INVESTIGATION OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) DEPOSITION IN ANKARA

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EFTADE O. GAGA

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Hüseyin İşçi
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Semra G. Tuncel

Supervisor

Examining Committee Members

Prof. Dr. O.Yavuz Ataman

Prof. Dr. Sezer Aygün

Assoc. Prof. Metin Zora

Asst.Prof. Nusret Ertaş

Prof. Dr. Semra G. Tuncel

ABSTRACT

INVESTIGATION OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) DEPOSITION IN ANKARA

Gaga, Eftade O.

Ph.D., Department of Chemistry
Supervisor: Prof. Dr. Semra G. Tuncel

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In this work, wet deposition samples were collected at Middle East Technical University campus, Ankara, between December 2000 and May 2002. Snow samples were collected from 50 grids in January, 2001 in Ankara to investigate dry deposition of PAHs. The collected samples were preconcentrated by Solid Phase Extraction and ultrasonic extraction tecniques. Extraction methodologies were improved prior to analysis of samples. Extracted samples were analyzed by Gas Chromotography-Mass Spectrometry for 14 Polycyclic Aromatic Hydrocarbons. Selected Ion Monitoring mode was used throughout the analysis.

Phenanthrene, fluoranthene, pyrene and benzo (b+k) fluoranthene were found to be dominant PAHs in wet deposition samples. Seasonal variation of PAHs were observed having higher concentrations in winter period.

Meterological parameters were also examined together with PAH concentrations. Contribution of PAHs coming from North East and South West direction were found to be dominant. Wet deposition fluxes were calculated and compared with other urban sites. Wet deposition fluxes are lower than industrial sites and comparable with urban sites in Europe. PAH ratios and factor analysis results demostrated combustion and traffic emissions are major sources of pollutants in the city.

Dry deposition of PAHs were invesigated using snow as a natural collecting surface. Dry deposition fluxes calculated using snow surface are compareble with other similar sites. Dry deposition pollution maps of PAHs were drawn by MapInfo software and it was observed that the major pollution regions are the localities where low income families live and low quality coal used for heating purpose. Ratio calculations showed that the central parts of the city is mostly affected from traffic emissions while coal emissions are dominating at the other parts of the city. Factor analysis applied to data set and 6 factors distinquished as coal, soil, traffic, oil combustion, mixed combustion and road dust.

Keywords: PAHs, dry deposition, wet deposition, snow, PAH ratios, deposition flux.

ÖZ

ANKARA'DA ÇOK HALKALI AROMATİK BİLEŞİKLERİN (PAH'LAR) ÇÖKELMESİNİN ARAŞTIRILMASI

Gaga, Eftade O.

Doktora, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Semra G. Tuncel

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Bu çalışma kapsamında Orta Doğu Teknik Üniversitesi, yerleşkesinde Aralık 2000- Mayıs 2002 tarihleri arasında yaş çökelme örnekleri toplanmıştır. PAH'ların kuru çökelmelerinin incelenmesi amacıyla Ocak 2001' de toplam 50 noktadan kar örnekleri toplanmıştır. Toplanan örnekler Katı Faz Ekstraksiyonu ve ultrasonic ekstraksiyon teknikleri ile önzenginleştirilmiştir. Ekstraksiyon teknikleri örneklerin analizinden önce geliştirilmiştir. Ekstrakt edilen örnekler Gaz Kromatografisi-Kütle Spektrometresi ile 14 Çok Halkalı Aromatik Hidrokarbon (PAH) için analiz edilmiştir. Analizler Seçilmiş İyon Modunda yapılmıştır.

Phenanthrene, fluoranthene, pyrene and benzo (b+k) fluoranthene yaş çökelme örneklerinde dominant olarak göze çarpmaktadırlar. Çok Halkalı

Aromatik Bileşikler kış mevsimlerinde daha yüksek miktarlarda bulunarak mevsimsel değişim göstermektedirler. Meteorolojik parametreler PAH konsantrasyonları ile birlikte değerlendirilmiş ve Kuzey doğu ve Güney Batı yönlerinden daha çok PAH taşındığı görülmüştür. Yaş çökelme örnekleri için yaş çökelme akıları hesaplanıp diğer kentsel bölgelerle karşılaştırılmıştır. Yaş çökelme akıları Avrupa'daki endüstriyel şehirlerden düşük gözlenirken, kentsel bölgelerle uyumluluk içerisindedir. PAH oranları ve Faktör Analiz sonuçları trafik ve kömür yakımının Ankara için önemli kirlilik kaynakları olduğunu göstermiştir.

PAH'ların kuru çökelmeleri kar yüzeyi doğal alıcı yüzey olarak kullanılarak araştırılmıştır. Hesaplanan kuru çökelme akıları benzer yörelerle karşılaştırılabilir düzeydedir. PAH'ların dağılım haritaları Map-Info Yazılımı kullanılarak oluşturulmuştur. Kirliliğin en çok gözlemlendiği yerler düşük kalitede kömür kullanımının çok olduğu ve genellikle düşük gelirli ailelerin yaşadığı yerler olarak saptanmıştır. Oran hesapları sonucu ise şehir merkezlerinde trafiğin, diğer bölgelerde ise kömür yakımının etken kirletici kaynakları olduğu ortaya çıkmıştır. Faktör analizi sonucunda ise 6 kirletici kaynağının katkısı ortaya çıkmıştı. Bu kaynaklar, kömür yakımı, toprak, trafik, yağ yakımı, karışık yanma ve yol tozudur. Kuru çökelme akıları kar yüzeyi kullanılarak hesaplanmış ve benzer çalışmalarla karşılaştırılmıştır.

Anahtar Kelimeler: PAH'lar, kuru çökelme, Katı Faz Ekstraksiyon, yaş çökelme, kar, PAH oranları, çökelme akısı.

TO MY HUSBAND, METE

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Ace	Acenapthene
Acy	Acenaphthylene
Ant	Anthracene
BaA	Benzo(a)anthracene
BaP	Benzo(a) pyrene
BbF	Benzo(b)fluoranthene
BgP	Benzo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
CFCs	Chlorofluorocarbons
Chr	Chrysene
CMB	Chemical mass balance
DahA	Dibenz(a,h) anthracene
EMEP	European Monitoring and Evaluation Program
EPA	Environmental Protection Agency
FID	Flame ionization detector
Flu	Fluorene
Flt	Fluoranthene
GC-MS	Gas Chromatography-Mass Spectrometry
HFCFs	Hydrochlorofluorocarbons
HOCs	Hydrophobic organic compounds
Ind	Indeno (1,2,3-cd) pyrene
LLE	Liquid-liquid extraction
MAE	Microwave assisted extraction

Nap	Naphthalene
OSPAR	Oslo and Paris Convention
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo- p-dioxins and furans
PFE	Pressurized fluid extraction
Phe	Phenanthrene
POPs	Persistent organic pollutants
Pyr	Pyrene
SCOT	Support-coated open tubular
SFE	Supercritical fluid extraction
SPE	Solid phase extraction
SPME	Solid Phase Microextraction
TIC	Total Ion Chromatogram
USE	Ultrasonic extraction
VOCs	Volatile organic compounds
WCOT	Wall coated open tubular

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CHAPTER 1

INTRODUCTION

1.1. Urban Air Quality

Intensive development of civilisation together with evolution of industry has caused deep changes in the quality of the environment in which human beings live in. Our world is full of synthetic chemicals which pollute air, water, soil and food. They can be found even in places at a very long distance from the place of their production or their use. For instance, lead and polychlorinated biphenyls was found in Greenland snow.

Human activities introduce many kinds of chemical components into the atmospheric environments of urban areas through industry, automobiles, etc. They contribute to many environmental problems, such as photochemical smog and asthmatic disease. They also influence not only the composition of the atmosphere but also the composition of atmospheric fallout. Although numerous studies of inorganic constituents in atmospheric fallout have been carried out, little attention has been paid to its organic constituents (Matsumoto and Hanya, 1980).

Air pollution path in the atmosphere was shown in Figure 1.1. Emitted air pollutants are dispersed and diluted in the atmosphere. Chemical reactions produce many pollutants, for example, ozone is produced as a result of photochemical reactions. Dispersion and dilution of air pollutants are strongly influenced by meteorological conditions, especially by wind direction, wind speed, turbulence, and atmospheric stability. Chemical reactions also depend on ambient weather conditions because they are influenced by short wave radiation, air temperature, and air humidity (Mayer, 1999).

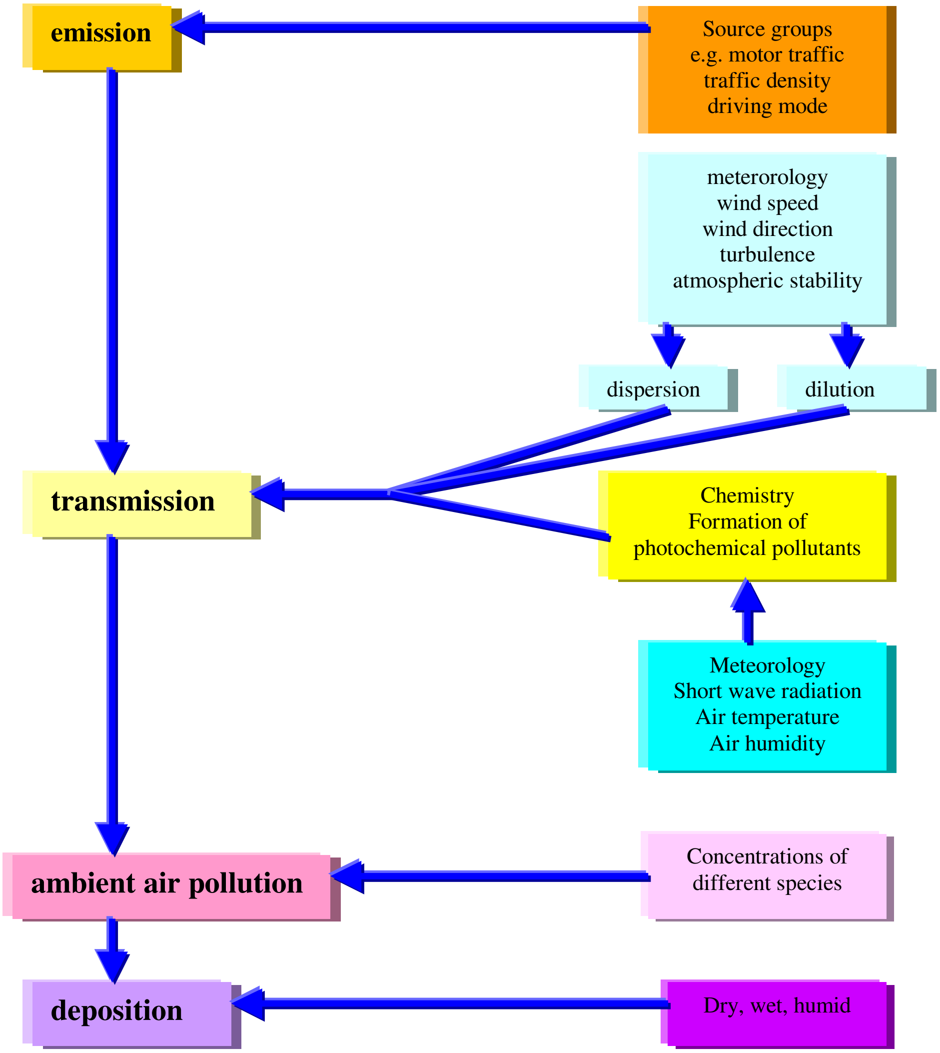


Fig 1.1. Schematic illustration of the air pollution path in the atmosphere

Since combustion is the dominant cause of urban air pollution, the various sources emit a large extent the same pollutants- only in varying proportions. Table 1.1 indicates the typical relative importance of source categories for emissin of the main pollutants. The distribution of course varies, thus e.g. in Eastern Europe SO_2 from space heating play a relatively more important role compared to western and Southern Europe (Fenger, 1999).

Table 1.1. Main emission sources and pollutants in air pollution in commercial non industrial cities.

Source category		Pollutant						
		SO_2	NO_2	CO	TSP	Organic	Pb	Heavy metals*
Power generation (Fossil fuel)		xx	x	x				x/xx
Space heating	coal	xx	x	xx	xx	xx/x		x/xx
	oil	xx	x					
	wood				xx	xx/x		
Traffic	gasoline		xx	xxx		xx	xxx	
	diesel	x	xx		xx	xx		
Solvents						x		
Industry		x		x	x	x	x	xx/xxx

The table indicates the relative importance of urban sources for the main urban pollutants. X:5-25%; xx:25-50 %; xxx:More than 50%
*with the exception of Pb

Not long ago, mainly inorganic analysis of precipitation took place, which was due to the intensification of acid rain. Nowadays, more often the attention of analysts is focused on the presence of organic pollutants in precipitation. The studies of precipitation conducted in the last few years showed the presence of more than 600 organic compounds, the most important of which belong to the following classes; petroleum hydrocarbons, polycyclic aromatic hydrocarbons, ketones, aldehydes, volatile organohalogen compounds, monocarboxylic acids, pesticides, alcohols, dicarboxylic amines, fatty acids, saccharides and amino acids (Polkowska et al., 2000).

1.2. Organic Pollutants

Organic substances brought to the atmosphere due to their evaporation from the earth's surface or emission from the human activities and subsequently transported with the masses of air over long distances. Water in clouds becomes saturated with these substances and precipitation contaminates surface waters and soils, sometimes far away from the emission sources (Grynkiewicz et al., 2002).

The class of volatile organic compounds (VOCs) includes species with different physical and chemical behaviors. Pure hydrocarbons containing C and H as the only elements (e.g., alkanes, alkenes, alkyns, and aromatics) are important VOC classes. However, volatile organic compounds containing oxygen, chlorine, or other elements besides carbon and hydrogen are important too. These latter classes include, for example, aldehydes, ethers, alcohols, ketones, esters, chlorinated alkanes and alkenes, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HFCFs) (Hewitt ,1999).

The class of persistent organic pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. With the evidence of long-range transport of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment of the whole globe (http://www.chem.unep.ch/pops/).

There is a growing concern about pollution by persistent organic pollutants (POPs) including PAHs. In may 2001, a global treaty for the regulation of POPs was signed: the "Stockholm Convention" which includes instruments for the total elimination of 12 POPs on a global scale. Large-scale programs are conducted in relation to the long-range transboundary atmospheric pollution (European Montoring and Evaluation Program, EMEP) or their discharge in to the sea (Oslo and Paris Convention, OSPAR). To these 12 POPs, the United Nations-European Community added to the PAHs of which benzo(a)pyrene (BaP) is the most toxic. The objective is to control, reduce or eliminate discharges, emissions and losses of POPs (Garban et al., 2002).

1.3. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various functional groups which may contain several elements. An important group of polycyclic aromatic compounds are the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzonoid rings and no elements other than carbon and hydrogen (Henner et al., 1997). They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs (Marce and Borrull, 2000).

Organic compounds can be released from their sources in gas phase or can be associated with particles by nucleation and condensation, forming particulate matter. The particulate form of PAHs are initially in the gaseous phase at high combustion temperature, however when the temperature decreases, gaseous phase PAHs adsorb or deposit on fly ash particles. The smaller the particle size, the greater the surface area for the adsorption of PAHs. The ambient temperature is very important for the gas-particle distribution of PAHs.

For instance napthalane was 100 % found in the gas phase, while benzo (a) pyrene (BaP) and other compounds with 5 and 6 rings are adsorbed on particulate matter. However napthalene was also found at high levels in the ashed from pulverized coal power generation, therefore associated to the particulate matter. (Mastral and Callen., 2000).

PAH can be formed in any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing C and H (Baek et al., 1991). The mechanism of formation of PAH involves the production of reactive free radicals by pyrolysis (at ~ 500-800 ° C) of fuel hydrocarbons in the chemically reducing zone of a flame burning with an insufficient supply of oxygen. The C_2 fragments, as well as C_1 and higher radicals, combine rapidly in the reducing atmosphere to form partially condensed aromatic molecules. On cooling the reaction mixture these PAH condense from the vapor phase onto co-existing particulate substrates, with a product distribution that generally reflects their thermodynamic stabilities in the oxygen-deficient flame (Finlayson and Pitts, 1986).

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

PAH formation in pyrolysis oils has been attributed by Diels-Alder reactions of alkenes to form cyclic alkenes. Upon dehydrogenation reactions of cyclic alkenes, stable rings of aromatic compounds form which further lead to formation of PAH compounds.However complex hydrocarbons do not have to necessarily break into small fragments before recombination processes. Compounds with several rings can suffer partial cracking. On the other hand, phenyl radicals also play an important role besides intermolecular and intramolecular hydrogen transfers at intermediary compounds in high temperature reactions that lead to PAH formation (Mastral and Callen., 2000).

1.3.1. Molecular Structure and Chemical Properties of PAHs

The molecular structures of PAHs were shown in Figure 1.2. PAHs are relatively neutral and stable molecules. PAHs have low solubilities and low volatilities except small components like napthalene. Solubilities of PAHs in water decreases with increasing molecular weight. Their liphophilicity is high, as measured by water –octanol partition coefficients (Kow). Due to their hydrophobic nature, the concentrations of dissolved PAHs in water are very low. PAHs show long half- lives in geological media. In an eorobic sediment, for example, half lives range from three weeks for napthalene up to 300 weeks for benzo (a) pyrene. PAHs are regarded as persistent organic pollutants (POPs) in the environment. This persistence increases with ring number and condensation degree (Henner et al., 1997).

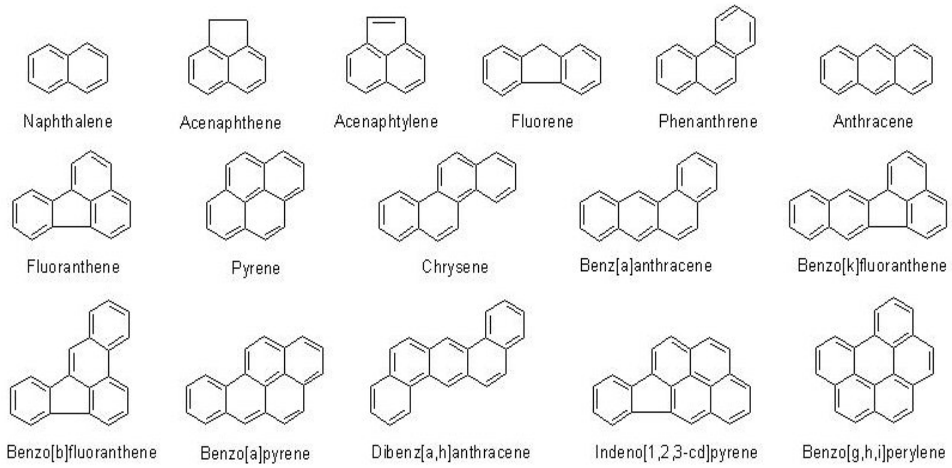


Figure 1.2. Molecular structures of PAHs

Physical properties of the 16 PAHs defined as priority pollutants by the American Environmental Protection agency (EPA) were shown in Table 1.2.

Table 1.2. Chemical structures and physical properties of selected PAHs

Compound	Formula	Molecular Weight	Melting Point °C	Boiling Point °C	Vapor Pressure kPa
Naphthalene	$C_{10}H_8$	128.18	80.2	218	$1.1x10^{-2}$
Acenaphtylene	$C_{12}H_8$	152.20	92-93	265-280	$3.9x10^{-3}$
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	$2.1x10^{-3}$
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	$8.7x10^{-5}$
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	$36x10^{-6}$
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	$2.3x10^{-5}$
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	$6.5x10^{-7}$
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	$3.1x10^{-6}$
Benzo(a)anthracene	$C_{18}H_{12}$	228.30	157-167	435	$1.5x10^{-8}$
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	$5.7x10^{-10}$
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	$6.7x10^{-8}$
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-471	$2.1x10^{-8}$
Perylene	$C_{20}H_{12}$	252.32	273-278	500-503	$7.0x10^{-10}$
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177-179	493-496	$7.3x10^{-10}$
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	493	$7.4x10^{-10}$
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	275-278	525	$1.3x10^{-11}$
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	162-163	-	$cax10^{-11}$
Dibenz(a,h)anthracene	$C_{22}H_{14}$	278.35	266-270	524	$1.3x10^{-11}$
Coronene	$C_{24}H_{12}$	300.36	438-440	525	$2.0x10^{-13}$

1.3.2. Toxicity and Carcinogenicity of PAHs

It has been known that coal tar is occupationally hazardous. Hovewer after discovery of carcinogenicity found in organic extracts of coal tar, potential environmental hazards of coal tar were suggested. This kind of biological activity was observed with extracts of respirable ambient particulates collected from Los Angeles photochemical smog, and then from major centers throughout the world. These observations are related to earlier studies on the carcinogenicity of coal tar extracts because many carcinogenic PAH are present in both industrial and ambient air environments. Thus in 1949, BaP was identified in domestic soot, while in 1952 it was found in ambient particles collected at ten stations throughout Great Britain. By 1970, BaP and related carcinogenic PAH were recognized being distributed throughout the world in respirable ambient urban aerosols. Furthemore, they were found in combustion-generated respirable particles collected from such primary sources as motor vehicle exhaust, smoke from residential wood combustion, and fly ash from coal-fired electric generating plants.

Concurrently, certain PAHs were shown to react with near ambient levels of NO_2+HNO_3 and with O_3 in synthetic atmospheres, to form directly mutagenic nitro-PAH and oxy-PAH (Finlayson and Pitts, 1986).

Some of the PAHs and their metabolites can induce stable genetic alterations that have the potential to irreversibly alter the control of cell division. This may result in tumor growth and cancer in fish and mammals. Since PAHs are soluble in fatty tissue, they may bioaccumulate and be transferred in the food chain. Some of PAHs have been identified as possible or probable carcinogens in humans, notably benzo(a)anthracene, chrysene, benzo(b and k) fluoranthene, benzo(a) pyrene and others (Golomb et al., 1997). Epidemiological studies have shown that people exposed to mixtures containing PAH’s (chimneys, coke oven emissions, cigarette smoke, roofing tar emissions) have increased rates of lung cancer (Fisher, 2001).

Although PAHs constitute only about 20 % of total hydrocarbons in petroleum (NRC,1985), they are responsible for the majority of its toxicity. The lower weight PAHs, known to be less toxic, are reported to be found predominantly in the vapor phase in an urban air where they can react with other pollutants (O_3 and NOx) to form more toxic derivatives. For example, PAHs react with NO_3, forming carcinogenic nitro-derivatives (June-Joo Park et al.,2001).

Not only does the PAH itself play a major role in the adverse biological outcomes of the exposure, but so does the size of the particle on which it may be adsorbed. Particulates less than 10 µm in diameter are more likely to contain greater amounts (per unit mass) of PAHs due to their large surface area to volume ratio. This is a great concern since it is the smaller diameter particles that are retained by the lung (Duggon, 2001). In human respiratory system, particles with diameters larger than 10 µm do not reach the thorax, particles ranging from 2.1 to 10 µm are preferentially retained by pharynx, trachea and bronchi and particles below 2.1 µm can reach terminal bronchi and alveoli. Therefore, a physical detrimental action of inhalable particles (i.e., the development of a pulmonory emphysema) is observed along with the chemical impact due to their toxicity (Cecinato et al., 1999).

The extent to which humansare exposed to PAHs is a function of several parameters, including the prevailing atmospheric conditions, concentrations in ambient air, partition between the gas and particle phase and the size distribution of airborne particulates. Risk assessment associated with inhalatory PAHs uptake is often estimated on the basis of the B[a]Py concentration in air. The evaluation of the health risk due to inhalatory exposure to PAHs is based on epidemiological findings. However, it has to be considerethat B[a]Py is just one carcinogenic compound in a mixture of carcinogens in the atmsophere (Papageorgopoulou et al., 1999).

1.3.3. Sources of PAHs

It has been estimated that stationary sources contribute for approximately 90 % of total PAH emission, but this is not true in urban and suburban areas, where the mobile sources are prevailing. The highest concentrations of atmospheric PAH can be found in the urban environment, due to the increasing vehicular traffic and the scarce dispersion of the atmospheric pollutants. The risk associated with human exposure to atmospheric PAH is highest in the cities, considering the density of population (Caricchia et al., 1999).

Part of the PAH in the atmosphere arises from natural combustion such as forest fires and volcanic eruptions, but emissions from human activities are the predominant source. The anthropogenic sources of PAH can be divided into stationary and mobile categories. Within the mobile category, the major contributors are vehicular petrol and diesel engines. The stationary category encompasses a wide variety of combustion processes including residential heating, industrial activities (e.g. aluminum production and coke manufacture), incineration and power generation which result in high atmospheric PAH concentrations in the vicinity of the major sources. The amount and range of PAH produced from any pyrolytic process varies widely, being dependent upon the fuel type and combustion conditions. The contribution of any PAH source to the atmosphere will depend on a number of factors including the emission rate of the source, its geographical location and the local climatic conditions (Baek et al., 1991).

1.3.4. Distribution in the Environment (air, water, sediments, biota)

Atmospheric PAHs are distributed between the gas and particulate phases depending on their physicochemical properties. They can be transported through the atmosphere over long distances entering into the aquatic environment by wet and dry deposition and/or gas water interchange. Once in the aquatic systems, most of the PAHs are associated to the particulate phase due to their hydrophobic properties giving rise to accumulation in the sediments. Sediments are therefore good environmental compartments for the record of long-range distribution of these compounds (Fernandez et al., 1999).

The main pathways of PAHs in the soil-plant system are shown in Figure 1.3. PAHs are hydrophobic compounds whose mobility in the soil-plant system is low. Equilibrium between solid, aqueous and vapor phase are very slow. As for pesticides, PAHs and their metabolites are expelled from the aqueous phase to adsorb on hydrophobic surfaces such as organic matter. They are either trapped in the pores, fixed with covalent or hydrogen bonds, or bound during humification processes. PAHs structure and stability stand in the way of their biodegradation by microorganisms, eg, fungi and bacteria. Biodegradation is slow and is a function of environmental parameters such as oxygen, water and nutrient contents. Migration of PAHs from the top soil is slow. PAHs seem to migrate bounded to particles. The major ways of entry of PAHs into plants seem to be through the leaves, from the vapor phase and by contact with contaminated soil particles. PAHs seem also to adsorb on the root cell walls. (Henner et al., 1997).

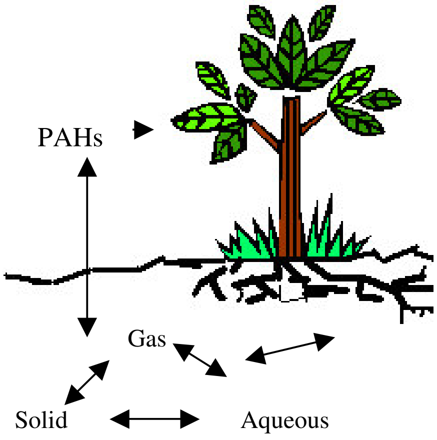


Figure 1.3. Main possible pathways of PAHs in the soil-plant system.

Historical records of PAHs in soil and sediment from rural ares and in ice from sites as remote as Greenland document the wide spread environmental contamination. Calculations by Wild and Jones on the distribution of PAHs in the United Kingdom demonstrate that the atmosphere has a low storage capacity and that the top of 15 cm of soil acts as a major repository, containing 94 % of all PAHs in the environment (Van Brummelen et al., 1996).

Natural waters like oceans, seas and lakes are another important sink for PAHs. There are some standard concentrations of PAHs for natural waters set by European Community. For instance, the reference concentrations for most dangerous PAHs are 10 ng/liter for benzo(a)pyrene, 20 ng/liter for fluoranthene and pyrene, 100 ng/liter for phenanthrene and anthracene in ground water (Djozan and Assadi, 1999).

Chemical exchange across the air-water interface is one of the major processes that controls concentrations and residence times of synthetic organic chemicals in natural waters. Hydrophobic organic chemicals (HOCs) such as chlorinated pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are transported long distances in the atmosphere and enter surface waters via wet and dry deposition. Atmospheric fluxes often dominate HOC inputs to remote lakes and the oceans. Once in the surface waters, dissolved HOCs may re-volatilize and the net HOC flux across the air-water interface is the difference between gross deposition and volatilization (Baker and Eisenreich., 1990).

1.4. PAHs in the Atmosphere

Polycyclic Aromatic hydrocarbons are emitted into the atmosphere either as vapors or associated with primary aerosol particles. Once in the atmosphere, the residence times and ultimate fates of these semivolatile chemicals depend upon their distributions among vapor, particle, and droplet phases. This partitioning is in turn controlled by the vapor pressures, Henry's law constants, and aqueous solubilities of the compounds and by the concentrations and size distributions of particles and droplets in the atmosphere. Chemical transformations and wet and dry deposition remove gaseous and particle-associated PAHs from the atmosphere (Poster and Baker, 1996).

As the particle associated and gas phase PAHs are transported through the atmosphere, they may be lost to the vegetation, soil, rivers, lakes, and oceans through the processes of dry and wet deposition. Neither mechanism is adequately understood. However, since pollutant concentrations can be measured directly in precipitation, wet deposition is better characterized quantitatively than is dry depositon.

Factors affecting the precipitation scavenging of PAH include the Henrys law constant (which is the ratio of the vapor pressure to the aqueous solubility of the component), precipitation intensity, storm type, as well as other meteorological parameters (Hansen and Eatough, 1991).

1.4.1. Gas to Particle Distribution of PAHs in the Atmosphere

The distribution of PAH in the atmosphere between the gas and particulate phases is determined by several factors, which include; the vapor pressure of the PAH (as a function of temperature); the amount of fine particles (in terms of available surface area for adsorption of PAHs); the ambient temperature; PAH concentration; and the affinity of individual PAH for the particles organic matrix (Baek et al., 1991).

Low molecular weight PAH compounds were primarily in the gas phase while high molecular weight PAHs were primarily found in the particulate phase. Gas phase percentages were generally higher in summer than in winter due to increasing temperature which increases the vapor pressure of the compounds (Odabaşı, 1998, Kaupp and MacLachlan, 1999).

The vapor pressure of a PAH molecule determines to a large extent, the phase (particulate or vapor) in which the chemical will be found. Junge (1977) showed, to a first approximation for urban particulate matter, that compounds with vapor pressures above $1 * 10^{-5}$ kPa should occur almost entirely in the gas phase, whereas compounds with vapor pressures less than $1*10^{-9}$ kPa should exist predominantly in the particulate phase. Any compound with a vapor pressure between these approximate limits would be expected to occur in both the vapor and particle phase (Hansen and Eatough,1991).

The effect of ambient temperature on the vapor pressure of the PAH is significant and must also be considered. Murroy et al (1974) showed that there is approximately an order of magnitude change in the vapor pressure of compounds such as benzo(a)pyrene and coronene for a temperature change of 20 °C. Since many regions can experience summer to winter variations of 50 °C or more, the vapor pressure of the PAH in the ambient environment can vary over two orders of magnitude. This, as a result, will cause a shift in the vapor to particle distribution of PAHs. As a consequence, one would expect to find more PAH associated with particulate matter in the winter than in the summer (Hansen and Eatough,1991).

Junge-Pankow adsorption model is another approach to obtain gas/particle phase distribution of PAHs. The basis of the model is a linear Langmuir isotherm with compound adsorption expressed by the relation of aerosol surface area available for adsorption (θ, cm^2/cm^3 air) and the subcooled liquid vapor pressure (P_L^0, Pa). The fraction of total atmospheric concentration of a semivolatile organic compound adsorbed on the particles (ϕ) is expressed as:

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

where c (Pa.cm) depends on the thermodynamics of the adsorption process and the surface properties of the aerosol. The suggested value for particle surface area is 1.1×10^{-5} (cm^2/cm^3) for urban air and 17.2 Pa.cm for the constant c (Odabaşı, 1998).

1.4.2. Air Water Gas Exchange of PAHs

Vapor phase PAHs can transfer from the air to the water and vice-versa. This transfer is governed by Henry's law which states that the concentration in water is proportional to the partial pressure of PAHs in air

$$p_a = H_a X_w$$

where p_a is the partial pressure in air, H_a is Henry's constant (both in pressure units), and X_w is the mole fraction in water. The lower Henry's constant, the more likely the gas will partition from air to water (Fisher, 2001).

1.4.3. Chemical Transformations of PAHs

The atmospheric chemical and photochemical reactions of the PAH are important for two reasons;

a) particular PAHs can be removed from the atmosphere as a result of chemical reactions,

b) decomposition product of the PAHs may be more hazardous to human health than the PAH from which they were derived (Hansen and Eatough, 1991).

A number of experimental studies have demonstrated that many PAHs are susceptible to photochemical and/or chemical oxidation under simulated atmospheric conditions (Pitts et al., 1985a, Nielsen, 1984; Kamens et al., 1988). Although results from the laboratory simulation studies are difficult to extrapolate to the reactivities of PAH under real atmospheric conditions, there is however potential for chemical transformation of PAH by gas-particle interactions in emission plumes, exhaust systems or even during atmospheric transport (Baek et al., 1991).

Nitro PAHs are emitted as a result of incomplete combustion processes. For instance diesel engines is one of the most important nitro PAH source in the urban environments. Other combustion sources are gasoline vehicles, aluminum smelters and coal-fired power plants. Nitro-PAHs may also be formed in the atmosphere via reactions of their parent PAH with OH or NO_3 radicals (in the presence of NO_2) in the gas phase as well as N_2O_5 or HNO_3 when the parent PAH is associated with aerosols. The mechanism of N_2O_5 nitration has been proposed to involve dissociation of N_2O_5 to NO_2^+ and NO_3^- followed by electrophile attack of NO_2^+. This mechanism could be of importance in strongly acidic sulphuric acid aerosols.

There are different mechanisms proposed for the gas phase formation of nitro-PAHs. For instance, below was proposed by Atkinsen and Arey (1994) and Fan et al., (1995) for the formation of nitro-PAHs in the gas phase.

Fluoranthene + OH$\rightarrow$ Fluoranthene-OH
Fluoranthene-OH+ $NO_2$$\rightarrow$ 2 nitrofluoranthene

It is not clear whether reaction with O_2 represents an important additional pathway for the OH-adduct (Feilberg et al., 2001).

Photochemical transformation have generally considered to be the most important mode of atmospheric decomposition of PAH of both phases and extent of photochemical decay is strongly depend on the nature of the substrate on which they are adsorbed. Although photochemistry is the major mechanism for decomposition of PAHs, various PAHs may also degrade by non-photochemical pathways such as evaporative or oxidative reactions with gaseous pollutants (Baek et al.,1991). Korfmacher et al., reported that fluorene and benzo(a/b) fluorene oxidized without the presence of light. Reactions of PAHs with ambient levels of O_3 have been reported by a number of experimental studies (Pitts et al., 1986, Peters and Seifert, 1980). Pitts et al.,(1986) demonstrated that five PAH, found at ngm^{-3} levels in ambient particulate organic matter, reacted with ozone in the range 50 to 300 ppb, regardless of the relative humidity of the simulated system. According to the experimental results PAHs may react readily with O_3 in polluted atmospheres.

Besides the reaction of PAHs with O_3 and NO_x, degradation of PAHs may also occur in the presence of SOx, however little is known about the products from the reaction of PAH with SO_x (Baek et al.,1991).

1.5. Atmospheric Pollutant Removal Processes

Atmospheric pollutant removal processes can be conveniently grouped into two categories: dry deposition of particles and vapors and wet deposition of particles and vapors. Dry deposition proceeds without the aid of precipitation and denotes the direct transfer of gaseous and particulate air pollutants to the Earth's surface. Wet deposition, on the other hand, encompasses all processes by which airborne pollutants are transferred to the Earth's surface in an aqueous form (i.e., rain, snow, or fog). The prevailing removal mechanism depends on the compound physico-chemical properties (solubility in water, Henry's law constant, vapor pressure), its vapor-to-particle partitioning and meteorological parameters(rain height, intensity and temperature). For instance, benzo(a)pyrene, which is predominantly bound to fine particles, is expected to be removed mainly by particle washout and dry particle deposition, on the other hand napthalene which has higher vapor pressure hence mainly occurs in the vapor phase, is removed by vapor washout and/or dry vapor deposition (Grynkiewicz et al., Scroeder and Lane, 1988).

Since PAHs in the atmosphere are mostly associated with particulate matter, their atmospheric residence time is closely related to the behavior of the carrier particles. The physical removal or transport of airborne particles is a function of the particle size and meteorological conditions. It has been established that both coarse particles (larger than 3 to 5 μm) and nuclei range particles (below 0.1μm) are similarly limited in their atmospheric residence times, and consequently in their effects, although their removal mechanisims are different. The former tend to be removed from the atmosphere by simple sedimentation, such as dry or wet deposition, while the latter are removed predominantly by coagulation with each other and larger particles. Particles in the size range between 0,1 and 3 µm, with which airborne PAH are predominantly associated, are known to diffuse only slowly and have little inertia, and can be expected to remain airborne for a few days or longer. Particle of this size range are not removed efficiently by rain and may be transferred over long distances, dependent upon atmospheric conditions (Baek et al., 1991).

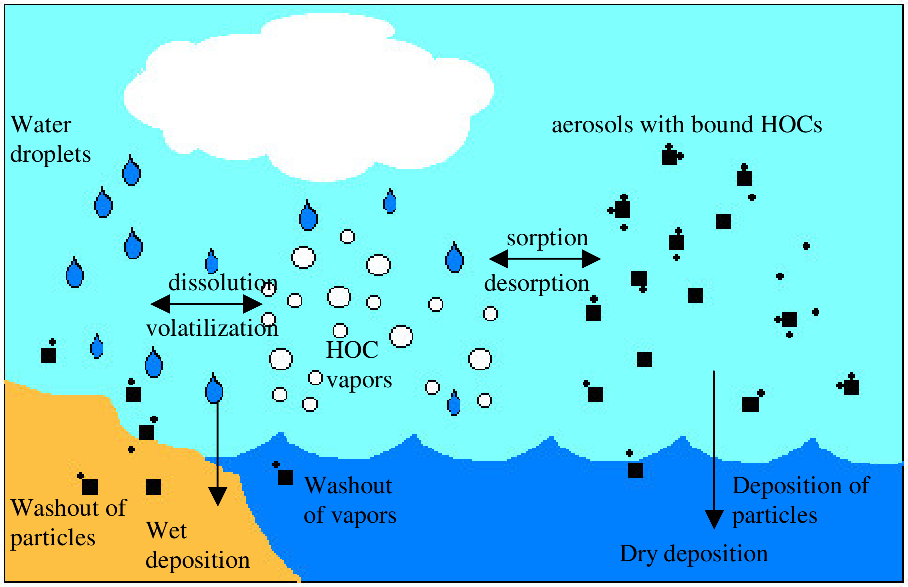


Figure 1.4. Atmospheric deposition of HOCs

Figure 1.4 shows schematically atmospheric deposition processes for Hydrophobic organic compounds (HOCs). As it is seen in Figure 1.4, particles and vapors are removed from the atmosphere with both dry and wet deposition. Gas- particle and gas liquid partitioning mechanisms are also important for the deposition of HOCs to earth surface. (Leister and Baker , 1994).

1.6. Wet Deposition of PAHs

PAHs were originally emitted from sources in the gas phase, adsorbed on to particulates, in part resisting degradation in the environment, and then went through atmospheric transport leading to a wider distribution. (Lin Sheu et al., 1997).

Aerial fluxes of semivolatile organic compounds occur by rain and snow scavenging of vapors and particles and by dry deposition (Bidleman., 1998). In the case of wet deposition, pollutant removal occurs by two mechanisms; in cloud scavenging or rain out and below cloud scavenging or washout. Particle scavenging by snow is a complex process occurring both in and below cloud.

Contribution of particle scavenging to wet deposition of hydrophobic organic contaminants (HOCs) depends on many factors such as concentration of aerosols, the size distribution of both snowflakes and aerosols, the hygroscopic nature of the particulate matter and ambient conditions (Schumann et al., 1988, Mitra et al., 1990, Sparmacher et al., 1993). Particles serve as seeds for condensation nuclei in in-cloud scavenging and called nucleation scavenging. The below cloud scavenging of particles may be viewed as a physical process in which falling snow flakes act like filters (Wania et al., 1998). Snow fall has the potential to significantly contribute to the deposition of airborne contaminants by washing out the aerosol and sorbing the vapor (Franz, 1994).

Snow may be more efficient than rain at below-cloud scavenging of particles because of the larger size and surface area of snowflakes. Snowflakes and dendritic crystals exhibit a “filtering effect” on atmospheric particles enroute to the surface due to their porosity, which allows air to pass through the falling solid. This ventillation enhances the ability of snowflakes and dendrites to scavenge small particles (0.2-2 µm), which tend to follow the streamlines around a non-porous raindrop. Field experiments have demonstrated that below-cloud scavenging of particles by snow is about five times more efficient than by rain (Franz and Eisenreich, 1998).

In the atmosphere, trace organic compounds are expected to partition between the aerosol and vapor phases. For a given compound, the extent of association with the aerosol will depend on its vapor pressure, the ambient temperature, and the amount and type of aerosol present. The mechanism of wet removal from the atmosphere are very different for particle associated compounds than for gas phase compounds. Non reactive gaseous organic compounds will be scavenged by rain according to the Henry's Law equilibrium between the vapor and aqueous phases (Ligocki et al., 1985). Particle scavenging is more difficult to predict theoretically since it is a complex process which depends upon the meteorological conditions in the cloud as well as the chemical and physical properties of the aerosol. When there is no exchange of material between the particulate and dissolved phases in the rain, the total degree of scavenging of a given compound can be expressed (Pankow et al., 1984).

$$W = W_g(1-\phi) + W_p\phi$$

Where W is the overall scavenging ratio:

$$W= [\text{rain, total}] / [\text{air, total}]$$

Wg is the gas scavenging ratio:

$$W_g= [\text{rain,dissolved}] / [\text{air, gas}]$$

Wp is the particle scavenging ratio:

$$W_p= [\text{rain, particulate}] / [\text{air, particulate}]$$

And ϕ is the fraction of the atmospheric concentration which is associated with particles. W will differ from the equilibrium Wq value for compounds which: (1)

are scavenged to some degree from the atmospheric particulate phase; and (2) remain on particulate material inside the raindrop. The second condition is necessary because material which is transferred to the dissolved phase will re-equilibrate rapidly with the atmosphere.

The simplest model for in-cloud particle scavenging involves nucleation scavenging followed by coalescence of the cloud droplets into raindrops. Of the order of 10^6 ~ 10 μm cloud droplets must combine to form one 1-mm raindrop. Hence, scavenging ratios under these conditions are expected to be of the order 10^6μm (Scott, 1981). This process alone seldom produces precipitation. Moreover, since cloud droplets form around hygroscopic particles, carbonaceous particles are not likely to act as condensation nuclei. In cold clouds, ice crystals grow by vapor accretion and by collection of supercooled droplets (riming) (Scott, 1981). Scavenging ratios may be considerably lower than 10^6 under these conditions. In the case of below cloud scavenging; Wp values have been estimated to be 10^3-10^5 for 0.01-1.0 um particles (Slinn et al., 1978). From this limited information, one may expect to observe overall particle scavenging ratios in the range of 10^3-10^6. Gas scavenging ratios for neutral organic compounds have been found to range from 10^0 to 10^5. Particle scavenging may therefore contribute significantly to the overall scavenging of many trace organic compounds which exist in both the aerosol and gas phases (Ligocki et al., 1985).

1.7. Dry Deposition of PAHs

Dry deposition is the transfer of airborne gases and particulates to the earth's surface, including soil, water, and vegetation, where they are removed (Seinfeld, 1986).

Current understanding of wet deposition is far beyond the dry deposition. Wet deposition is relatively simple to measure, even though the precipitation processes themselves are complicated and considerable uncertainity exists if one attempts rigorous conceptual or mathematical descriptions. By comparison, dry deposition is difficult to measure; therefore existing data base on this process is relatively small and still contains many uncertainities. It is important to recognize that, for both dry and wet deposition, the atmospheric pathways and characteristics for criteria as well as noncriteria contaminants are much better described and understood for the aerosols than for the gaseous substances (Scroeder and Lane, 1988).

The process of dry deposition for particulate PAH comprises three mechanisms; diffusion, impaction, and sedimentation. These three mechanisms depend upon the shape and size of the particle upon which PAHs are adsorbed, wind speed, and the atmospheric friction velocity. Similarly for gaseous PAH, the dry deposition will depend upon the moleculer weight and the polarity of the molecule.

Airborne PAHs are relatively short-lived, in order of a few to tens of hours. Thus, in dry air PAHs may not travel very far from the emission sources, to a distance of a few to tens of kilometer (Golomb et al., 2001).

1.7.1. Sampler Characteristics in Deposition Measurements and Difficulties in Dry Deposition Sampling

Many different type of samplers have been used to collect atmospherically transported contaminants. These samplers can be divided into two basic varieties: deposition samplers which collect material being deposited, usually passively, to a controlled surface; and, ambient samplers which actively draw a measured volume of air through a sampling medium, providing a measurement of contaminant concentration in the atmosphere. Dry and bulk deposition pans are true passive samplers which do not activelly draw air and suspended materials to themselves. Deposited materials are, however, exposed to sunlight and the atmosphere which may result in photodegradation, volatilization or wind removal of particulate material. Since samples collected by this way are bulk samples, it is not possible to quantitate wet and dry parts separately. Bulk samplers can be equipped with movable parts and rain sensors to permit the separation of wet and dry deposits but the dry part is still susceptible to photodegradation, volatilisation and removal by wind action (Waite et al., 1999). In addition, the majority of organic chemical analyses of rain water do not clearly distiguish between the dissolved and particulate fractions. Such a distriction is critically important to study of precipitation organic chemistry as it relates to nucleation, washout, and chemical transformations occuring within the atmospheric boundary layer (Mazurek et al., 1987).

Wet deposition of hydrophobic organic compounds can be measured directly by event-only collecters however dry deposition measurements are not easy to conduct. Several surfaces such as glycerol-coated plates or pans, teflon sheets, filter paper, or water surfaces have been used in the literature but they are not reliable and do not simulate natural environmental surfaces very well. Besides real measurements, model calculations also used to derive information about the dry deposition but they are also lack of real world information (Swackhamer et al., 1988). Dry deposition rates of some compounds have been mathematically estimated from ambient air concentrations and the atmospheric chemical dynamics of the compound (Eisenreich et al., 1981, Barrie et al., 1992, Bidleman and McConnell, 1995). However these calculations are based on some variables like, atmospheric particle size distribution, partitioning between particulate and gas phase which are in turn controlled by temperature, humidity and other climatic conditions (Waite et al., 1999).

1.7.2. Snow as a Surrogate Surface for Dry Deposition of PAHs

Snow can be a good collecting surface for measuring the accumulation of both organic and inorganic pollutants, because the deposition time is easy to define and snow samples are easy to analyse (Viskari et al., 1997).

Snow fall has the potential to significantly contribute to the deposition of airborne contaminants by washing out the aerosol and sorbing the vapour. In a snow pack, the large specific surface area of ice crystals has the potential to sorb appreciable quantities of hydrophobic organic compounds (HOCs). Snow may be a valuble medium for monitoring contaminant levels in any region as it is less transient than rain. Figure 1.5. shows the processes which may occur in a snow pack on land.

