentrations were low (0.79 to 12.98 pg m^{-3}). It can be concluded that PCB 209 was volatilized as a result of elevated temperatures.

CHAPTER 5

CONCLUSIONS

Twenty successive daytime and nighttime, and forty daytime air samples were collected during May, 2003-March, 2004, for representing short-term and long-term periods, respectively. They were analyzed for 41 polychlorinated biphenyls (PCBs). Ambient air gas and particulate concentrations and their temperature dependency were investigated.

The short term average $\Sigma PCB_{(41)}$ (gas+particle) concentration was higher than long term average concentration, but all the values were in the range of the values reported in the literature. Particulate phase total concentration were found one order of magnitude than literature value. In the congener base evaluation resulted in absence of PCB 169, which has adioxin-like toxicity, in long-term samples.

Lower chlorinated congeners (tri-and tetra-chlorinated biphenyls) were the abundant group in both term samplings. This can be attributed to their high vapor pressures which make their volatilization easier than the higher chlorinated congeners.

Temperature dependency of PCBs were investigated by using Clasius-Clapeyron equation. The slope of the function of ln P versus 1/T helps to describe the source of these chemicals whether they originated from long or short-range atmospheric transport. Short-term data was analysed for this model and the partial pressures of 12 PCB congeners (PCB 74, 70, 101, 99, 87, 82/151, 153, 138, 158, and 128) were significantly correlated with the inverse temperature (<0.05). The slopes belong to statistically significant congeners were negative indicating that their concentrations increased with increasing temperature. were relatively steep and ranged between -5845.43 and -10088.8 suggesting that their ambient concentrations were influenced by short-range or regional transport. The sudden temperature change between day and night-time made the change more clear to see this steep slope, but the wind change showed its effect with a scattering data resulted in low correlation values. For the PCBs that did not have significant correlation with the temperature, wind speed and wind direction could be other meteorological parameters which effected gas phase PCB concentrations. In order to investigate these effects another model including wind speed and direction as factors were incorporated and it was observed that two more congeners yielded significant correlations with temperature. These PCBs were the lighter congeners which could easily be influenced by the wind.

In the long-term data analysis with respect to Clasius-Clapeyron relationship 13 PCB (PCB 18, 17, 31, 28, 33, 74, 70, 95, 99, 153, 138, 187, and 209) congeners were statistically significant ($p<0.05$) with temperature. Introduction of wind speed and wind direction did not yield a significant model. The sources of these congeners were attributed as the PCBs originated from short-range transport due to their significant temperature correlations having coefficients -2508.9 to -5643. The others with lower R^2 values and poor correlations exhibited that their sources might be originated from long-range transport.

When compared with the short-term values the slopes obtained in long-term analysis were relatively shallow. It is predicted that, in the long-term other environmental factors affecting PCB concentrations interfere and effectiveness of temperature variation is reduced when compared with the short-term. Besides, seasonal investigations exhibited intermediate slopes for the temperature dependent correlation.

The only positive slope obtained for PCB 209 and this can be attributed to the influence of its ongoing source. Since the usage and production of PCBs were banned the source may be the exchange processes from buildings, indoor air, soils, urban dust etc., to overlying atmosphere.

FUTURE RECCOMENDATIONS

In the study, even though the slopes were statistically significant for some congeners, the correlation coefficient was too low to conclude a strong temperature dependency. Back trajectory analysis could give more idea about dominating transport mechanisms in the area.

Additionally, the average particle phase concentration in the area was one order of magnitude higher than the other measured data in the literature. At the same time, the organic content of the particulate phase was higher than that was assume in the literature. Due to high particulate phase concentration and organic matter content in the suspended particle, dry deposition would play an important role in the surface contamination. Therefore, dry deposition concentrations onto surfaces (buildings, soil, vegetation etc.) can be a future study.

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