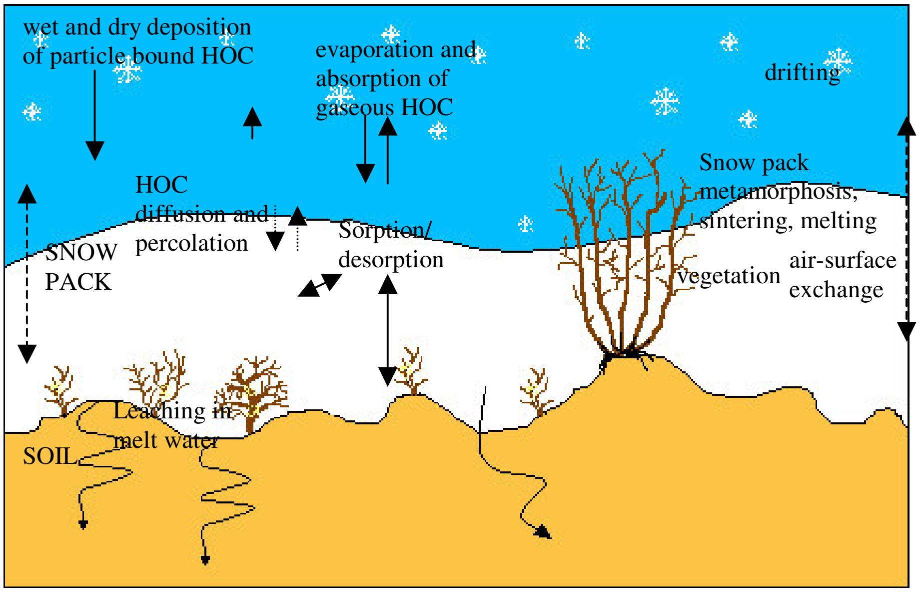


Figure 1.5. Post depositional processes affecting hydrophobic organic chemicals (HOCs) fate in a terrestial snow pack (Wania et al., 1998).

As a result of gas and particle scavenging processes a snow pack contains HOC in four forms; bound to the ice surface, sorbed to particles, as vapour in the interstitial air, and dissolved in liquid water. Their relative contributions are determined by physical and chemical properties of the chemical and the snow pack. In fresh snow, ice surface-partitioning usually dominates, particularly for less volatile HOCs. It is probably errorneous to asume that HOC which is particle bound in the freshly fallen snow remains as such in the pack. It is likely that there is a continuous redistribution between the four forms as the snow pack ages. Since the area, volume and volume fractions change, the sorptive capacity of a snow pack is time dependent. Depending on ambient conditions, fallen snow undergoes many physical changes, such as subliming, compacting, sintering, freezing, and melting. In a dry snow pack when temperatures are below the freezing point, sintering can lead to a continuous reduction in a specific surface area and porosity with the corresponding increase in grain size and the decrease in grain population by vapour transfer (Wania et al., 1998).

1.8. Organic Molecules as Tracers

Determination of source contributions from ambient monitoring data by receptor modeling techniques relies on the ability to characterize and distinquish differences in the chemical composition of different source types. The elemental composition of source emissions has been used on many times to identify separately different sources of airborne particles. Unfortunately, a large number of sources that emit fine particulate matter do not produce emissions that have unique elemental compositions, instead many sources emit principally organic compounds and elemental carbon. (Schauer et al., 1996).

Over the past decades chemical mass balance (CMB) models, based on trace element spectra, have been widely used for motor vehicle source apportionment. However in recent years typical lead concentrations associated with motor vehicle emissions declined and in 1990 lead containing gasoline became unavailable in many parts of the U.S.A. Therefore, an alternative tracer for motor vehicle emissions is necessary (Gordon, 1988; Daisey et al., 1986). Diesel engines for instance emit particulate matter at a rate 30-100 times higher than an equivalent-sized gasoline powered engine (NRC, 1982) and a unique tracer needs to be find. Other sources, such as domestic heating,oil combustion, home heating wood combustion and petroleum refinery operations also lack of effective element tracers for source identification (Li and Kamens, 1993).

When such important sources of primary particle emissions can not be identified in ambient samples, then much of the true nature of a particulate air pollution problem remains obscured. Recent advances in source testing techniques make it possible to measure the concentrations of hundreds of specific organic compounds in the fine aerosol emitted from air pollution sources. By analogous methods, the organic compounds present in the fine aerosol collected at ambient sampling sites can be determined. The relative distribution of single organic compounds in source emissions provides a means to fingerprint sources that can not be uniquely identified by elemental composition alone. These advances in measurement methods therefore create the practical possibility of devising receptor models for aerosol source apportionment that rely on organic compound concentration data and that potentially can identify separately the contributions of many more source types than has been possible based on elemental data alone (Schauer et al., 1996).

Because certain compounds are characteristic of specific sources, rain water analysis for specific components provides a tool to trace the sources of organic matter in rain water as well as the origin of an air mass moving over the sampling site during rain events. For example, PAHs are incomplete combustion products of biomass and fossil fuels, thus they are good indicators of combustion sources. By contrast, fatty acids are excellent indicators of biological contribution to the atmosphere. Although individual markers have been used alone, the combination of different tracers provides powerful tools to evaluate the relative importance of biogenic and anthropogenic inputs to the atmosphere (Hansen and Eatough, 1991).

Same PAH may be generated by each source, the utility of using PAH depends on how different the patterns of the PAH are from each source. Many studies have suggested that some specific PAH or ratios between PAH compounds may be used for source identification. (Li and Kamens, 1993).

There are two significant concerns regarding the use of PAHs in source apportionment studies. First, partitioning of various PAHs between gas and particulate phases complicates both the sampling methodology and characteristic source signatures. The second concern is the loss of the source signature by destruction of PAHs by photochemical processes (Larsen and Baker., 2003).There are number of studies to identify organic tracers for number of source categories (Harrison et al., 1996, Simcik et al.,1999, Park et al., 2002, Yunker et al., 2002). However, often data sets are complex with certain source signatures being masked (Hopke et al., 1991). It was mentioned in Daisey's work that existing data indicated that it is possible to use PAHs as well as other organic compounds (such as alkenes) to assist in distinquishing emissions from particular pollutant sources (Daisey et al., 1987, 1986). Organic compounds might also be used together with trace elemental data by simultaneously for source apportionment studies (Harrison et al., 1996).

Duval and Friedlander (1991) utilized PAH data in Los Angeles to identify the following source fingerprints, coal combustion: anthracene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene and chrysene, coke production: anthracene, phenanthrene, benzo(a)pyrene and benzo(g,h,i)perylene, incineration phenanthrene, fluoranthene, pyrene, wood combustion: anthracene, phenanthrene, fluoranthene, pyrene, oil burning: fluoranthene, pyrene, petrol powered cars fluoranthene, pyrene, benzo(g,h,i)perylene, coronene, diesel powered cars: similar to petrol with higher ratios of benzo(b, k) fluorathene plus thiophene compounds. Rogge et al., (1993) reported high concentrations of chrysene, Benzo(a) anthracene, fluoranthene, pyrene in aerosols emitted from natural gas home appliences. As can be noticed above there is much similarity and overlap between profiles from different sources.

Parent and alkyl-substituted PAHs have both natural sources (oil seeps, bitumens, coal, plant-debris, forest and prairie fires) and anthropogenic sources (fossil fuels and combustion). Since the PAH compositions of the two sources overlap, especially for parent PAHs, the significance of anthropogenic PAH in the environment must be evaluated against a dynamic background of natural PAH. Despite the widespread applicibility of PAHs, most studies have been limited to a specific location or type of sample, with the result that few studies have comprehensively addressed the relative suitability of various commonly applied ratios as indicators. Parent PAH ratios have been widely used to detect combustion derived PAH. To minimise confounding factors such as differences in volatility, water solubility, adsorption etc. ratio calculations are restricted to PAHs within a given molecular mass. For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable “kinetic” PAH isomers relative to the more stable “thermodynamic” isomers. However some PAH react faster than others in the atmospheric chemical processes. PAH ratios in the atmosphere often will depart from those seen in source emissions. Various studies have demonstrated that benzo[a]pyrene, benzo[a]anthracene and anthracene degrade photolytically in the atmosphere at much faster rates than their isomers or other commonly measured parent PAH (Kamens et al.,1986, 1988; Maschlet et al., 1986; Behymer and Hites, 1988). In Mediterranean aerosol the most photoreactive components (typically benzo[a]anthracene and benzo[a]pyrene) show depletion between urban and remote areas for PAHs that have primary source in vehicle emissions (Sicre et al., 1987; Gogou et al., 1996, Tolosa et al., 1996). Ambient air data for

Los Angeles demonstrate that anthracene proportions are lowest in day time and indicate that anthracene undergoes more rapid photochemical reaction in the atmosphere than phenanthrene (Fraser et al.,1998). In contrast, the fluoranthene/pyrene and indeno[1,2,3-cd]pyrene/benzo[g,h,i]perylene isomer pairs degrade photolytically at comparable rates (Masclet et al., 1986; Behymer and Hites, 1988), suggesting that the original composition information is preserved during atmospheric transport. Biomass and fossil fuel combustion processes produce aerosols with very different particle sizes and physical properties and these differences affect both the dispersion pathways in the environment and the physical protection afforded combustion products such as the PAHs. Black carbon forms in two fundamentally different ways. Char (and charcoal) black carbon forms during the flaming and smouldering of the cellulose-rich solid residues of plant tissues and is a common product of wildfires. In contrast, soot black carbon is generated from volatiles formed within flames and subsequently recondensed by free radical reactions to form the graphite rich material that is more typical of fossil fuel combustion. (Yunker et al., 2002). Pyrogenic PAH generally associate with soot-rich particles that protect them from degradation in the atmosphere, water column and sediments. Greater protection would be expected with a larger particle size or with the encapsulation of PAHs within a particle, rather than adsorption on the surface. The amount of protection also is dependent on the particle colour, because PAHs associated with light coloured or grey substrates photodegrade much faster that PAHs associated with dark coloured or black substrates. Because the char black carbon of wood soot consists of large, dark, refractory particles that provide a solid matrix that traps and stabilizes PAH, a recognisable PAH fingerprint of combustion can survive over geological time scales. Accordingly it is likely that char from wildfires affords much greater protection towards photolysis than is observed for carbon black or other black soot from fossil fuel combustion (Yunker et al., 2002).

However during winter, photolysis can be expected negligible due to the low angle of the sun and substantial reduction in the photolytic degradation of particle-assosciated PAH at lower temperatures and humidity (Kamens et al., 1986, 1988).

Data about the ratios were collected from literature by Yunker et al.,(2003) and given in Table1.3

Table 1.3. Literature PAH ratios for petroleum, single-source combustion and environmental samples

Source	Ant/178	Flt/Flt+Pyr	BaA/228	Ind/Ind+ BgP
Petroleum				
Kerosene [b]	0.04	0.46	0.35	0.48
Diesel oil (n=8) [b,c,d,e]	0.09± 0.05	0.26±0.16	0.35±0.24	0.40±0.18
Crude oil (n=9) [f-h]	0.07	0.22±0.07	0.12±0.06	0.09
Australian crude oils and fluid inclusion oils (n=102) [i]	0.03±0.03	0.43±0.13	-	-
Shale oil [g]	0.26	0.34	0.45	0.39
Lubricating oil [j]	-	0.29	0.10	0.12
Coal (n=27) [k]	0.20±0.13	-	-	-
Asphalt [l,m]	-	-	0.50	0.52-0.54
Combustion				
Lignite and brown coal (n=3) [n,o]	0.08	0.72	0.44	0.57
Bituminous coal (n=3) [o,p]	0.33	0.53±0.05	0.34	0.48
Hard coal briquettes (n=9) [q,r]	-	0.57±0.03	0.43±0.04	0.52±0.04
Coal tar (SRM 1597)[s]	0.18	0.58	0.54	0.53
Wood soot (n=2) [p,t]	0.26	0.50	0.43-0.49	0.55-0.55
Wood (n=19) [u,v,w,x,y]	0.19±0.04	0.51±0.06	0.46±0.06	0.64±0.07
Grasses (n=6) [v]	0.17±0.04	0.58±0.04	0.46±0.02	0.58±0.10
Gasoline (n=2) [t,z]	0.11	0.44	0.33-0.38	0.09-0.22
Kerosene (n=3) [aa, bb]	0.14±0.02	0.5	0.37	0.37
Diesel (n=25) [c, d, e, g ,t, z, bb]	0.11±0.05	0.39±0.11	0.38±0.11	0.35±0.10
No. 2 fuel il (n=2) [cc]	0.06	0.51	0.17	-
Crude oil (n=4) [h]	0.22	0.44±0.02	0.49±0.01	0.47±0.01
Environmental samples				
Bush fire [u]	-	0.61	0.23	0.70
Savanna fire particulate (n=3) [dd]	-	0.59±0.01	-	0.39± 0.07

Table 1.3. continued

Source	An/178	Fl/Flt+Pyr	BaA/228	Ind/Ind+ BgP
Road dust [l, ee]	0.18	0.42	0.13	0.51
Lubricating oil, re-refined [ff]	-	0.74	-	0.36
Used engine oil,gasoline, passenger car [ff]	0.22	0.30	0.50	0.18
Used engine oil, diesel car, truck, and bus [ff]	-	0.37	-	0.29
Tunnel with light duty gasoline vehicles (n=4) [gg, hh]	-	0.45±0.03	0.46±0.06	0.30±0.04
Tunnel with heavy duty diesel trucks and gasoline vehicles (n=5) [gg, hh]	-	0.42±0.01	0.57±0.04	0.30±0.07
Roadway tunnels (n=2) [ii, jj]	0.13	0.43	0.42	0.30
Urban air (including SRM 1648 and 1649a: n=3)[bg, kk, ll]	0.08±0.02	0.56±0.01	0.30±0.05	0.40±0.11
Creosote treated wood piling (n=4) [mm]	0.20±0.05	0.62±0.01	0.5±0.03	0.64±0.04

[a] The mean and range (in brackets) are given where replicates are available (n=1 unless otherwise specified). The mean ± SD is provided when n > 2; - indicates not measured.
[b]Westerholm and Li, 1994. [c]Wang et al., 1999. [d]Schauer et al., 1999. [e]Westerholm et al., 2001. [f]Grimmer et al., 1983a. [g]Wise et al., 1988b. [h]Benner et al., 1990. [i]CSIRO Australia petroleum data base; Simon George, pers. Commun. [j]Grimmer et al., 1981a. [k]Radke et al., 1982 (measured peak heights). [l]Wakeham et al., 1980a (measured peak heights). [m]Readman et al., 1987 (measured peak heights). [n]Grimmer et al., 1983b. [o]Oros and Simoneit, 2000. [p]Lee et al., 1977 (measured peak heights). [q]Ratajczak et al., 1984. [r]Grimmer et al., 1985. [s]Wise et al., 1988a. [t]Li and Kamens, 1993. [u] Freeman and Cattell, 1990. [v] Jenkins et al., 1996. [w]Oanh et al., 1999. [x]Schauer et al., 2001. [y]Fine et al., 2001. [z]Rogge et al., 1993b. [aa]Laflamme and Hites, 1978 (measured peak heights). [bb]Sjögren et al., 1996. [cc]Rogge et al., 1997. [dd]Masclet et al., 1995. [ee]Rogge et al., 1993a. [ff]Grimmer et al., 1981b. [gg]Miguel et al., 1998. [hh]Marr et al., 1999. ii Benner et al., 1989. [jj]Fraser et al., 1998a. [kk]NIST SRM 1649a certificate of analysis. Ll Fraser et al., 1998b. [mm]Goyette and Brooks (1998) and Goyette, unpublished

PAHs of molecular mass 178 and 202 are commonly used to distinquish between combustion and petroleum sources (Soclo et al., 2000, Sicre et al., 1987). For mass 178, anthracene to anthracene plus phenanthrene (Ant/178) ratio< 0.10 usually is taken as an indication of petroleum while a ratio > 0.10 indicates the dominance of combustion.

For mass 202 a fluoranthene to fluoranthene plus pyrene (Flt/Flt+Pyr) ratio of 0.5 is usually defined as the petroleum/combustion transition point, but in practice this boundary appears to be less definitive than 0.1 for Ant/178. The Flt/Flt+Py ratio is below 0.5 for most petroleum samples and above 0.5 in kerosene, grass, most coal and wood combustion samples and creosote, but is below 0.5 for gasoline, diesel, fuel oil, and crude oil combustion and emissions from cars and diesel trucks (Table 1.3.). Crude oil samples from most studies have ratios < 0.40, but the mean ratio for Australian crude oil is > 0.40, and a few oils have very high proportions of fluoranthene. Vehicle and crude oil combustion particulates are more uniform(0.41-0.49) and closer to the 0.5 boundary than diesel exhaust (particulate plus vapour 0.20-0.58; Table 1.3.) suggesting that unburned diesel depress the fluoranthene proportion in exhaust samples. Overall, however, the petroleum boundary ratio appears closer to 0.4 than 0.5 for Flt/Fl+Pyr and ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas ratios > 0.5 are characteristic of grass, wood or coal combustion.

PAHs of molecular masses 228 and 276 are used less frequently as parent PAH indicators and few guidelines have been established for their interpretation. Because very low proportions of benz[a]anthracene or indeno [1,2,3-cd] pyrene are rarely observed in combustion samples (Table 1.3.), a BaA/228 or Ind/Ind +BgP ratio less than 0.20 likely indicates petroleum.

A BaA/228 ratio over 0.50 has been taken to indicate combustion while a ratio below 0.5 has been attributed to low temperature diagenesis. The data summarised in Table 1.3. suggests that 0.50 is probably too high for the diagenesis/combustion transition and that BaA/228 ratios < 0.20 imply petroleum, from 0.20 to 0.35 indicate either petroleum or combustion and > 0.35 imply combustion.

Combustion products of gasoline, kerosene, diesel and crude oil have ratios of IP/IP+Bghi below 0.5, with vehicle emissions falling between 0.24 and 0.40. Accordingly, Ind/Ind+BgP ratios < 0.20 likely imply petroleum, between 0.20 and 0.50 liquid fossil fuel (vehicle and crude oil) combustion, and ratios > 0.5 imply grass, wood and coal combustion (Yunker et al., 2002)

Low molecular weight PAHs/High molecular weight PAH ratios (LMW/HMW, Phe+Ant+Pyr+Flt/BaA+Chry+BbF+BaP+BeP+DahA+BgP+Ind) used by Soclo et al., (2000) was based on the fact that petrogenic contamination is characterized by the predominance of the lower molecular weight PAHs while the higher molecular weight PAHs dominated in the pyrolytic contamination.

Fluoranthene:pyrene ratio of 0.6 has been suggested as an indicative of vehicle emissions (Neilson, 1998).

PAH emission profiles vary among engine types. Low molecular weight PAHs are mainly emitted from diesel engines, whereas petrol engines release the greatest amounts of high molecular weight PAHs (Castellano et al., 2003).

Ratios of fluoranthene to fluoranthene plus pyrene on the order of 0.40-0.45 have been reported in exhausts of gasoline-fueled vehicles (Aceves et al.,1993).

Diesel exhausts is believed to be enriched in fluoranthene, chrysene and pyrene relative to gasoline fuel exhaust (Masclet et al., 1986).

1.9. Importance of Organic Analytical Chemistry in Environmental Research

The growing extent of pollution of the environment as a result of human activities initiated a wide complex of legislative measures. Reliable and relevant data on concentrations of pollutants in the environment is necessary for environmental protection policy. The largest problems were encountered in the case of organic micro pollutants, where the analysts had to cope with many different compounds occurring at trace concentrations. Thus the need for reliable data on occurrence of organic micro pollutants in the environment was an important driving force initiating the development of modern analytical techniques and procedures. Two major target areas of interest can be distinguished in the process of development of environmental organic trace analysis. The first area that was given major attention in the past was analytical separation and detection. In this field remarkable progress has been achieved during several decades. The second field, sample preparation has always been in the shadow of the first one, often being considered as a boring, inevitable part of the whole analytical method. Only after the highly sensitive analytical systems had become a common standard for environmental analysts, it was realized that the preparation of samples was an important braking factor in general progress in environmental analysis (Liśka, 2000).

Analytical objectives for environmental samples are governed by the necessity of obtaining reliable measurements at very low concentration levels in complex matrices. Many factors are of critical importance at very low concentrations considering the reliability of results. Analytical accuracy is normally measured directly by analysis of certified reference materials or by confirmatory testing. The latter consists of applying two inherently different analytical procedures to the same set of samples containing a range of determinant concentrations and comparing the resulting data statistically, in particular by regression method. (Manoli and Samara , 1999).

1.9.1 Varieties of Organic Analytes in Environmental Matrices

Man has put thousands of organic compounds to use this century, often in large quantities. In the 1960s it became increasingly obvious that certain chemicals have found their way into the natural environment in large quantities. Some of them came to be known as environmental poisons, animals exposed to them often displayed symptoms of illness or injury. All toxins entering the environment can be regarded as environmental poisons. Certain pollutants can, acting over long periods, harm living organisms even in low concentrations. This means that pollutants that are stable and thus persistent have a great ability to act as environmental poisons. Their stability means not only that their effects are long-lasting, but also that they are dispersed over large areas before broken down. The risk of a stable compound causing biological effects increases if it is capable of bioaccumulation, i.e., of being stored in living tissue. Stable organic compounds that are fat-soluble are usually able to bioaccumulate. Fat-soluble pollutants can accumulate in fatty tissues of living organisms in concentrations many times higher than in the surrounding environment. Many aromatic hydrocarbons are both fat-soluble and persistent. If these compounds become halogenated, their stability and their solubility in fat tend to increase yet further. POPs can be divided into three categories. Some of the "classic" environmental poisons- such as DDT, toxaphene, chlordane and hexachlorocyclohexane (HCH) are insecticides. These have been deliberately dispersed over agricultural land. Industrial chemicals never intended for dispersal outdoors can also leak into the environment. PCBs are the best-known example; other compounds of this kind are polychlorinated napthalenes (PCNs), chloroparaffins and brominated flame retardants. Some industrial chemicals are no longer manufactured. A third category of POPs occurs mainly as by-products of various manufacturing or combustive processes. These include hexachlorobenzene (HCB), polycyclic aromatic hydrocarbons (PAHs) and dioxins. To a limited extent many of these compounds can also be formed naturally, but anthropogenic emissions have now declined substantially.

1.9.2 Methods of Extraction

There is a growing realization that faster and more efficient methods for sample pretreatment are essential. Usually most of the time (60%) is spent in sample preparation while only 7% for analysis of the samples by instruments (Fritz and Masso, 2001).

Trace analysis of organic pollutants in water by GC-MS is basically hindered by two problems. The first problem is that the water sample is generally too dilute for direct injection, so the water sample has to be concentrated. The second problem is that water is not compatible with most GC stationary phases and therefore its transfer onto GC column should be prevented. To overcome these problems a number of different methods for phase switching, i.e., transferring the analytes from a large volume of water to a small volume of an organic solvent have been developed (Baltussen et al., 1998).

Determination of semi volatile organic compounds in liquid matrices frequently involves the use of conventional techniques, such as liquid-liquid extraction (LLE) and solid phase extraction (SPE). Compared to SPE, LLE is a time consuming multi step method for which large amounts of solvents are necessary. For that reasons LLE has been largely replaced in past few years by SPE using a variety of sorbents. However SPE is limited to semi-volatile compounds because the boiling points of the analytes must be substantially above that of the solvents. (Eisert and Levsen 1996, Santos and Galceran, 2002, Manoli and Samara, 1999).

More recently, several solvent-less extraction techniques were proposed. Solid Phase Microextraction (SPME) which has recently been evaluated for the extraction of a wide variety of pesticides, PAHs and polychlorinated biphenyls (PCBs) and the other solutes from water samples. SPME is based on the sorption (partitioning) of the analytes present in water sample into a layer of stationary phase coated onto a syringe like device. The main advantage of this method is its simplicity; besides the SPME device only standard GC instrumentation is required. The main disadvantage is that since this method is based on partitioning equilibrium, extraction is in some cases incomplete which render quantification difficult. Each analyte should be individually calibrated and the extraction yield should be determined for each solute (Baltussen et al., 1998).

Extractions of organic compounds from solid matrices have been done traditionally by Soxthlet or shake-flask extraction. However, in recent years instrumental extraction techniques have been developed which usually saves time and organic solvent. The most important instrumental extraction techniques are; supercritical fluid extraction (SFE), Microwave assisted extraction (MAE) and pressurized fluid extraction (PFE) ultrasonic extraction.

Supercritical fluid extraction has appeared on the market 20 years ago which was the first instrumental extraction technique among all. Basically, this technique exploits gas like and liquid like properties of supercritical fluid, typically carbon dioxide. Initial limitations of the technique centered around its inability to extract polar analytes from sample. However use of organic modifiers allows to extract analytes with wide range of polarities. SFE is an environmental friendly extraction technique which uses CO_2 as a solvent.

In MAE organic solvent and the sample are subjected to radiation from a magnetron in either a sealed vessel (pressurized MAE) or an open vessel (atmospheric MAE). Unlike SFE where samples are extracted sequentially, pressurized MAE allows up to 14 samples to be extracted simultaneously. The major limitation of MAE is that solvent needs to be physically removed from the sample matrix upon completion of the extraction prior to the analysis.

Pressurized fluid extraction is commercially available in the form of Accelerated Solvent Extraction (ASE). In this technique which has first appeared in the market in 1995, organic solvent is used together with heat and pressure to extract analytes from matrix. In contrast to other techniques PFE is an automated instrument capable of extraction 24 samples sequentially and a typical extraction time is 12 min per sample (Dean et al., 2000).

1.9.2.1 Solid Phase Extraction (SPE)

Organic compounds are a great concern in rivers, streams and ground water of the world. The waste water analysis protocol used in the United States for phenols, benzidines, pthalate esters, nitrosoamines, organochlorine pesticides, nitroaromatics, polynuclear aromatic hydrocarbons, haloesters, chlorinated hydrocarbons and acid-base neutrals requires chlorinated solvents for extraction. As much as 150 ml of methylene chloride may be used per sample of water. The methylene chloride is removed by evaporation under nitrogen, with as much as 5 to 10 million liter per year released to the atmosphere by the Superfund Contract Laboratory Program alone. It has been known that methylene chloride removes the ozone from the upper atmosphere and is suspected carcinogen. For that reasons, US EPA decided to reduce methylene chloride in their current analytical methods. SPE is one of the extraction methods applied to reduce the amount of organic solvents in the laboratory. It is also faster than liquid extraction and requires one tenth of the volume of solvent to extract the comparable volume of sample (Thurman and Snavely, 2000).

Solid Phase Extraction is a sample treatment technique in which a liquid sample was passed through a sorbent. Both the analytes to be determined or the interferences of the samples are retained on the sorbent by different mechanisms. In the first case, the analytes are eluted in a small volume of a solvent and so, the analytes are concentrated; in the second case the function of the solid-phase extraction is to clean the sample. The first case is mainly used for liquid samples and the second for solids, gases or liquids, usually after another sample-treatment technique. So, SPE is extremely versatile in the sense that it can be applied to a wide range of samples (Marcè and Borrull, 2000).

Compared to other extraction techniques such as liquid-liquid extraction, sonication, soxthlet extraction, SPE consumes less amount of toxic solvents which is a great concern in environmental point of view. The amount of solvent does not exceed 30 ml which is much less than that when miniaturized SPE was used. It is not even comparable with the classical extraction techniques which requires sometimes hundreds of mililiters of solvent.

Time is also another important parameter that must be taken into account considering huge number of samples collected in environmental studies. SPE saves substantial amount of time. If the sample is not loaded heavily with particles, extraction of a sample does not exceed 1 hour which is one day in the case of soxthlet extraction.

Considering the trace amount (ng/L) to of analytes present in environmental matrices, SPE is very advantageous since it is possible to enrich analytes 1000 times or more.

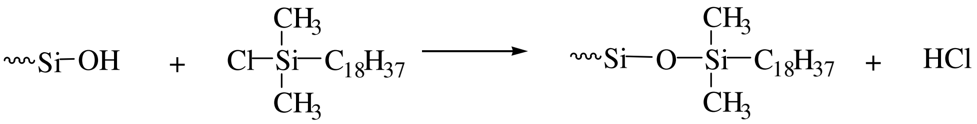
It is always desirable to extract the samples in situ to avoid decomposition or losses of samples during transport. Samples can be eluted even extracted in field using SPE. However, it is not always possible to maintain all the laboratory equipment in the field, in that case samples can be eluted through SPE disks or cartridges and brought to laboratory for further steps and analysis.The studies have shown that organics retained on SPE disks or cartridges are stable over 30 days as long as they are stored at dark and cold.

1.9.2.1.1. Reversed Phase SPE

The modes of SPE can be classified similarly to those of LC that are normal phase, reversed phase and ion exchange. Reversed phase separations involve a polar (usually aqueous) or moderately polar sample matrix (mobile phase) and a nonpolar stationary phase. The analyte of interest is typically mid- to nonpolar. Several SPE materials, such as the alkyl- or aryl-bonded silicates are in the reversed phase category.

In reversed phase SPE, the hydrophilic silanol groups at the surface of raw silica packing (typically 60 Å pore size, 40 um particle size) have been chemically modified with hydropobic alkyl or aryl functional groups by reaction with the corresponding silanes.

Retention of organic analytes from polar solutions (e.g. water) onto these SPE materials is due to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the silica surface (Supelco Bulletin, 1998).



$$\sim\mathrm{Si{-}OH} \quad + \quad \mathrm{Cl{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}C_{18}H_{37}} \longrightarrow \sim\mathrm{Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}C_{18}H_{37}} \quad + \quad \mathrm{HCl}$$

The sorbents used in SPE include graphitized carbon black (GCB), reversed –phase (RP) materials (modified silica gels) and polymeric materials. The most widely used RP material (and SPE sorbent in general) is the octadecyl (C_{18}) phase, but ethyl, butyl, cyclohexyl, octyl, phenyl, propylamino, dimethylaminopropyl and cyanopropyl reversed phase have been applied as well. The best known polymeric sorbents are styrene- divinylbenzene copolymers (Polysorb S, Amberlite XAD-2 and XAD-4) and polyacrylates (Amberlite XAD-7 and XAD-8). Unsatisfactory recovery rates and poor reproducibility were observed for XAD resins. Especially for the XAD resins excessive cleaning procedures are required prior to their use (Weigel et al., 2001). Bonded- phase silica sorbents have several advantages over polymeric resins. They do not require extensive clean-up, there are usually fewer chromatographic interferences during analyses and they permit faster analyses and less consumption of solvents. On the other hand, XAD- resins are less expensive and allow the extraction of larger volumes of water with higher flow-rates (Tolosa et al., 1996).

1.9.2.1.2. SPE Apparatus

Solid phase extraction disks and cartridges has been widely used to extract PAHs from different types of environmental liquid matrices. Figure 1.6. shows the differences among the three types of SPE formats.

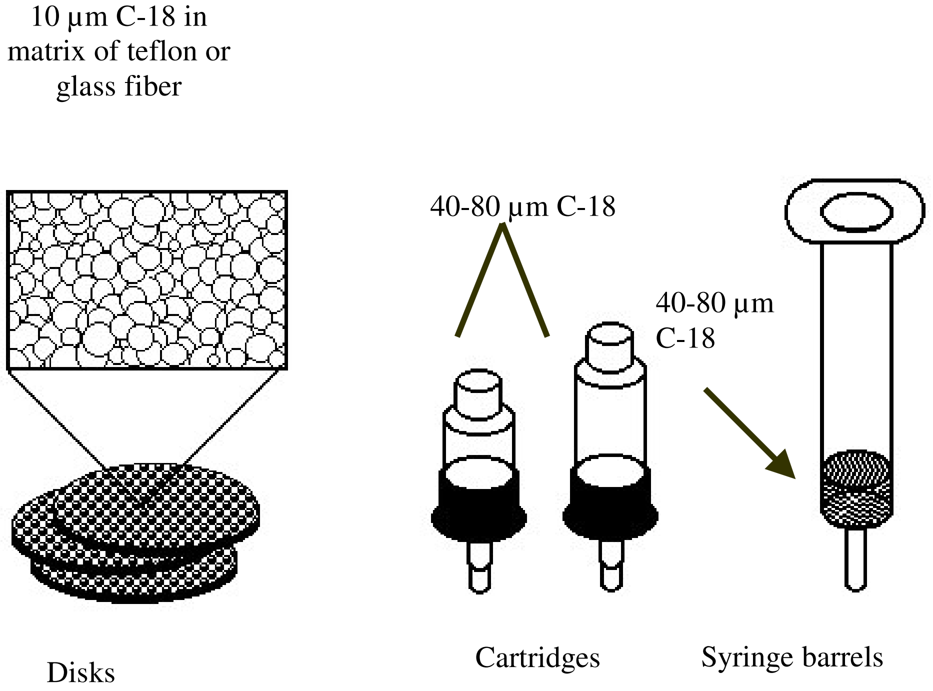


Figure 1.6. Three formats for solid phase extraction, disks, cartridges, and syringe barrels (Thurman and Snavely, 2000).

SPE disks differ from SPE cartridges or syringes in that the disk is a membrane loaded with a solid sorbent whereas the cartridge or syringe contain sorbent. Disks have two distinct advantages over conventional SPE cartridges. Firstly, they often can be operated with smaller elution volumes and higher flow rates. The improved performance of the disk can be attributed to the small particle size (8-12 µm) of the sorbent embedded in the polytetrafluoraethylene (PTFE of Teflon) of the disk (compared to 40-80 µm in a conventional cartridge). Secondly, the increase in density and uniformity of packing provided by the smaller particles mitigates breakthrough and channeling, which permits the use of high flow rates and low extraction time (Thurman and Snavely, 2000). Moreover, disks give lower interference levels when compared to conventional SPE cartridges with polyethylene frits (Tolosa et al., 1996).

The discs are used much like the filter paper in a filtration apparatus (Figure 1.7.). After sample elution, sample is transferred from the flask and a thin collection tube is placed in to the flask to collect eluate.

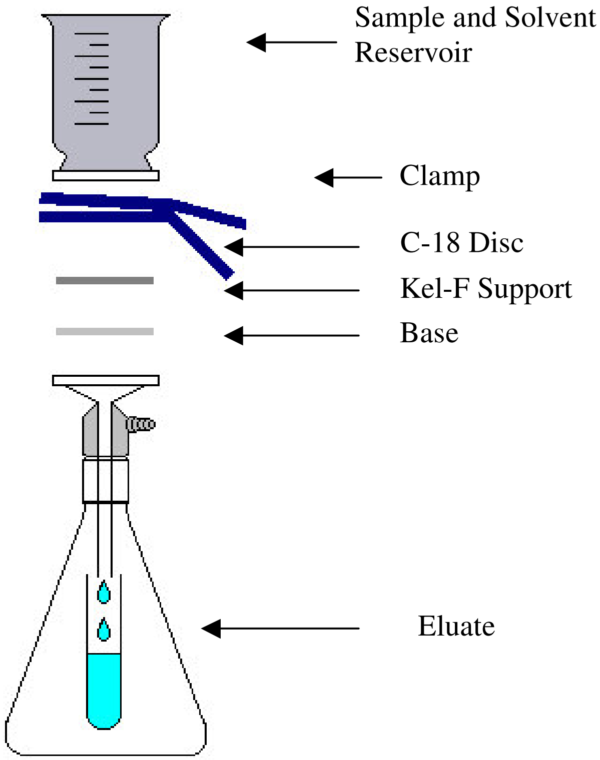


Figure 1.7. SPE apparatus for disc extractions in an extraction process

1.9.2.1.3. SPE Procedure

SPE can be used off-line (i.e., the sample praparation is completely separated from the subsequent chromatographic analysis) or online (i.e., it is directly connected to the chromatographic system). In off-line methodologies, samples are treated through a sorbent packed in a disposable cartridges or asserted on an inert matrix of a membrane-based extraction disk (Hennion and Pichon 1994). A typical off-line SPE sequence for cartridges is described below (Figure 1.8.). To show the procedure schematically, cartridges are preffered because of the visual easiness, all the procedural steps are same for the SPE disks. The SPE procedure can be divided into four main steps: conditioning, application of sample, removal of interferences and water (rinsing), and elution of the sorbed analytes.

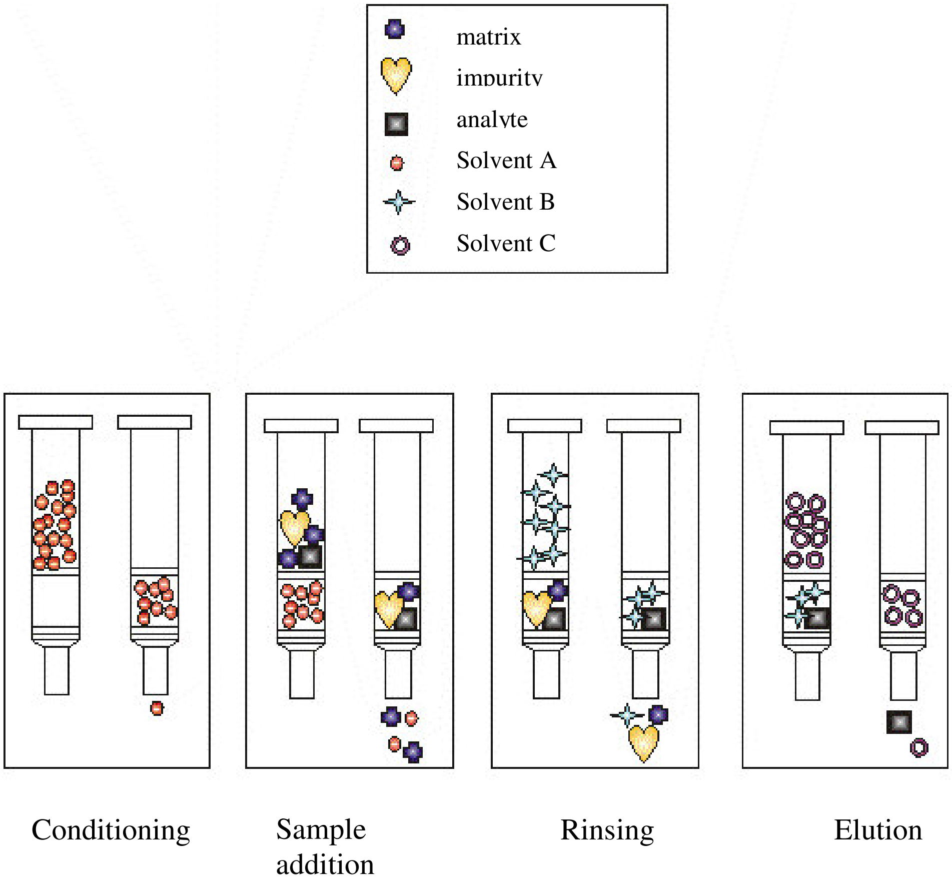


Figure 1.8. A schematic view SPE procedure

Conditioning is usually necessary to prepare the SPE column or disk for the extraction process. For retention of analytes to occur, the bonded phase must be able to interact with the sample matrix. In the dry form of C-18 sorbent, the C-18 chains tend to be coiled up. After application of solvent , these chains will uncoil as shown in Figure 1.9. (Fritz,1999).

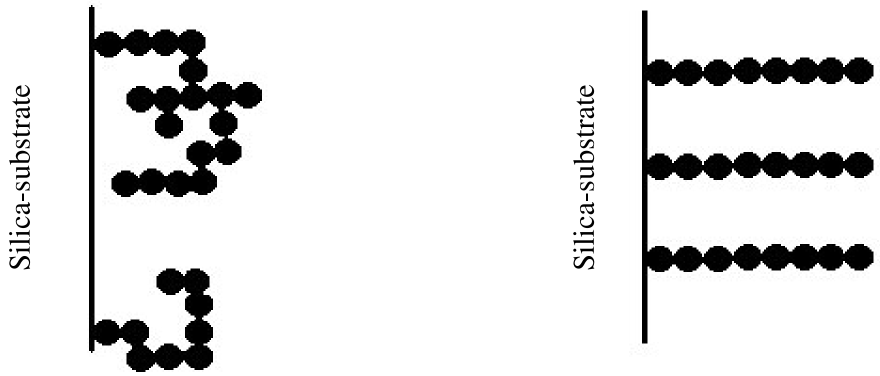


Figure 1.9. Activation of C-18 chains with organic solvent (Fritz, 1999)

A solvent is passed through the column to ‘wet” the sorbent , an ensure interaction. The sorbent bed sould not be allowed to dry out after solvation. Reversed phase type silicas and nonpolar adsorption media usually are conditioned with a water-miscible organic solvent such as methanol, followed by water or an aqueous buffer. Methanol wets the surface of the sorbent and penetrates bonded alkyl phases, allowing water to wet the silica surface efficiently. Sometimes a pre-conditioning solvent is used before the methanol step. This solvent is usually the same as the elution solvent, and is used to remove any impurities on the SPE tube that could interfere with the analysis, and may be soluble only in a strong elution solvent.

The aqueous sample is applied to the disk or tube under gentle vacuum. It should be noted that surface of the disk or tube should be wet before application of the sample. If drying occurs, the surface should be reconditioned before the application of the sample. During the sample loading other matrix components may retain on the sorbent surface due to some specific chemical interactions (e.g., Van der Waals or nonpolar interactions) or other matrix components may pass through the cartridge unretained.

The flow rate can affect the retention of certain compounds. Generally, the flow rate should not exceed 2 mL/min for ion exchange SPE tubes, 5 mL/min for other SPE tubes, and may be up to 50 mL/min for disks. Dropwise flow is best, when time is not a factor.

The SPE disk or tube is usually rinsed with a solution to remove unwanted compounds or interferences. However one should be very careful about the selection of the rinsing solvent to avoid partial elution of the analyte.

The elution of analytes from the sorbent is the reverse of the sorption process. The analyte(s) is/are removed from the sorbent by applying a suitable solvent or combination of solvents to the SPE disk or cartridge. For instance, a nonpolar eluting solvent can be used to remove the nonpolar analytes from a reversed phase SPE disk.

Because the analytes are retained on the sorbent by a partitioning process, the eluting solvent needs to have sufficient contact with the organic phase (C-18) and strenght in order to elute the analytes from the sorbent. Since stationary phase consists of silica matrices, it has an increased polarity compared to the original hydrophobicity of the C-18. The choice of an appropriate eluting solvent can be considered by the values of eluotropic strength. The solvent that has lower ε^0 is a stronger eluting solvent for non-polar analytes from reversed phase stationary phases (Varanusupakul, 2000). Eluotropic strength and polarity of solvents was shown in Table 1.4.

Table 1.4. Solvent eluotropic strength and polarity (Zief and Kiser, 1994)

Solvent	ε^0	p’
Acetic acid, Glacial	> 0.73	6.2
Water	> 0.73	10.2
Methanol	0.73	6.6
2-Propanol	0.63	4.3
20%Methanol, 80% Methylene chloride	0.63	-
20%Methanol, 80 % Diethyl ether	0.65	-
40 %Methanol, 60 % Acetonitrile	0.67	-
Pyridine	0.55	5.30
Isobutyl alcohol	0.54	3.00
Acetonitrile	0.50	6.20
Ethyl acetate	0.45	4.30
Acetone	0.43	5.40
Methyl ethyl ketone	0.39	4.50
Tetrahydrofuran	0.35	4.20
Methylene chloride	0.32	3.40
Chloroform	0.31	4.40
Tert-butyl methyl ether	0.29	-
Ether, anhydrous	0.29	2.90
Benzene	0.27	3.00
Toluene	0.22	2.40
Carbon tetrachloride	0.14	1.60
Cyclohexane	0.03	0.00
Pentane	0.00	0.00
n-Hexane	0.00	0.06
n-Heptane	0.00	0.20
Hexanes	0.00	0.06

ε^0= Eluotropic strength, eluting solvent strength on silica
p’= polarity index, measure of solvent’s ability to interact as proton donor, proton acceptor or dipole

1.9.2.2. Ultrasonic Extraction

Ultrasonic extraction is one of the widely used methods for the extraction of PAHs from aerosol and filter samples (Rocha et al., 1999, Zheng et al., 1997, Nielsen 1996, Park et al., 2002, Fernandez et al., 1999, Menichini et al., 1999).

Ultrasonic extraction is based on enhacement of mass exchange in pores of the solid phase when exposed to ultrasound.

Soxthlet extraction is one of the oldest and most widely used approaches for conventional extraction of solid samples. The advantages of this method are: (a) the sample phase is always in contact with fresh solvent, thereby enhancing the displacement of the target compounds from the matrix and (b) the compounds are not decomposed due to moderate extraction conditions. The drawbacks of this technique are the effect of water in the sample that can affect the extraction efficiency and long extraction time. (usually 8 hr or more). To shorten the extraction time alternative methods, e.g. SFE, ultrasonic extraction (USE) and microwave-assisted extraction (MAE), etc were developed. Ultrasonic extraction has proven to be equally or more efficient than Soxthlet extraction. The major advantages of this method are as follows;

a) reproducibility of the technique;
b) the applicability of the method to a range of sample sizes;
c) the dramatic reduction in time needed to perform highly efficient extractions
d) efficient extraction of polar organic compounds.

Traditional ultrasonic extraction, uses water as agitation energy transportation medium and total recovery can be reached within a relatively short time (usually 45-60 min) (Lee et al., 2001).

1.9.3. Methods of Analysis

A number of analytical techniques have been developed for the determination of PAHs in complex environmental samples. Gas chromatography coupled with Flame ionization detector (FID) or mass detector or liquid chromatography coupled with time programmed fluorescence detector has been used for the analysis of PAHs.

Recently, tandem mass spectrometry (MS-MS) is gradually becoming more important for environmental analysis. The MS fragmentation pattern is a powerful tool for obtaining such confidence in compound verification. MS-MS allows the analysis without chromatographic separation between analytes and, therefore, low chromatographic time can be used (Hernandez et al., 2001). Supercritical fluid chromatography has also been used, the main advantages of which are its high separation efficiencies and short analysis time. By gas chromatography several PAH isomers are not resolved and although GC-MS spectrometry is a good technique, it requires using surrogate standards to quantify and clean-up after extraction of both liquid and solid samples (Marce et al., 2000). These techniques are successfully applied to the analyses of environmental samples and detection of environmental analytes including volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo- p-dioxins and furans (PCDD/Fs).

Nowadays, the analysis of environmental samples for PAHs and for other organic pollutants has been developed to high standards. Neverthless, the complexity of the samples and the low concentration levels of organic contaminants continue to promote research interest and directed towards achieving more convenient, and cost effective methods (Manoli and Samara, 1999).

A fundamental problem in interpreting analytical results from such investigations is the lack of knowledge on the comparability of data, especially if different analytical methods are used or if methods are changed in time. The absence of standardized procedures is strongly felt as inter laboratory studies have clearly shown that the determination of PAHs is quite complex (Berset et al., 1999).

1.9.3.1. Gas Chromatography-Mass Spectrometry

Gas Chromatography (GC) is a very popular technique in organic analytical research, because of its very high selectivity and resolution, good accuracy and precision, wide dynamic range and high sensitivity. Capillary GC was first applied to analyse PAHs in the early 1960's and its use has progressed to the point that it now comprises one of the standard methods for determination of these compounds in environmental matrices. Nevertheless, PAHs with more than 24 carbon atoms can not be analysed by GC because of their lack of volatility. Mixtures to be analyzed are injected into an inert gas stream and swept into a tube packed with a solid support coated with a resolving liquid phase. Sample was injected to the GC via split/splitless injector (Figure 1.10).

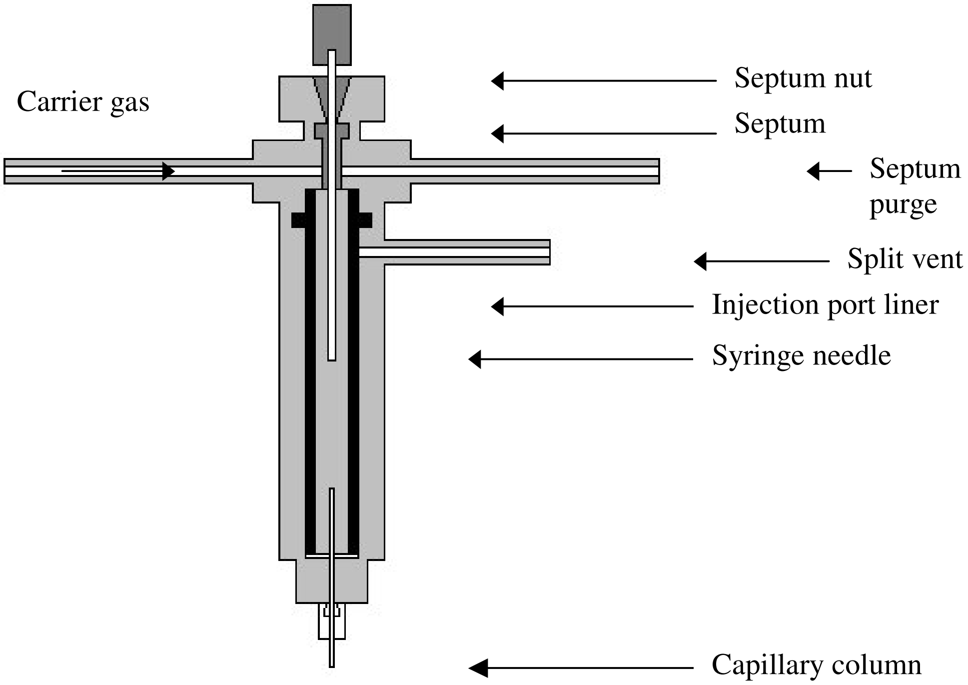


Figure 1.10. Split/Splitless GC injector (McMaster and McMaster, 1998).

Sample is vaporized in the injector throat the split valve is used to control the amount of sample allowed to enter the column. This is used to prevent overloading of the column. Since sample discrimination can occur during volatilization and splitting, a variety of throat liners are available that provide variations in surface area and composition to control these changes. The simplest throat liner is a plug of glass wool, but a variety of borosilicate glass and silica restricted tubes with constructions are available.

There are two types of columns encountered in gas chromatography, packed and capillary. Chromatographic columns vary in length from less than 2 m to 50 m or more. They are constructed of stainless steel, glass, fused silica, or teflon. Packed columns are densely packed with a uniform, finely divided packing material or solid support, that is coated with a thin layer (0.05 to 1 um) of the stationary liquid phase. Capillary columns are of two basic types namely, wall coated open tubular (WCOT) and support-coated open tubular (SCOT). Wall coated columns are simply capillary tubes coated with a thin layer of the stationary phase. In SCOTs , the inner surface of the capillary is lined with a thin film (~ 30 um) of a support material. This type of column holds several times as much stationary phase as does a wall coated column and greater sample capacity. Generally, the efficiency of SCOT column is less than that of WCOT but significantly greater than packed column (Skoog and Leary., 1992). In this study 5% (phenyl)methylpolysiloxane (HP 5-MS) WCOT column which has a nonpolar stationary phase was used.

Many capillary GC stationary phases designed for optimally separate complex PAH mixtures are commercially available from different suppliers. In general, nonpolar stationary phases, such as methyl polysiloxane or phenyl methyl polysiloxane, are the most suitable for the separation of these compounds (Santos and Galceran, 2002). Absorptive interaction between the components in the gas stream and the coating leads to a differential separation of the components of the mixture, which are then swept in order through a detector flow cell. Gas chromatography suffers from a few weaknesses, such as its requirement for volatile compounds, but its major problem is the lack of definitive proof of the nature of the detected compounds as they are separated. For most GC detectors, identification is based solely on retention time on the column. Since many compounds may possess the same retention time, we are left in doubt as to the nature and purity of compound (s) in the separated peak (McMaster and McMaster, 1998). A FID is normally adequate for sensitive detection, but coupling GC with MS affords greater selectivity through the application of selected ion monitoring (SIM). (Santos and Galceran, 2002).

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

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

The system diagram of GC-MS used in our research is shown in Figure 1.11. The MS system was composed of an electron impact source, a quadropole mass analyzer and electron multiplier as a detector.

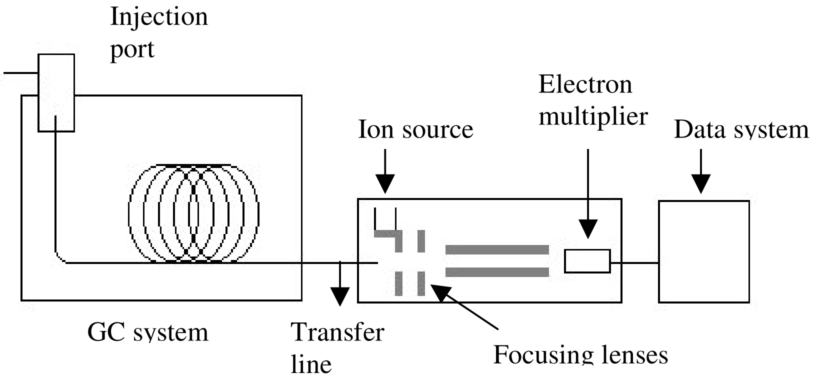


Figure 1.11. A typical GC/MS system diagram (Masucci and Caldwell,1995).

Electron impact source is widely used in organic mass spectrometry. As shown in Figure 1.12, this source consists of a heated filement giving off electrons.The latter are accelerated toward an anode and collide with gaseous molecules injected into the source.

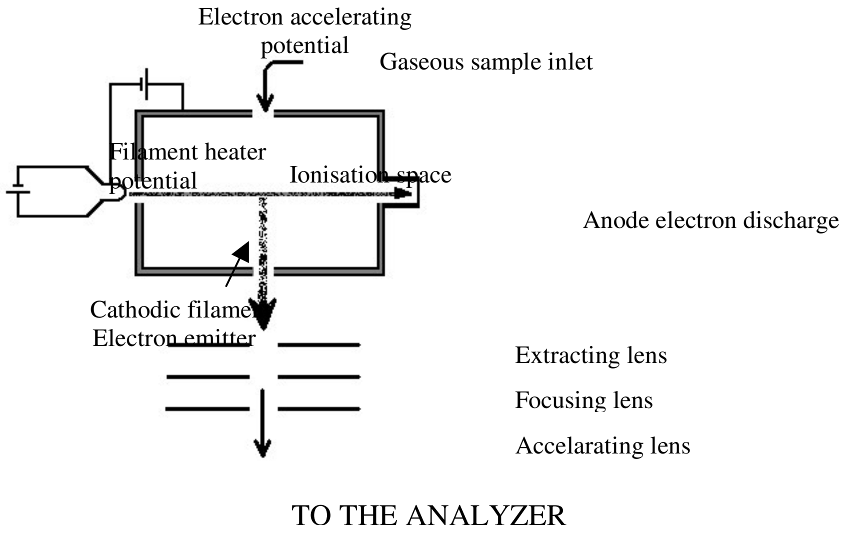


Figure 1.12. Diagram of an electron impact source

Each electron is associated to a wave whose wavelength λ is given by $\lambda = \frac{h}{mv}$ where m is its mass, v, its velocity and h, Plank's constant. When this wavelength is close to the bond lengths, the wave is disturbed and becomes complex. If one of the frequencies has an energy corresponding to a transition in the molecule, an energy transfer can occur. When there is an energy transfer, an electron can be expelled (Hoffman et al., 1996).

Once the sample is ionized, itself and its ionization fragments must be focused, propelled into the analyzer, and selected, and the number of each fragment formed must be counted in the detector. The quadrupole mass analyzer is the heart of the mass spectrometer (McMaster and McMaster,1998).

The mass filter separates ions according to their mass-to-charge ratio (m/z). At a given time, only ions of a selected mass-to-charge ratio can pass through the filter to the detector. The mass filter in the Mass Spectrometry is the quadropole. The quadropole (Figure 1.13.) is a fused-silica (quartz) tube coated with a thin layer of gold. The four hyperbolic surface create the complex electric field necessary for mass selection. Opposing segments are connected; adjacent segments are electrically isolated. One pair has positive voltages applied, the other negative. A combined direct current (dc) and a radio frequency (RF) signal is applied to the two pairs of segments. The magnitude of the RF voltage determines the mass-to-charge ratio of the ions that pass through the mass filter and reach the detector. The ratio of dc-to-RF voltage determines the resolution (widths of the mass peaks). There are several parameters that control the dc and RF voltages.

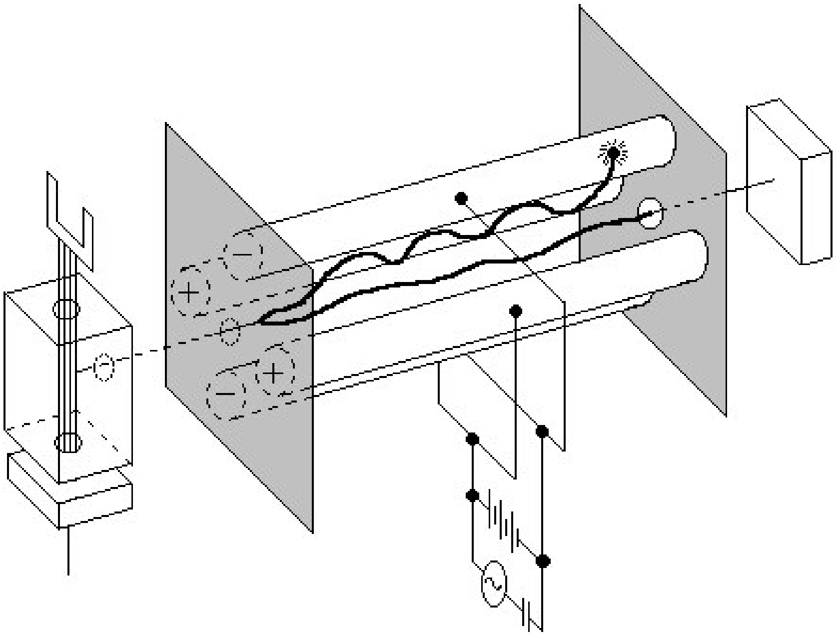


Figure 1.13. Quadropole analyzer

1.9.4. Quality Control

The purpose of quality control is to check that the analytical procedure functions correctly during routine use. It is designed to guarantee that no unrecognized changes during analysis influence the analytical result. Specific checking and monitoring procedures must be prescribed so that the person responsible for the analysis can be sure that the whole analytical system always yields tolerable results.

Validation must always be carried out for newly developed or modified procedures. This takes place either by

- analysis of reference materials or
- comparison of the results of the analyses with those of a validated or
- an independent analytical procedure, or by
- control samples prepared in the laboratory itself.

In the above list the methods are listed in order of priority, the preferred methods first. The equal validity of the procedures is shown by testing for systematic differences between the analytical results. In analyses of reference samples and prescribed control samples, the result of the analysis is compared with the given reference value. For the validation of analytical results, reference materials or certified materials must be available. Certified reference materials, i.e. materials containing a confirmed concentration of analytes, are produced and distributed by internationally recognized organizations or institutions. In analytical laboratories reference materials are used for calibration ("calibration standards") and as controls ("control standards"). Certified data alone, however, do not guarantee success; the reference materials must be used correctly. Depending on the samples to be analyzed and the technique used, the correct understanding of the problem and appropriate choice of reference material is important. Requirements for control material:

- Representative with regard to the matrix and concentration
- The substance levels in the control material cover the analytically important ranges

- Available in sufficient amounts
- Stability over several months has been demonstrated
- Not influenced by the storage vessel
- The removal of samples does not lead to changes in the remaining control material

1.10. Literature

One of the earliest studies on the organic pollutants in precipitation samples has been performed by Lunde et al (1977) in Norway. 22 samples of snow and rain collected and fractionation of components adsorbed on particles and dissolved in water phase was also carried out. They have analyzed the samples for organic micro pollutants and identified 4 chemical groups namely, alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters, fatty acid ethylesters. Electron microscopic analyses of particulate material was also carried out and presence of alkanes and PAHs in precipitation samples was related with the fuel use.

Polkowska et al., (2000) measured the PAHs and pesticides in atmosperic precipitation samples in Poland. Concentration of PAHs in rain and snow samples was found to be 2 to 4 times higher in winter season because of the residential heating. Besides that traffic has been the second major contributor to the observed pollution in the city. Among all the PAHs phenanthrene, fluoranthene and pyrene were the most often determined compounds.

PAH deposition into the Galveston Bay, Texas, via wet and dry deposition and gas exchange was estimated by Park et al., (2001). Particulate and vapor phase PAHs in ambient air and particulate and dissolved phase in rain samples were collected and analyzed. They have found that 95 % of the atmospheric PAHs were in the vapor phase and 73% of PAHs in the rain were in the dissolved phases, respectively. Phenanthrene and napthalene were the dominant species in air vapor and rain dissolved phase, while 5 and 6 ring PAH were dominant in the particulate phase of both air and rain samples. The major sources of PAHs in Galveston Bay determined as combustion and petroleum vaporization. Gas exchange from the atmosphere to the surface water has been estimated to be the major deposition process for PAHs relative to wet deposition.

Atmospheric loadings of PCBs and PAHs to a small lake in UK were estimated by Gevao et al.(1998). Atmospheric concentrations and deposition fluxes of several PAHs and PCBs were measured over a one year period. Total deposition fluxes (wet+dry) of 12 PAHs were 33.5 µg m^{-2} $month^{-1}$. Regression analysis was performed between annual average deposition fluxes and atmospheric concentrations for PAH compounds. A strong positive correlation was identified for PAH compounds with four or more rings (r^2= 0.92) whereas this relationship was relatively week if tricyclic PAHs were included in the analysis (r^2=0.63). This tendency showed the effective scavenging of high molecular weight particulate PAHs from the atmosphere. Air water gas exchange of PCBs and PAHs were also investigated. The two film model (Liss and Slater, 1974) was used for decribing air-water gas exchange. For that purpose, atmospheric gas and dissolved surface water concentrations of ΣPCBs and ΣPAHs were measured. The gas phase PAHs were dominated by the more volatile three and four ring compounds, likely dissolved PAHs were dominated by the more aqueous soluble low molecular weight compounds (tri- and tetracyclics). The net fluxes for both PCBs and PAHs from water to air was calculated and it was indicated that volatilisation of PCBs and low molecular weight PAHs dominates for most of the year. The annual loss of ΣPCBs and ΣPAHs from the water column due to outgassing was estimated to be 0.9 g $year^{-1}$ and 0.95 kg $year^{-1}$, respectively.

Spatial and temporal patterns of PAHs and other groups of semivolatile organic compounds were investigated by Brun et al (1991) in Atlantic Canada. Wet deposition samples were collected on a monthly basis from three locations of Atlantic Canada. PAHs were shown to follow seasonal patterns, with increasing concentrations during colder months of the year. Spatial influences were also observed indicating localized and long-range transport atmospheric inputs. Fluoranthene was found to be dominant PAH compound and almost detected in every sample.

Golomb et al (2001) measured the wet and dry deposition of PAHs at Nahant, Massachusetts. In this study dry deposition samples were collected onto an exposed water surface simulating dry deposition of particles onto the ocean surface. The same temporal trend was observed having higher concentrations in winter times. Chemical Mass Balance Model was used to apportion the dry deposition sources. In addition, PAH concentrations found in wet deposition samples did not correlate the amount of precipitation.

Bulk precipitation and runoff concentrations of PAHs were determined in Greece (Manoli et al., 2000). Deposition fluxes of PAHs were calculated and higher fluxes were found when high concentrations of PAHs were coincided with large amounts of precipitation. The concentrations of PAHs was found to be lower in surface waters than bulk precipitation. Finally it has been concluded that atmospheric deposition and domestic effluents are the major sources into surface waters.

Monthly PAH amounts were determined in bulk (wet and dry) deposition samples collected in Paris (France) and fluoranthene and pyrene was found to be major components, averaging 20.2 % and 18.7 % , respectively of the total. A relationship between PAH concentrations and temperature was established with a good correlation for fluoranthene and pyrene (R^2 of 0.77 and 0.83, respectively), giving evidence of mainly temperature- dependent scavenging processes for the lightest molecular weight PAHs. The heating contribution to the overall annual PAH loading was estimated to be 41 % (Ollivon et al., 2002).

Atmospheric particle size distributions of PAHs and PCDD/Fs were investigated by Kaupp et al.,(1999). They have sampled air with a five-stage Berner low pressure cascade impactor. The particles were separated into the following size ranges, < 0.15,0.15-0.45, 0.45-1.35, 1.35-4.05, 4.05-12.2, > 12.2 μm aerodynamic diameter (d_{ae}). They have suggested that PCDD/Fs and PAHs in wet deposition originate predominantly from the atmospheric removal of small particles with $d_{ae} < 1\mu m$, whereas larger particles contribute a large portion of dry deposition flux. Their calculations also indicated that dry deposition of large particles accounts for only a relatively small fraction of the bulk deposition flux.

Grynkiewicz et al., (2002) measured the concentrations of PAHs in bulk precipitation at ten sites of an urban area in Poland between January 1998 and April 1999. Napthalene, phenanthrene + anthracene has been found at maximum concentrations detected in every sample. Concentrations of acenapthylene, acenapthene, fluorene benzo(b+k) fluoranthene, indeno (1,2,3-cd) pyrene, benzo(a)anthracene and benzo(g,h,i)perylene remained at trace level. Concentrations of PAHs was found to be higher in winter period and average concentrations of PAHs in precipitation samples depend 85% on the fraction of coal heating. They have also investigated the relation of traffic density with PAHs concentrations and found 40% dependence of the average concentrations of PAHs on the average traffic intensity.

Kawamura and Kaplan (1986) investigated compositional change of organic matter during precipitation events. They have collected ten rain samples during two precipitation events and analyzed for n alkanes, UCM of hydrocarbons, PAHs, fatty acids (FAs), benzoic acid and phenols.

The deposition rates of these compounds did not linearly decrease with time and fluctuated during precipitation events. It was not an expected result since washout removes pollutants during precipitation. This finding was explained by two major factor; wind direction and anthropogenic activities around the sampling location. They have also concluded that origins of the air masses during a rain event may be traced by analysis of organic compounds of both biogenic and anthropogenic origin.

Hydrophobic organic contaminants (HOCs) are present in the atmosphere in both gaseous and aerosol sorbed forms, and both forms become associated with hydrometeors (snow flakes, rain drops, fog particles) and are thus transferred from the atmosphere to the ground. The efficiency of scavenging and atmospheric concentrations presumably determine the concentrations of HOCs in snow fall and therefore the flux by deposition. In addition, chemicals identified in snow pack samples may include contribution of direct dry deposition of aerosols and adsorption of gaseous HOCs (Wania et al., 1998).

Odabaşı et al., (1999) measured dry deposition fluxes of PAHs by water surface samples (WSS) and smooth greased plate and compared the results. The range for particulate $\sum_{14}$ PAH flux measured by dry deposition plates was 27.4-229 μg/ m^2d (average 144± 60 μg/ m^2d) and particulate $\sum_{14}$ PAH fluxes were dominated by phenanthrene, fluoranthene, and pyrene. They have also compared the dry deposition fluxes of PAHs measured by WSS and dry deposition plate. It has been found that except for acenapthene, fluorene, phenanthrene and pyrene, the rest of the PAHs fluxes were not statistically different (paired t test, 95 % confidence level). The difference between the particulate fluxes for some PAHs measured with WSS and dry deposition plates may be due to sampling artifacts associated with these two samplers.

In a study performed by Garban et al., (2002) 58 weekly samples of atmospheric bulk deposition (dry + wet) were collected in France at six specific sites representing, urban, semi-rural, rural, coastal, coastal-rural and forested sites. Seasonal variations were recorded that winter time concentrations were 2-3 times higher than summer. Higher PAH concentrations were observed in Paris which is the most urbanised and industrial site among 6 sampling sites. PAH concentrations in Paris were 4 to 20 times higher than coastal, rural and forested sites. In this study, population density was well correlated with PAH concentrations in bulk precipitation supporting local emission sources.Besides population, relation of distance from main pollutant sources with PAH was shown. PAH concentrations decreased proportionally from the distance to the main pollution sources. Deposition fluxes were also calculated and compared with other sites in the world. At Paris site bulk deposition was 2.5 to 6 times higher than those in the rural and forested sites but daily fluxes were lower than those reported by Halsall et al (1997) in 1991-1992 at Manchester and Cardiff (U.K). By using the calculated fluxes for 6 sites, they have estimated total PAH atmospheric deposition to the whole country (Garban et al., 2002).

Principal Component Analysis (PCA) was applied to bulk deposition data collected from France. PCA analysis was performed in 14 active variables consisting of PAH concentrations and 3 supplementary variables: total concentration, temperature and rainfall which are represented in PCA as weekly averages (38 weeks). As a result of PCA analysis three axes representing 68 %, 12.4 % and 7.3 % of the variance were obtained. Relationships between subjects (weeks) and between variables (PAH concentrations) were well represented in a 2D plot (explained variance: 80.4 of the total variance). Consequently, the interpretation is restricted to the study of first two axes. In the correlation matrix

14 variables were found to be strongly and positively correlated to the first factor with the exception of acenapthene. While inserting the temperature and rainfall in to the correlation matrix, it was found that distribution of the weeks along the first axis is connected to the temperature. In the distribution of PAH concentrations along second axis, two groups were distinguished, lighter weight PAHs and heaviest weight PAHs. The coordinates of the meteorological parameters on the second axis revealed contribution by both rainfall and temperature (Motelay-Massei et al., 2003).

Clouds and precipitation contribute significantly to the removal of atmospheric pollutants. Pollutant removal by ice has been less studied than removal by drops. Snow flakes are aggregates of individual, mostly dentritic snow crystals to cling together once they have collided. Aggregates of snow crystals may scavenge aerosol particles by means of impaction scavenging. The individual snow crystals of which they are composed may scavenge aerosol particles by nucleation scavenging and impaction scavenging. The former mechanism is a result of aerosol particles becoming incorporated into the snow crystals by aerosol particles acting as ice forming nuclei, while the latter mechanism is a result of aerosol particles becoming attached to the snow crystals by Brownian motion, inertial, hydrodynamic, phoretic and electric forces (Mitra et al., 1990).

Occurence of stable organic compounds at the Swedish west coast has been carried out by Brorström et al., (1994). Bulk deposition samples and gas and particulate phase air samples have been collected during 1989 and 1990. The determination of individual PAH compounds was carried out using a high performance liquid chromatography. Atmospheric concentrations of PAHs in air samples and deposition samples fluctuated significantly for the 1989 data. Information about the meteorological parameters have been collected for the evaluation of long range transport of air pollutants. There was a better aggrement between PAH concentrations in air and deposition samples collected in 1991. More volatile PAHs such as phenanthrene and anthracene found to be higher in air samples. Besides that the ratios of the PAHs in the gas phase to that in deposition samples varied markedly between different sampling points. It has been observed that greatest amounts of PAHs and total hydrocarbons are deposited in connection with episodes together with heavy precipitation. Long range trasport of PAHs from Europe also increase the atmospheric input to the Swedish coasts.

Influence of submicron particles on hydrophobic organic contaminants (HOCs) in precipitation samples was investigated by Poster and Baker (1996). They have analyzed rain water samples and ambient particulate and vapor phase PCBs and PAHs during 5 storm events. The rain was collected by wet only precipitation sampler and samples were insitu filtered through glass fibre filters (mean pore size, 2.9 µm) and amberlite XAD-2 resin. Ambient air and particulate samples were collected by drawing air through glass fibre filter and a polyurethane foam. By this way, particle associated and gaseous contaminants were isolated from the atmosphere before, during or immediately after each rain event. They have calculated aqueous PCB and PAH concentrations in rain by using ambient gaseous concentrations and Henry's law. Predicted PCB and PAH concentrations in rain was found to be less than measured concentrations by an average factor of about 100. This was explained by the scavenging of HOC enriched submicron particles which are not filter retained. Besides that, partition coefficients to filter retained particles were found to be 10 times lower than the partition coefficients to non-filter retained particles. It was concluded that, PAHs emitted during combustion processes may be incorporated into the matrix of primary aerosols and fraction of PAHs associated with particulate matter in the atmosphere is likely to bound within particle matrix and not exchangeable with the surrounding gas phase. Another finding of this study was that, nonfilter retained and filter retained particulate matter in rain water play an important role in the overall removal of contaminants from the atmosphere. Hydrophobic organic contaminants were found to be up to 80 % bound to nonfilterable particulate material and < 9 % truly dissolved. Besides that, chemical characteristics of particles retained by glass fiber filter are different than those submicron particles that are able to pass through the filter.

1.11. Objectives of the Study

The main objective of the study is to understand composition of wet and dry deposition of Polycyclic Aromatic Hydrocarbons (PAHs) in Ankara.To achieve main objective, application and improvement of analytical methodologies were also investigated. Understanding of PAH composition in deposition is important as such data do not exist in Ankara or anywhere else in Turkey.

Since wet and dry PAH deposition fluxes were estimated through analysis of rain water and surface snow samples; additional assessments could be made from the same data. This allowed us to set additional objectives at the beginning of the study. These additional objectives can be summarized as

1- To examine the PAH composition of wet deposition in Ankara to assess the levels of these compounds in urban precipitation and such data will be unique in Turkey.
2- To examine the temporal variations of PAHs
3- To investigate the sources of PAHs observed in precipitation samples by using multivariate techniques.
4- To investigate the suitability of snow surface as a surrogate to determine dry deposition fluxes of PAHs
5- To develop a sampling strategy for the assessment of PAH dry deposition fluxes throughout the city, which can be applied to similar studies in other urban environments.

6- To determine spatial distribution of PAH dry deposition in different parts of the city.

Following were the objectives for the analytical part of the study.

7- To develop Solid Phase Extraction method to isolate and preconcentrate trace level PAHs from rain and snow matrices.

8- To develop ultrasonic extraction method for trace enrichement of PAHs from glass fiber filters.

9- To optimise parameters for analysis of PAHs by GC-MS with SIM mode.

10- To apply the methods for determination of PAHs from snow and rain samples

CHAPTER 2

EXPERIMENTAL

2.1. Sampling

In this chapter rain and snow sampling strategies were summarized.

2.1.1. Rain Sampling

Sampling site selection is an important step in environmental studies. In this study, sampler was placed on the roof of METU observatory in the campus. METU is 12 km far from city center and major roads around the campus are Konya and Eskişehir roads. METU observatory is on the north of the campus and it is approximately 2 km far from the Eskişehir road and 6km far from the Konya road. It is 15 minutes walking distance from the chemistry department which makes easier to visit sampling site. Sampling station was shown in Figure 2.1

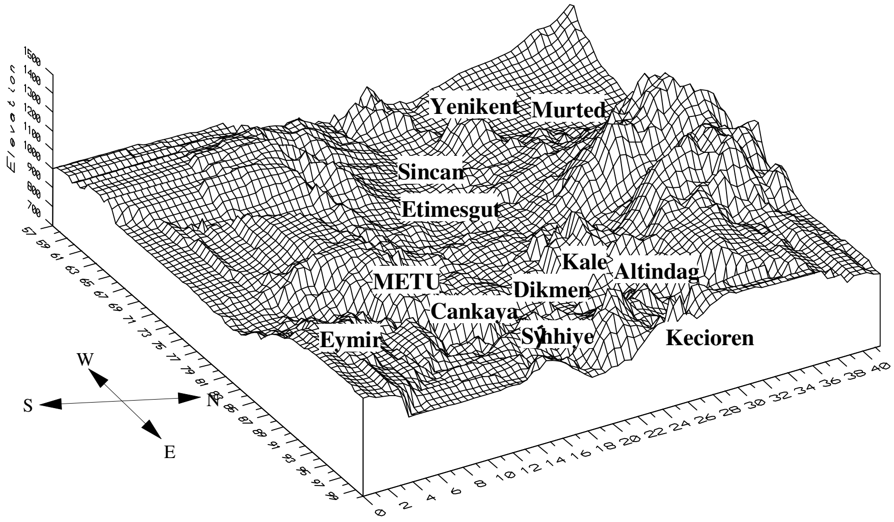


Figure 2.1. Topographic view of sampling station (METU)

Electricity is available in the observatory and there is no major industrial activity or point source around the sampling site. Sampling site at METU and close view of sampler were shown in Figures 2.2 and 2.3.

Figure 2.2. Picture of rain sampler on top of METU Observatory

Figure 2.3. Close view of Andersen wet only sampler

Samples were collected starting from December 2000 till June 2002. Ankara does not take too much rain; for that reason a total of 62 samples have been collected. Rain was continuously sampled and a rain sample may represent several individual rain events. Over 90 % of the precipitation occured in sampling period was collected. Few events were missed due to malfunctioning of the sampler or power shortages. Filtered rain samples were taken from sampler and capped with teflon lids. Glass fiber filters were removed from the filtration system and transferred to glass petri dishes by using teflon twizers. Samples were brought to the laboratory, tagged and sample information was recorded and kept in refrigerators. However some of the samples were discarded due to very low volume of sample collected (less than 20 ml).

2.1.1.1. Rain Sampling Strategy

Rain water samples were collected by a Andersen wet only sampler. The original sampler was modified for the collection of rain samples for the analysis of PAHs. A picture of modified sampler was shown in Figure 2.4.

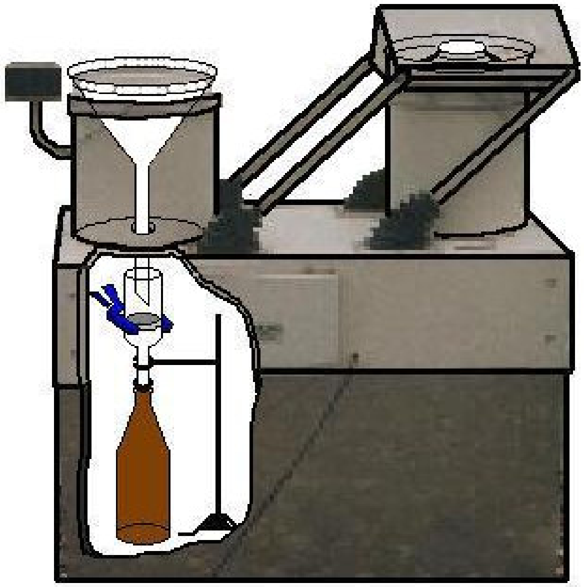


Figure 2.4. A picture of modified rain sampler

Sampler originally consists of two polyethylene buckets placed in stainless steel cyclindirical containers; the one on the right is for the collection of liquid samples and the one on the left is for the dry deposition samples. There is a a lid on the sampler which is activated by a humidity sensor. When the sensor gets wet, it moves and covers the dry deposition part and then move over the wet part just after the end of rain or snow event. There is a time and event counter in the inner part of the sampler. The original buckets were made of polyethylene which is a potential contaminant for the organic analytes and there was not any in situ filtration system for the collection of particulate and dissolved phases of rain. For the reasons mentioned above, the sampler was modified. Firstly, a 32 cm diameter glass funnel was placed inside the stainless steel wet compartment and the tip of the funnel was directed to a

90 mm filtration apparatus which was purchased from Cole Palmer company. A 90mm glass fibre filter (Cole Palmer) was used for the in situ filtration of samples. Samples were collected into 1 liter amber glass bottles.

2.1.2. Snow Sampling

Snow samples were collected in Ankara city which is a typical urban site with a population of 4.5 Million. There are no major industrial sources in the city other than some small scale industry has been settled down in Ostim region. There is also a cement factory on the north. Considering the other emission sources, domestic heating seems to be a major one. Natural gas has been used in some parts of the city for space heating. But low quality coal which has been used especially in many parts of the city where low income people lives makes an important contribution to the pollution in the city.

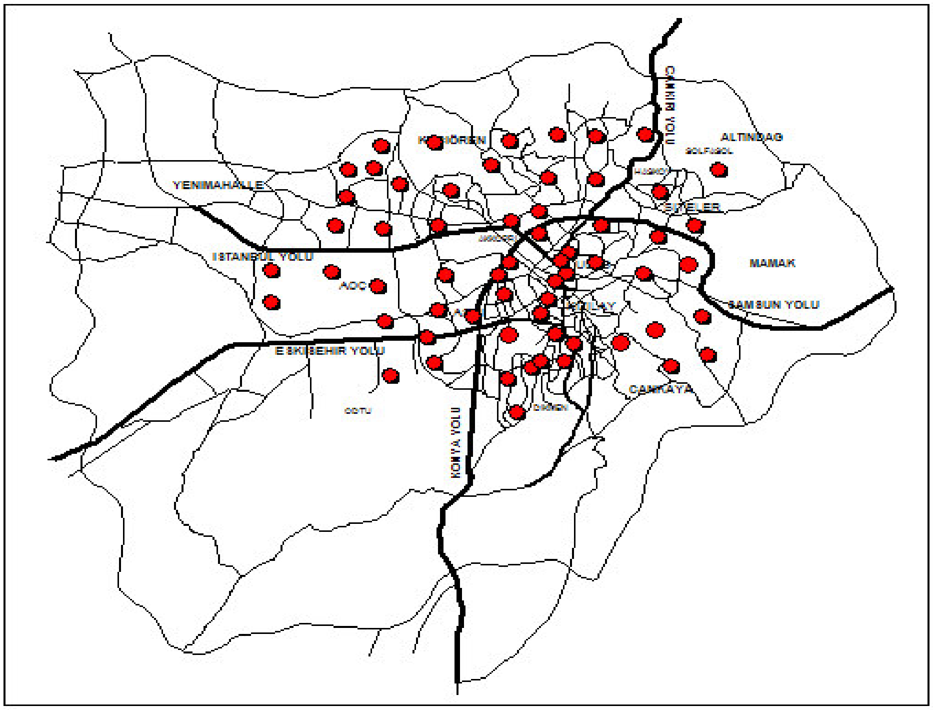


Figure 2.5. Snow sampling points in Ankara

2.1.2.1. Snow Sampling Strategy

In order to assess the dry deposition of PAHs on snow surface, first sampling points are defined. The sampling area was divided into 2*2 km grids by using 1:25 000 scaled maps. The sampling points were shown in Figure 2.5. After defining sampling points, sampling periods were determined. The idea was to use snow surface as surrogate for dry deposition. The period in between two snow events was used as dry deposition period. Therefore two sampling campaigns were conducted in a definite period of time. Reference fresh snow samples were collected just after a major snow fall from certain grids to analyze the fresh snow PAH content. Second sampling campaign was done after 13 days later from the first sampling from all grids in that case. During this 15 days period there was no other snow event. This time interval was determined by considering amount of dry deposition and the time of following possible event. Since it was not easy to collect all the samples by one person in a one day period, 5 sampling teams were constructed. Each group was assigned to a specific part of the city to collect samples from predefined grids. The snow samples were collected in 5 liter glass jars. All of the glass jars were washed with hot detergent and rinsed with hexane, acetone and deionized water several times and dried in oven. Extrapure solvents were used for the cleaning purpose. Each group was equipped with deionized water, polyethylene gloves, aluminum shovels, and solvent prerinsed (acetone and hexane) aluminum foils to cover the lid of the glass jars and GPS to locate the sampling points. Since it was very important to collect the snow from a certain depth in a definite area, a sampling tool was designed. It is basically like a tray and made of stainless steel and 45*30 cm dimensions which is shown in Figure 2.6.

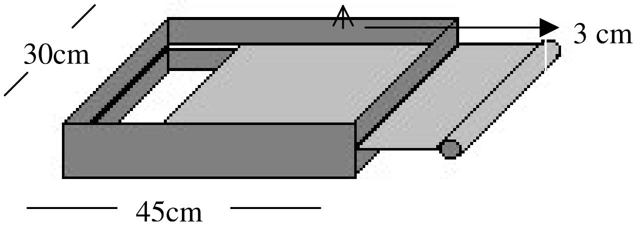


Figure 2.6. Snow sampling tool

This basic tool allows to collect surface snow samples from a definite depth (3 cm) in a definite area. The dimensions and snow depth were determined by making calculations using snow density so that 1 litre melted snow will be obtained which is sufficient for the analysis.

After sampling, glass jars were brought to the laboratory and stored in cold and dark untill the analysis.

2.2. Preconcentration and Extraction Techniques Used Throughout The Study

In the content of this study, snow and rain samples were collected. Analytical procedures applied both for snow and rain samples were summarized in Figure 2.7

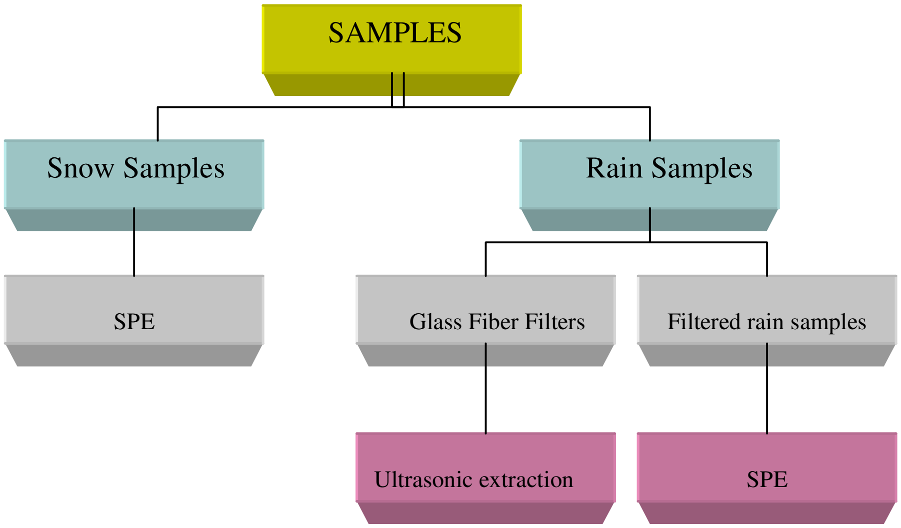


Figure 2.7. Preconcentration techniques used for the extraction of rain and snow samples.

Briefly, snow samples were directly preconcentrated by SPE without prefiltration. Rain samples were insitu filtrated in the sampling site and filtered rain samples were extracted using SPE while Glass Fiber Filters were ultrasonically extracted. Different SPE extraction procedures were used for the snow and rain samples. In the following sections extraction techniques used throughout the study will be summarized.

2.3. Reagents and Materials

C18 Solid Phase Extraction discs (ENVI discs) were purchased from Supelco. Millipore Filtration apparatus was used for the SPE of samples. Glass Fiber filters were from Cole-Palmer. All the solvents were chromatographic grade and purchased from Merck Company. Certified PAH standard solutions and deutorated standards (Restek, Supelco, Dr Ehrenstorfer) were used throught the study and intermediate standard solutions were prepared from the stock standards with appropriate dilutions with dichloromethane. All the stock, intermediate and standard solutions were stored in refrigerator. Hamilton gas tight glass syringes (500, 100, 10 µl) were used for the preparation of the standards into 2 ml amber vials. Ultrasonic extractions were preformed by using Branson ultrasonic bath. A Supelco minivap evaporator was used to reduce the volumes of extracts. The extracted samples were transferred to 2 ml amber glass vials (Supelco) for further reduction of the volume. Standard reference materials (SRM 1597a, SRM 1649a) were purchased from National Institute of Standards (NIST).

2.3.1. Preparation of Na_2SO_4 and Glass Wool

Sodium Sulfate (Na_2SO_4) was used to dry the extracts. Six g of Na_2SO_4 were put in a column and tip of the column was filled with glass wool. The extract is loaded to the column and washed with solvent. Although extrapure Na_2SO_4 was purchased from the company, it was cleaned before use. For that purpose, Na_2SO_4 was put in a glass column and sequentially washed twice with hexane and twice with dichloromethane. The volume of solvent used for each washing is twice the estimated volume of the Na_2SO_4 in the column. Washed Na_2SO_4 was transferred to a large beaker, covered loosely with solvent rinsed aluminum foil and oven dried at 50 °C for 1 hour and conditioned at 225 °C overnight. Dry Na_2SO_4 was transferred to an amber glass bottle with a teflon lined cap and stored in a desiccator.

Glass wool used in the experiments were also cleaned before use. A quantity of a glass wool was compressed into a large glass column and washed sequentially hexane and dichloromethane and treated like Na_2SO_4 and storred in a desiccator.

2.3.2.Cleaning of Glassware

Since the amount of analytes were very low in samples, extreme precautions were taken to eliminate the contamination. Besides that, since all the solvents and analytes were toxic, all the extractions were performed in a special fume hood which is ventilated very well and used only for sample preparation for organic analysis. All the glassware were rinsed with hexane and acetone and washed with detergent (Alconox) in hot water following several rinses with tap water and deionized water. The washed glassware was placed in an oven and dried. Cleaned glassware were kept in closed boxes.

2.4. Instrument and Apparatus

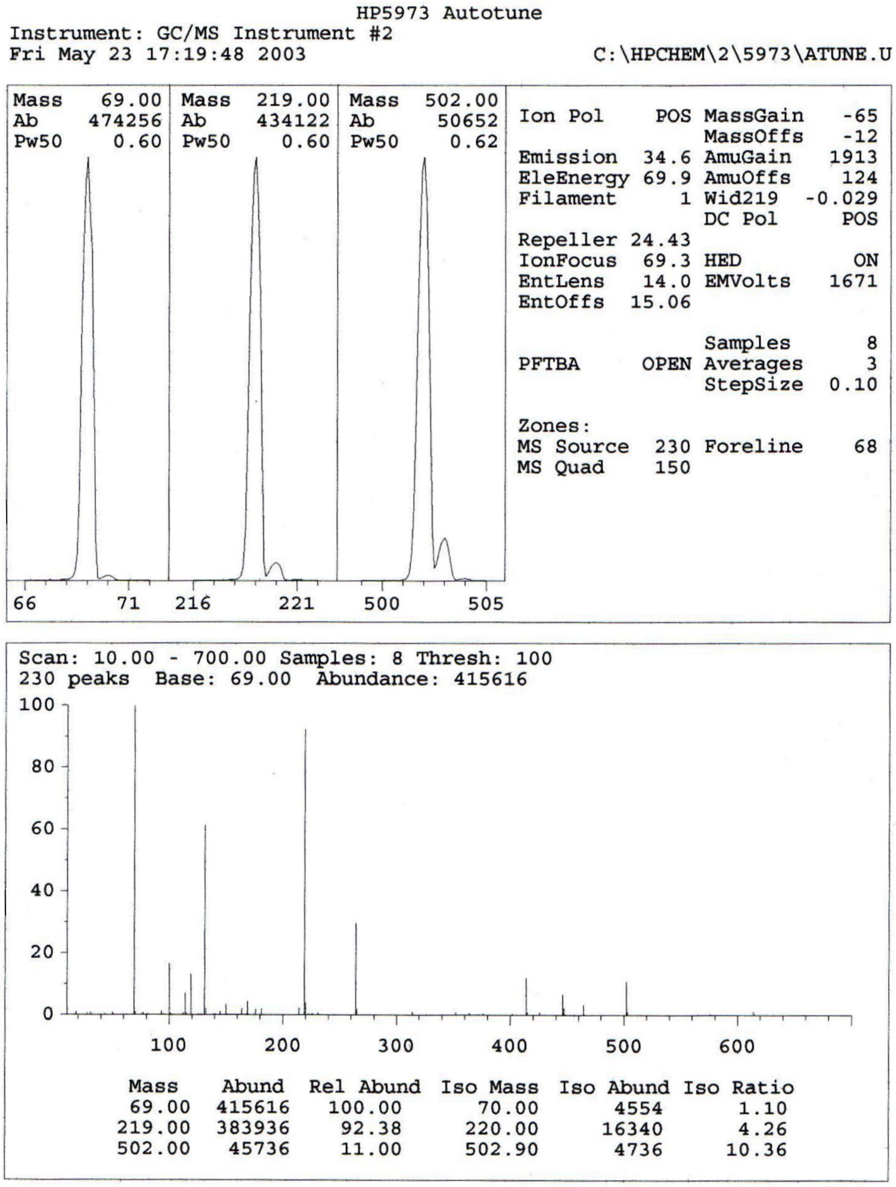
A HP (Hewlett Packard) 6890 series gas chromatograph coupled with HP 5973 mass spectrometer was used for the analysis. Instrument is also equipped with Flame Ionization and Electron Capture detectors. A 30m, 0.25 mm id., 0.25µm film thickness, crosslinked 5% Phenyl methyl siloxane, HP 5MS, capillary column (Agilent Tech.) was used for the separation of PAHs throughout the study. A 4 mm id. deactivated glass liner (Agilent Tech.) packed with glass wool was used to prevent contamination of the analytical column from sample particulates and pieces of septum.

2.4.1. Mass Spectrometer Calibration

Perflourotributylamine (PTFBA) has been the predominat calibration gas used in mass spectrometry because of the mass range of its fragments, their evenly spaced major fragments, and the volatility of the gas under the analyzer vacuum.

PFTBA is a clear, volatile liquid under the high vacuum conditions of mass spectrometer analysis. It is kept in a vial valved off the sample inlet. When the instrument needs to be calibrated, the calibration gas valve is opened and calibration gas is allowed to vaporize into the source chamber. Calibration gas is ionized in the mass spectrometer's source by the electron beam from the filament and passed into the analyzer where its fragments are separated and detected. The major masses for calibration compound are 69, 131, 219, 264, 414, 464, 502, 614. In a well-tuned mass spectrometer, the 69 mass is the base mass; fragments 131 and 219 have approximately the same heights, equal to 45-60 % of the 69 peak; the 414 peak is about the 3-6 % of the 69 peak; and 502 will be 3% or less than 69 peak height.

Current status of the instrument is always monitored by autotune. Autotune report also provides information about the possible leaks. If 28 (N_2) or 44 (CO_2) exist in high percentages in the autotune report, source of leak was investigated. Usually leaks may occur in the GC inlet or MS interface parts. Electron multiplier voltage is another parameter showing the status of the ion source. Higher voltage is an indication of polluted ion source. If the volatge is around 2000 ev MS is vented and ion source is cleaned. An autotune report was shown in Figure 2.8.(McMaster and McMaster,1998).



```
                          HP5973 Autotune
Instrument: GC/MS Instrument #2
Fri May 23 17:19:48 2003                          C:\HPCHEM\2\5973\ATUNE.U

Mass    69.00  Mass   219.00  Mass   502.00
Ab     474256  Ab     434122  Ab      50652
Pw50     0.60  Pw50     0.60  Pw50     0.62

Ion Pol      POS MassGain    -65
                 MassOffs    -12
Emission    34.6 AmuGain    1913
EleEnergy   69.9 AmuOffs     124
Filament       1 Wid219   -0.029
                 DC Pol      POS
Repeller   24.43
IonFocus    69.3 HED          ON
EntLens     14.0 EMVolts    1671
EntOffs    15.06

                 Samples       8
PFTBA       OPEN Averages      3
                 StepSize   0.10

Zones:
MS Source    230 Foreline     68
MS Quad      150

Scan: 10.00 - 700.00 Samples: 8 Thresh: 100
230 peaks  Base: 69.00  Abundance: 415616

   Mass    Abund  Rel Abund  Iso Mass  Iso Abund  Iso Ratio
  69.00   415616     100.00     70.00       4554       1.10
 219.00   383936      92.38    220.00      16340       4.26
 502.00    45736      11.00    502.90       4736      10.36
```

Figure 2.8. An example of an autotune report

2.5. Optimization of GC-MS Parameters for Snow and Rain Samples

GC-MS parameters were optimized prior to analysis of samples. A splitless glass liner with glass wool was chosen to prevent the contamination of the column since glass wool prevents the entrance of small particles to the column. Injection port temperature was set at 280 °C. Several temperature programs were experimented to obtain the best resolution of PAHs and the one given in Table 2.1. was found to be optimum and used for determination of PAHs in both snow and rain analysis.

Table 2.1. Operating GC-MS conditions

GC column	30 m × 0.25mm i.d., 0.25 μm film thickness 5% Phenyl methyl siloxane, HP 5MS, capillary column
Liner	Splitless glass liner with glass wool, deactivated (Agilent technologies)
Carrier gas	Ultra purified Helium, 99.999%, 1ml/min
Injection type	Splitless
Injection port temperature	280 °C
Oven temperature	70 °C (4 min), 7 °C /min to 300 °C (10 min)
Injection volume	1μl
Mass spectrometer	Electron impact, 70 eV
Mass spectrometer quadropole temperature	150 °C
Mass spectrometer source temperature	230 °C

Mass spectrometer quadropole and source temperatures were set at 150 °C and 230 °C respectively. The standard was analyzed in scan mode first in order to see the fragmentation pattern of each PAH. All the ions in between 35 and 550 amu were scanned. Scan mode is very useful for qualitative purposes because one can see everything in the sample. By this way standard purity can be examined before starting analyses. If standard is not in good condition, decomposition products appear in SCAN mode. After scanning the standard, target and qualifier ions were determined for each PAH compound. One target and 2 qualifier ions were usually monitored for quantitative analysis.

SIM mode improves sensitivity by limiting the mass of the ions detected to one or more specific fragment ions of known mass. As a consequence, it is highly selective and it eliminates a large portion of the noise inherent in full scan detection mode. The most popular method of spectral interpretation and identification remains the comparison of sample spectra with collections of reference spectra (Ragunathan et al., 1999). The presence of a target compound was established when two criteria were met. A first criterion is the retention time; retention time of the compound in the sample which should match with the one in the standard. A second criterion is the ratios of the ions monitored; ion ratios of the compound in the sample should be the same with the one in the library database spectra.

Mass software performs automatic integration of the peaks according to the written data analysis method. However, visual inspection of the produced chromatogram is essential since sometimes automatic integrations produce wrong results especially for closely eluting compounds. Each time, for each analysis, all the chromatograms were inspected before further calculations.

The monitored ions and SIM windows were given separately for snow and rain analyses in Tables 2.2, 2.3, 2.4. and 2.5. There are some differences in Tables considering the compounds monitored. Restek mixture calibration standard was used for snow analyses and this standard does not contain benzoic (k) fluoranthene. A new mix standard containing benzoic (k) fluoranthene purchased from the company and added to analyte list for rain analysis. The surrogate standard mixture used for the snow analyses contains acenapthene d10, phenanthrene d10, chrysene d12, and perylene d12 whereas new surrogate mixture for rain analysis contains naphthalene d8 plus other four surrogates. External calibration were used for quantification of PAHs in snow samples, whereas internal standard calibration was preferred for the determination of PAHs in rain samples hence internal standards, pyrene d10 and benzo(a) anthracene were added to the list for rain analysis.

Table 2.2. Monitored ions for PAHs (target ions underlined) used for rain analyses

PAHs		Ions	R.T (min)
Naphthalene-d8 (Nap-d8)	Surrogate std	136, 68, 137	9.13
Naphthalene (Nap)		128, 129, 127	9.17
Pyrene-d10 (pyr-d10)	Internal std	212, 106, 213	24.56
Acenaphtylene (Acy)		152, 151, 153	14.51
Acenaphthene		154, 153, 152	15.16
Acenaphthene-d10 (Ace-d10)	Surrogate std	164, 162, 165	15.04
Fluorene (Flu)		166, 165, 167	16.86
Phenanthrene- d10 (Phe-d10)	Surrogate std	188, 94, 189	19.90
Phenanthrene (Phe)		178, 179, 176	19.96
Anthracene (Ant)		178, 179, 176	20.12
Fluoranthene (Flt)		202, 101, 203	23.92
Pyrene (Pyr)		202, 101, 203	24.61
Benzo(a)anthracene (BaA)		228, 229, 226	28.73
Chysene (Chr)		228, 229, 226	28.85
Chysene d12 (Chr-d12)	Surrogate std	240, 120, 241	28.78
Benzo(a) pyrene-d12 (BaP-d12)	Internal std	264, 132, 265	32.94
Benzo(b)fluoranthene (BbF)		252, 253, 126	32.11
Benzo(k)fluoranthene (BkF)		252, 253, 126	32.13
Benzo(a) pyrene (BaP)		252, 253, 126	33.00
Perylene-d12 (Per-d12)	Surrogate std	264, 260, 265	33.18
Indeno (1,2,3-cd) pyrene (Ind)		276, 138, 277	35.97
Dibenz(a,h) anthracene (DahA)		278, 139, 279	36.09
Benzo(g,h,i)perylene (BgP)		276, 138, 277	36.55

Entire chromatogram was divided in 5 time intervals in which specific ions were monitored, by this way sensitivity of the measurements were increased by decreasing backgrounds in the entire chromatogram.

Table 2.3. Adjustment of SIM parameters for rain analyses

Windows	Time period (min)	Ions monitored
1	8-19	128, 129, 127, 136, 68, 137, 152, 151, 153, 164, 162, 165, 166, 167, 154
2	19-23	188, 189, 178, 176, 179, 94, 80
3	23-31	202, 101, 203, 228, 226, 229, 240, 120, 241, 212, 213, 106, 236
4	31-35.5	252, 253, 126, 264, 260, 265, 132
5	35.5-47	276, 138, 227, 278, 139, 279, 277

Table 2.4. Monitored ions for PAHs (target ions underlined) used for snow analyses

PAHs		Ions	R.T (min)
Naphthalene (Nap)		128, 129, 127	10.41
Acenaphtylene (Acy)		152, 151, 153	15.80
Acenaphthene		154, 153, 152	16.43
Acenaphthene-d10 (Ace-d10)	Surrogate std.	164, 162, 165	16.33
Fluorene (Flu)		166, 165, 167	18.21
Phenanthrene- d10 (Phe-d10)	Surrogate std.	188, 94, 189	21.27
Phenanthrene (Phe)		178, 179, 176	21.30
Anthracene (Ant)		178, 179, 176	21.46
Fluoranthene (Flt)		202, 101, 203	25.35
Pyrene (Pyr)		202, 101, 203	26.03
Benzo(a)anthracene (BaA)		228, 229, 226	30.19
Chysene (Chr)		228, 229, 226	30.30
Chysene d12 (Chr-d12)	Surrogate std.	240, 120, 241	30.23
Benzo(b)fluoranthene (BbF)		252, 253, 126	33.61
Benzo(a) pyrene (BaP)		252, 253, 126	34.51
Perylene-d12 (Per-d12)	Surrogate std.	264, 260, 265	34.66
Indeno (1,2,3-cd) pyrene (Ind)		276, 138, 277	37.53
Dibenz(a,h) anthracene (DahA)		278, 139, 279	37.66
Benzo(g,h,i)perylene (BgP)		276, 138, 277	38.18

Table 2.5. Adjustment of SIM parameters for snow analyses

Windows	Time period (min)	Ions monitored
1	8-19	128, 129, 127, 152, 151, 153, 164, 162, 165, 166, 167, 154
2	19-23	188, 189, 178, 176, 179, 94, 80
3	23-31	202, 101, 203, 228, 226, 229, 240, 120, 241, 212, 213, 236
4	31-35.5	252, 253, 126, 264, 260,
5	35.5-47	276, 138, 227, 278, 139, 279, 277

Total Ion chromatograms (TIC) of PAHs in SIM mode for snow analysis obtained by optimized conditions were given in Figure 2.9.

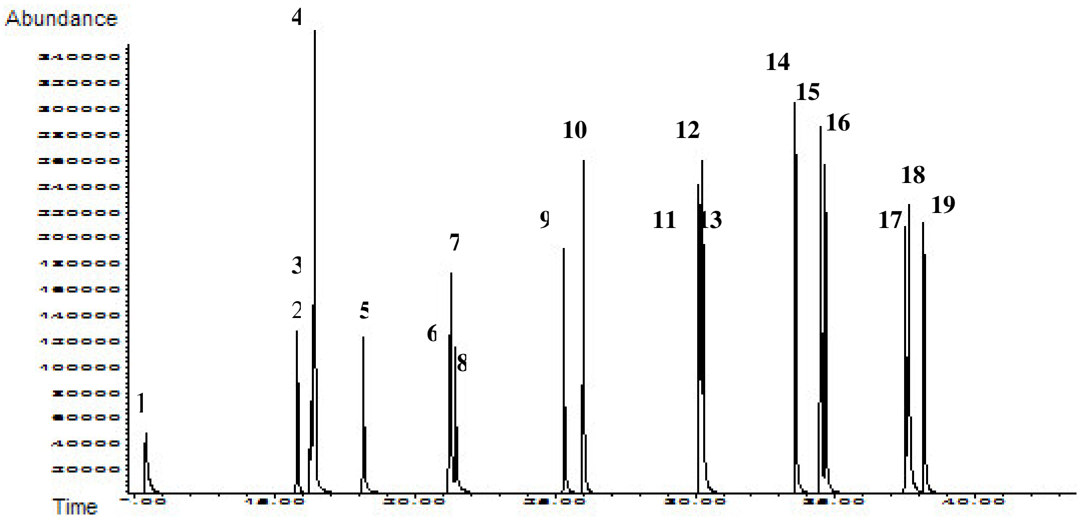


Figure 2.9. SIM chromatogram of 3 ng of PAHs and surrogates for snow analysis;

1. Napthalene, **2.**Acenapthylene, **3.**Acenapthene d10 (surrogate std.), **4.** Acenapthene, **5.**Fluorene, **6.** Phenanthrene d10 (surrogate std.),**7.** Phenanthrene, **8.** Anthracene, **9.**Fluoranthene, **10.** Pyrene, **11**.Benzo(a)anthracene, **12**. Chrysene d12(surrogate) , **13**.Chrysene, **14**.Benzo (b)fluoranthene, **15**. Benzo(a)pyrene, **16**. Perylened12(surrogatestd.),**17**.Indeno(1,2,3cd)pyrene,**18**.Dibenzo(a,h)anthracene **19**. Benzo(g,h,i)perylene

All the compounds were well separated from each other except for benzo(a)anthracene and chrysene d12 (Figure 2.10.).

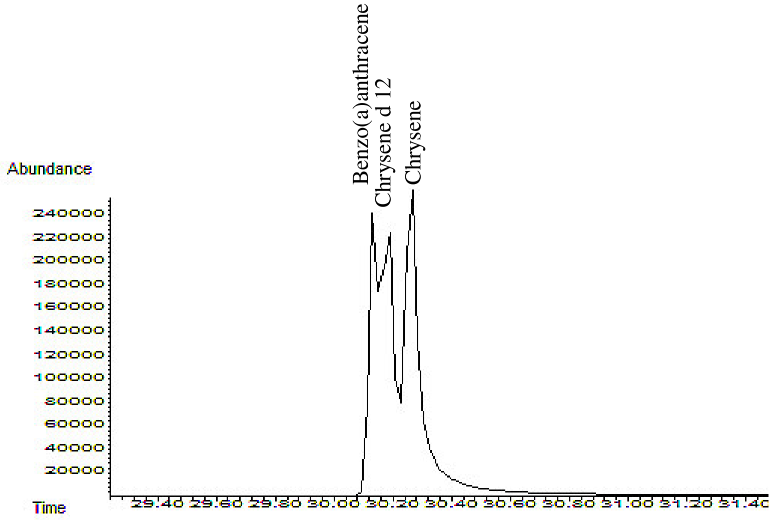


Figure 2.10. TIC chromatogram for unresolved benzo(a)anthracene and chrysene d12.

However, extracted ion chromatograms of benzo(a)anthracene and chrysene d12 is resolved very well (Figure 2.11.). Since the ions used for quantification of benzo(a)anthracene and chrysene d12 is different 228 for benzo(a)anthracene and 240 for chrysene d12 it does not make any confusion on their quantification. In such cases mass spectrometry is very useful since it is not always possible to separate all peaks by using a GC column.

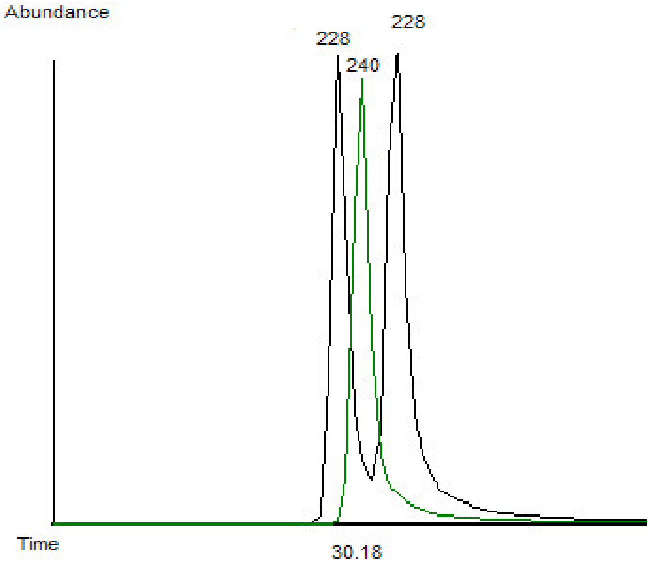


Figure 2.11. Extracted Ion chromatograms of benzo(a)anthracene, chrysene d12 and chrysene

Total ion chromatogram obtained for the determination of PAHs in rain matrix was shown in Figure 2.12. Since same temperature programs applied, peak behaviours were the same for benzo(a)anthracene and chrysene d12. Apart from that, Pyrene d10 and pyrene could not be resolved in the column (Figure 2.13). Since the quantification ions used for pyrene d10 (212) and pyrene (202) were not the same, quantification of compounds successfully performed (Figure 2.14.).

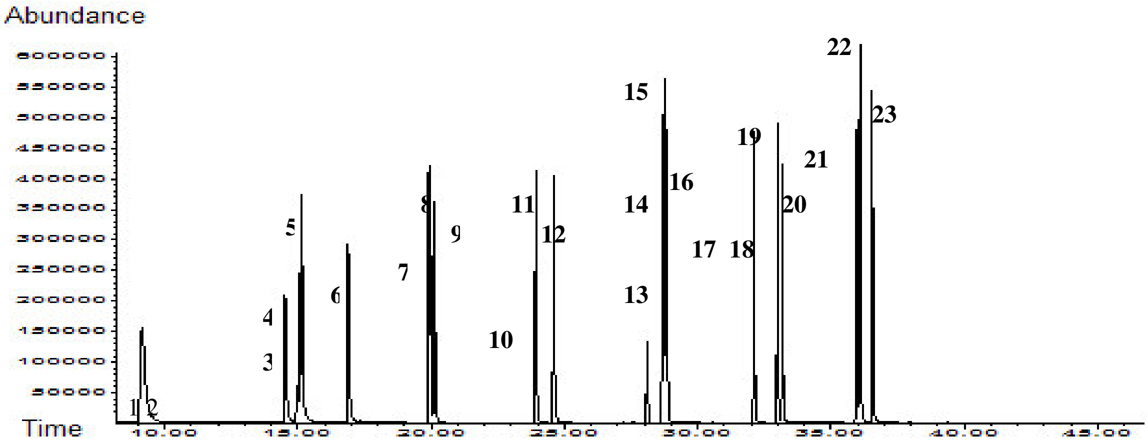


Figure 2.12. SIM mode chromatogram of 2.5 ng of PAHs , 2.5 ng surrogates and 0.5 ng internal standards for rain analysis; **1.** Napthalene d8 (surrogate std.), **2**. Napthalene,**3.**Acenapthylene,**4.**Acenapthene d10 (surrogate std.), **5.**Acenapthene, **6.**Fluorene, **7.**Phenanthrene d10(surrogate std.), **8.** Phenanthrene, **9.** Anthracene, **10.**Fluoranthene,**11.**Pyrened10(internal std.),**12**. Pyrene **13**.Benzo(a)anthracene d12(internalstd.),**14**.Benzo(a)anthracene, **15**. Chrysene d12(surrogatestd.), **16**.Chrysene,**17**.Benzo(b)fluoranthene,**18**.Benzo(k)fluoranthene,**19.**Benzo(a)pyrene,**20**.Perylened12(surrogatestd.),**21.**Indeno(1,2,3-cd)pyrene, **22**.Dibenzo(a,h)anthracene, **23**. Benzo(g,h,i)perylene

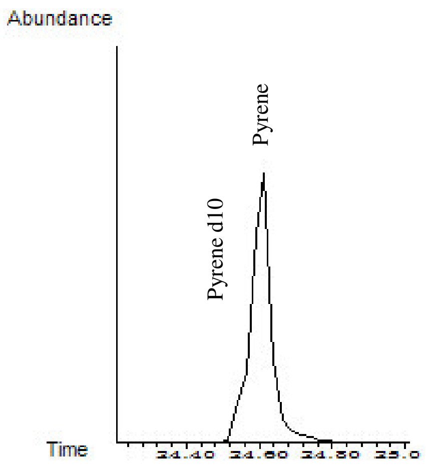


Figure 2.13. TIC chromatogram for overlapped pyrene d10 and Pyrene

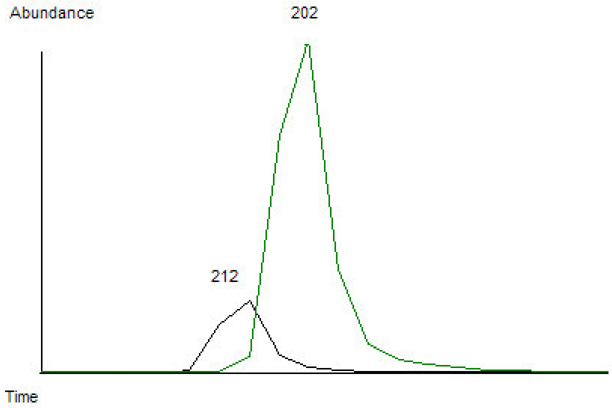


Figure 2.14. Extracted Ion chromatograms of pyrene d10 and pyrene.

2.5.1 Calibration of the Instrument for Rain Analysis

Before the analysis of the unknown, a calibration curve is prepared by running at least four standards. There are two ways in which calibration is performed: external standard calibration method and internal standard calibration method. External standard method involves preparation of a calibration curve by plotting area or height response against concentrations of analyte(s) in the standards. The calibration factor is then calculated as the ratio of concentrations to area/height response and should be constant over a wide range of concentrations.

The internal standard method is more reliable than the external standard method. Equal amounts of one or more internal standards are added onto equal volumes of sample extracts and the calibration standards. The response factor (RF) is then calculated as follows:

$$\mathrm{RF}=\frac{As*Cis}{Ais*Cs}$$

where As and Ais are the area (or height) response for the analyte and the internal standard, respectively; while Cs and Cis are their concentrations. Thus RF for analytes may be determined by running standard solutions of the analytes containing internal standards. If the RF values over the working range of concentrations fall within ± 20% relative standard deviation an average RF value should be used in the above equations to determine the concentration of the analytes in the sample. Alternatively, a calibration curve may be plotted between response ratio (As/Ais) vs RF.

The concentration of the analyte in the sample= $\frac{As * Cis * D}{Ais * RF}$ where D is the dilution factor (Patnaik, 1997).

Internal standard calibration was used for quantification of PAHs from rain matrix and pyrene-d10 (pyr-d10) and Benzo(a) pyrene-d12 (BaP-d12) were used as internal standards which were added to the final extract in the same amount with standards. Linear calibration curves with a linear regressions greater then 0.99 were obtained for all the PAHs and surrogates. Calibration curves for surrogates and some of PAHs were shown in Figures 2.15 and 2.16.

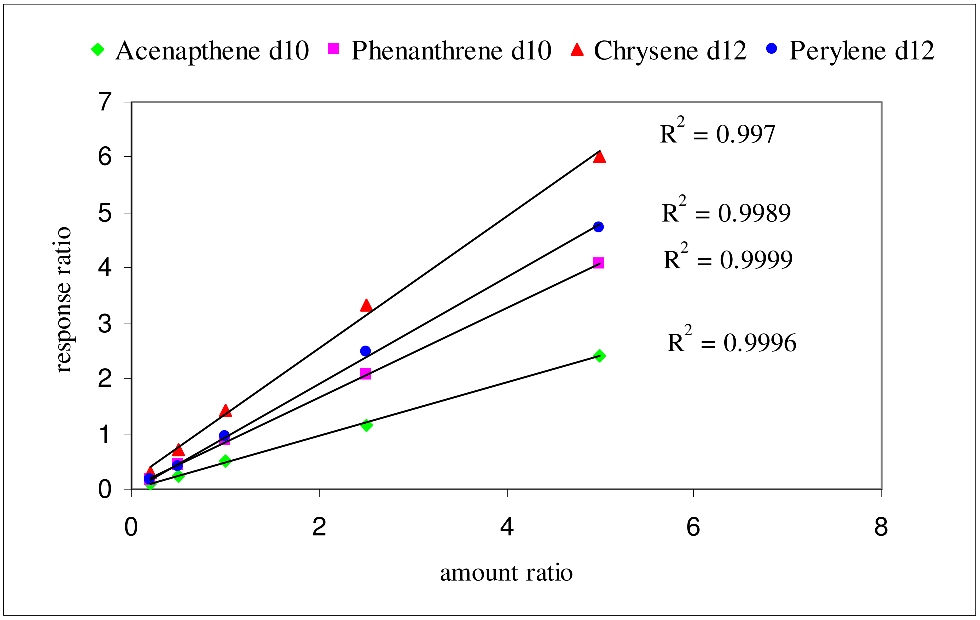


Figure 2.15. Calibration curves of surrogates

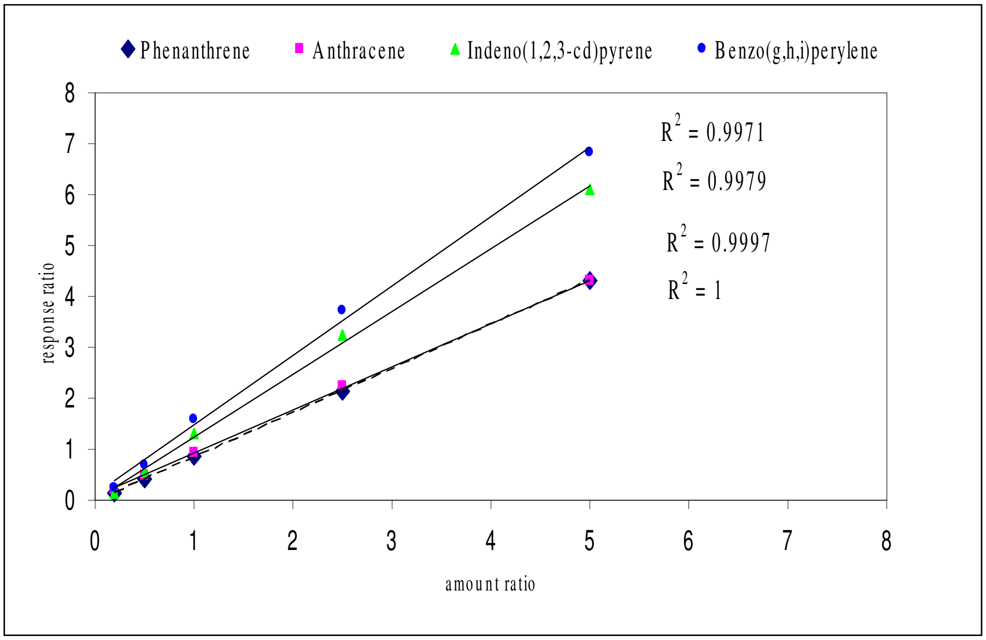


Figure 2.16. Calibration curves of some of PAHs

2.5.2. Calibration of the Instrument for Snow Analysis

Since internal standards were not available at the time of snow sample analyses, analytes were quantified by external calibration method. Although internal standard calibration method was not used, good correlation coefficients were obtained for all the PAHs and surrogates. Calibration curves were given in Figures 2.17, 2.18 and 2.19.

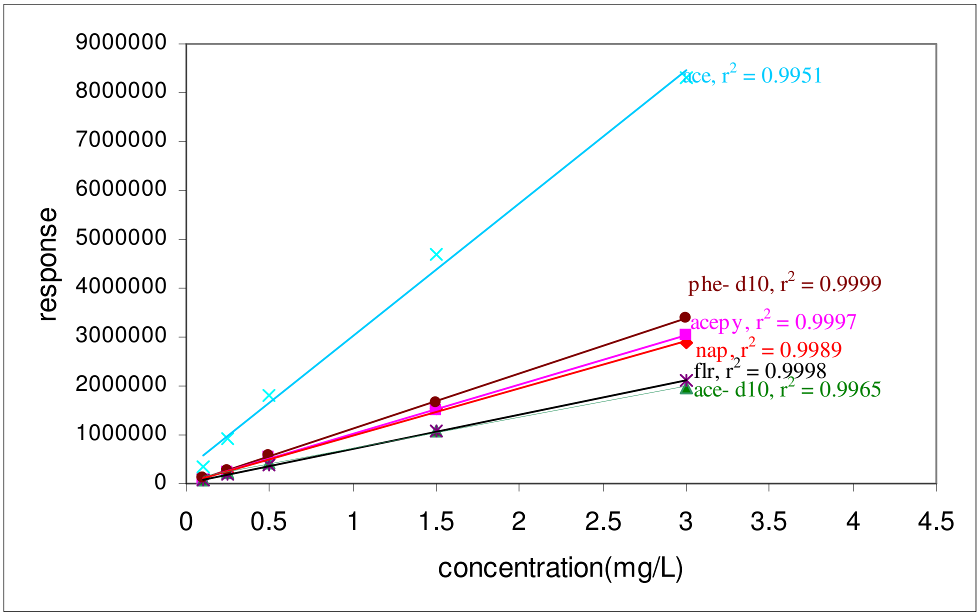


Figure 2.17. Calibration curves of Phe, Acy, Nap, Fl, Ace-d10

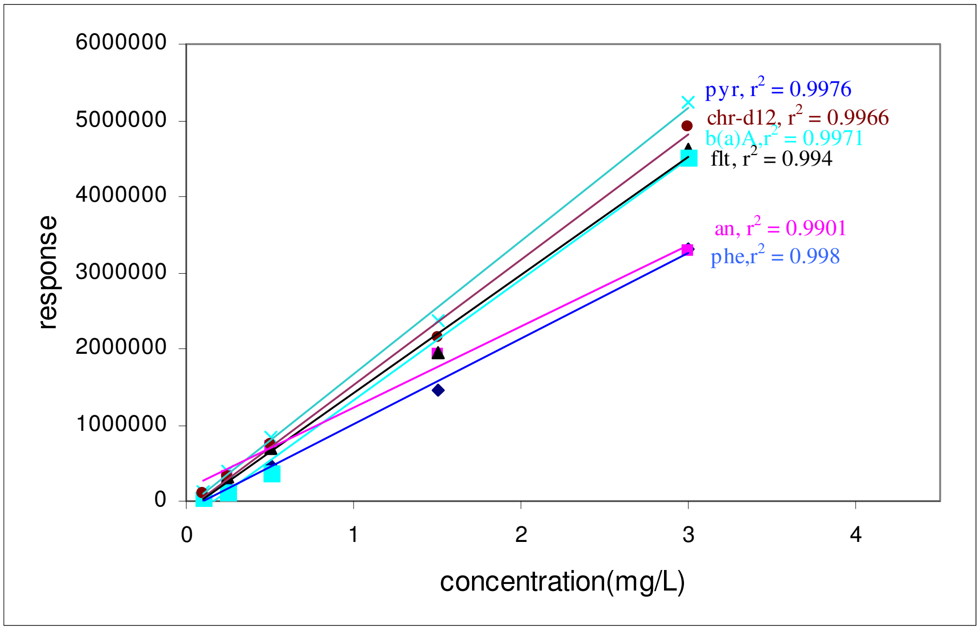


Figure 2.18. Calibration curves of Pyr, Chr-d12, BaA, Flt, Ant, Phe

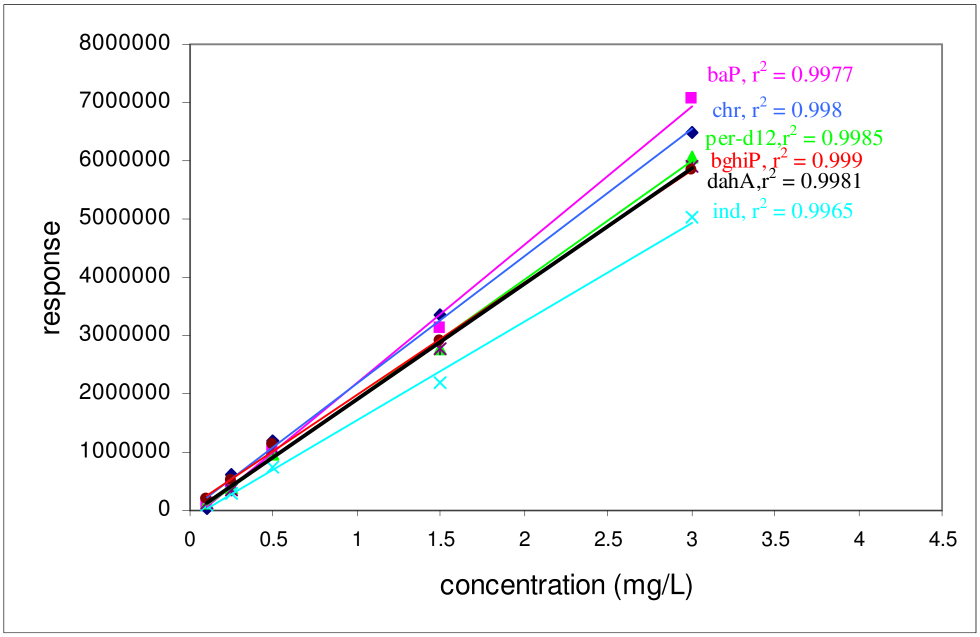


Figure 2.19. Calibration curves of BaP, Chr, Per-d12, BgP, DahA, Ind

2.6. Application of SPE to the Filtered Rain and Snow Samples

SPE procedure used for the analysis of snow and rain samples were adapted from Carrera et al., (2001) and applied to snow samples (Figure 2.20). However some modifications were done in the procedure. Surrogate compounds (acenapthene d10, phenanthrene d10, chrysene d12 and perylene d12) were added to samples prior to extraction. Use of surrogates is necessary in environmental samples and use of real samples rather than prepared solutions are more informative and real regarding the recovery of PAHs from samples. Certain surrogates were used for the assessment of recovery of certain PAH compounds. Table 2.6. shows the surrogates and their use for the correction of each PAH recoveries.

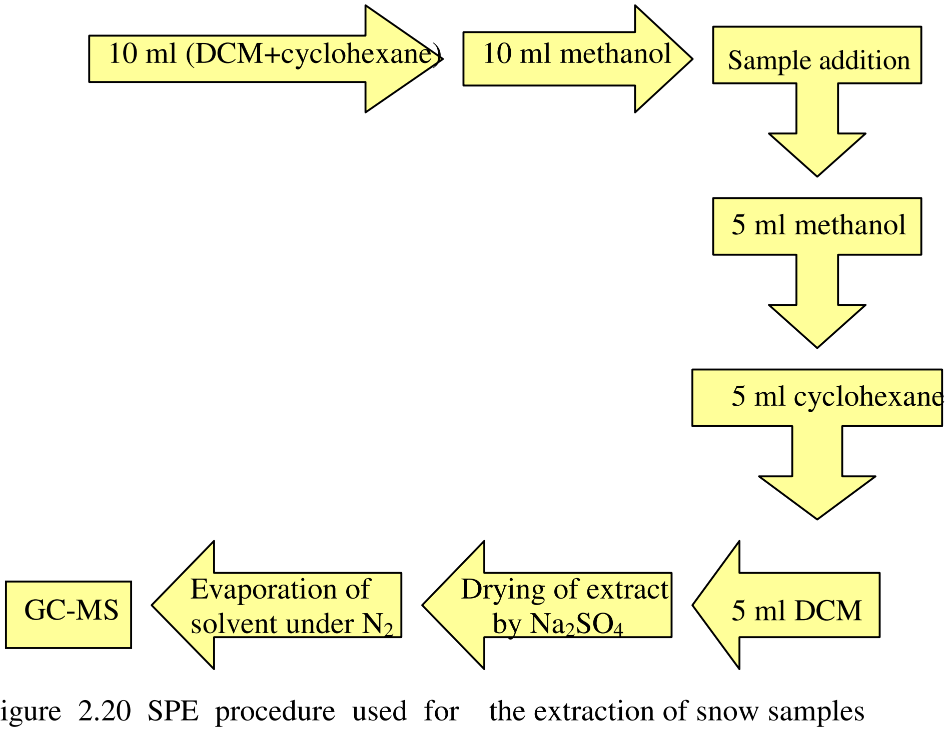


Figure 2.20 SPE procedure used for the extraction of snow samples

Table 2.6. Surrogates and their representative PAHs

Acenaphthene-d10 (Ace-d10)	Naphthalene (Nap) Acenaphtylene (Acy) Acenapthene (Ace) Fluorene (Flu)
Phenanthrene-d10 (Ant-d10)	Anthracene (Ant) Phenanthrene (Phe)
Chrysene-d12 (Chr-d12)	Fluoranthene (Flt) Pyrene (Pyr) Benzo(a)anthracene (BaA) Chysene (Chr)
Perylene-d12 (Per-d12)	Benzo(b)fluoranthene (BbF) Benzo(k)fluoranthene (BkF) Benzo(a) pyrene (BaP) Dibenz(a,h) anthracene (DahA) Indeno (1,2,3-cd) pyrene (Ind) Benzo(g,h,i)perylene (BgP)

Acenapthene-d10 and phenanthrene-d10 were used for the recovery calculations of 3 ring PAHs, Chrysene-d12 for 4 ring PAHs and Perylene-d12 for the 5 and 6 ring PAHs. Calculated average recoveries of surrogates for the snow samples were 67 %, 90 %, 65 %, 43 % for Ace-d10, Phe-d10, Chr-d10, Per-d12 correspondingly.

However, different SPE procedures were considered to obtain higher recoveries of PAHs from filtered rain matrix. For that purpose surrogate standards namely; napthhalene d8, acenapthene d10, phenanthrene d10, chrysene d12 and perylene d12 were added to deionized water and extracted accordingly. Surrogate standards were added in 500 ml deionized water at a concentration of 0.1 μg/L. Duplicate extractions were done for each extraction procedure.

The procedures used for the optimization of SPE were summarized in Table 2.7.

Table 2.7. A summary of extraction procedures used for SPE optimization

No	Extraction procedure
1	10 ml DCM+ 10 ml Methanol+10ml deionized water+sample addition+ elution with 2 portions of 10 ml DCM
2	10 ml (ethylacetate+DCM, 1:1)+10 ml methanol+10 ml deionized water+sample addition+elution with 2 portions of 10 ml (ethylacetate+DCM, 1:1)
3	10 ml (ethylacetate+DCM, 1:1)+ 10 ml methanol+sample addition+elution with 2 portions of 10 ml ethylacetate)
4	10 ml(ethylacetate+DCM, 1:1)+10 ml methanol+sample addition+elution with 10 ml ethylacetate+10 ml DCM
5	10 ml hexane+10 ml DCM+10 ml methanol+10 ml deionized water+sample addition+elution with 2 portions of (hexane+DCM, 1:1)

For each kind of procedures, solvent was retained on the C18 disk for 4 minutes in order to maintain enough time for solvent, sorbent interaction. Comparison of different SPE procedures were shown in Figure 2.21.

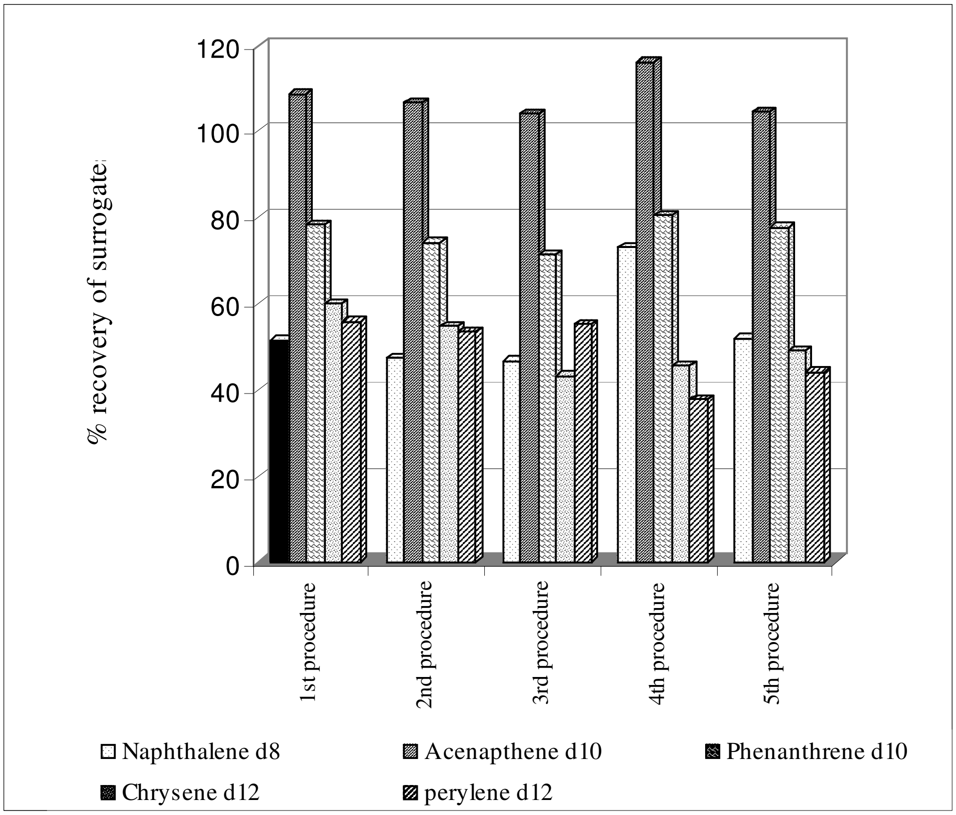


Figure 2.21. Comparison of different SPE procedures

All procedures resulted similar recoveries for acenepthene d10 and phenanthrene d10. 4th procedure give higher recovery for napthalene d8 however chrysene d12 and perylene d12 recoveries were lower than other 4 procedures. Chrysene d12 and perylene d12 recoveries were lower in 5th procedure compared to others. Considering all the surrogate recoveries 1st and 2nd procedures were found to be similar and higher recoveries were obtained for all the surrogates in the first procedure. For that reasons, 1st procedure was chosen to be optimum for extraction of PAHs from rain matrix and procedural details were given in Figure 2.22.

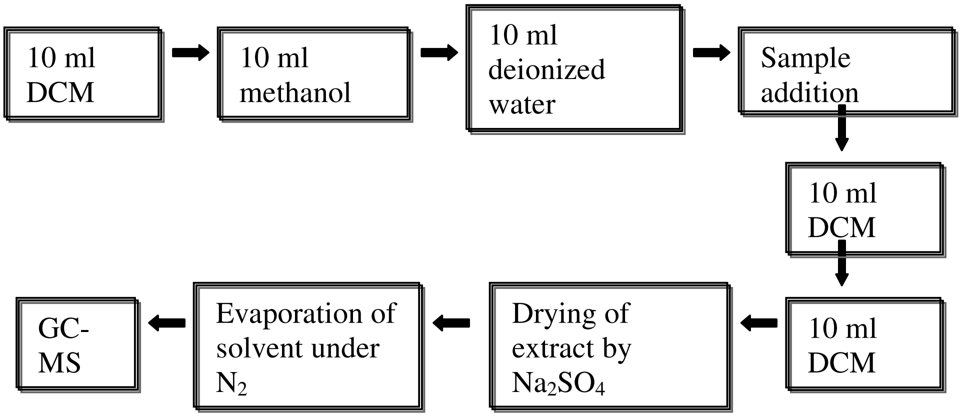


Figure 2.22.SPE procedure used for the extraction of filtered rain samples.

Addition of solvents before sample addition provides conditioning and cleaning of the C18 disk. Sample was added to the filtration funnel and sucked with a pumb with an average flow rate of 10ml/min. Disk was dried completely after sample elution since water layer remaining on the surface of the disk hinder the effective contact of eluting solvent with disk. Eluted sample in the flask was poured out and a collection tube was placed inside the erlenmayer flask. The PAHs on the disk were eluted through two fractions of 10 ml DCM. The extract in the collection tube was removed and dried with Na_2SO_4. Dried extract was placed in a fume hood and volume of the extract was reduced around 2 ml under gentle nitrogen stream. For further volume reduction extract was transferred to 2 ml amber vial by a glass syringe and solvent was evaporated near to dryness. Exact volume of the extract was measured by glass syringe and appropriate amount of internal standards were added and volume was completed to 50 µL by solvent for analysis by GC-MS.

Final concentrations of PAHs were obtained after recovery correction of the PAHs using surrogates. The surrogates and their represantative PAHs for recovery calculations for rain samples were shown in Table 2.8.

Table 2.8. Surrogates and Their Representative PAHs for rain samples

Naphthalene-d8 (Nap-d8)	Naphthalene (Nap)
Acenaphthene-d10 (Ace-d10)	Acenaphtylene (Acy) Acenapthene (Ace) Fluorene (Flu)
Phenanthrene-d10 (Ant-d10)	Anthracene (Ant) Phenanthrene (Phe)
Chrysene-d12 (Chr-d12)	Fluoranthene (Flt) Pyrene (Pyr) Benzo(a)anthracene (BaA) Chysene (Chr)
Perylene-d12 (Per-d12)	Benzo(b)fluoranthene (BbF) Benzo(k)fluoranthene (BkF) Benzo(a) pyrene (BaP) Dibenz(a,h) anthracene (DahA) Indeno (1,2,3-cd) pyrene (Ind) Benzo(g,h,i)perylene (BgP)

2.7. Application of Ultrasonic Extraction to the GFFs

SRM 1649a, an urban particulate material was used for the optimization of the ultrasonic extraction. Different solvents; toluene, acetone and dichloromethane (DCM) were used. Approximately 0.05 gr SRM 1649 a was taken in a small beaker and 20 ml of solvent were added and put in ultrasonic bath. Extracted samples were filtered from Glass Fiber Filters and dried by eluting from Na_2SO_4 column. After volume reduction under gentle stream of nitrogen, internal standards were added and analyzed. Results were shown in Figure 2.23.

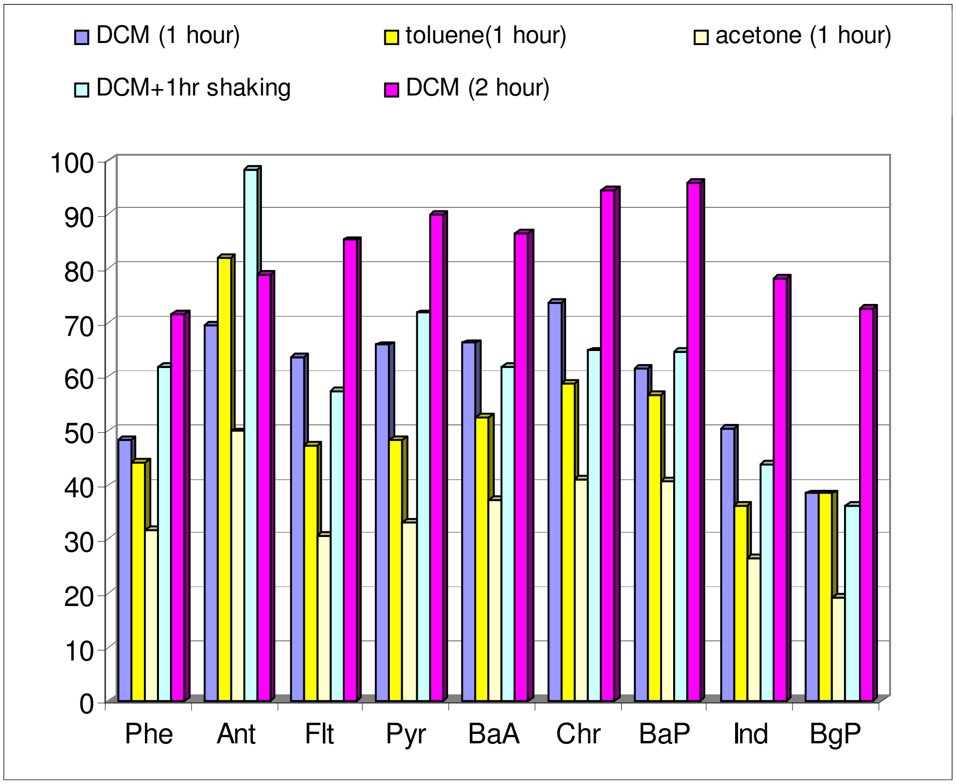


Figure 2.23. Comparison of different solvents for ultrasonic extraction of GFF filters

Higher recoveries of PAHs from urban dust matrix were obtained by 2 hour DCM extraction, all the analyte recoveries were higher than 70%. Two hour ultrasonic extraction with DCM followed by 1 hour shaking was also tried but no further improvement of recovery was observed. Standard deviations and average recoveries obtained by 2 hour ultrasonic extraction with DCM were shown in Table 2.9.

Table 2.9. Average recovery of PAHs from SRM 1649a matrix using 2 hr ultrasonic extraction with DCM (n=3)

	Average recoveries
Phenanthrene	71.6±2.4
Anthracene	78.6±3.3
Fluoranthene	85.2±3.9
Pyrene	89.9±3.6
Benzo(a)anthracene	86.4±2.7
Chrysene	94.5±3.3
Benzo(a)pyrene	95.7±1.6
Indeno	78.1±4.2
Benzo(g,h,i) perylene	72.6±3.1
Benzo(b)fluorathene	89.5±11.2
Benzo(k)fluoranthene	94.4±3.3

For the extraction filter samples, glass fiber filters were cut into stripes, placed in a beaker and surrogate standards were added on to the filters and 30 ml of ultrapure DCM were added. Samples were extracted for 2 hours continuously in ultrasonic bath. Extracted samples were filtrated by glass fiber filters to remove the particulates from the extract and then dried by eluting from Na_2SO_4 column. Solvent was evaporated under nitrogen stream and transferred to 2 ml amber glass vials and volume was further reduced and internal standards were added. Concentrated extracts were analyzed by GC-MS.

2.8. Quality Control

Standard Reference Materials (SRMs) are commonly used to assure quality in environmental and analytical works. However organic reference materials are quite new in the market compared to other inorganic standard reference materials. The available SRMs on the market are SRM 1649a and SRM 1597. These two SRMs were frequently applied to assure quality in our work.

Standard Reference Material (SRM) 1649a is an atmospheric particulate material collected in an urban area (Washington DC) over a period in excess of 12 months and is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, and total carbon in atmospheric particulate material and similar matrices Since it is a natural matrix it is also very suitable for the evaluation of extraction efficiencies of different extraction methods and clean-up procedures for the analysis of PAHs in similar matrices.

Standard Reference Material (SRM) 1597 is a natural, combustion related mixture of polycyclic aromatic hydrocarbons (PAHs) isolated from a coal tar sample and dissolved in toluene. 63 PAH compound was identified in SRM by GC-MS however 12 of them were reported as a reference concentration and 18 of them was reported as an information value. It is suitable for direct analysis since it is dissolved in organic phase and no clean up is needed. For that reasons, it is suitable for the evaluation of analytical technigues such as Gas Chromatography, liquid chromatography or gas chromatography-mass spectrometry. This SRM can also be used for the evaluation of the analytical performance of an analytical column.

The stability of the instrument and organic standards were checked by serial injections of the 20 fold diluted SRM 1597a shown in Figure 2.24. The same SRM solution was used during 20 days period. There was no significant change in instruments response and SRM solution concentration during that time period.

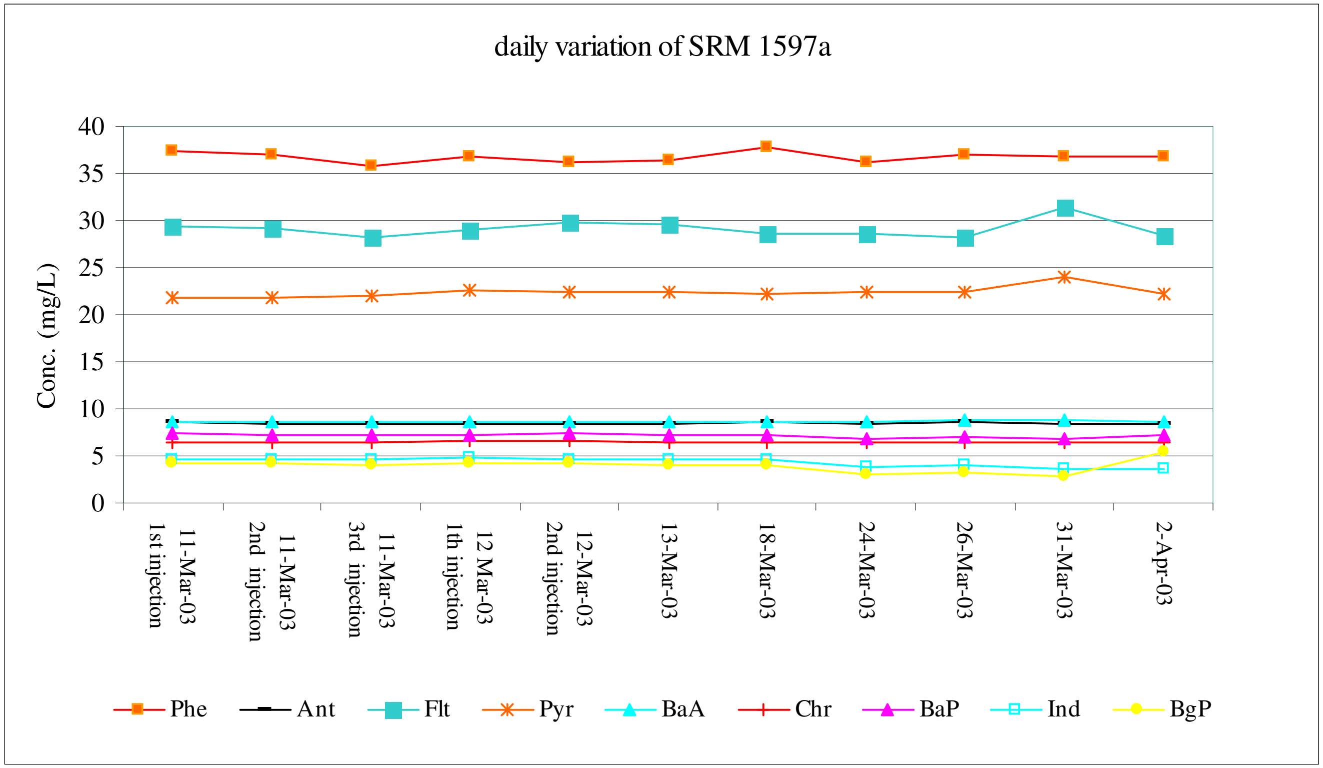


Figure 2.24. Daily variation of SRM 1597a

SRM 1597 a was also used to check the accuracy of the standard calibration curve. Standard deviation of the SRM concentrations and accuracy for each PAH compound were given in Table 2.10. Generally, standard deviations are relatively low and accuracy of the calibration curve is adequate for quantitative analysis of samples.

Table 2.10. Analysis Results of SRM 1597a (ppm)

PAHs	Certified conc.	Average conc.	% Error
Naphthalene	1000 ± 50	1038 ± 12	3.82
Phenanthrene	400 ± 4	369 ± 7	7.89
Anthracene	87.4 ± 2	84.7 ± 1	3.12
Fluoranthene	278 ± 4	291 ± 6	4.70
Pyrene	204 ± 3	222 ± 3	8.76
Benzo (a) anthracene	85.3 ± 3.4	85.7 ± 0.6	0.42
Chrysene	62.0 ± 1.1	64.5 ± 0.7	4.01
Benzo (a) pyrene	82.9 ± 5.3	72.5 ± 0.5	12.5
Indeno(1,2,3-cd) pyrene	52.1 ± 4.0	45.7 ± 0.75	12.3
Benzo(g,h,i) perylene	46.5 ± 6.7	40.9 ± 0.7	12.0

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Wet deposition research

3.1.1. Overview of the produced data set and summary statistics for rain study

Samples were collected in between December 2000 and June 2002. A total of 61 samples were collected in this period.

As it was mentioned in experimental section rain water samples were in situ filtrated from glass fiber filter (2.7 μm pore size) in the field. Particulate phase (insoluble) concentrations refers to amount collected on glass fiber filter (GFF) whereas aqueous phase (soluble) concentration is the rain filtrate collected in dark glass bottles. There is a large body of evidence indicating that PAHs are predominantly associated with small particles of less than 2 μm (Sicre et al., 1987). However glass fiber filters are not very efficient to retain small particles. So there is always some particles in the filtrate which makes PAHs concentration in aqueous phase otherwise they have extremely low solubilities. Average soluble and insoluble fractions for all samples are shown in Table 3.1. Almost all the measured PAHs have higher concentrations in insoluble fraction except for Ace, Flu and Ant. The results obtained for Ace and Ant might be misleading as they were not measured in most of the samples because of their high volatility and rapid degradation in the atmosphere. This is especially important for Ant obtaining higher concentrations in insoluble fraction.

Table 3.1. Summary Statistic of measured PAHs.

PAHs	Units	Soluble	Insoluble
Acy	ngL^{-1}	10.9± 16.3	13.2±12.4
Ace	ngL^{-1}	21.8± 34.1	11.6±30.0
Flu	ngL^{-1}	43.7±59	30.4±44.5
Phe	ngL^{-1}	91.6±111	114±141
Ant	ngL^{-1}	76.0±187	0.18±1.32
Flt	ngL^{-1}	63.5±98.6	83.6±125
Pyr	ngL^{-1}	53.8±90.9	55.9±90.5
BaA	ngL^{-1}	16±14.6	24.4±42.6
Chr	ngL^{-1}	28.3±30.1	53±105
B(b+k)F	ngL^{-1}	41.7±40.0	113±193
BaP	ngL^{-1}	19.7±17.1	30.1±30.0
Ind	ngL^{-1}	17.9±15.8	50.4±79.7
DahA	ngL^{-1}	5.87±6.43	9.24±10.7
BgP	ngL^{-1}	12.0±12.3	37.9±58

The same data is shown in terms of percent contribution of each PAH to the total PAH concentration (Fig 3.1)

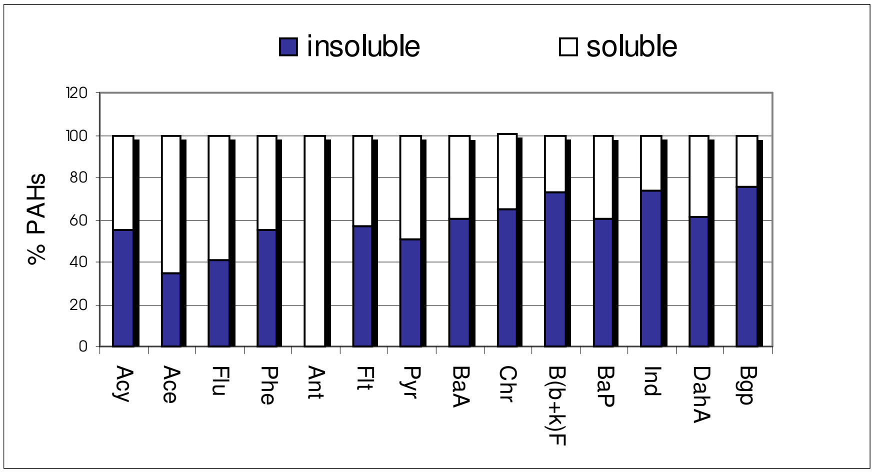


Figure 3.1. Percent distribution of soluble and insoluble fraction

As can be seen from Figure 3.1. insoluble fraction contribute more than 60 % of the total for most PAHs. But many samples have concentrations in the level of detection limit for soluble part. If we take into account this fact, insoluble fraction is a lot more than 60%.

Average concentrations and standard deviations of measured PAHs both in particulate and aqueous phase are shown in Table 3.2. Total concentrations of PAHs were found by adding particulate and soluble fraction concentrations which were expressed as nanogram per liter. Fifteen PAHs namely; Acenapthylene (Acy), Acenapthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b) fluoranthene(BbF), benzo(k) fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (Ind), Dibenzo(a,h)anthracene (DahA),Benzo(g,h,i)perylene (BgP) were measured both in particulate and aqueous phase. Since BbF and BkF peaks are not well resolved in samples, they were integrated together and reported as a sum. Although basic statistics were given for all of the PAHs, Acenapthene and Anthracene were found to be below detection limits for 80% of the data so these two compounds were eliminated from analyte list for further discussions. Highest concentrations obtained for Phe followed by Flt, B(b+k)F and Pyr.

Table 3.2. Summary Statistic of measured PAHs (ngL^{-1})

	Size	Average	Stand. Deviation	Median	Geometric mean
Acy	52	18.3	20.6	9.77	11.2
Ace	19	20.0	24.1	9.78	10.5
Flu	57	66.4	68.7	43.8	43.2
Phe	59	196	171	140	138
Ant	12	70	178	13.6	17.6
Flt	59	137	142	101	94.2
Pyr	59	93.0	111	57.2	56.2
BaA	54	29.0	42.0	14.1	15.7
Chr	54	63.1	106	29.9	30.4
B(b+k)F	55	128	189	84.7	73.3
BaP	38	35.0	30.1	25.9	22.4
Ind	48	55.2	78.8	32.6	31.3
DahA	17	9.70	10.6	5.91	5.94
BgP	42	40.4	57.2	20.0	21.34

Standard deviations of almost all measured PAHs are in the order of concentrations indicating high fluctuations from one sample to another. If the data are normally distributed arithmetic means and standard deviations are used to describe the data. But, atmospheric concentrations are controlled by many different parameters that is why atmospheric species are usually log-normally distributed. There are several ways of testing distribution of data statistically. Closeness of the geometric mean and median with each other is an indication of log-normal distribution. As it was seen in Table 3.2, geometric mean and median are very close to each other for most of the PAHs and they are lower than the aritmetic mean and this observation is due to very high concentrations of PAHs detected in few of the samples. For instance, geometric mean and median values for Phe are 138 and 140 respectively which are very close to each other. However, arithmetic mean for Phe is 257 which is significantly higher than geometric mean and median and it corresponds to concentration values where only small numbers of data points exist. For that reason use of arithmetic means is not correct way to represent a lognormaly distributed data.

Frequency histograms were prepared for each PAH and smooth curve fitted to distributions were hypotized to be log normal. The goodness of the fit was then tested using Kolmogorov-Smirnov (K-S DN) statistics. Frequency histograms for selected PAHs (Flt, Phe and Pye) are given in Figure 3.2 and parameters obtained from Kolmogorov-Simirnow statistics are presented in Table 3.3.

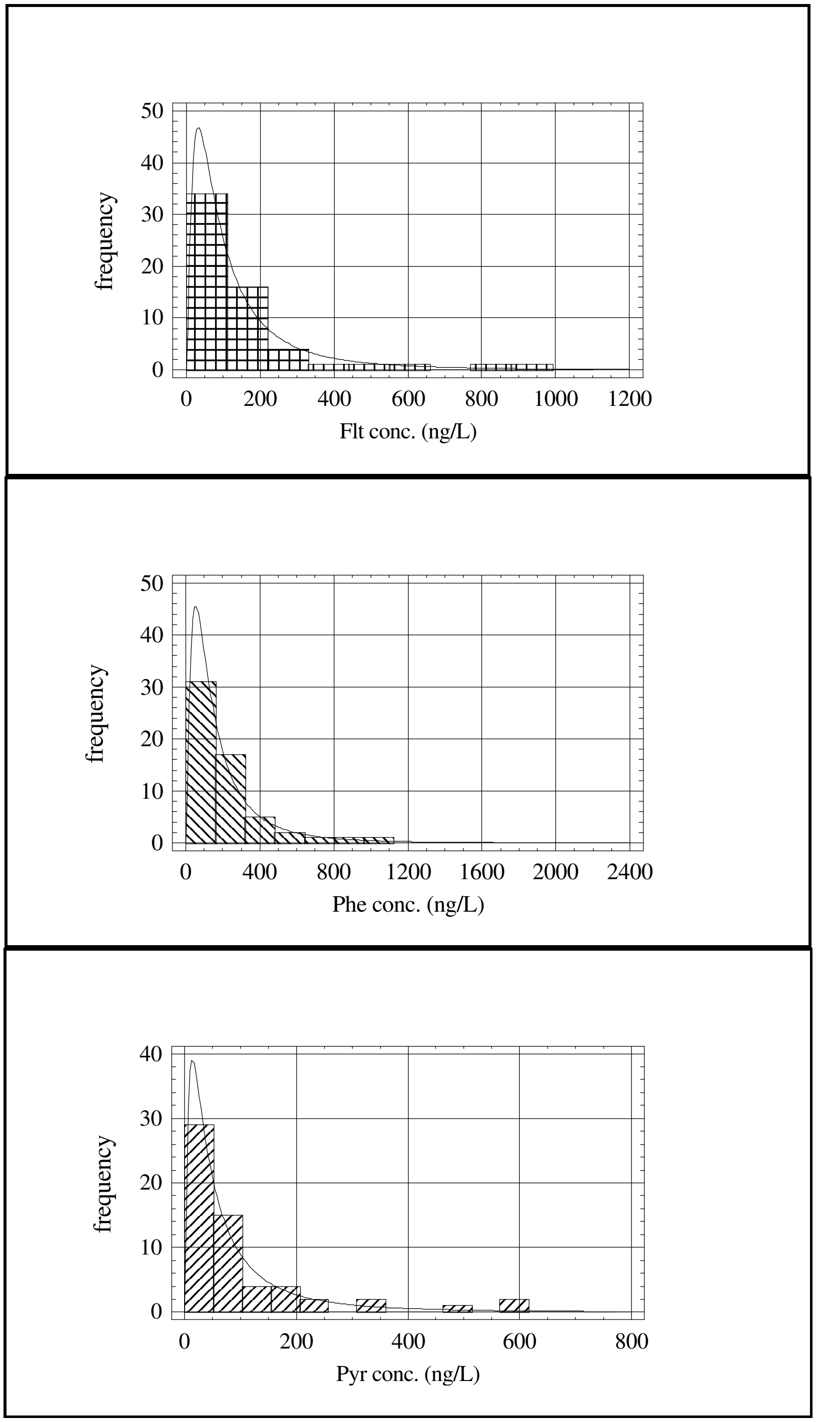


Figure 3.2. Frequency histograms of Flt, Phe and Pyr

Table 3.3. Kolmogorov-Smirnov Test of Normality, Skewness, Standard Kurtosis

PAHs	K-S DN	Std. Skewness	Std. Kurtosis	Alpha	Distribution type
Acy	0.107	6.14	6.72	0.79	Log-normal
Ace		1.69	0.49		
Flu	0.087	6.24	6.82	0.67	Log-normal
Phe	0.08	3.59	3.86	0.62	Log-normal
Ant		2.13	1.98		Log-normal
Flt	0.088	4.30	4.74	0.69	Log-normal
Pyr	0.074	3.95	4.1	0.58	Log-normal
BaA	0.0648	4.42	4.93	0.48	Log-normal
Chr	0.067	4.69	5.24	0.50	Log-normal
BbF	0.0838	4.59	5.11	0.63	Log-normal
BaP	0.086	4.35	5.16	0.54	Log-normal
Ind	0.091	4.00	4.39	0.64	Log-normal
DahA					
Bgp	0.1	3.85	4.30	0.65	Log-normal

Skewness is a measure of the symetry or shape of the data. Data departs from normality when standard skewness values are outside the range of -2.0 to +2.0. Skewness values higher than zero indicates right-tailed distribution and values smaller than zero is an indication of left tailed distribution. As can be seen from Table 2 all the standard skewness values are higher than 0 showing right tailes distribution. Kurtosis is a measure of flatness or stepness with respect to gaussian distribution. Again kurtosis values outside of -2 to +2 shows departures from normality. Kolmogorov-Smirnov test compares the empirical cumulative distribution function to that of hypotesized distribution. K-S DN values are calculated from the Statgraph software when lognormal distribution is chosen. The K-S DN values which are lower than critical values at 95% confidence level shows lognormal distribution of data. Alpha values are also added in Table 3.3 as a disproof of of null hypothesis that the distribution is

lognormal. Alpha values are computed from the following equation;

$$\text{Alpha}=\left[\sqrt{N}+0.12+\frac{0.11}{\sqrt{N}}\right]*DN$$

Critical value of alpha is 1.36 at a 95% confidence level. If calculated alpha values are higher than 1.36 it means that data do not fit the hypothesized lognormal distribution. Alpha values are meaningfull when sample size exceeds 40. In our case, since number of data points for Ant and Ace is less than 40, alpha values were not calculated for them. Calculated alpha values are in the range of 0.48-0.79 showing lognormal distribution of the data for all PAHs (Table 3.3). Lognormal distribution of data is due to presence of large number of colinear factors such as meteorology, chemistry etc.

3.1.2 Comparison of the data with literature

Comparison with similar sites is always recommended in environmental studies for observing similarities and differences from one site to another and to assess the amount of pollution observed in studied site. For our data, it would be better to compare with other studies conducted in urban areas which are under the direct influence of anthropogenic emissions. But, because of the limited urban data present in the literature, we also compared with rural data sets. However comparison of PAHs in wet deposition samples is not easy because of the following reasons;

- Most of the data considering PAH measurements were done on aerosols and measurement of PAHs in precipitation is scarce.
- Sampling methodologies may differ according the purpose of the studies. For instance, in most of the studies collection of bulk deposition samples

were preffered to estimate the total pollutant load into the lakes and seas (Golomb et al., 2001, Gevao et al., 1998). Different sampling methodologies are used for different information needed. Therefore, making a direct

comparison of our data with other studies is not easy for the reasons mentioned above.

Considering all uncertanities, data in this study were compared with data reported in literature for other locations. As pointed out before, literature data for both urban and rural sites were included in comparison to see the differences. Urban sites are under the influence of local sources but rural sites are affected from distant sources.

In the scope of the EMEP (European Monitoring and Evaluation Program), concentrations of metals have been monitored in 100 rural stations in Europe since 1988. Heavy metals and persistent organic pollutants (POPs) were included in EMEP's monitoring program in 1999. However, earlier data has been available and collected, and the EMEP database thus also includes older data, even back to 1988 for a few sites. The strategic long-term plans on POPs recommended to take a stepwise approach, and the following compounds or groups of compounds should be included in the first step: polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), HCB, chlordane, lindane, alpha-HCH, DDT/DDE. In 69 of them, metals in air and precipitation have been monitored, however, in 2001 it was 6 sites measuring POPs in both air and precipitation, and together it was 13 measurement sites. Among this 13 stations, PAHs there are only 5 stations measuring PAHs in deposition samples (two in Germany, two in Sweden and one in Finland) (EMEP report).

Data from EMEP stations (European Montoring and Evaluation Program) were also included in comparison. Data from Germany stations were obtained from monthly by wet only collectors while bulk concentrations were measured on monthly basis in Sweden and Finland. Concentrations are reported as volume weighted average for this sites. Our concentrations are also converted to volume weighted averages.

The use of raw concentrations of PAHs (and other pollutants as well) for comparison is misleading, because concentrations of pollutants in rain water is shown to vary with the precipitation amount. Volume weighted concentrations of pollutants in rain water are preferred for comparison, dilution effect is eliminated in calculation of volume weighted concentrations.

Volume weigted averages were calculated using the following relation (Acker et al., 1998, Valenta et al., 1986):

$$\bar{c} = \frac{1}{\sum_i p_i} \cdot \sum_i c_i \cdot p_i$$

Where, $\bar{c}$ is the precipitation weighted arithmetic mean concentration of a pollutant,

p_i is precipitation amount in day i and c_i is the measured concentration in that particular day.

Remaining data used in the Figure 3.3 were obtained from literature. Sampling locations and periods, sampling methodologies and relevant information gathered from the literature for each study was summarized below for comparison purpose;

Poland (Grykiewicz et al., 2002): Bulk deposition samples were collected at ten points of a large urban location (Gdansk, Sopot and Gydinia) over a period of 16 months (January 1998 to April 1999). At each site 16 samples were collected as a total of 160 samples. Arithmetic mean concentrations of 10 sites were used for comparison.

France (Motelay-Massei et al., 2003): Weekly bulk deposition samples were collected at a suburban site in Evreux (100 km west of Paris) from March 2001 to March 2002. 38 bulk deposition samples were collected in this period and mean concentrations of all samples were reported.

France (Ollivon et al., 2002): Twelve monthly bulk deposition samples were collected at Paris which is a typical urban location, in between November 1999 to October 2000. Monthly concentrations of PAHs were reported and average of 12 months were used for comparison.

India (Sahu et al., 2003): Rain samples were collected between end of May and end of June 2001 at Mumbai, India. Mumbai can represent an urban site however traffic emissions are very restricted. Thirteen rain events were collected and average concentrations of measured PAHs were reported.

Greece (Manoli et al., 2000): This study was undertaken in Imathia, a Greek Province in Central Macedonia. Monthly bulk deposition samples were collected from seven sampling sites during the period of September 1996-May 1997.

Switzerland (Leuenberger et al., 1988): Study was undertaken in an urban site, Dübendorf in Switzerland in 1985. Wet deposition samples were collected and particulate and aqueous phases were separated during sampling. Four winter rain and 3 summer rain samples were collected. Major emission source in the winter time stated as oil burning for residential heating.

Hungary (Kiss et al., 2001): Samples were collected at a rural site by Lake Balaton, Hungary. Both rain and snow samples were collected by wet only collector from January 1995 to March 1996.

Usually observed PAH concentrations measured in Ankara are higher than other European sites. However, BaA, BaP and BgP concentrations are close to measured concentrations in Hungary. Flt and Pyr concentrations are higher than other sites except for Hungary. Phe concentration in Ankara is higher than other cities but very close to urban Switzerland. While Chr concentrations measured in our site is comparable with urban Paris and urban India, Flu concentrations are almost equal with urban India.

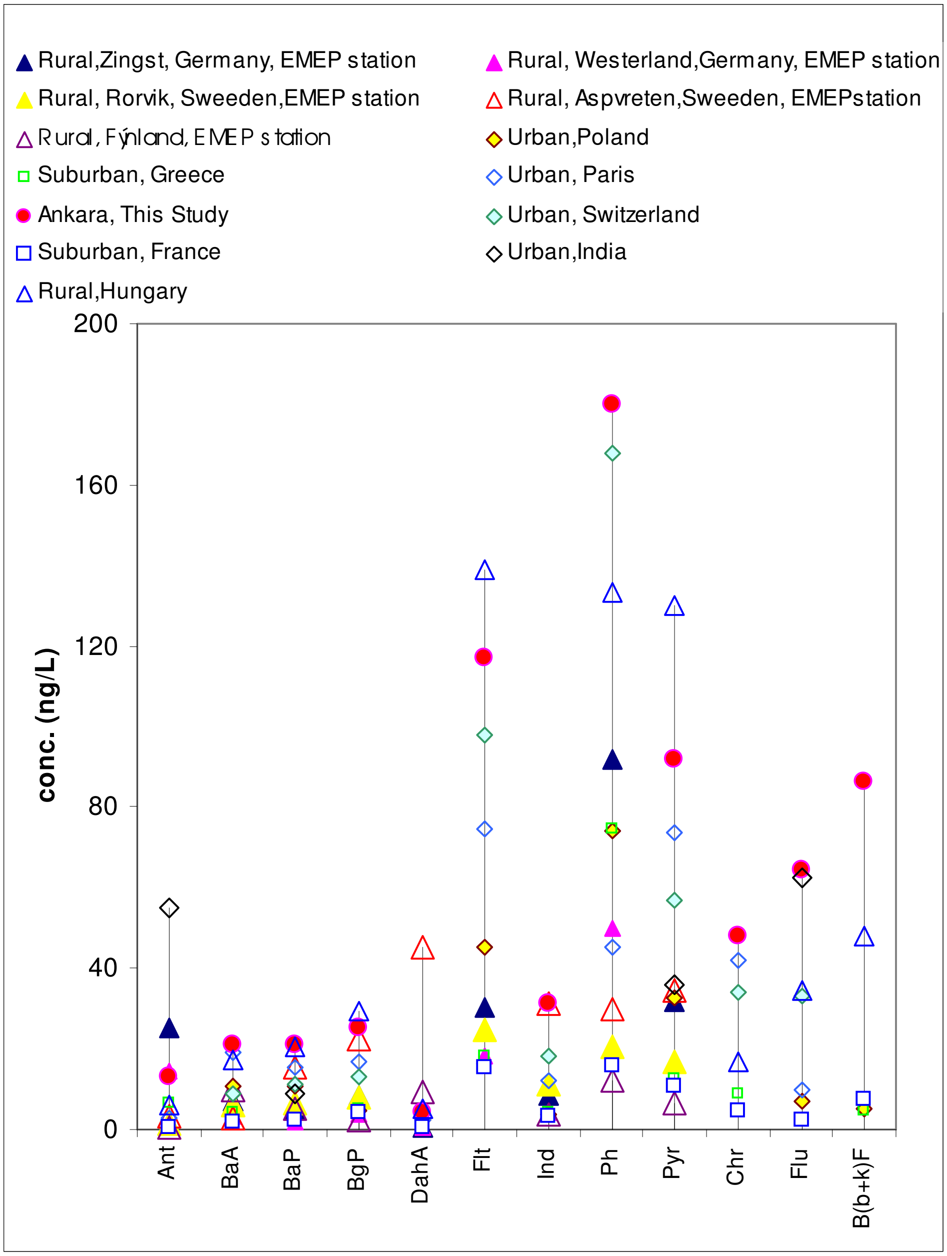


Figure 3.3. Comparison of our study with literature

Winter and summer concentrations were provided for Hungary by Kiss et al. (2001) and used for seasonal comparison with our data (Figure 3.4). Sampling site, Tihany is a summer resort village near Lake Blaton, with a population of 1500 inhabitants It is mentioned that major local anthropogenic sources of air pollution are traffic in summer and residential heating in winter. Results represent concentrations of PAHs in rain samples collected by using wet only sampler. Our results were compared according to winter and summer seasons were shown in Figure 3.4. Initial observation of the figure shows that concentration profiles of PAHs is similar in two sites considering the monthly variation of species. Concentrations of Flt and Pyr are significantly higher than Ankara while others are comparable in winter season. This is due to form of the precipitation in Hungary since snow was the only form of the precipitation in cold winter. It is known that snow scavenging of pollutants 20 times higher than rain and this may be the reason for elevated concentration in winter period. However summer concentrations are higher in Ankara. Ankara is a big city and anthropogenic emissions are quite higher as compared to Hungary.

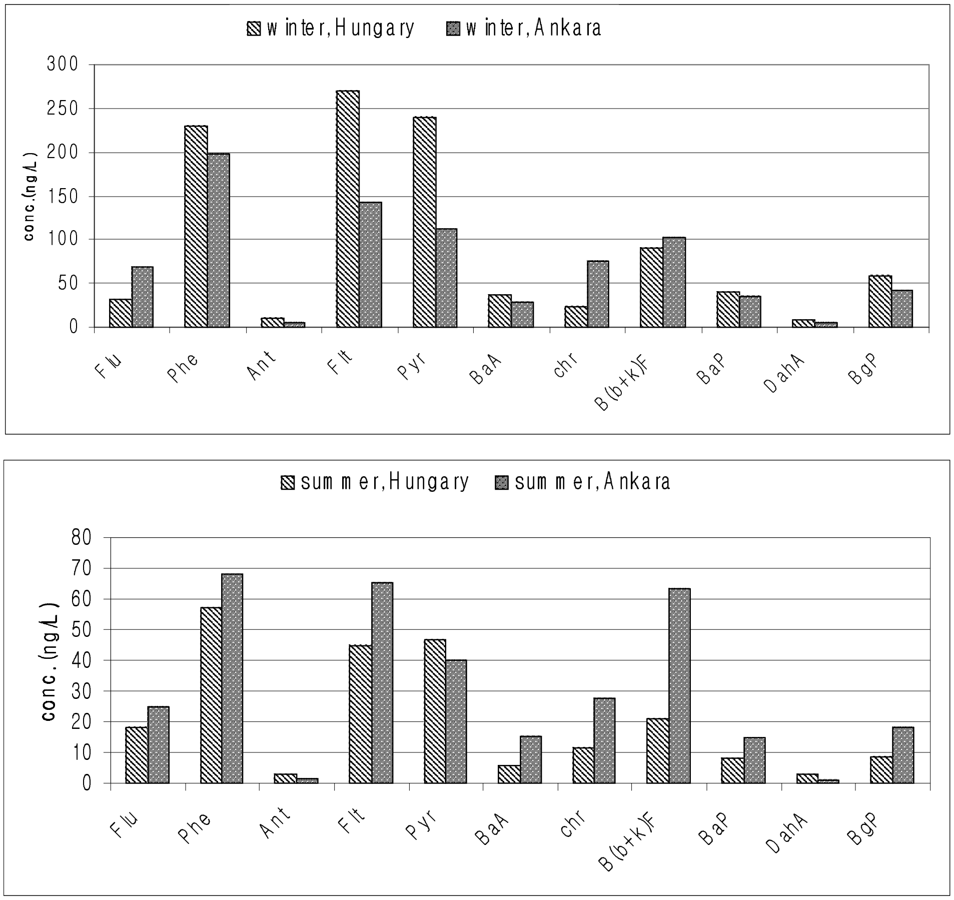


Figure 3.4. Comparison of the study with Hungary

Data from Switzerland includes winter and summer concentrations were also used for comparison (Figure 3.5).

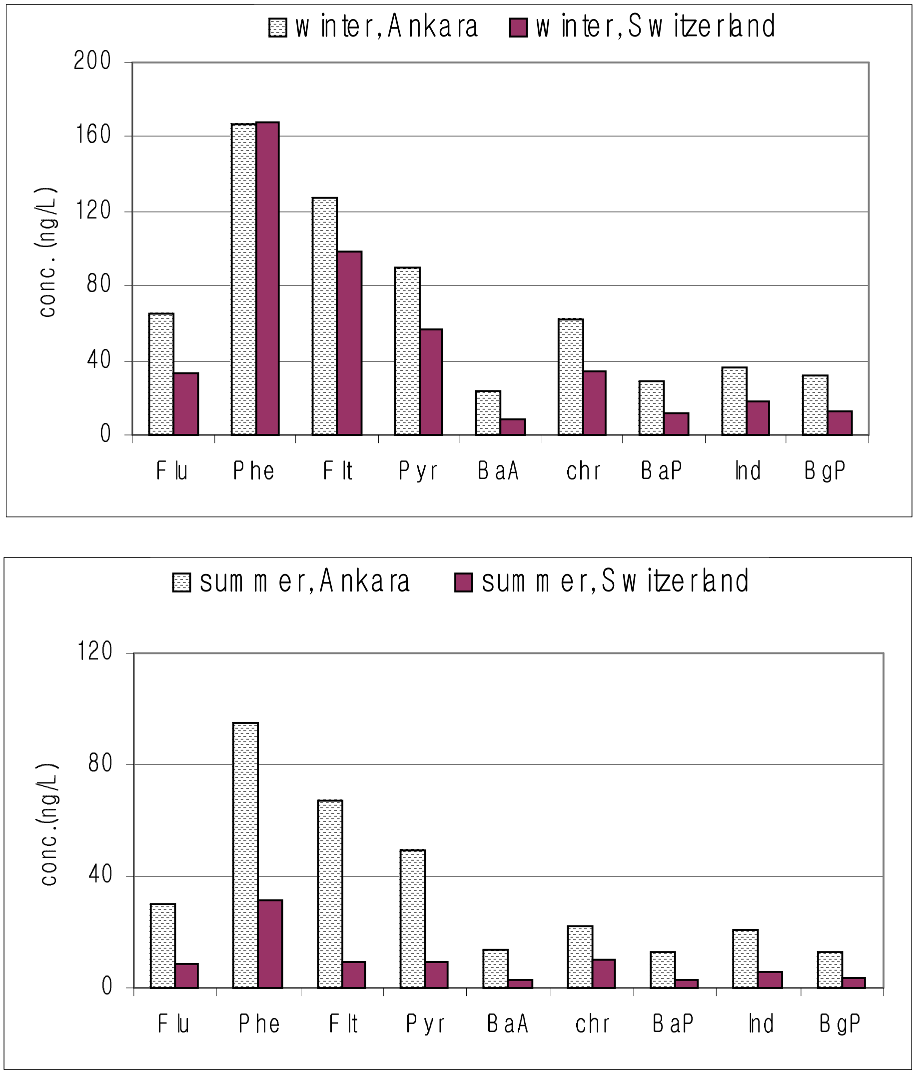


Figure 3.5. Comparison of our study with Switzerland

Usually winter concentrations are comparable however, summer concentrations are higher in Ankara again. For the time being this observation could be explained by the presence of road dust in Ankara atmosphere. Station is 7 km far from the major roads. Number of cars having catalytic converter is relatively less in Turkey since average age of automobiles are quite higher than European cities and it is known that automobiles without catalytic converter emits PAHs at a rate of 25 times higher than automobiles with catalytic converters (Simoneit et al., 1993). Diesel motor vehicle emissions of PAHs are also 10 times higher than gasoline powered vehicles (Lang et al., 2002). Suspended dust particles are efficiently removed by wash out process increasing summer concentrations in Ankara.

3.1.3. Relation of PAHs with Meteorological Parameters

Air mass movement is believed to be a major controlling factor for the dispersion, distribution and deposition of atmospheric organic compounds (Kawamura and Kaplan, 1986b, Jaffe et al., 1993a). For that reason, the direction, velocity and frequency of air masses could have a significant effect on the content as well as composition or organic aerosols associated with them (Lee and Jones, 1999). For instance, temperature is especially important as it may affect the partitioning behavior of PAHs in gas and solid phase which determine the amount of PAHs in rain water since the efficiency of scavenging from the atmosphere for gaseous and aerosol forms of PAHs are different during precipitation.

Measurement of wind speed and wind direction is important in air quality monitoring. It can help to identify the location of the source of the pollution, and also provide a better overall picture of what is happening in the air.

The characteristic meteorological feature of Ankara is low annual wind speed. The calculated average wind speed in Ankara is 2 cm/s. Topographical features of Ankara and lower wind speeds enhances the accumulation of pollutants in the region. During calm conditions particles emitted from sources reside over the city for sufficiently long time to mix both vertically and horizantally resulting a homogeneous air mass.

PAHs emitted from their sources are primarily in the gas phase, however they quickly adsorbed on particles and resist degradation in the environment. PAHs adsorbed on aerosols can be removed from the atmosphere and settle on the ground either by washout and/or dry deposition. For that reasons, meteorological conditions which certainly affect aerosols are also affect the rain water composition especially in urban environments. We will start with wind speed to discuss the affect of meterological parameters on PAH concentrations in rain water samples. Meterological parameters were taken from Turkish Meteorological Organization for the corresponding sampling period.

Relation of wind speed with observed PAH concentrations were shown in Figure 3.6. As it was seen in Figure concentrations of PAHs in rain samples are inversely related with wind speed. Such behaviour is expected, as pollutants accumulate over the city at low wind speeds resulting in high concentration events.

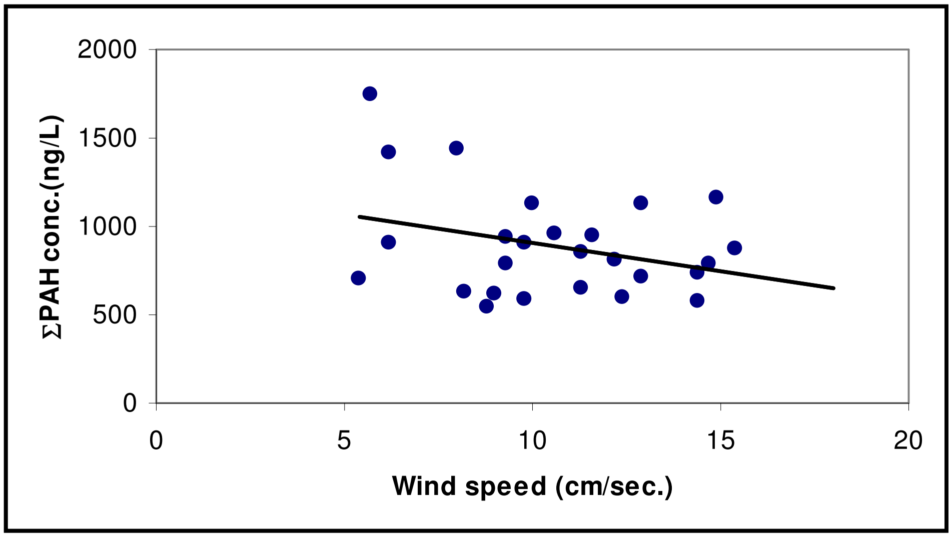


Figure 3.6.The relation between ΣPAHs and wind speed.

To examine the affect of wind direction to the observed PAH concentrations, we treated wind data in two steps. First we investigated the relation of wind direction with total amount of PAHs. For that reason, data has been sorted according to total PAH concentrations in each sample and the highest 25 samples were taken and corresponding wind patterns were investigated (Figure 3.7.) In this way we got a qualitative information about the wind direction which carries highest concentrations to the sampling site.

Wind patterns were classified according to wind directions and 3 classes are distinguished 36 percent from the NE (north east), 32 percent from the WSW (west) and 32 percent from mix directions but mainly from NE and WSW.

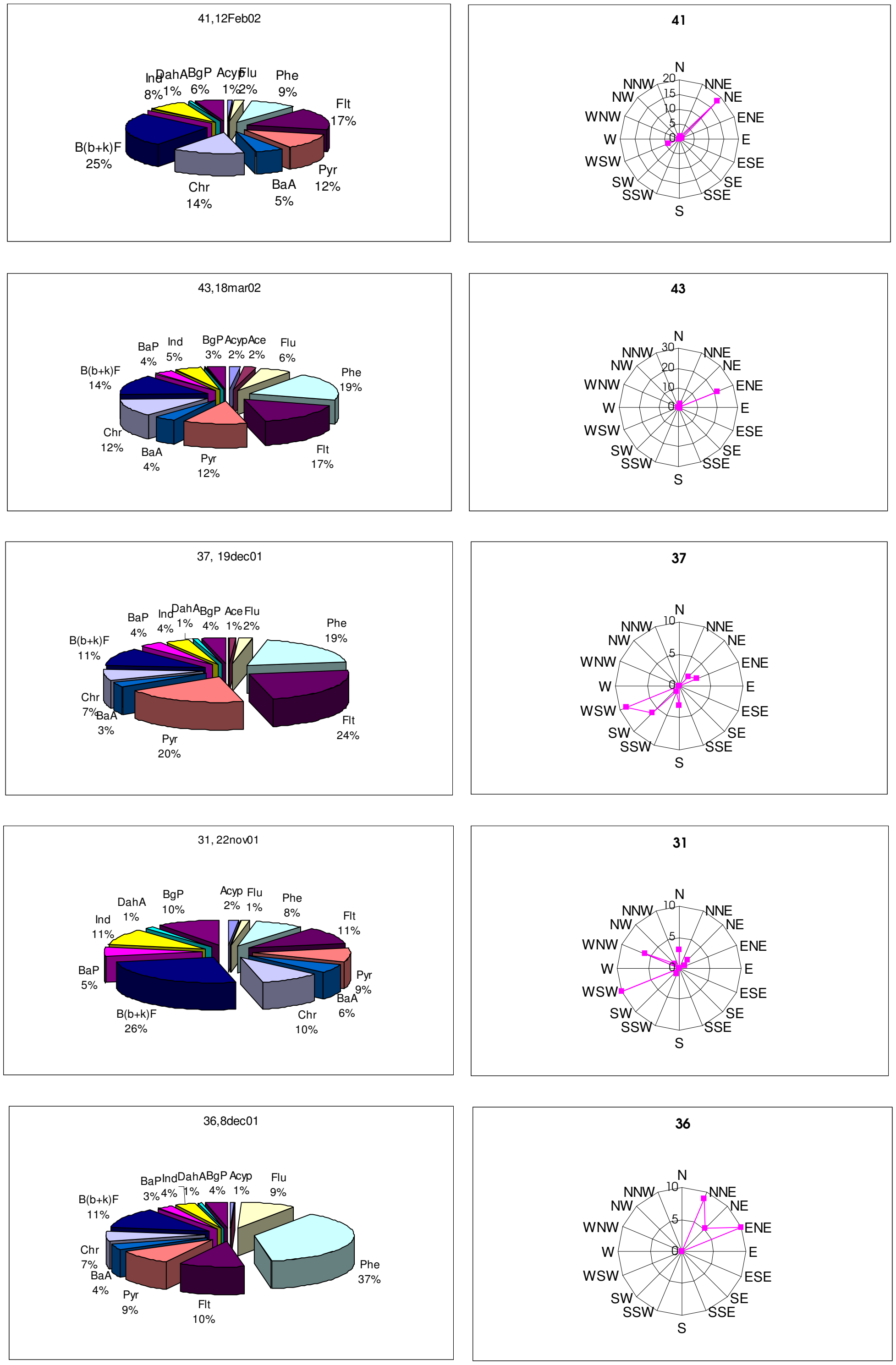


Figure 3.7. PAH concentration distribution and corresponding wind patterns

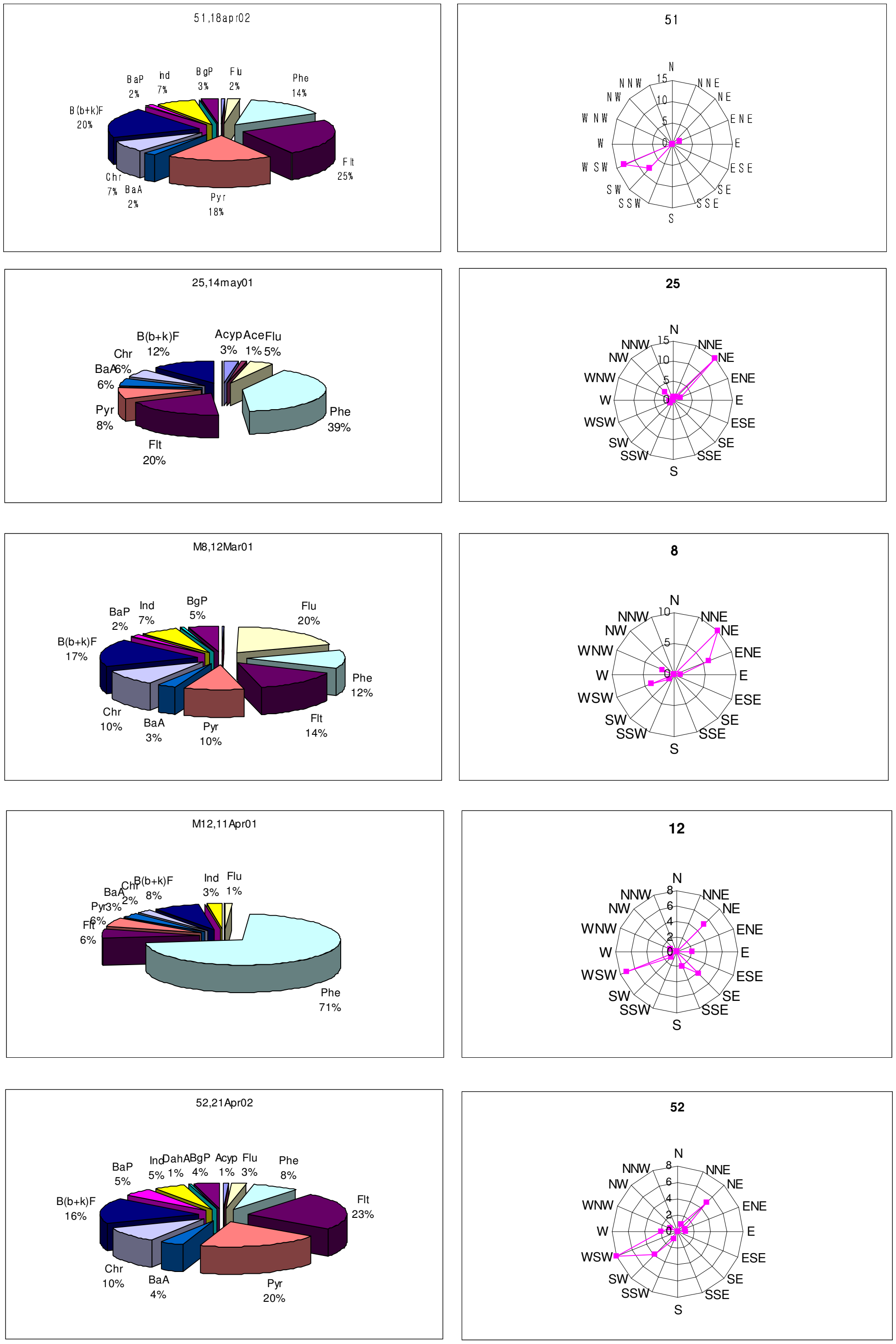
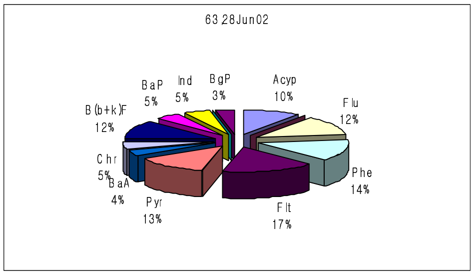
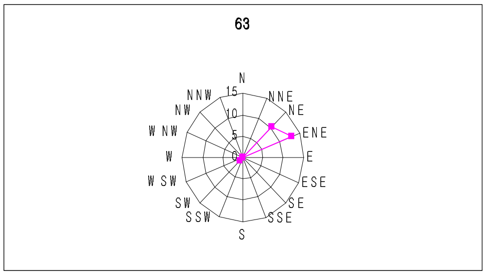
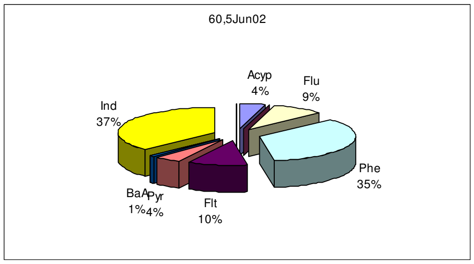
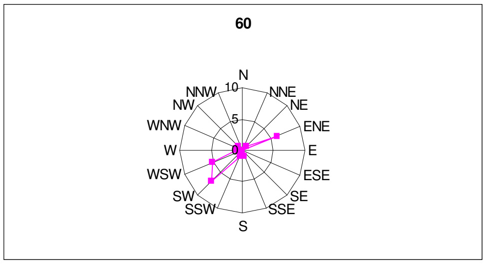


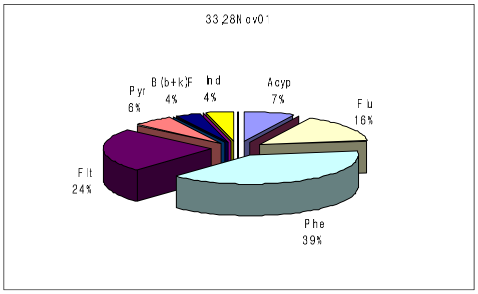
Figure 3.7 continued

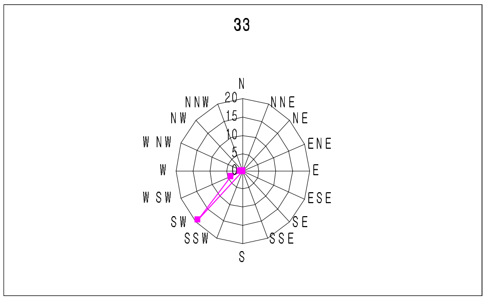


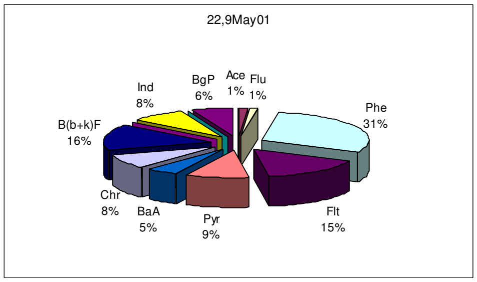


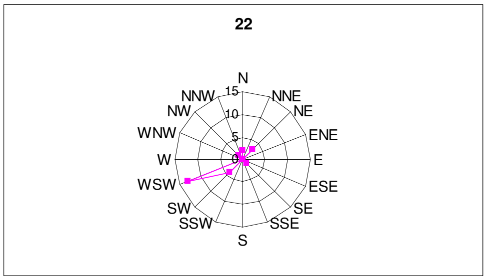


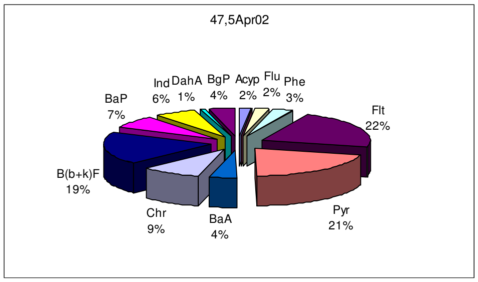


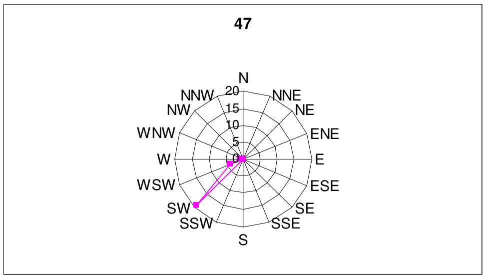












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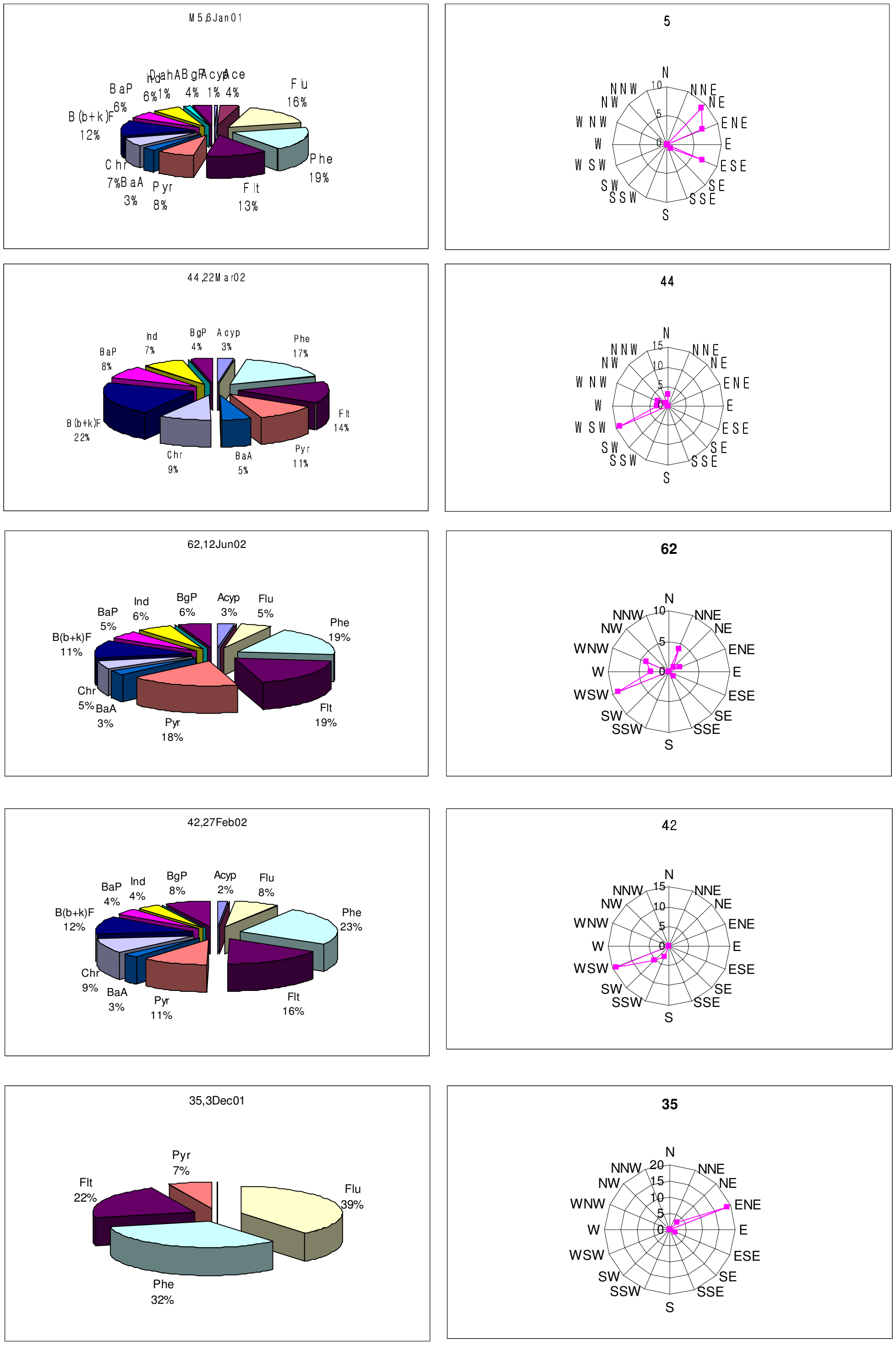

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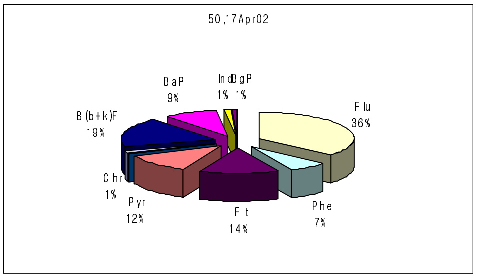
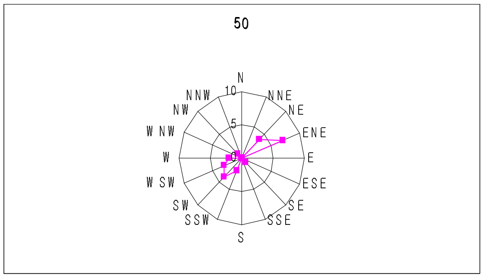
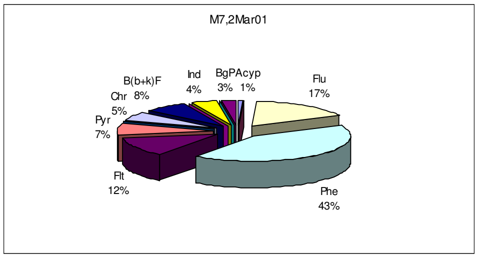
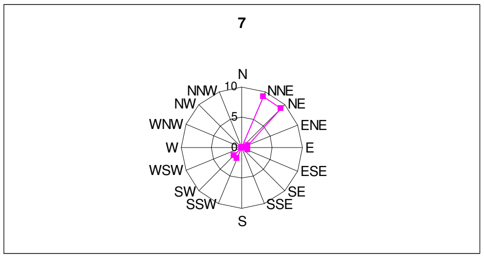
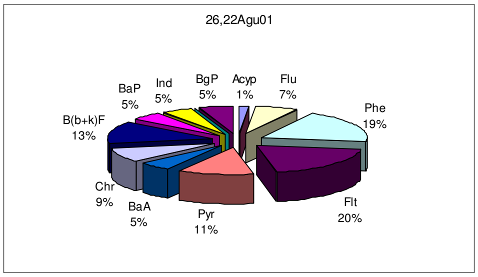
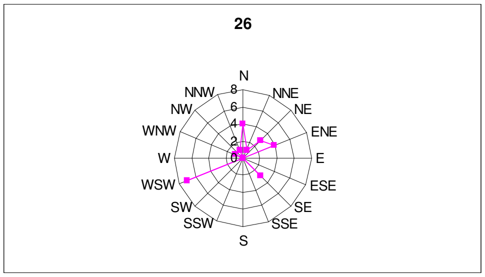


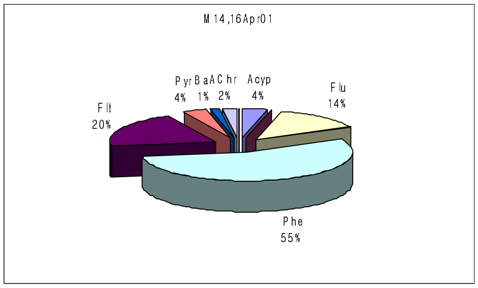


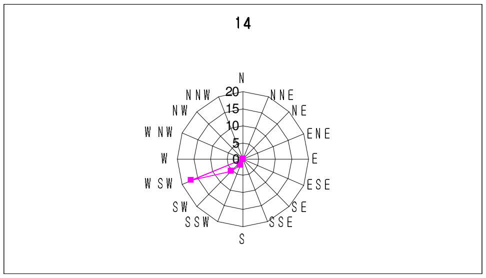


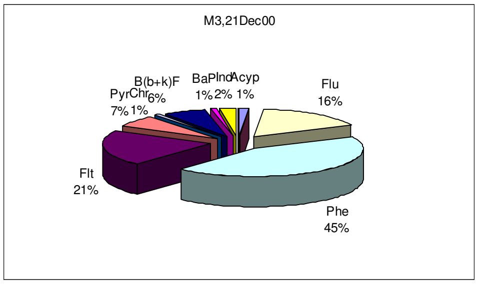












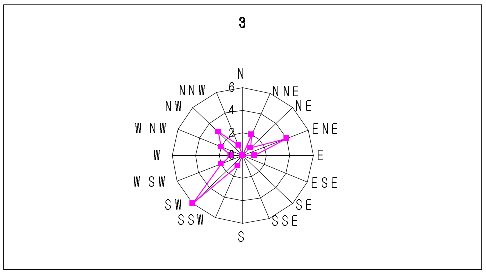


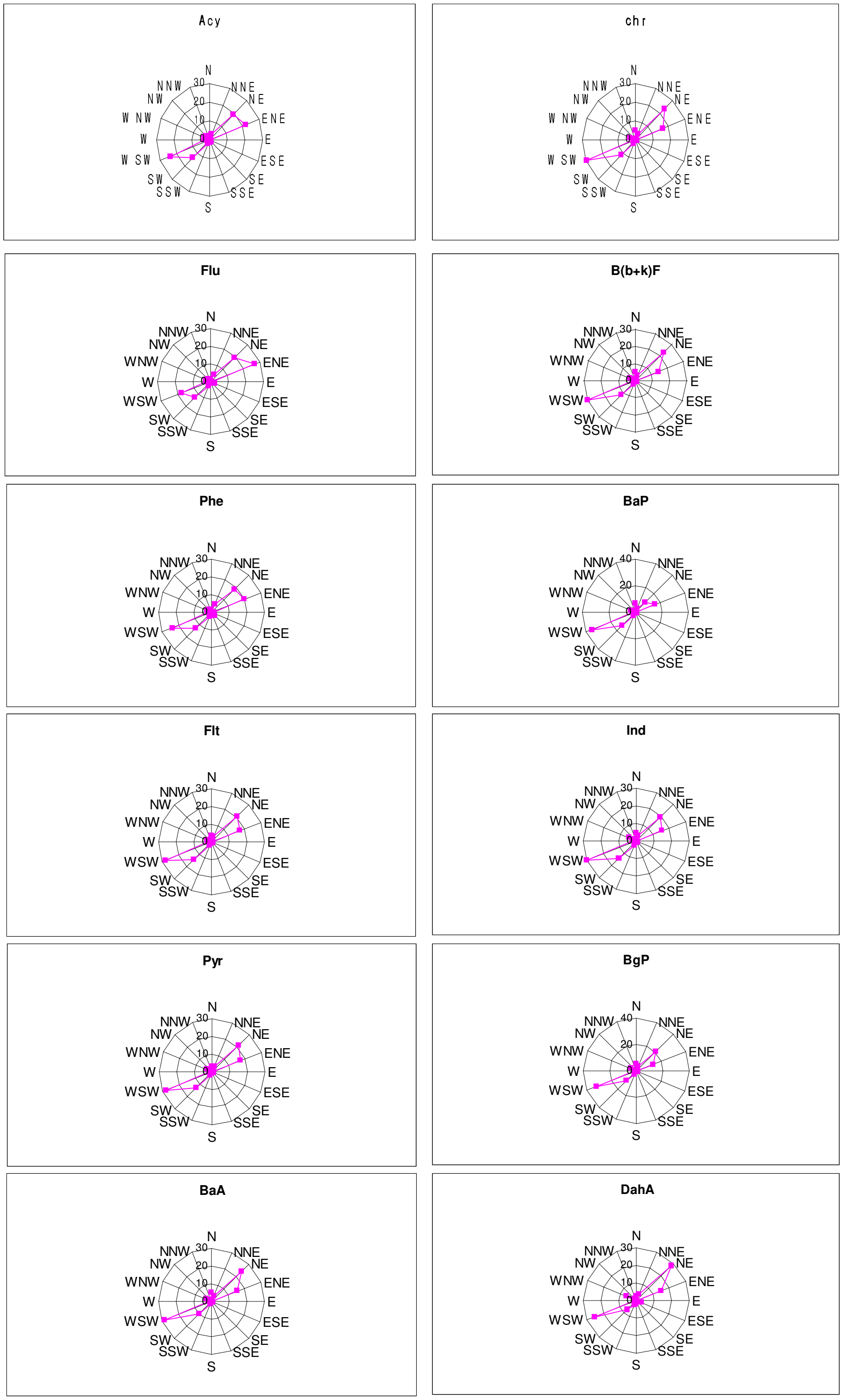
Figure 3.7. Continued

In order to investigate how different air masses affect the variability of PAHs, concentrations of total PAHs in each sector was calculated and it was found that 46 % of the PAHs come from NE sector, 28 percent from SW and 26 percent from mix sector. When air masses moving into the sampling site from the NE direction, pass over the heavily populated and polluted sites, Mamak, Tuzluçayır, Altındağ and Siteler. This sites are low income districts and polluted sites. Low quality coal combustion is common in winter times enhancing concentration of pollutants in this districts. It is likely that air masses incorporate locally emitted aerosols and carry them to the sampling site. On the other hand major industrial activities are located on west (Ostim) and SW (Şaşmaz, Cement Factory) of Ankara. It is very clear that pollutants emitted from that sites are carried by prevailing winds to other localities.

After having qualitative data we examined the whole data considering wind frequency and wind direction since the contribution of emissions from different parts of the city on observed concentrations of PAHs at the station site is not only a function of average concentrations in different wind sectors but also of the frequency of surface winds from different sectors. Frequency of wind flow from different sectors particularly important during days with low wind speed because the air mass over the city is fairly uniform and concentrations of PAHs do not change from one sector to another. Contribution of each wind sector on observed concentrations of measured parameters was determined by the procedure used by Vossler et al.(1989). In this procedure, the average wind sector frequency Fj for wind sector j was first calculated. The average fractional contribution to a parameter k from each wind sector j was then calculated using the following relation.

$$\frac{Ckj}{Ck} = \frac{1}{N} \sum \frac{Cik * Fj}{Ck}$$

where Fj is the wind frequency, Ckj is the average concentration of parameter k from wind sector j, Ck is the average concentration of the parameter k in all samples and Cik is the concentration of parameter k for the sampling period i. The percent concentrations of PAHs in each wind sector were shown in Figure 3.8. as pie charts and in Figure 3.9. as a bar graph..



Acy

chr

Flu

B(b+k)F

Phe

BaP

Flt

Ind

Pyr

BgP

BaA

DahA

Figure 3.8. Fractional contribution of PAHs from wind directions

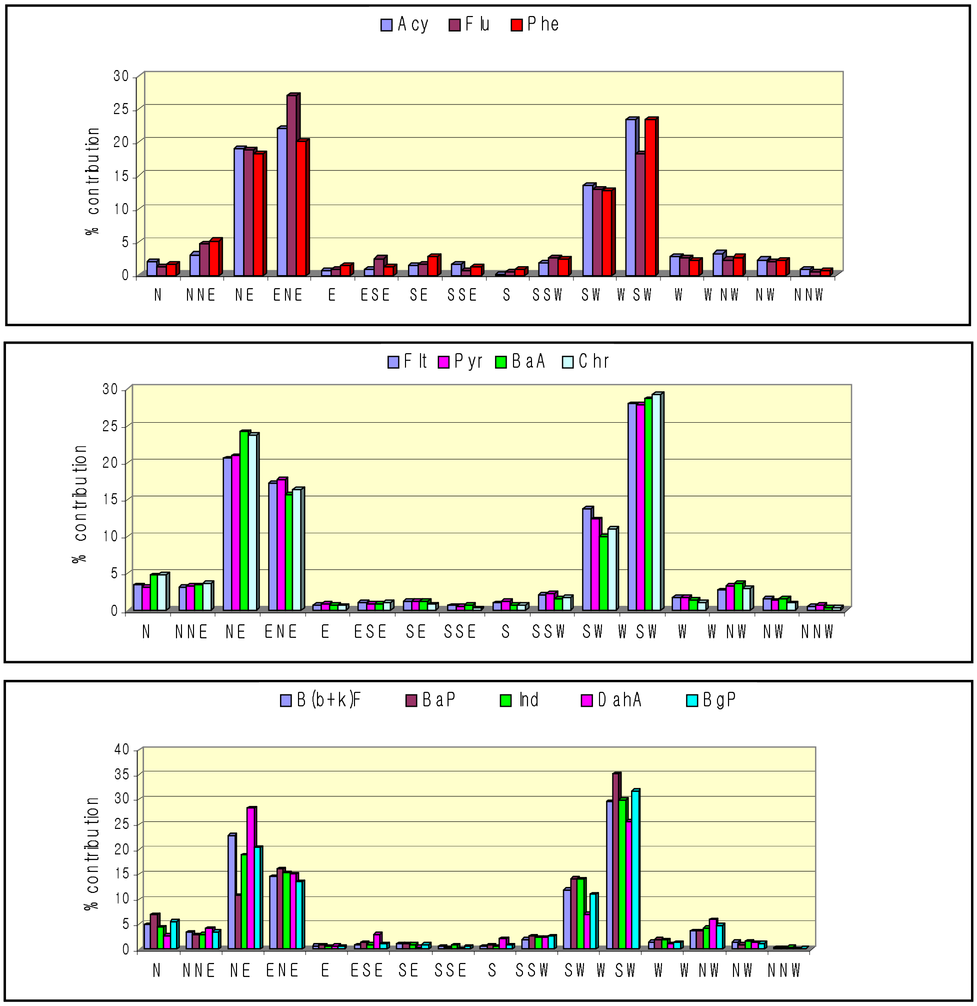


Figure 3.9. Percent Concentrations of PAHs in different wind sectors.

Since densely populated districts (which indicate high emission intensity) are located to the north, northeast and east of the sampling site, it is not unusual to observe high contributions of PAHs with winds from these sectors. Usually contributions of winds from NW and SW directions for all PAHs higher than other directions. Although the concentrations of PAHs are slightly higher in SW direction, there is not much difference between two sectors. Besides that topographical properties of Ankara is very suitable for the accumulation of pollutants in low altitude sites. Ankara is located on a shallow plate surrounded by the mountains. That is why pollutants can accumulate and stay long times in the lower troposphere.

3.1.4. Short-Term variations in PAH concentrations

Short term variations refer to the unusual event changes in the concentrations. Concentrations of all species increase by an order of magnitude or more and then decrease back to the pre-event levels within few days, generating episode. For the remote sites, long range transport might be the reason as well as meteorological changes on the observed changes. However for urban sites more likely reason for these fluctuations is the sudden changes of meteorological parameters like wind speed, wind direction or mixing height. Usually concentrations of pollutants increase as mixing height decrease. In Figures 3.10, 3.11, 3.12, time series plots of PAHs were plotted to illustrate their temporal variations. In Figure 3.10, 6 episodes identified for Phe and Flu; four in winter season, one in spring and one in summer season. In figure 3.11 (Flt, Pyr, BaA, Chr) 5 episodes having 1 in spring 3 in winter, and in Figure 3.12 (B(b+k)F, BaP, Ind, DahA, BgP) three episodes, all in winter period is detected. Most of the episodes appear in winter time.

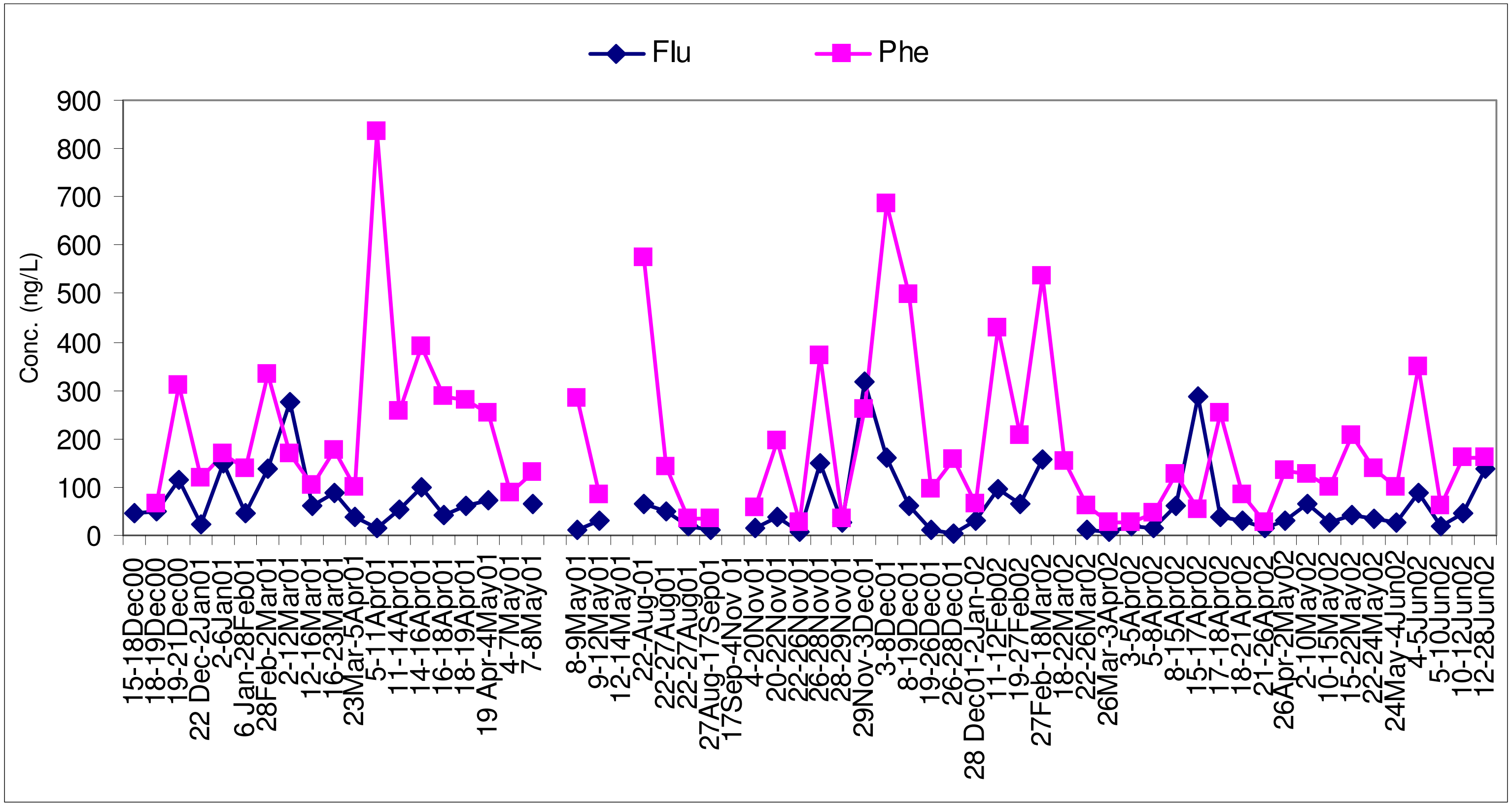


Figure 3.10. Temporal variation of Flu and Phe

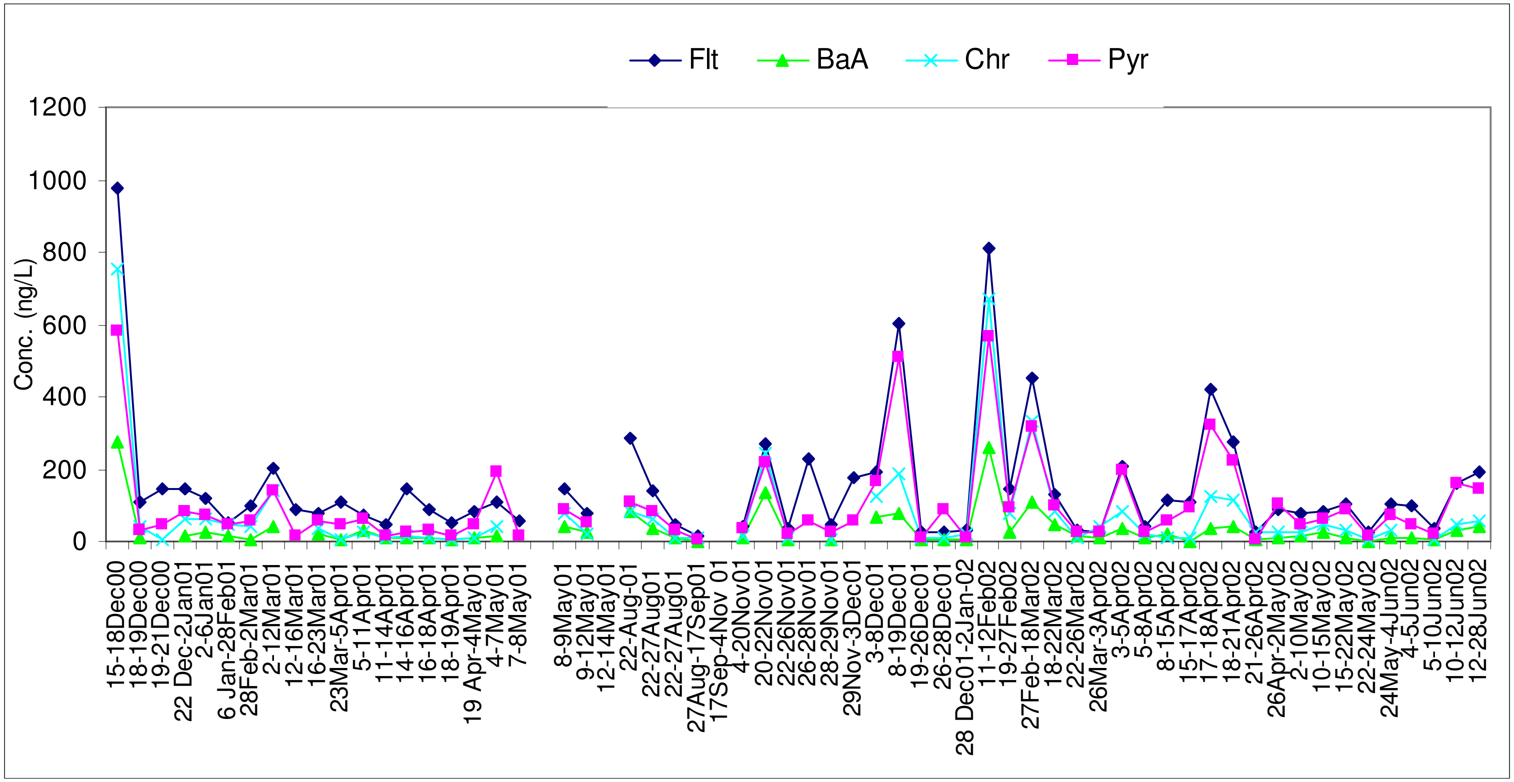


Figure 3.11. Temporal variation of Flt, BaA, Chr, Pyr

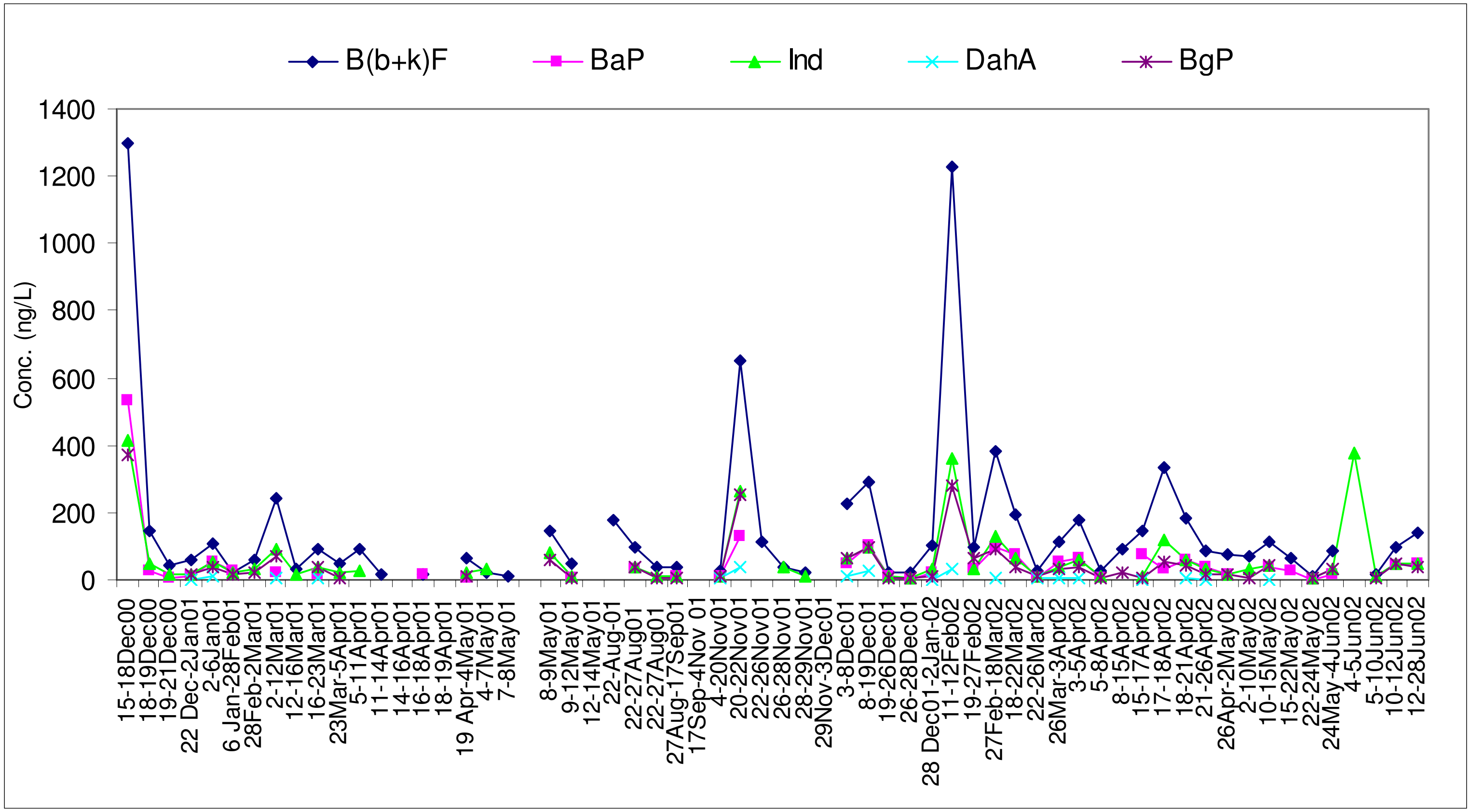


Figure 3.12. Temporal variations of B(B+k)F, BaP, Ind, BgP

3.1.5 Monthly variations of PAH concentrations

Monthly volume weighted average concentrations of PAHs were given in Figure 3.13. Although they were given in monthly averages, in some of the months there are two or three data points calculated because Ankara does not receive so much precipitation in summer and fall. For instance, September and August data is the average of only two rain events and there is no wet precipitation occurred in June, July and October 2000. The rest of the data is more representative considering of the given month.

When the Figure 3.13 is inspected, it can be seen that all the PAHs shows similar behaviour. Acy and Flu have higher concentrations in March 2001 and Apr 2002. In the second group of compounds (Phe, Flt, Pyr, BaA, Chr) higher concentrations appear in March and April 2001, December and February 2002. In the third group of compounds (B(b+k)F, BaP, DahA and BgP) December ad March 2001, February and April 2002 shows higher concentrations.

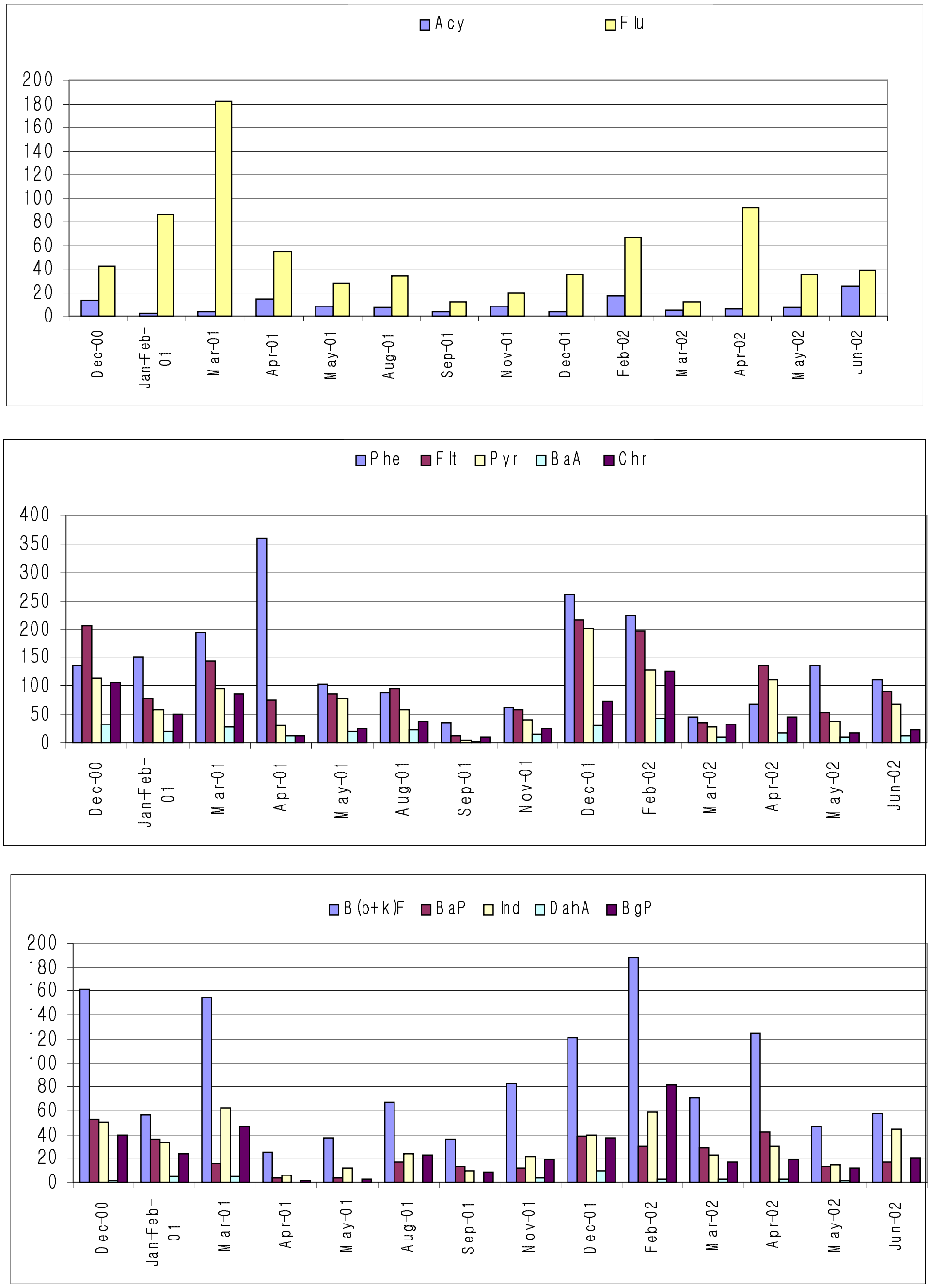


Figure 3.13. .Monthly volume weighted averages of measured PAHs

It has been mentioned before that temperature is an important factor for observed PAH concentrations. Temperature affect the partitioning behaviour of PAHs hence their gas and particle scavenging by wet deposition. On the other hand temperature is indirectly related with PAH emissions since heating activities increase in cold periods enhancing anthropogenic contribution to the observed concentrations. Average monthly temperatures and Total PAH concentrations were shown in Figure 3.14. When the ambient temperature increases, total PAH concentrations decrease.

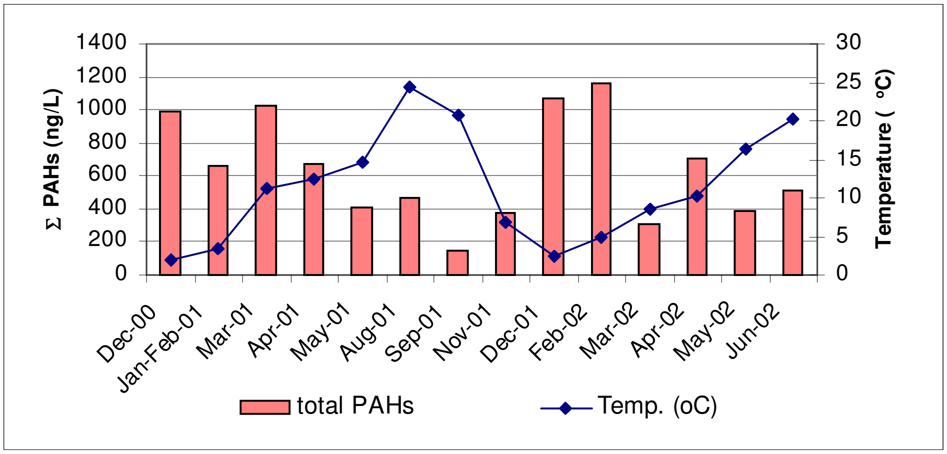


Figure 3.14. Temperature and concentration change in study period.

3.1.6. Seasonal variation of PAHs

Seasonal variation of PAHs investigated by many researchers (Golomb et al., 2001, Garban 2002, Manoli et al., 2000). Seasonal trends were observed having higher PAH concentrations in winter and lower in summer. Increasing combustion activities and decreasing mixing height thought to be important factors for the observed high concentrations of PAHs in winter period for most of the studies.

Urban and rural aerosol PAH concentrations were well studied compared to rain. Urban PAH concentrations can be 2 times higher than rural concentrations suggesting influence of local sources (Jaffrezo et al., 1993, Sicre et al., 1987, Greenberg et al., 1985) and for the urban atmospheres combustion activities are predominant sources for PAHs.

We have investigated the seasonal concentrations of PAHs in Figure 3.15. Rather than considering four seasons, we divided 12 months of the year into two as heating and nonheating season. The heating units in Ankara are allowed to operate only when the ambient temperature is below 15 ºC. Consequently, most of the residential units starts to operate at October 15 and stops at second half of the April.

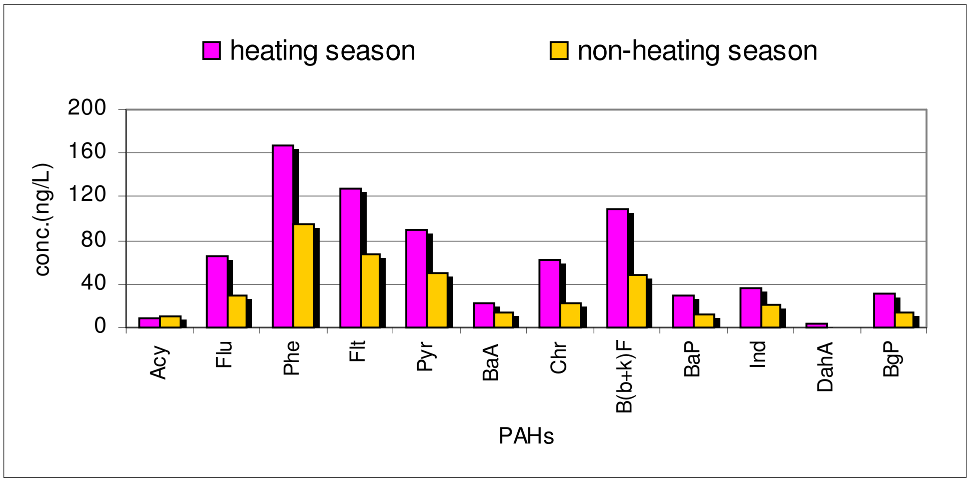


Figure 3.15. Volume weighted concentrations of PAHs in heating and non-heating season

Ankara is a typical urban city with a population of 4 Million. There is limited industrial activity in and around Ankara. Major sources of PAHs thought to be combustion activities resulting from domestic heating and traffic. Concentration profiles of PAHs in two periods were shown in Figure 3.15. It is very clear from figures that concentrations of PAHs are higher in winter months and lower in summer and spring. Although it is early to talk about the common sources of PAHs in Ankara, it seems that there are common sources of PAHs and it is more likely that combustion might be a dominant source of PAHs in Ankara.

Winter to summer ratios of PAHs were summarized in Table 3.4. As can be seen from Table, concentrations of PAHs in heating period are approximately 2 times higher than non-heating season. Similar trends were observed in most of the studies in literature (Golomb et al., 2001, Ollivon et al., 2002, Hart et al., 1993, Kiss et al., 2001, Garban et al., 2002).

Table 3.4. Winter to summer ratios of PAHs

	Winter/summer ratio
Acy	0.77
Flu	2.21
Phe	1.75
Flt	1.89
Pyr	1.82
BaA	1.71
Chr	2.75
B(b+k)F	2.23
BaP	2.27
Ind	1.7
DahA	
BgP	2.45

Several ratios were used to investigate the seasonal behavior and sources of PAHs in literature (Yunker et al.,2002, Park et al., 2002). Use of ratios will be discussed in more detail in the coming pages. However certain PAH ratios were calculated in winter and summer period to estimate the sources of PAHs. Corresponding values for certain sources collected from literature together with calculated ratios were given in Table 3.5.

Table 3.5. PAH ratios in winter and summer period.

	BaA/BaA+Chr	Ind(Ind+BgP)	Ind/BgP
winter	0.29	0.62	2.11
summer	0.37	0.42	1.07
Vehicles			
Gasoline	<0.5	0.05-0.22	0.4
Diesel	0.38	0.35	1
Coal	>0.5	0.57	

BaA/BaA+Chr is usually used to identify traffic emissions (Masclet et al., 1987) and it is very close to ratio for diesel emissions in summer however it indicates coal combustion in winter. Another ratio (Ind/Ind+BgP) is very close to diesel ratio in summer and close to coal ratio in winter. Third ratio (Ind/BgP) is also supports the previous findings indicating the influence of diesel emissions in summer period. It can be concluded from the ratio calculations that motor vehicle emissions are very dominant on the concentrations of PAHs observed in summer season in Ankara. On the other hand coal combustion is an important source for PAHs in winter. Besides combustion sources, meteorological conditions may also affect the concentrations of PAHs in winter time as mentioned before. Especially low mixing height and low solar radiation in winter season enhances the concentrations of PAHs.

3.1.7. Relation of PAH concentrations with amount of precipitation

Concentrations of PAHs expected to be related to the precipitation amount due to factors such as (1) diffusive aerosol capture, in which maximum diffusion of aerosol particle to the rain drops occur before it start raining. The rate of diffusion will decrease with time after it starts raining because number of particle in the atmosphere will decrease also. This will increase the concentrations of species in first few drops of the rain samples, (2) initial rain evaporation, in which the evaporation processes occur maximally in the cloud droplets before it start raining. As a result of evaporation the first few drops of the rain event will be more concentrated than the others, (3) Dilution of the chemical species by heavy rain. After a short time of raining, large fractions of the airborne particles will be washed out. Consequently, large rain volumes will dilute the concentrated first few drops (Al-Momani, 1995, Al-Momani et al., 1998, Pierson et al., 1987).

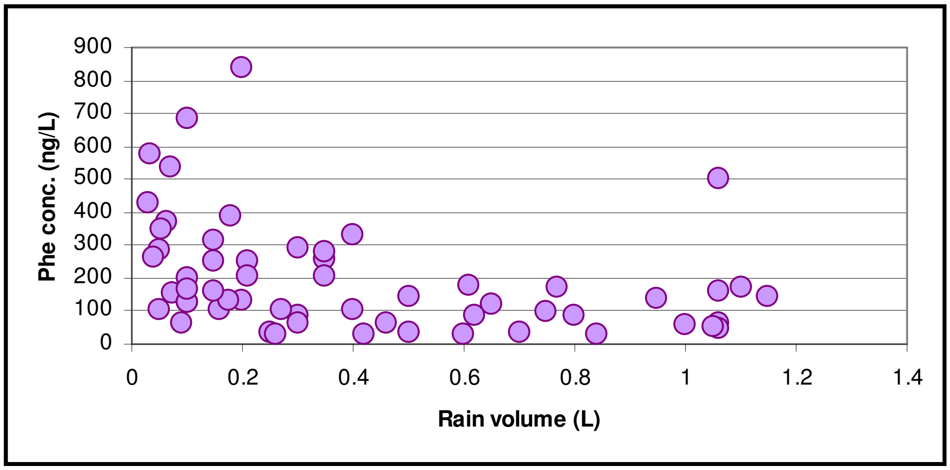


Figure 3.16. Concentration vs. rain volume for Phe

It has been observed that, concentrations of PAHs usually decrease with increasing rain volume (Figure 3.16). A relationship between concentrations of PAHs in precipitation and precipitation amount was also investigated. A linear regression analysis was performed using SGPLUS software in which dependent variable is concentration of PAH and independent variable is the amount of precipitation. In regression analysis Reciprocal X model was fitted where relation is described by a hyperbolic equation; $Y= a + b/ X$. In this equation, Y is the concentration of certain PAH, a and b are regression coefficients and X is the precipitation volume (Baeyens et al., 1990, Pierson et al., 1987). Regression coefficients, equations and degree of relationships were shown in Table 3.6. As depicted in Table 3.6 there is a statistically significant relation between amount of PAHs and volume of precipitation.

Table 3.6. Results of Regression analysis

PAHs	Reg. Coeff.	Regression equation	Relationship	Conf. level (%)
Acy	0.62	$Conc_{Acy}$= 6.75+23.3/volume	Exist	99
Ace	0.30	$Conc_{Ace}$= 16.9+12.8/volume	Exist	90
Flu	0.29	$Conc_{Flu}$= 48.3+33.9/volume	Exist	95
Phe	0.44	$Conc_{Phe}$= 129+129/volume	Exist	99
Ant	0.30	$Conc_{Ant}$= 32.6+167/volume	Exist	90
Flt	0.48	$Conc_{Flt}$= 74.4+145/volume	Exist	99
Pyr	0.34	$Conc_{Pyr}$= 62.2+73.9/volume	Exist	95
BaA	0.63	$Conc_{BaA}$= 4.78+61.7/volume	Exist	99
Chr	0.58	$Conc_{Chr}$= 6.74+154/volume	Exist	99
B(b+k)F	0.53	$Conc_{B(b+k)F}$= 34.9+234/volume	Exist	99
BaP	0.50	$Conc_{BaP}$= 3.49+130/volume	Exist	99
Ind	0.62	$Conc_{Ind}$= 10.4+108/volume	Exist	99
DahA	0.61	$Conc_{DahA}$= 5.78+9.96/volume	Exist	99
BgP	0.61	$Conc_{BgP}$= 10.3+90.2/volume	Exist	99

Regression plots of some of PAHs were shown in Figure 3.17. Plots drawn were fitted to reciprocal X model by SGPLUS software. Amount of precipitation in terms of mm were calculated using the sample volumes (ml) and collection area. It is clear from figure that as the amount of precipitation increase concentrations decrease. As a result, it can be said that amount of rain is an important factor on the concentrations of PAHs in deposition samples. However, there are other factors that may affect the concentration, such as, strength of the pollution source, origin of air masses and effect of meteorological parameters like wind speed and wind direction.

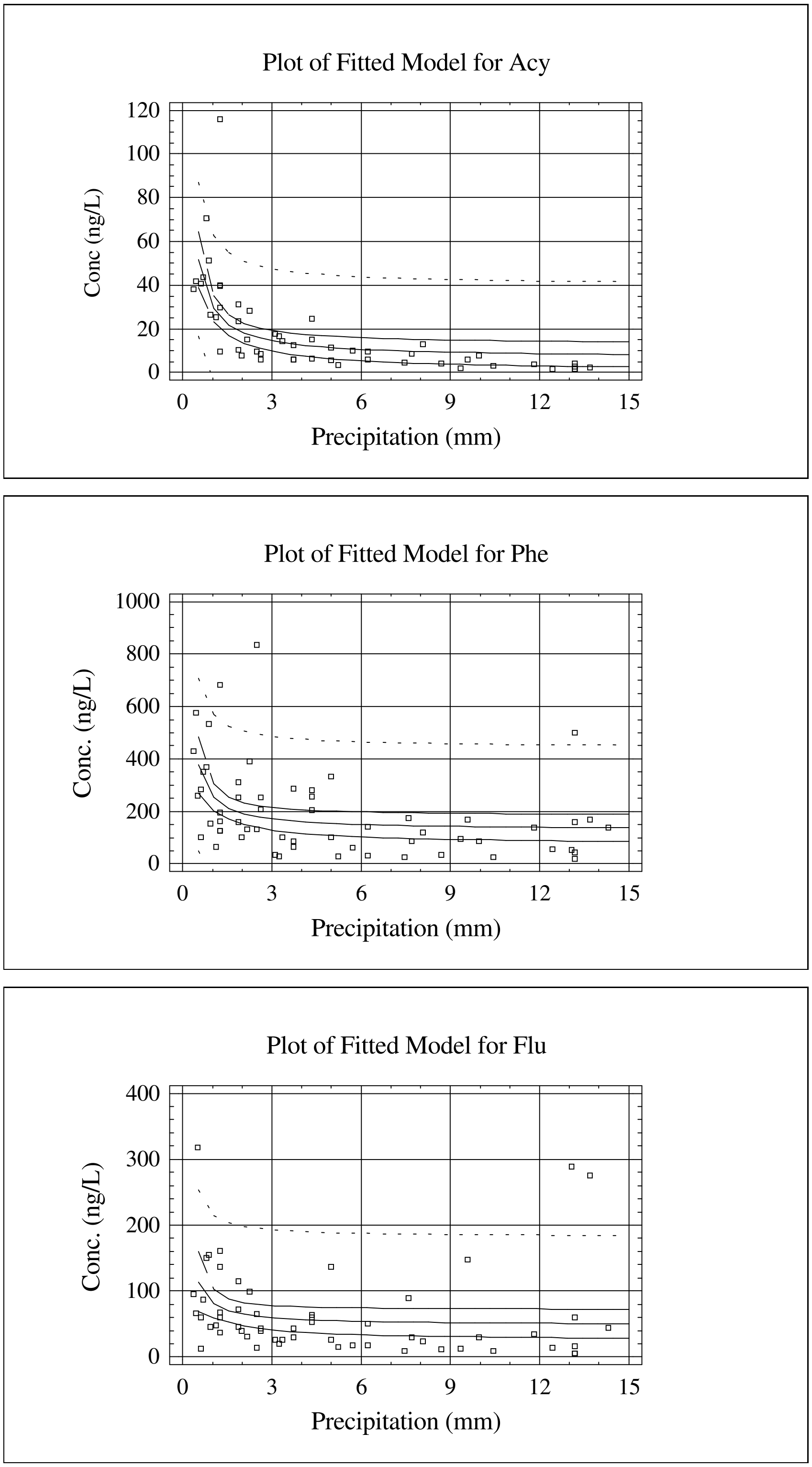


Figure 3.17. Fitted Regression plots for Acy, Phe and Flu.

3.1.8. Wet deposition fluxes

Atmospheric transport and deposition is an important pathway of persistent organic pollutants both far from and near source areas. Precipitation is one of the removal processes for air pollutants and thus responsible for fluxes of pollutants from air to soil. Extended knowledge has been gained concerning the the concentrations of inorganic elements in rain water, however less investigations have been carried out on organic pollutants.

It was our concern to calculate the total deposited amount of each PAH to the Ankara for the first time. This calculation enabled us to express quantitatively the deposited amount of each PAHs to the surface.

Wet deposition fluxes for PAHs were calculated by multiplying the measured concentrations with the volume of collected rain sample. This calculation can be performed for different sampling periods like monthly, seasonal or annual bases. This choice is determined by the sampling duration. Since we sampled the whole year, fluxes were calculate on an annual bases. Results of annual wet deposition fluxes of PAHs are shown in Figure 3.18. Ph, Flt, Pyr and B(b+k)F deposition of PAHs are higher than other PAHs .

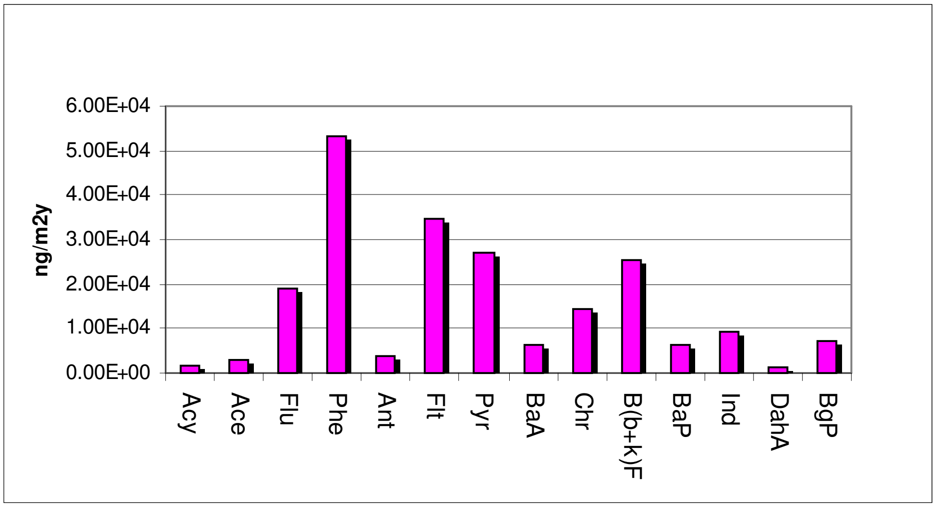
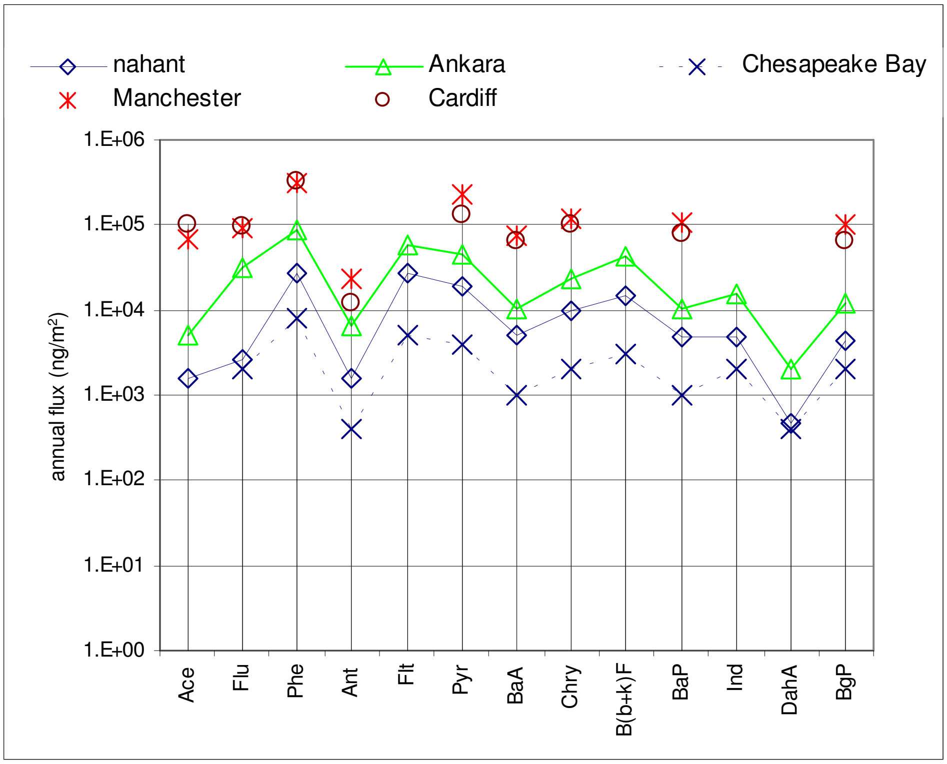


Figure 3.18. Annual wet deposition fluxes of PAHs in Ankara

We compared the PAH deposition fluxes in Ankara with literature values (Figure 3.19).



Nahant: Golomb et al.,1997, Machester and Cardiff:Halsall et al., 1997, Chesapeake Bay: Dickhut et al., 1995.

Figure 3.19. Comparison of deposition fluxes with literature.

Usually, deposition fluxes measured in Ankara are quite lower than Manchester and Cardiff, which are highly industrialized cities and reported fluxes are sum of wet and dry deposition measurements. On the other hand our results are comparable with the fluxes measured at Nahant, USA which is more similar site for our comparison considering site features and sampling methodology since they collected wet and dry deposition separately. Fluxes measured at Chesapeake Bay representing a rural location where wet only sampler was used for collection of samples are usually lower than Ankara. Besides the absolute values, the trend for fluxes are similar for all the sites. Highest fluxes were observed for Phe followed by Flt, Pyr and B(b+k)F.

We compared the annual wet deposition flux of total PAHs with Paris (Ollivon et al., 2002). Annual flux of total PAHs was reported as 234 $\mu g/m^2$ in Paris while it was 213 $\mu g/m^2$ for our data. Bulk deposition fluxes of total PAHs were reported as in the range of 74.7-393.6 $\mu g/m^2$ by Manoli et al., (2000) in Northern Greece and it was 334.8 $\mu g/m^2$ for Swedish west coast (Brorstrom-Lunden et al., 1994). Our results are in agreement with all studies.

3.1.9. Hierarchical Cluster Analysis

After we examine the trends in the data, as a next step we investigated the relations between measured parameters using statistical techniques. Statistical treatment of the data was achieved from simple to complicated methods. Therefore before the application of FA we first used cluster analyses in order to see related parameters.

Cluster analysis is an exploratory multivariate method that can be used to describe the relationships among variables. Classification of variables into groups using cluster analysis does not require a priori information on the number and the properties of the groups. Several mathematical criteria can be used to examine similarity (or difference) between variables and cases. The Euclidean distance defined as the length of the straight line between two points. Shorter the distance higher the similarity in between two variables. The initial outcome of hierarchical cluster analysis is a number of clusters that is equal to the number of variables. This process is repeated as many times as required to form a single cluster. The similarities among the clusters decrease as clusters are merged into a single group. In this work average methods used to link the clusters. Using different methods to measure similarities and link clusters and/or adding small perturbations can examine the sensitivity and accuracy of the cluster analysis (Kavouras et al., 2001). Graphical representation of the clustering procedure can be seen by drawing dendogram. The vertical axis is made up of the objects or individuals; the horizontal axis represents the number of clusters formed at each step of the clustering procedure. Also known as a Tree Graph. (STATGRAPH manual). Our solution for cluster analysis is shown in Figure 3.20.

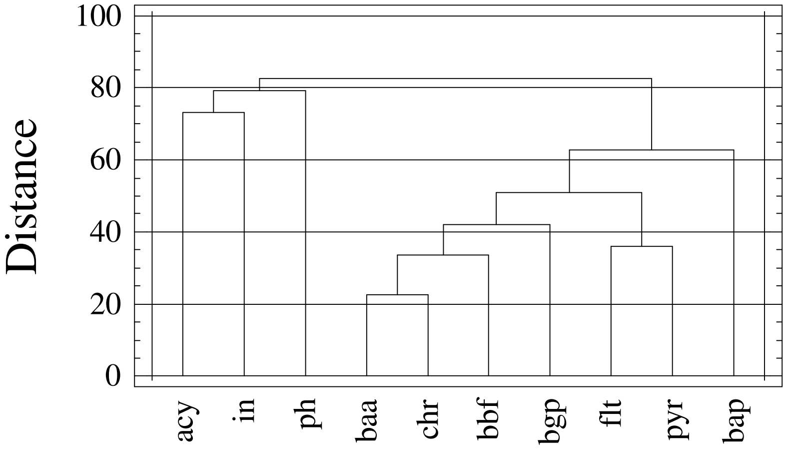


Figure 3.20. Hierarchical dendogram of PAHs

The closest couples are (Acy, Ind), (BaA, Chr) and (Pyr, Flt). Next similar parameters to these couples are Ph, BbF and BaP. We used this observation to interpret Factor analysis solutions. The above mentioned couples are also seen in different factors which will be discussed in the following pages.

3.1.10. Use of PAH ratios

In previous chapters we stated that measured PAH concentrations will be used for source identification and resolution of similar sources from each other. Source resolution is a major problem in source identification. Using trace metal data may not be enough to differentiate one similar source from another. That is why having PAH data is a big help to solve this problem. But bulk concentrations of PAHs alone may not be conservative as the concentration changes from one locality from another. So ratios are being used in literature (Yunker et al.,2002) to identify sources. For that reason before we discuss FA we looked at PAH ratios.

Certain PAH ratios have been used to characterize the sources of PAHs in literature (Simcik et al.,1999, Park et al., 2002). Some of PAH ratios collected from the literature and corresponding ratios obtained from our study was shown in Table 3.7. Geometric means and standard deviations (in parantheses) were provided for each ratio.

One of the most commonly used ratio is Flt/Flt+Pyr which is 0.61 in our study is close to coal combustion signal. Another ratio is BaP/BgP ratio which is 1.03 indicating again coal combustion signal. While BaA/BaA+chr ratio indicates coal as a source, BaA/chr ratio obtained in this study fall in between 0.28-1.2 indicating gasoline exhaust. Ind/BgP ratio is also very close to diesel emission signal. Out of 6 ratios, 4 indicates coal, one diesel and one gasoline as sources of PAHs in Ankara. Unfortunately there is not a good ratio for natural gas combustion. Based on the above ratios, Ankara is affected from different types of sources which are coal and traffic mainly.

Table 3.7. Diagnostic Ratios in atmospheric particles

	Flt/Flt+Pyr	BaP/BgP	BaA/BaA+Chr	BaA/Chr	Ind/BgP	Ind/Ind+BgP
This work	0.61 (0.11)	1.03 (1.95)	0.32 (0.1)	0.44 (0.34)	1.45 (0.98)	0.57 (0.1)
Vehicles		0.3-0.78 [a,b]		0.63[b]		
Gasoline exhaust	0.44[h]	0.3-0.4d	< 0.5 [h]	0.28-1.2 [c,d]	0.4[e]	0.09-0.22[h]
coal	> 0.5[h]	0.9-6.6[a]	> 0.5[h]	1-1.2 [c,f]		0.57[h]
Diesel	0.39[h]	0.46-0.8 [f]	0.38	0.17-0.36 [d,g]	1 [e]	0.35[h]

[a] Daisey et al., 1979
[b] Smith and Harrison, 1996
[c] Gschwend and Hites 1981
[d] Rogge et al., 1993
[e] Caricchia et al.,1999
[f] Masclet et al., 1987
[g] Khalili et al., 1995
[h] Yunker et al.,2002

3.1.11. Factor Analysis (FA)

Two approaches can be employed to evaluate source contributions from source emissions data and ambient monitoring data: source-oriented models and receptor oriented models. Source-oriented models use emissions data to predict pollutant concentrations at a specific receptor air monitoring locations. Receptor oriented models infer source contributions by determining the best-fit linear combination of emission source chemical composition profiles needed to reconstruct the measured chemical composition of ambient samples. Determination of source contributions from ambient monitoring data by receptor modeling techniques relies on the ability to characterize and distinquish differences in the chemical composition of different source types (Schauer et al., 1996)

Multivariate approaches are based on the idea that the time dependence of a chemical species at the receptor site will be the same for species from the same source. Species of similar variablity are grouped together in a number of factors that explain the variability of the data set (Liu et al., 2003).

The Factor analysis(FA) has been widely used in receptor modeling to identify source categories affecting a given receptor site. The purpose of FA is to represent the total variability of the original data in a minimum number of factors. Each factor is orthogonal to all others, which results in the smallest possible covariance. The first factor represents the weighted (factor loadings) linear combination of the original variables that account for the greatest variability. Each subsequent factor accounts for less variability than the previous. By critically evaluating the factor loadings, an estimate of the chemical source responsible for each factor can be made (Larsen and Baker., 2003).

Although there is no unambiguous criteria to determine the number of factors which should be retained, there are some general guidelines;

- the number of factors should be generally less than the number of variables
- Number of factors retained should explain a large fraction of the system variance and variances of individual species.
- Factors having eigen values larger than 1 should be retained. Factors with eigen values less than 1.0 do not have a significant contribution on the system variance.
- Factors retained should have some physical meaning (Al-Momani et al., 1995).

3.1.11.1. Treatment of Missing data

Before applying FA, whole data was inspected for missing values. Missing values are species having concentrations below detection limit. For instance, if there is a missing value in one of the samples for a certain variable, whole sample is discarded from the data set which may result loss of information. For that reason missing data treatment is very important especially in environmental studies considering very low levels of pollutants present in samples.

To obtain results that represents all data set, the missing data due to values below detection limits was replaced by the half of the detection limit. In literature many approaches were used to fill in the missing value. For instance a random value between zero and detection limit may be substituted or a stepwise regression can be used.

However number of missing values in data set is important. If a given species has too many missing data points (more than 10 %) it should be excluded from FA study. The underlying assumption in filling missing data is that, the missing values of every parameter are so small that, even if the generated numbers are too far from the true value, their influence on the FA are insignificant

Total wet deposition data generated from analyzing soluble plus insoluble fraction of rain water composition were used for FA. Factor analysis was performed using Statgraphic Plus package program. Ace and Ant were not included in FA since there were many missing values in data set for this two parameters. The Factor Analysis solution for rain data is given in Table 3.8.

Table 3.8. Varimax Rotated Factor Matrix

	Factor 1	Factor 2	Factor 3
Acy		0.39	0.68
BaA	0.52	0.73	
BaP	0.81		
B(b+k)F	0.79	0.31	
BgP	0.84		
Chr	0.80	0.45	
Flt	0.28	0.79	0.30
Ind			0.84
Phe		0.81	
Pyr	0.54	0.53	
Eigen value	4.35	1.8	1.07
Explained Variance	43.5	18.1	10.7
Total variance			72.3

Three factors extracted which explains 72.3 % of the total variance. First factor is highly loaded with high molecular weight PAHs. Most of the BaP, B(b+k)F and Chr variation is explained in this factor. Chr is usually emitted both from natural gas and diesel motor vehicles. BaP is emitted from non-catalyst and catalyst automobiles. Phenanthrene is not in the first factor indicating that this factor is not associated with unburned and residuel fossil fuels. Consequently this factor is attributed to the emissions from pyrolysis and combustion of fossil fuels. However, having higher contributions for most of the PAHs this factor is assigened as coal combustion

Second factor is highly loaded with BaA and moderately loaded with Chr suggesting that natural gas combustion might be source. High contribution from Phe is an indication of unburned fossil fuel and residual fossil fuels. As a result of above findings this factor is assigned is a mix of natural gas and unburned fossil fuel.

Factor 3 is highly loaded with Acy and Ind which are also in the same clusters in cluster analysis. Acy is another trace for vehicle emissions. Diesel emissions are characterized by high emissions of Ind also (Li et al., 1993). Based on that data and ratio calculations this factor is assigned to vehicle emissions.

All three factors indicate a kind of combustion source. Since PAH data are very limited and studies are new it is not easy to apportion factor composition for specific sources.

The clearest identified source is coal combustion as many PAHs are produced throughout coal combustion. The major difficulty in organic pollutants research is the limited data and experience. Research on organic pollutants is very new in the world and very first in Turkey. Use of PAH data alone have many difficulties since many PAHs are emitted from different sources and there is a great overlap of PAH profiles and sources. Therefore it has been suggested to use PAH data with trace metal data since trace metals have very well known sources.

3.2. Dry Deposition research

3.2.1. Overview of the produced data set and summary statistics for snow study

In this study surface snow samples were analyzed for 14 PAHs by Gas Chromatography-Mass Spectrometry. Some basic statistical calculations were shown in Table.3.9. Acenapthylene, Acenapthene and Anthracene concentrations were found to be under detection limit for most of the samples so they are not included in Table.

Table 3.9. Summary Statistics of PAHs (ng/L)

PAHs	N	Aritmetic mean	Geometric mean	Median	Minimum	Maximum
Fl	31	25.27± 40.56	9.792	13.08	0.157	189.9
Ph	25	77.40±76.30	42.68	54.30	2.549	281.3
Flt	38	78.55±77.97	42.81	45.94	3.232	289.7
Pyr	38	55.29±47.72	31.59	44.78	0.310	170.6
BaA	39	25.98±25.12	16.71	14.30	1.756	105.46
Chr	37	21.61±19.70	13.74	13.99	0.390	87.44
BbF	27	62.99±91.06	27.16	28.49	1.013	401.6
BaP	45	30.25±37.63	18.74	18.29	1.814	214.2
Ind	27	39.27±54.70	11.17	20.21	0.248	217.8
DahA	21	12.73±13.55	6.069	7.1	0.098	43.19
BgP	13	40.35±42.41	22.62	28.56	3.218	157.02

At first glance, standard deviations of measured species are very high indicating large variance of PAH concentrations from one site to another. Geometric mean and median values are very close for most of the PAHs and they are usually lower than arithmetic mean which is an indication of lognormal distribution.

Large differences between two mean values indicate that data is skewed toward right or left. Arithmetic mean that is significantly higher than geometric mean indicates skewness toward high values, whereas arithmetic mean that is lower than geometric mean indicates data that skewed toward low values. In environmental research right skewed data (skewed toward low values) is more common (Alagha, 2000).

Distributions of PAHs are skewed and skewness may indicate an anthropogenic input to snow surface. The frequency histogram for BaP, Fl, Flt and Pyr were shown in Figures 3.21, 3.22, 3.23, 3.24.

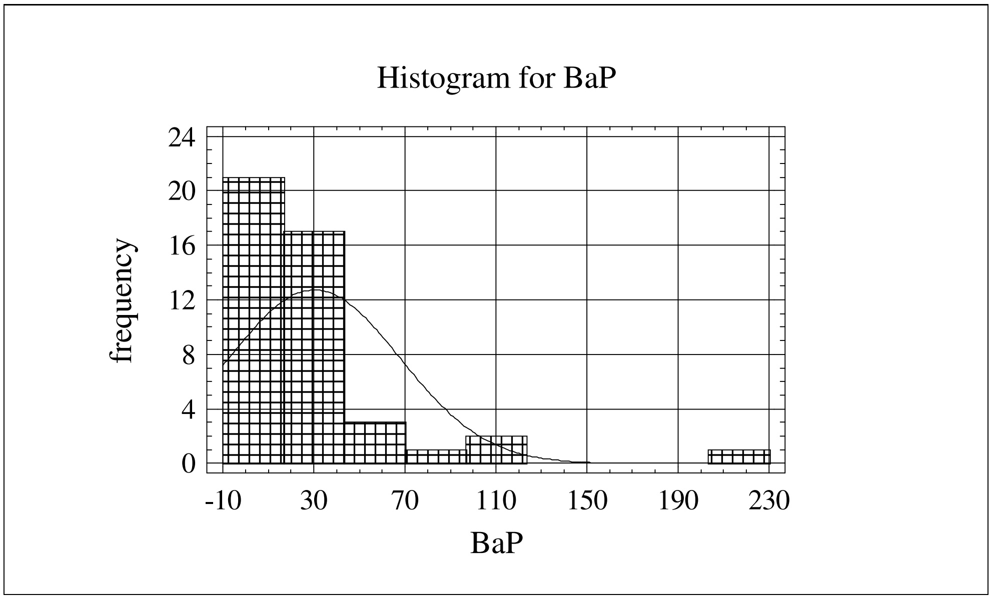


Figure 3.21 Frequency histogram for BaP

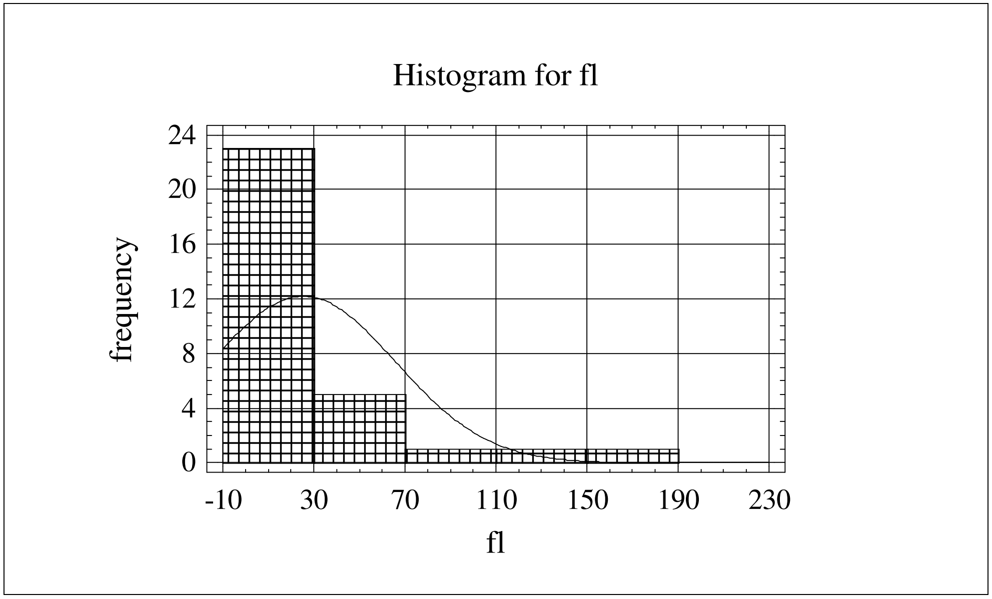


Figure 3.22. Frequency histogram for Fl

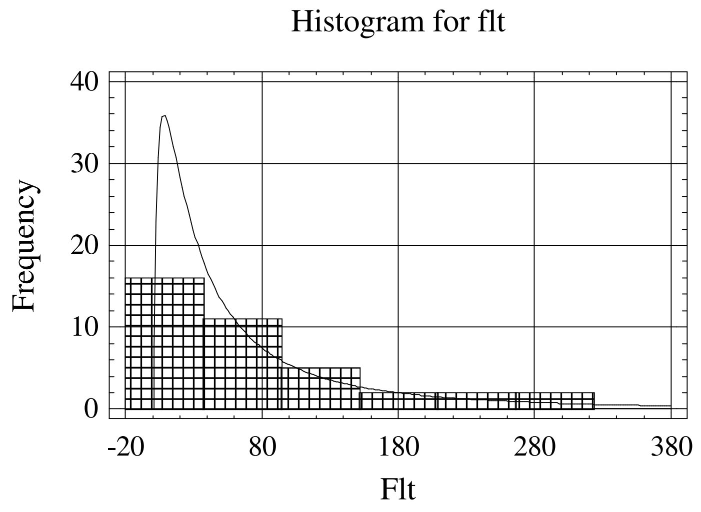


Figure 3. 23. Frequency histogram for Flt

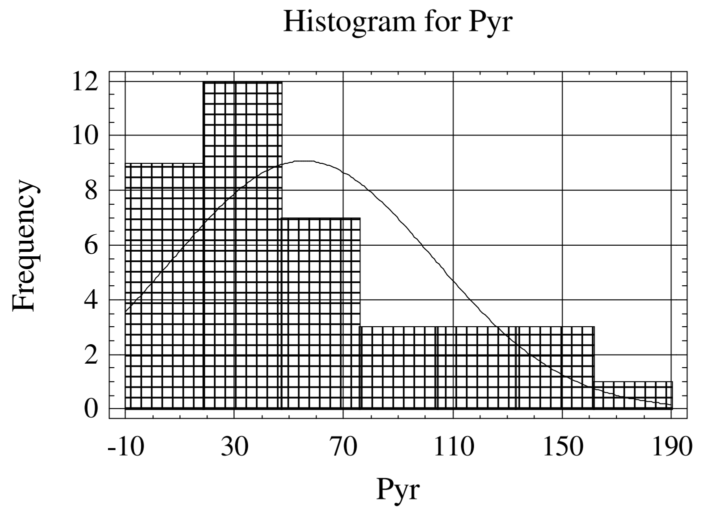


Figure 3.24 Frequency histogram for Pyr

3.2.2 Comparison of the fresh and aged snow PAH concentrations.

In order to evaluate dry deposition of PAHs on snow surface fresh snow PAH concentrations were compared with aged snow concentrations at the end of 15 days. Fresh snow samples were collected, immediately after the snowfall at December, 3 2000, from 3 points, including Organized industrial district (OSTIM), Kızılay and Sentepe, representing background concentrations, before any dry depositon takes place over the snow surface. The sampling points for fresh snow are depicted in Figure 3.25.

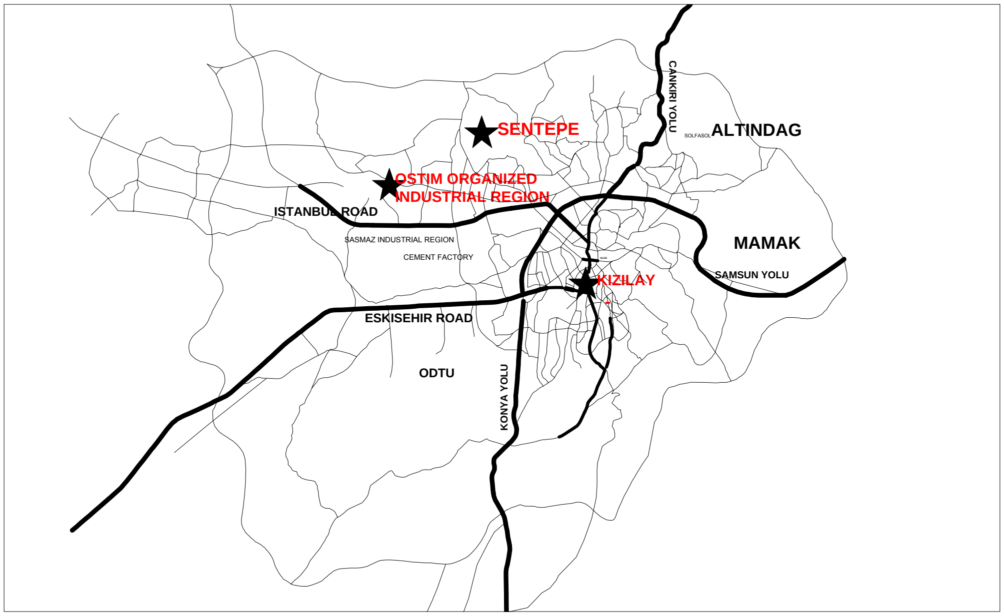


Figure 3.25. Sampling points

OSTIM, which is 20 km far from city center is an organized industrial region. There are large numbers of small and middle sized companies producing variety of products. The major activities are focused on production of dye, plastic, polyethylene pipes, asphalt, batteries and cleaning materials. Kızılay is the center of the city populated with government buildings and shopping centers. Sentepe site differs from other two sites in both social and physical characteristics. It is one of the lowest income districts in Ankara with insufficient infrastructure and unplanned cottage-like housing. Although natural gas is available at most districts in Ankara, main mode of heating in few low-income areas, such as Şentepe is still the poor quality coal (coal containing high S and refractory fractions) owing to relatively high cost of natural gas. The reference snow samples were collected far from the 4 major highways in the city, namely Eskisehir, Istanbul, Konya and Samsun roads. Samples were collected with the procedures described in section 2.1.2.1 and analyzed like regular samples as described in Section 2.5. Composition of fresh snow samples was depicted in Figure 3.26.

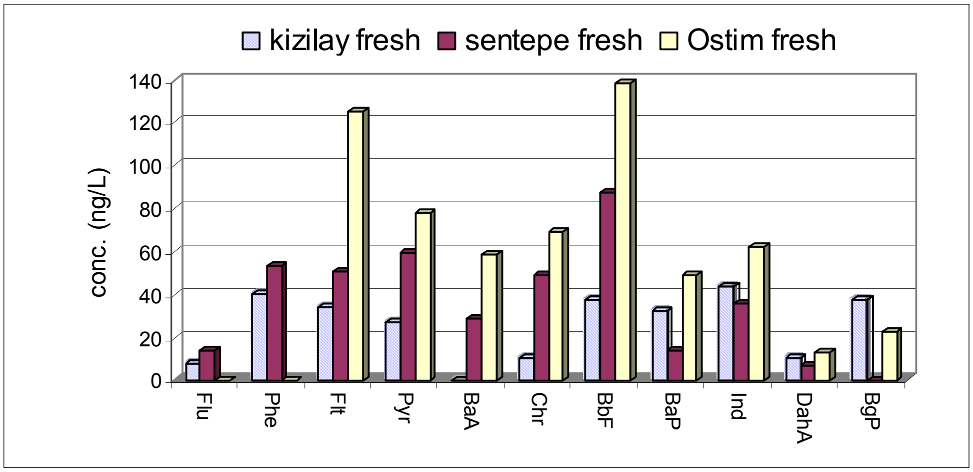


Figure 3.26. Comparison of fresh snow PAH concentrations

Difference of PAH concentrations in fresh snow samples can be explained as follows;

Snow is more efficient than rain at below cloud scavenging of particles because of the larger size and surface area of snow flakes. The particle scavenging efficiency of snow is related to crystalline shape. Snow flakes exhibit filtering effect on atmospheric particles and enhance the scavenging of small particles. Field experiments demonstrated that particle scavenging by snow is five time more efficient than rain (Sparmacher et al., 1993, Franz et al., 1998). Since all the samples were collected in the same day there will be no difference in pollutants concentrations scavenged by rain out process. However, local characteristics of the sites are very different, one might expect a difference in PAH concentrations in the first sampling, as a result of wash out process.

Usually fresh PAH concentrations in OSTIM snow were found to be higher than other two sites except for Flu, Phe and BgP (Figure 3.25). As pointed out before there are small scale industries operating at Ostim. The high PAH concentrations observed in Ostim are due to emissions from these industrial activities. Fresh-snow PAH concentrations measured at Şentepe site concentrations are lower than those observed at Ostim, but higher than the corresponding concentrations measured at Kızılay. Natural gas was used for heating purposes almost every parts of the Kızılay and it is reasonable to find lower concentrations. On the other hand, Sentepe PAH concentrations were higher than Kızılay which can be explained by the use of low quality coal for heating purposes in Şentepe.

Percent contributions each PAH to the total PAHs in fresh snow samples were shown in Figure 3.27. Phenanthrene, Fluoranthene and pyrene were found to be abundant in Kızılay and Sentepe. These three PAHs are always the most abundant in cities and populated rural areas, all over the world (Kiss et al., 2001; Simcik et al., 1999, Mastral et al., 1996). These two compounds were produced in combustion process (vehicular and industrial combustions, and biomass burning (Masclet et al., 2000). The dominance of these three compounds may be explained by their higher water solubility, higher emission rates and /or lower reactivity in the atmosphere (Kiss et al., 2001) It is quite usual to observe high percent contributions of BgP in Kızılay because it is a typical gasoline vehicle markers (Park et al., in press). BbF was found to be high in Sentepe and OSTIM.

Benzo(b)fluoranthene is most likely to result from the incomplete combustion of a variety of fuels including wood and fossil fuel which is used both sites for heating (EPA). Relatively high contribution of BaP was observed in Kızılay since automobile exhausts also emit high proportions of BaP (Oda et al., 2001) Benzo(g,h,i)perylene (BgP) contribution to total PAHs in Kızılay site is 14 % which is quite higher than Şentepe and Ostim. Indeno(1,2,3-cd)pyrene is also relatively higher in Kızılay and this compound is a diesel emissions marker (Li and Kamens, 1993, Harrison et al., 1996). This results support the idea that major source of pollution in Kızılay is traffic. Phenanthrene concentration in Ostim was found to be under detection limit but Flt contribution is very high.

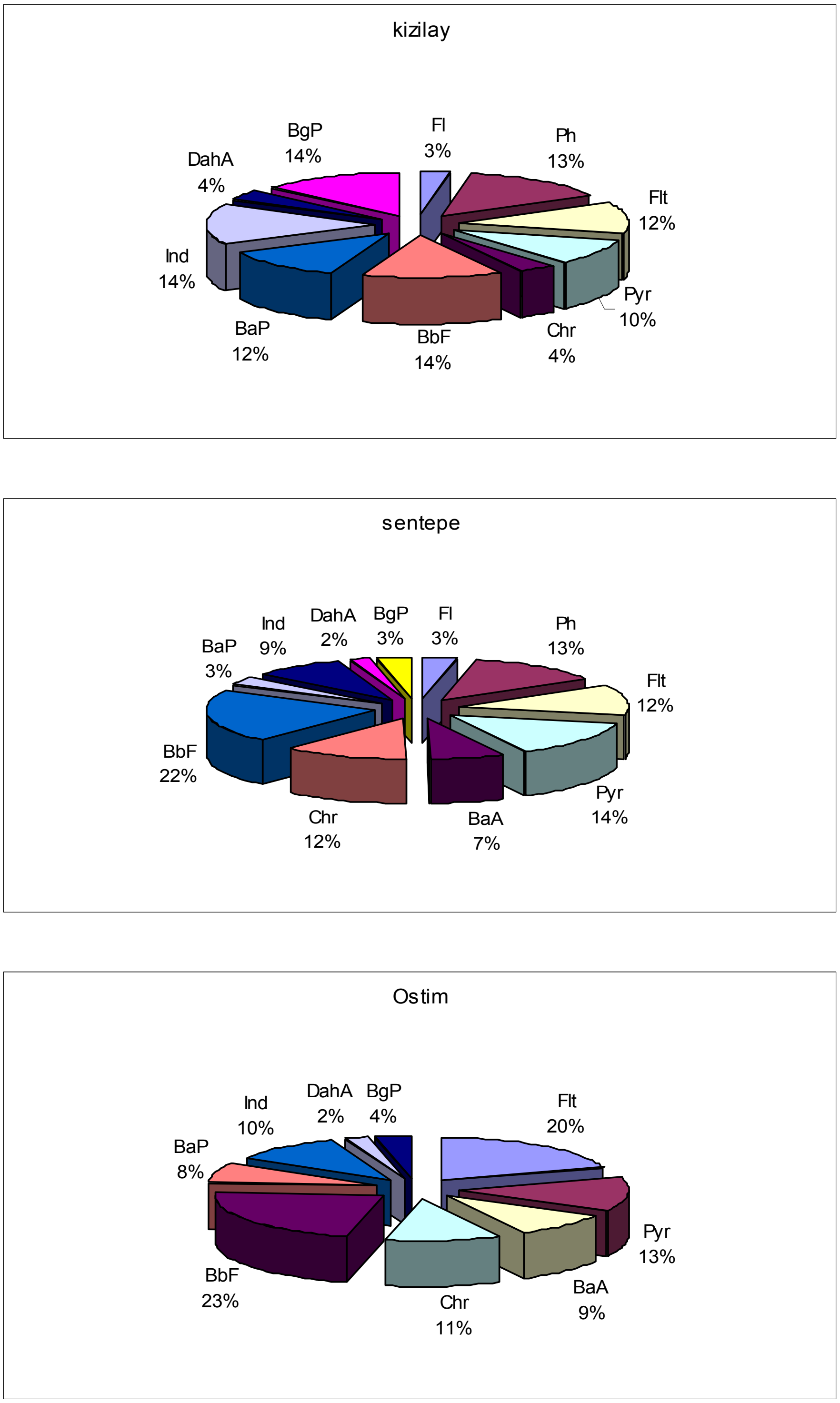


Figure 3.27. Percent contributions of individual PAHs in fresh snow samples.

The results demonstrated that concentrations of PAHs are not homogeneously distributed over the measurement area. The variability in PAH concentrations probably originates from washout process. The concentrations of PAHs in deposited snow originates from two sources; (1) PAHs that are incorporated into snow during transport of air masses or clouds to the region and that deposits when the cloud snows. This component which represent in-cloud or rainout (snow out in our case) are expected to be fairly uniform throughout Ankara, because air masses during their long range transport to the region are expected to mix well and form a uniform composition in whole cloud (2) PAHs that are washed out during snow. This is a local component and can be highly variable, because the washout component strongly depends on the atmospheric PAH concentrations at different parts of the city, which can be highly variable.

However, the important point is the differences between the PAH concentrations in fresh snow and concentrations after 15 days during which dry deposition occurs, if these differences are large enough, fresh snow concentrations can be subtracted from all samples no matter how variable they are and such subtraction would not cause a significant error in dry deposition estimates. However, if the PAH concentrations are not significantly different between fresh and aged snow, then subtraction of an average value of a highly variable values would cause large uncertainty in dry estimated dry deposition values.

Second sampling campaign was conducted 15 days later from 50 points, which were homogeneously distributed throughout the city. Reference points were also included in the second sampling to monitor the change in PAH concentrations due to dry deposition in 2 weeks. The key factor in this study, for determination of dry deposition of PAHs on snow surface is presence of no wet precipitation event in between two sampling campaigns. Luckly, no rain or snow event occured in that time period. Concentration profiles of each PAH at each site for 15 days period was shown in Figure 3.28.

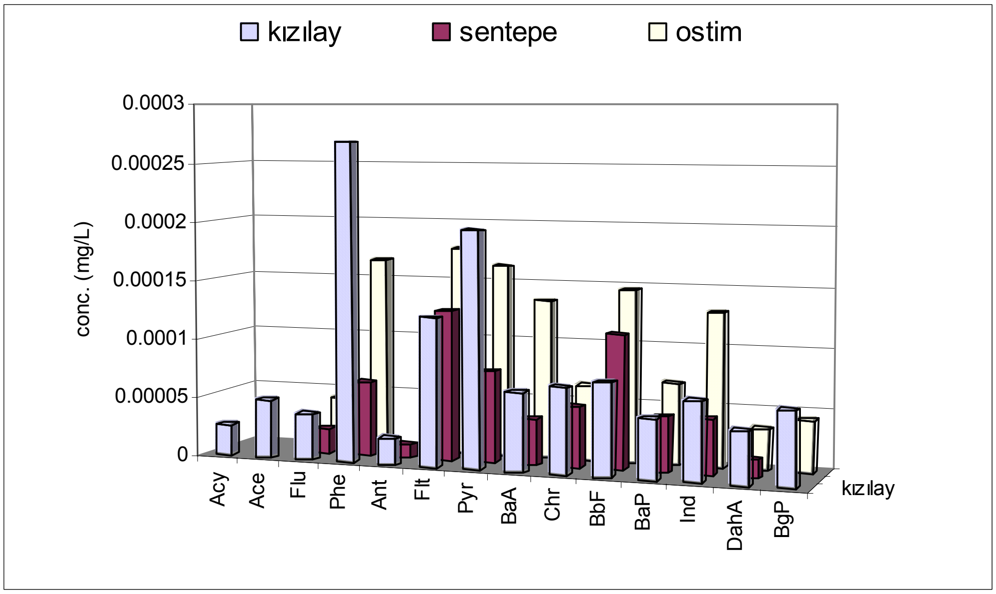


Figure 3.28. Concentrations of PAHs after 15 days

In Sentepe site Acy and Ace were not detected. This two compounds are the more volatile PAHs among 16 PAHs and volatility losses during sampling and extraction has been mentioned in literature (Kendall et al., 2001).

Percent contributions of each PAH to the total concentration for aged snow samples were shown in Figure 3.29. As it can be seen from 3.27 and 3.29 PAH profiles has changed at the end of 15 days indicating dry deposition of PAH from different sources.

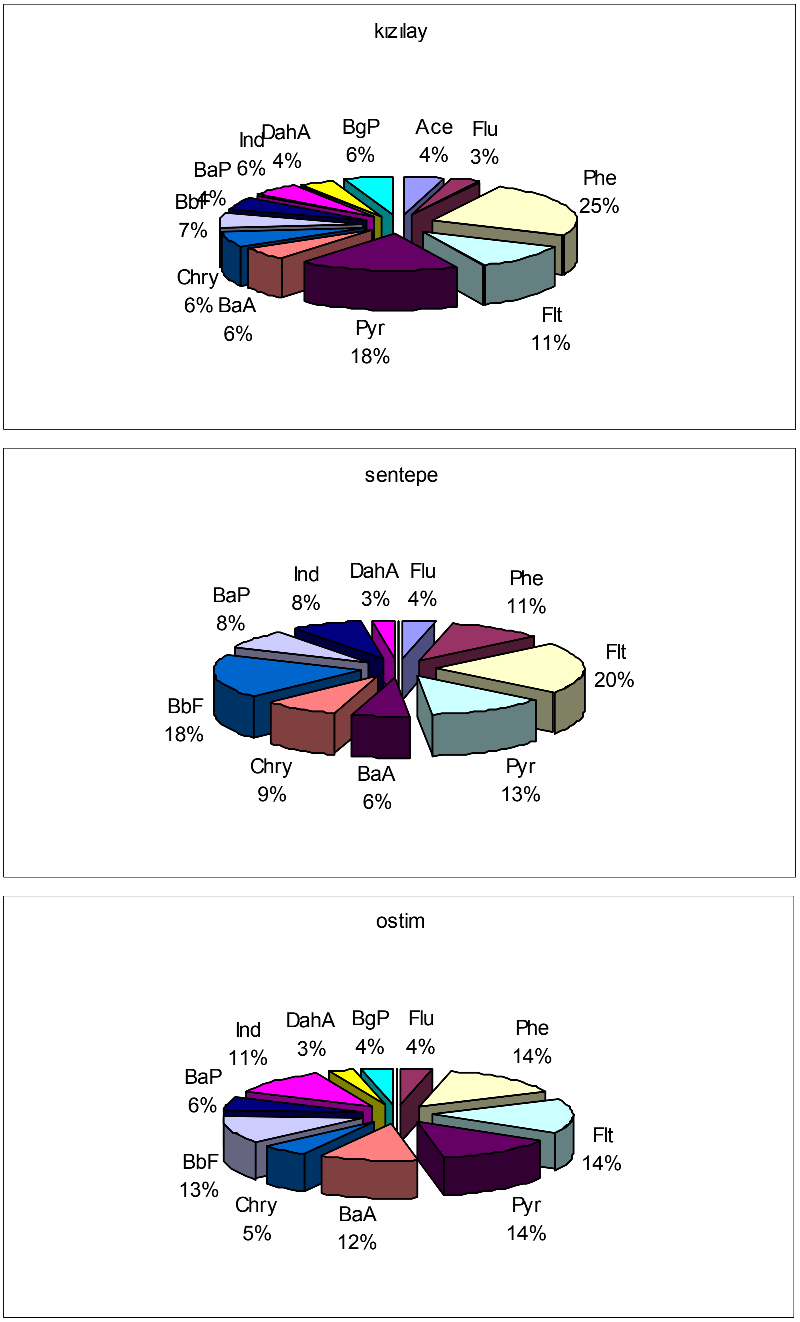


Figure 3.29. Percent contributions of individual PAHs in aged snow samples.

Usually phenanthrene, fluoranthene and pyrene, which are well-known marker species for coal combustion (Harrison et al., 1996), have the highest concentrations. Although seems attractive, identification of sources from high concentrations of specific PAH compounds is not possible, because some of these compounds are emitted to atmosphere from more than one source. For example, concentrations of fluoranthene, which is known to be high in emissions from coal combustion, is also is also high in emissions from combustion of natural gas (together with other PAHs, such as Benzo(a)anthracene, chrysene and pyrene) (Rogge et al., 1993).

3.2.3. Enrichment Ratios

Concentration changes of each PAH at the end of 2 weeks were shown separately in Figure 3.30. Concentrations were transferred to logarithms and put in Y axes. Some of the compounds were not shown in Figures because they were below the detection limit. In Kızılay site Acy, Ace, Ant and BaA concentrations in fresh snow was below detection limit. In Sentepe site, Acy, Ace, and BgP concentrations in both fresh and aged snow and Ant in fresh snow were below detection limit. In Ostim site, Acy, Ace in both fresh and aged snow, Flu and Phe in fresh snow were also found to be below detection limit. Concentrations of all PAHs were increased at the end of 15 days period.

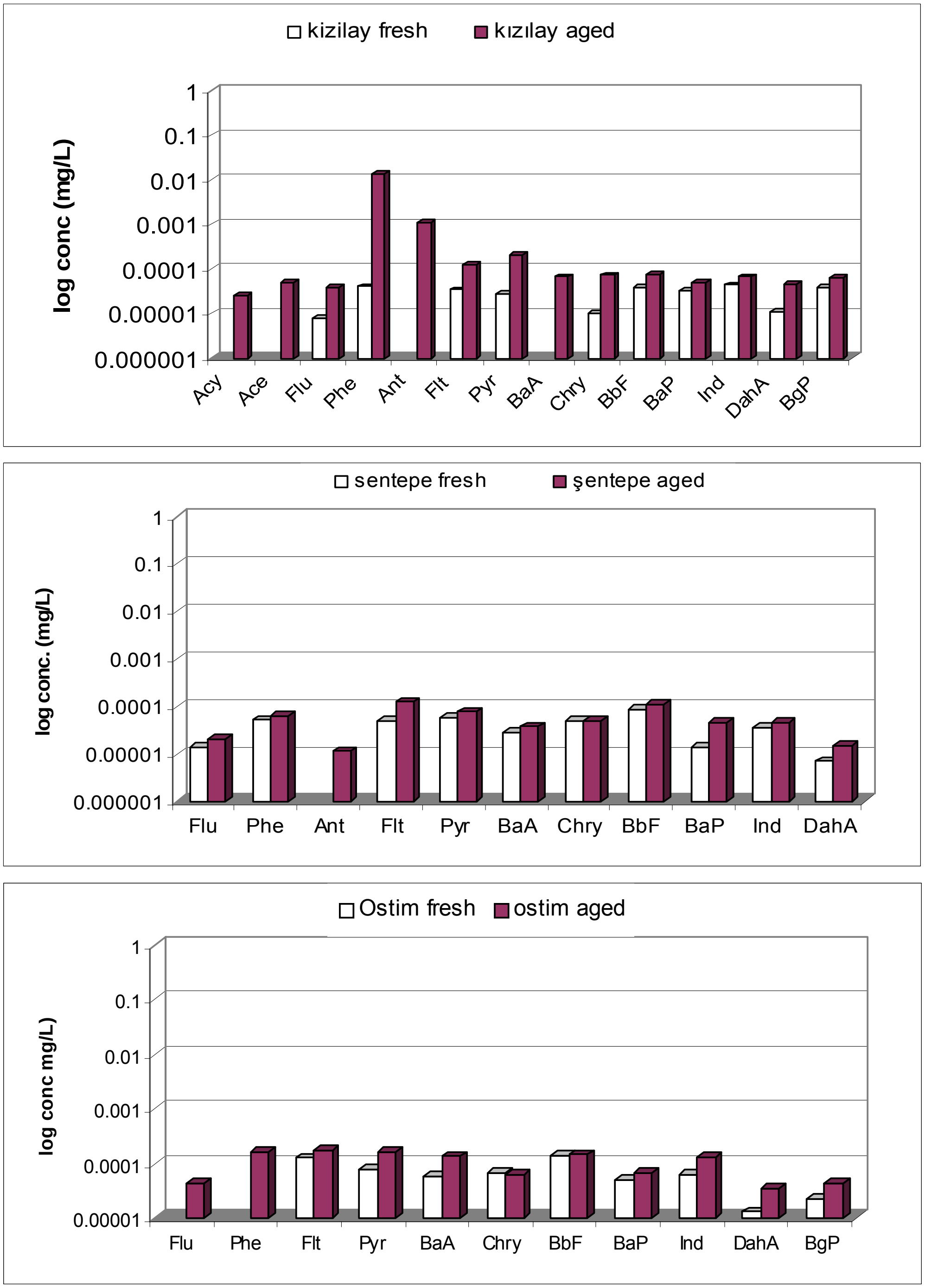


Figure 3.30. Concentration changes of PAHs in two sampling campaigns for all sites

Enrichment ratios for each PAH at each site was shown in Figure 3.31, Enrichment ratio was defined as;

$$ER_x = (C_x)_{\text{aged snow}}/(C_x)_{\text{fresh snow}}$$

Where $(C_x)_{\text{aged snow}}$ is the concentrations of PAH at the end of 15-day period and $(C_x)_{\text{fresh snow}}$ is the corresponding concentration in fresh snow.

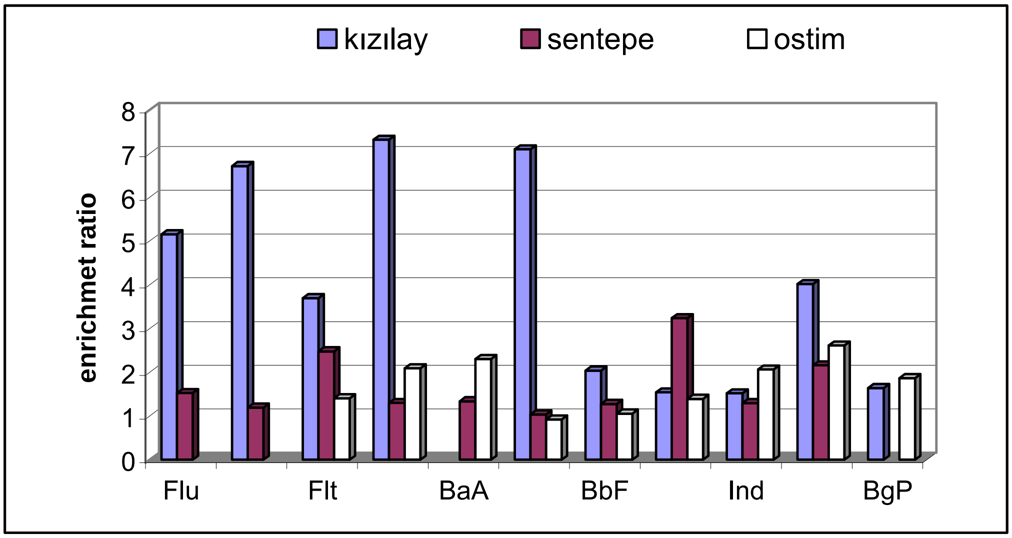


Figure 3.31. Enrichment ratios of PAHs in three sites

Enrichment ratios for Fl, Ph and BgP for Ostim and BaA for Kızılay sites were not calculated because the concentrations of these PAHs were below detection limit in fresh snow samples. All PAHs, except for BaP, Ind and BgP, were more enriched at Kızılay. The difference between Kızılay and other two sites were particularly high for Flu, Phe, Pyr, Chry and less pronounced for Flf, BbF and DahA. Enrichment ratios were comparable for BbF, Ind and BgP at all three sites. The BaP, on the other hand was more enriched at Şentepe.

There are two main reasons for high enrichments of majority of the PAHs at Kızılay, compared to other two sites. One of the reasons is the high emissions of motor vehicle and natural gas-related PAHs at the Kızılay. Kızılay is the most densely populated district in the city. It is also the business center and has the heaviest traffic load. The heating in Kızılay is mostly with natural gas combustion with negligibly small coal combustion. As a result of these factors, one would expect to have high emissions of traffic and natural coal combustion related PAHs at Kızılay.

The concentration ratios of both Flt/(Flt+Pyr) and Flt/Pyr are used markers to discriminate between gasoline and coal combustion in literature (Rogge et al., 1993, Yunker et al., 2002). These ratios will be discussed in more detail later in the text, but briefly, the Flt/(Flt+Pyr) > 0.5 is suggested to demonstrate the dominant coal combustion contribution on observed PAH levels, whereas ratios <0.5 probably originates from gasoline combustion (Li and Kamens, 1993, Yunker et al., 2002). Similarly, Flt/Pyr ratio close to 0.6 suggested indicating gasoline combustion. Higher ratios are indication of coal combustion (Müller et at., 1998).

The Flt/(Flt+Pyr) and Flt/Pyr ratios in aged snow samples at Kızılay, Şentepe and Ostim are given in Table 3.10.

Table 3.10. PAH ratios in aged snow samples

	Flt/(Flt+Pyr)	Flt/Pyr
Kızılay	0.4	0.6
Sentepe	0.5	1.6
Ostim	0.6	1.6

The Flt/(Flt+Pyr)and Flt/Pyr ratios in aged snow at the Kızılay station are 0.4 and 0.6, respectively. Both of them indicate that emissions from motor vehicles is the main source PAH observed at Kızılay region as expected. The Flt/(Flt+Pyr) ratios calculated for Şentepe and Ostim, are 0.5 and 0.6, and FLT/PYR at the same sites are 1.6 and 1.6, respectively. Both Flt/(Flt+Pyr) and

Flt/Pyr ratios at Şentepe and Ostim aged snow samples indicate that the coal combustion is the main source of PAHS measured in these districts. This observation is consistent with the demographic structure of the Şentepe and Ostim. Şentepe is one of the lowest income districts in the city and main mode of heating is still the combustion of coal. OSTIM, on the other hand is an industrial area. Although, natural gas is supplied to the industries, widespread coal, due to its cheaper price, use is well known.

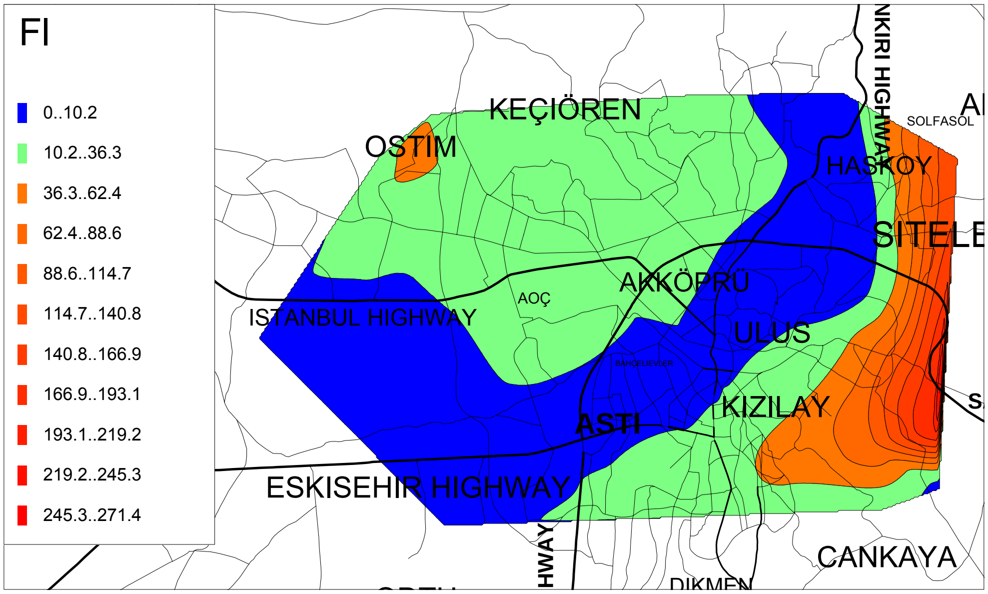
The Flt/(Flt+Pyr)and Flt/Pyr ratios in Kızılay fresh and aged snow samples are 0.6 and 1.3, respectively. These ratios indicate dominant coal source for PAH concentrations at Kızılay fresh snow samples, which is different from gasoline combustion source attributed based on the same ratios in aged snow samples at the same site. The difference observed in Flt/(Flt+Pyr)and Flt/Pyr ratios in fresh and aged snow samples at Kızılay indicates that the PAHs in falling snow is not directly related to what is being emitted to atmosphere at that particular region. Some of the PAHs in falling snow flakes are due to washout process and should be related to local emissions, but some, on the other hand, are due to rain out and represent profiles at the locations where they are incorporated into cloud. Obviously, this coal signature that exists in the falling snow flakes is modified by the dry deposited PAHs during 15 days of aging and PAH profiles after 15 days represent local emissions which is expected to be from motor vehicles at Kızılay. The Flt/(Flt+Pyr) and Flt/Pyr ratios calculated after subtracting concentrations of these PAHs in fresh snow from concentrations measured in aged snow (represents only dry deposition without the influence of wet deposition) are 0.3 and 0.5, respectively. Both of these ratios suggest gasoline influenced PAH profile as obtained from ratios calculated without subtraction. The similarity in the ratios both with and without subtracting fresh snow concentrations is due to large difference between the concentrations measured in fresh and aged snow samples.

At Şentepe and OSTİM stations calculations performed both with and without subtraction of fresh snow concentrations suggested that PAH observed in these stations (both in fresh and aged snow samples) are dominated by combustion sources, rather than traffic.

Another likely reason for high enrichments of at least some of the PAHs observed at Kızılay is the strong contribution of road dust (or mud in this case) on aged snow concentrations. Since the emissions of all pollutants from motor vehicles occurs at very low level (typically 50 cm from the ground), they quickly sediment out at the road or sticks on soil particles on the road surface. Consequently, soil particles on the road surface, which is called road dust, are highly enriched in PAHs and other pollutants such as Pb. If road dust particles find their way to collected samples, one can expect extremely high concentrations of traffic related PAH compounds. In fresh snow samples the contribution of road dust on samples, including the one collected at Kızılay is negligible, because all the roads are covered with snow and resuspension of dust particles is not possible. Within a day after the snow, the roads are salted and snow melted forming slurry of road dust in melted snow and remained in this form throughout the 15 day period. Normally road dust in such slurry can not be resuspended by wind action, but some road dust become airborne by physical action of passing vehicles. This can be visually seen as dirt on the snow around the roads. Some of these resuspended particles (or droplets) are small enough to reach the sampling point at Kızılay. This mechanism is not as important at Şentepe and Ostim, because the lack of heavy traffic around those stations.

3.2.4. Construction of pollution maps for PAHs

Dry deposition pollution maps of PAHs were constructed using a Geographical Information Systems (GIS) software, MAPInfo 5.5. Dry deposition amounts were determined by subtracting the fresh snow PAH concentrations from aged snow concentrations. Distribution maps, showing spatial distributions of PAHs were drawn using “triangulation with smoothing” interpolation approach. Interpolation is the procedure used to predict the unknown values with the help of known values at neighboring points. Triangulation is a process of grid generation that is most commonly applied to data that requires no regional averaging, such as elevation readings. Distribution maps were prepared for most of the PAHs, except for Ace, Acy, BgP and DahA. Distribution patterns were not calculated for these four compounds, because data were below detection limit in large number of sampling points. Distribution maps for each PAH were shown in following Figures.



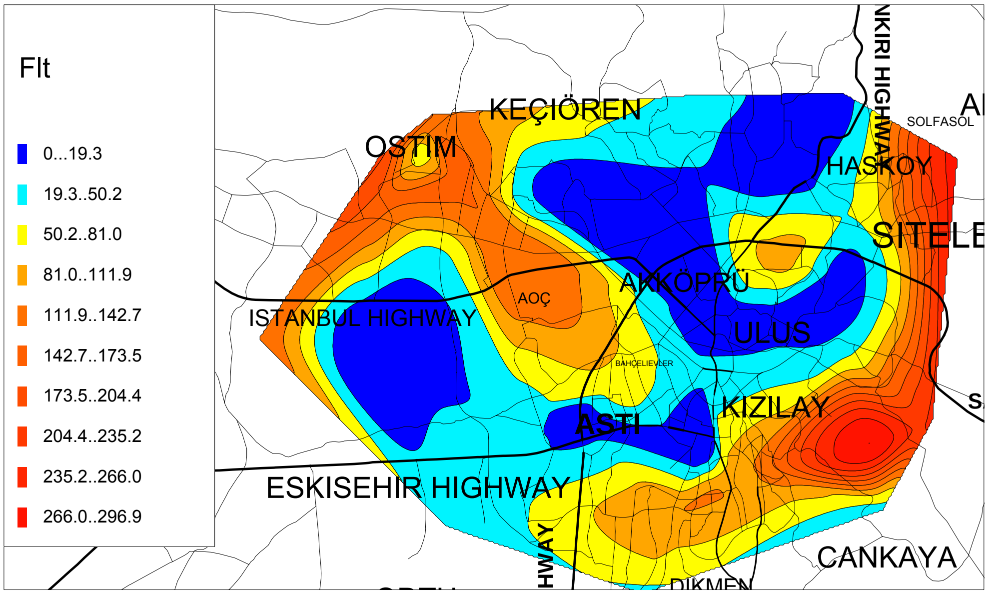


Figure 3.32.Pollution maps of Fl and Flt

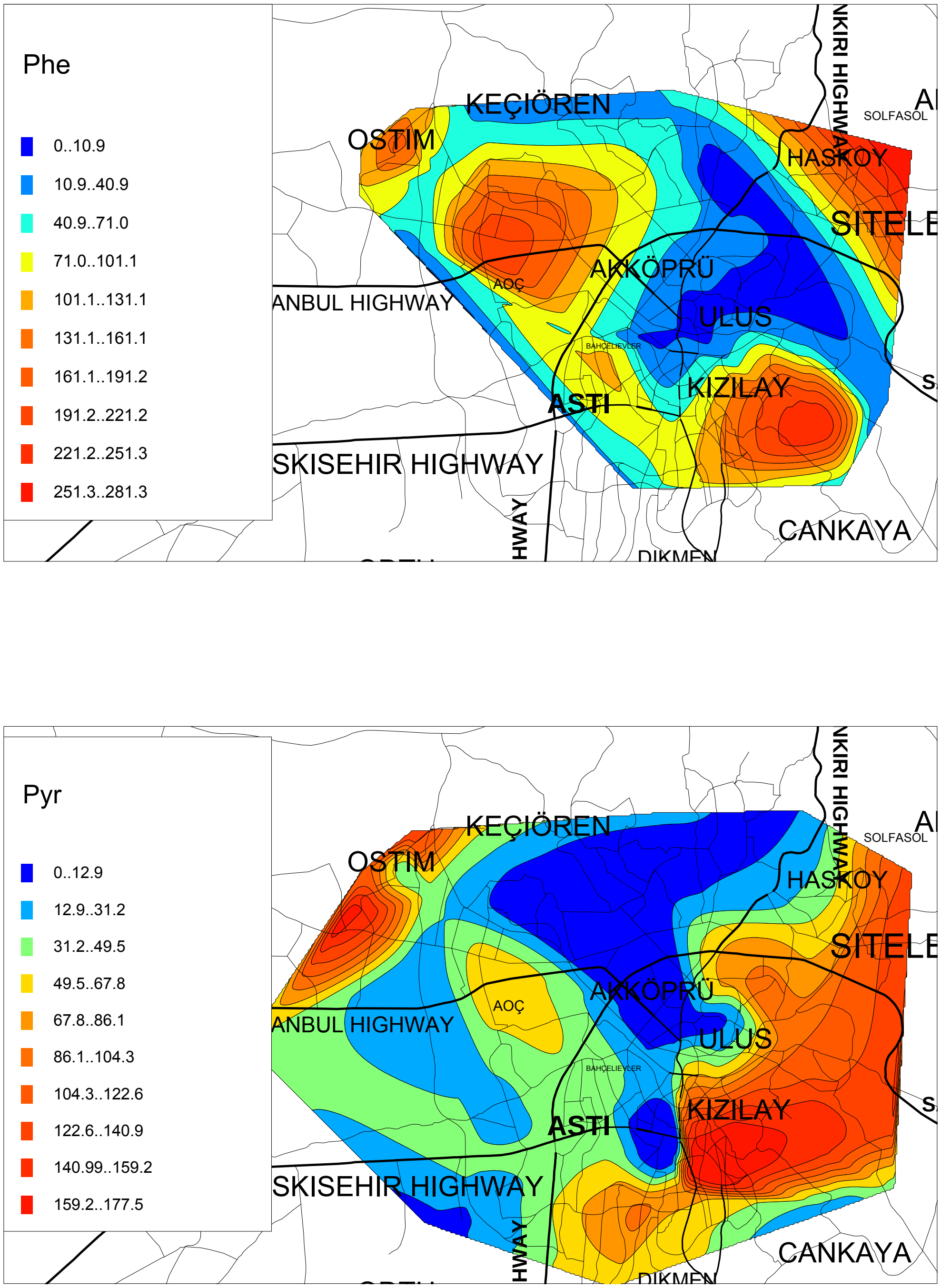


Figure 3.33. Pollution maps of Phe and Pyr

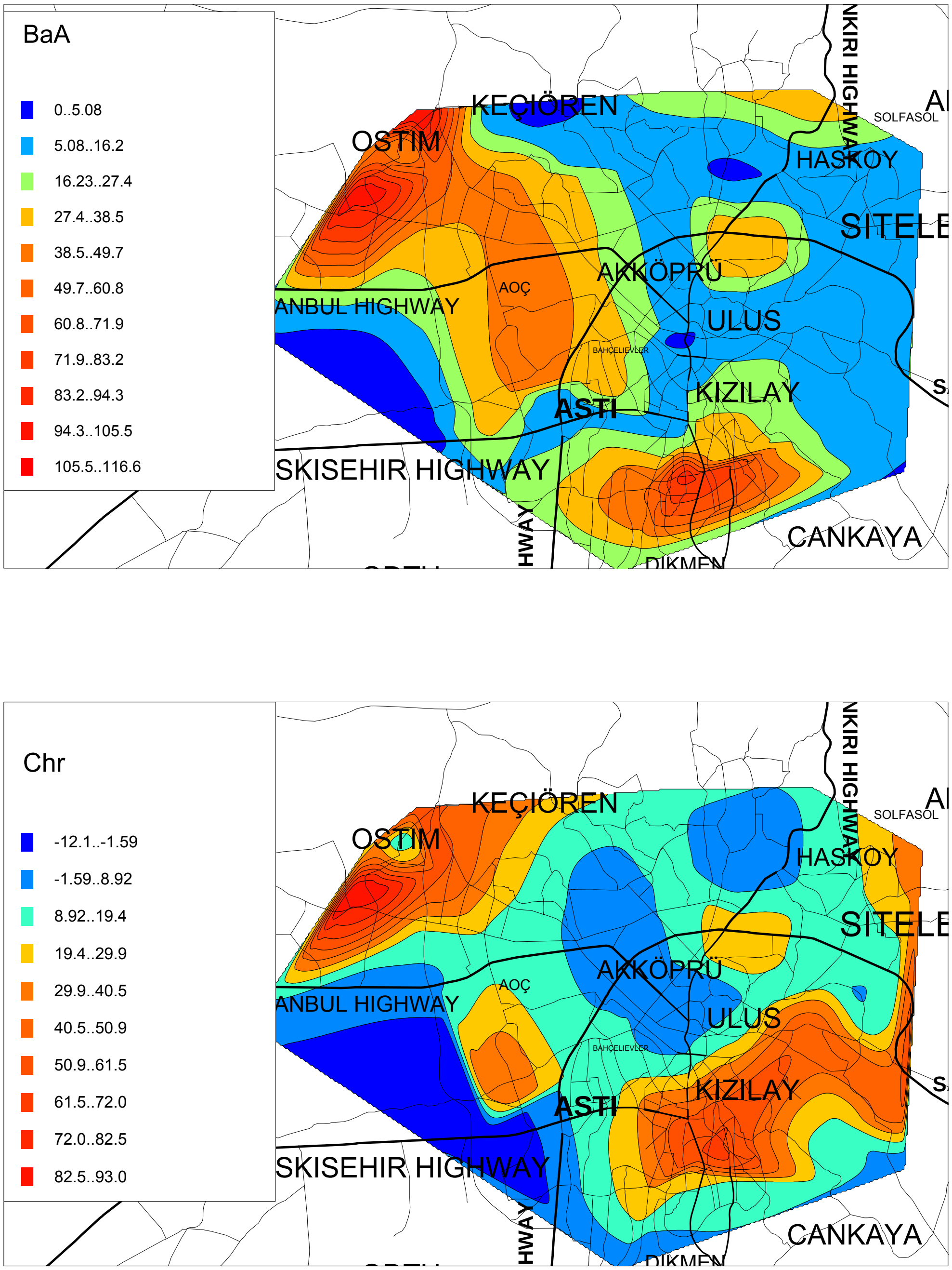


Figure 3.34. Pollution maps of BaA and Chr

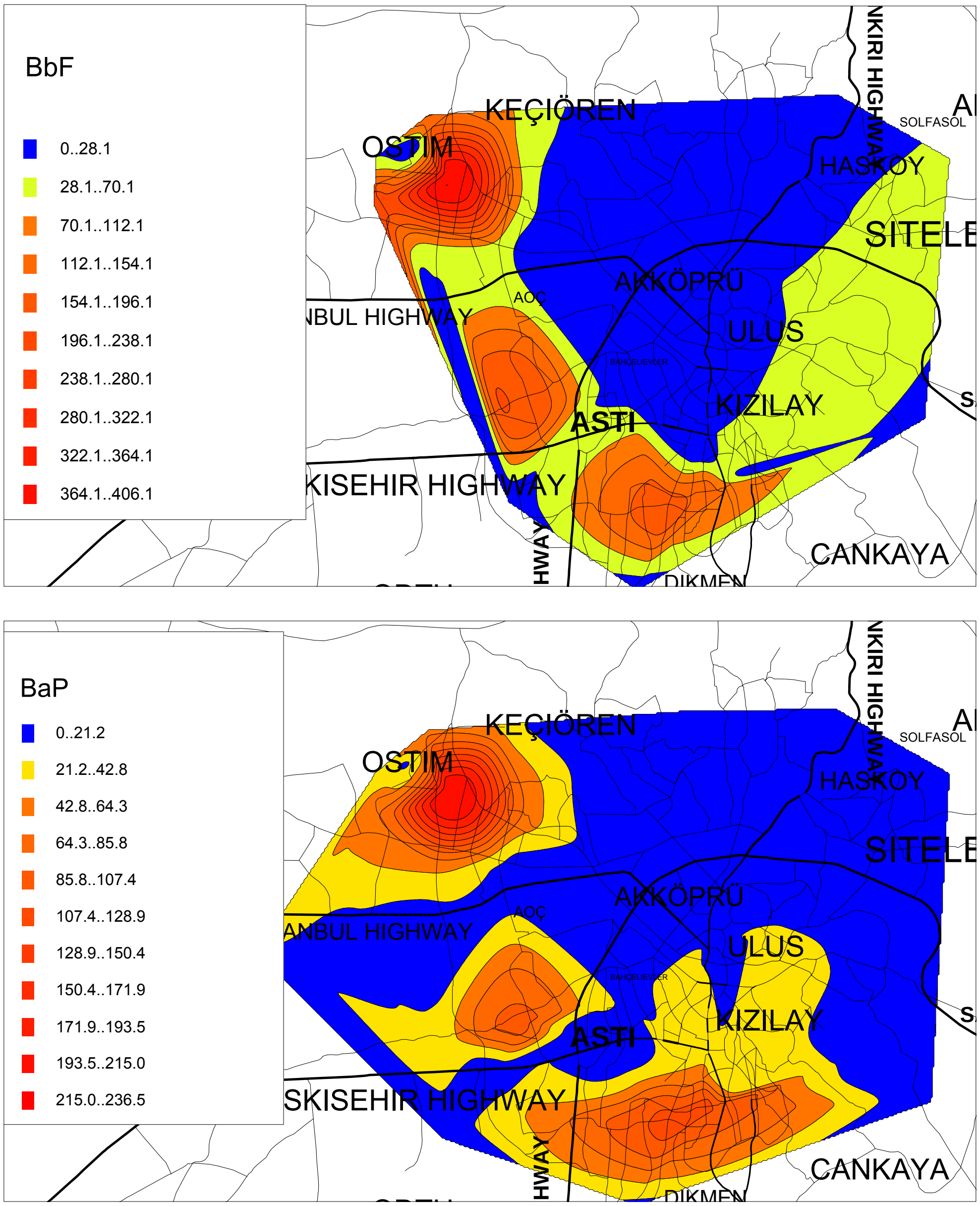


Figure 3.35 Pollution maps of BbF and BaP

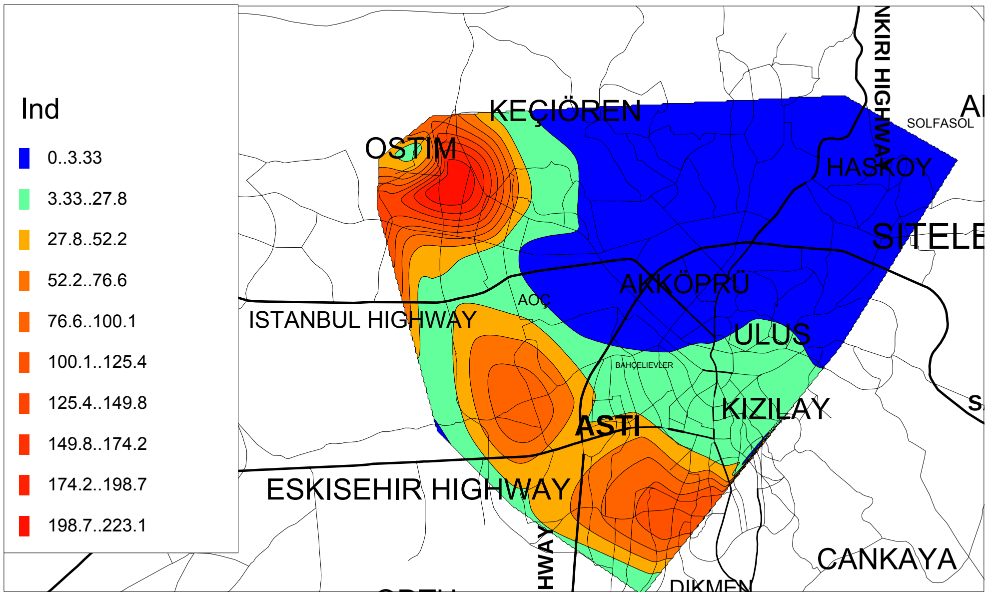


Figure 3.36. Pollution map of Ind

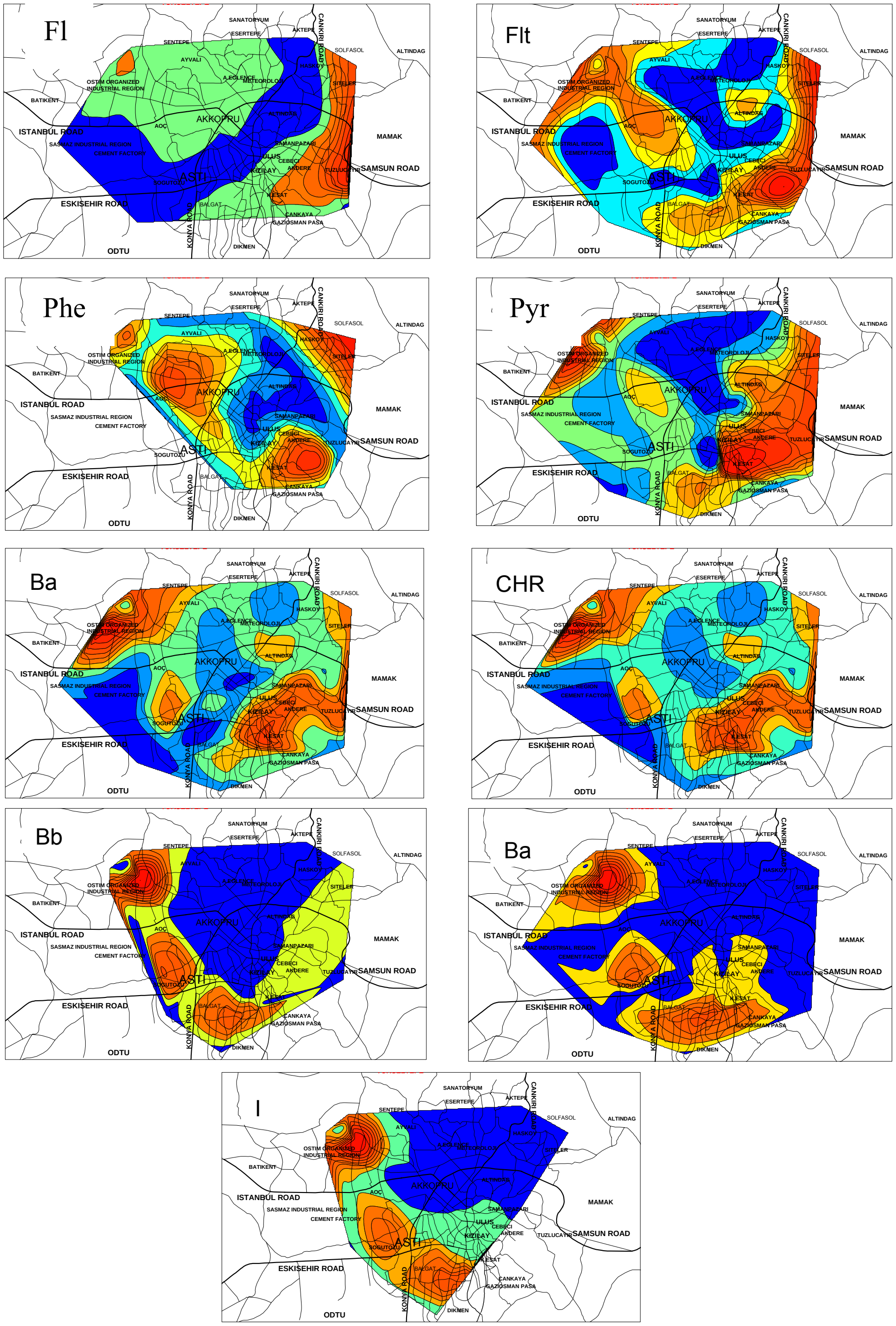


Figure 3.37. Pollution distribution maps of PAHs

Following points can be noted in the discussion of maps:

Concentrations of all PAHs, except for BaP are high on the east of Ankara, which is the region that includes, Mamak, Tuzluçayır and Siteler

Without any exception, concentrations of all PAHs are high in the northwest of the study area, which includes OSTIM industrialized district.

Another area that has high concentrations of all PAHs is the triangle between Atatürk Orman Çiftliği, Gazi Mahallesi and Eskişehir road.

Concentrations of most, if not all, of the PAHs are also high in the area that includes Balgat and öveçler.

The areas described above can be considered as the districts in the city with high PAH dry deposition fluxes and probably high PAH concentrations in the atmosphere. It should be noted that these districts with high PAH deposition are all low income districts in the city. A map of annual income of people living in Ankara city was shown in Figure 3.38. In figure, annual income decreases from A to G. As can be noticed from the figure locations where low income families overlap with the high polluted regions in the pollution distribution maps of PAHs .

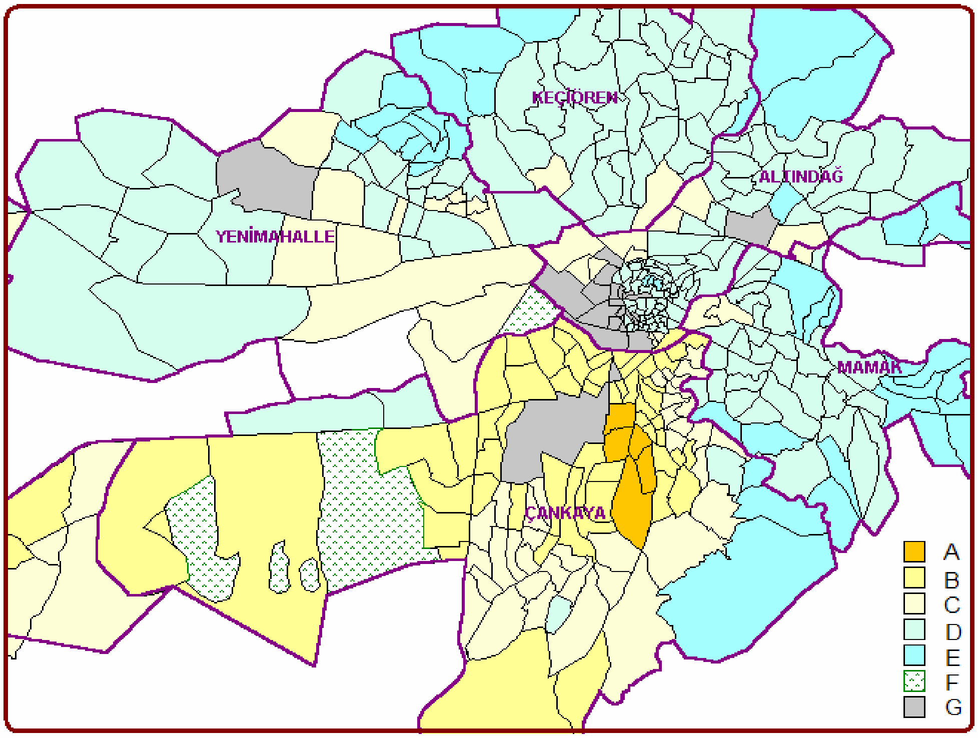


Figure 3.38. Annual income distribution of peoples living in Ankara

Since the incomplete combustion of coal is a well known important source of atmospheric PAH, These low-income areas are the ones where coal combustion is most likely.

Ankara suffered from severe coal-based air pollution in 70's and 80's, which reflected in SO_2 and PM concentrations that increase to few-thousand μg m^{-3} episodically during winter season. The levels of PAH were not known in those days as there were no PAH measurements. Air pollution problem that originated from coal and fuel oil combustion was eventually eliminated when natural gas was started to be used for space heating. Today natural gas is supplied to most of the city, except for gecekondu districts where settlement is not organized and do not have adequate infrastructure. Consequently, main mode of heating in Mamak and Tuzluçayır and Solfasol where high concentrations was observed for all PAHs measured in this study, is the coal combustion. Other districts where high PAH concentrations were measured, although are all areas where low-income population live, can not be described as gecekondu districts. They have adequate infrastructure and natural gas is supplied to all of them, but high PAH levels measured in these districts is still probably due to coal combustion.

Although natural gas is supplied to most of the city with planned and organized settlement, population in low income areas still prefer to burn coal, because it is significantly cheaper compared to the cost of natural gas. Local authorities encourage this illegal use of coal for space heating because of politics. The unexpected increase in SO_2 levels observed in the Ankara air quality monitoring network is attributed to such use coal for space heating in these districts (Ministry of Health, unpublished data). The cheapest coal that is being burned in stoves is the "kaçak kömür" which has low calorific value and has high S and refractory fractions. The use of such coal for space heating was banned several years ago, but every one knows that it is being used illegally in low income districts of the city. Consequently high PAH deposition fluxes measured in low income districts of the city is not a coincidence, but due to use of coal for space heating in these parts of the city.

In Gecekondu areas and in low income districts coal is combusted in stoves where combustion is far from being complete. Since PAHs are the products of incomplete combustion of coal, stoves are ideal sources for these compounds. Furthermore, since the calorific value of "kaçak kömür" used for heating is very low, large quantities of coal has to be burned to generate sufficient heat energy, which also aggravates PAH emissions.

Fairly high deposition fluxes were also measured in districts such as Kızılay, Küçük Esat, Çankaya, Gaziosmanpaşa etc. Some of these districts are the areas where the wealthiest people in Ankara reside. None of them can be classified as low-income settlement areas. Consequently, people living in these districts do not burn coal when natural gas is available, and observed high PAH deposition fluxes can not be explained by coal combustion.

There are probably two potential sources of PAH in these high-income areas. One of them is the dispersion of PAH from gecekondu and low income areas to these districts. For example dispersion of PAH emitted in Tuzluçayır in the atmosphere can appear as moderate PAH deposition at Cebeci, or PAH emitted at Balgat and Öveçler can appear as moderate PAH deposition at Dikmen.

The second potential source of observed high PAH levels in districts where coal combustion is not expected is the traffic emissions. Many of the high income areas with high PAH deposition values, such as Kızılay, Çankaya, Ulus etc are the most congested part of the city. Since traffic is also one of the main sources of PAHs in the atmosphere, high traffic emissions can also account for observed high PAH deposition fluxes in these areas.

3.2.5. Use of PAH Ratios

Since the emissions from incomplete coal combustion and traffic have different PAH profiles, the ratios of different PAHs can be used to differentiate between coal and traffic sources for observed PAH levels in the atmosphere. Since the PAHs in dry deposition is not different from PAHs in atmosphere, the ratios that are being used for atmospheric PAH concentrations can also be used in our snow data.

There are different PAH ratios that are being used to differentiate between traffic and combustion sources (Li and Kamens, 1993, Yunker et al., 2002)). The ratios used in this study are fluoranthene-to-(fluoranthene+pyrene) and fluoranthene-to-pyrene.The values of fluoranthene-to-(fluoranthene+pyrene) ratio that are higher than 0.5 is suggested to indicate a dominant source of coal combustion, whereas values smaller than 0.5 are indicative of dominant traffic emissions on observed PAH concentrations (Yunker et al., 2002, Kendall et al., 2002).

Similarly, fluoranthene-to-pyrene ratios close to 0.6 is suggested to indicate motor vehicles and ratios significantly different from 0.6 (smaller or higher) indicates coal combustion as the mains source of observed PAH in the atmosphere.

These two ratios were calculated for each sampling point and their distribution maps were prepared using the method used in generating concentration maps. The two maps prepared with ratios show the areas in the city where traffic emissions are influential on observed PAH depositions. The results are depicted in Figure 3.39 and 3.40

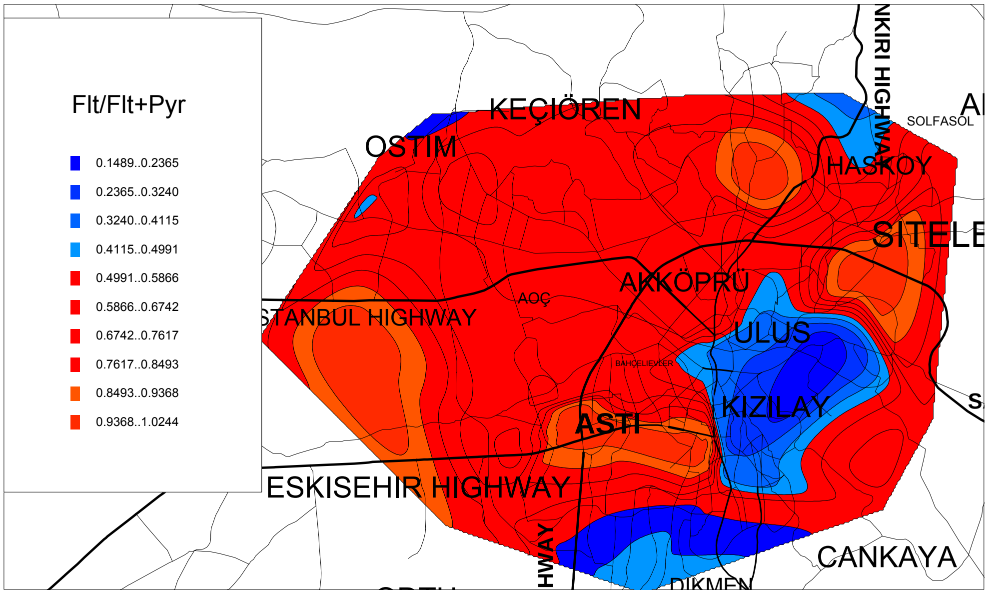


Figure 3.39. Fluoranthene/Fluoranthene+Pyrene map

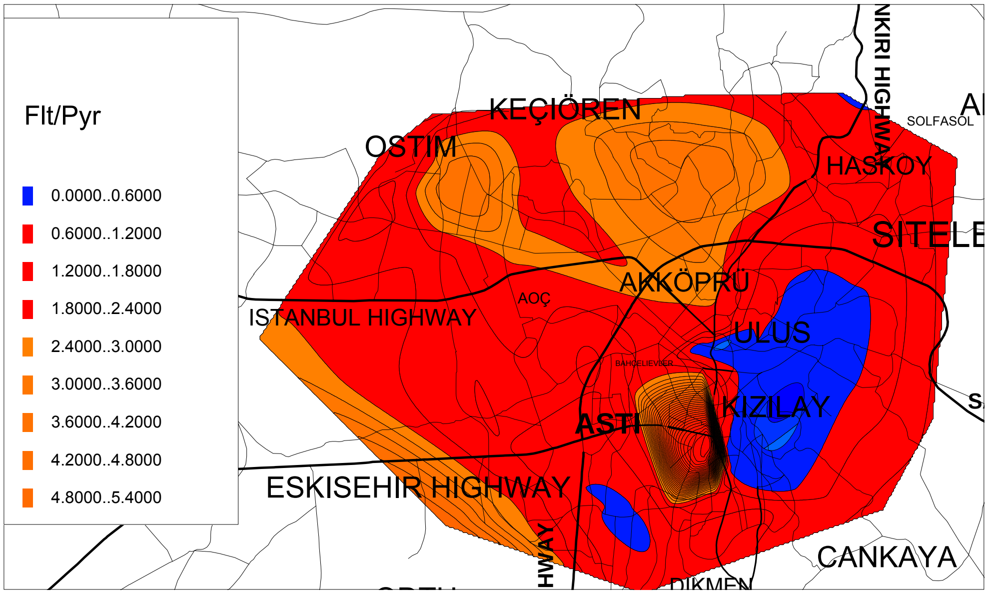


Figure 3.40 Fluoranthene / Pyrene map

The ratio maps nicely complement concentration maps and explain why high PAH deposition fluxes are observed in certain districts where coal combustion is not expected. In both maps it is very clear that traffic emissions significantly affect PAH deposition fluxes in a very limited part of the city. In the rest of the city coal combustion is determining on observed deposition fluxes.

The area in Ankara where PAH concentrations are significantly affected from motor vehicle emissions is at the center of the city including, districts, such as Kızılay, Cebeci, Küçük Esat. Note that these districts are the ones identified as areas with moderate PAH deposition levels, which can not be accounted for by coal combustion.

3.2.6. Depth profile of PAHs

In order to observe the vertical distribution of PAHs in snow, core sampling was performed. Core samples were taken from a certain point by using sampling apparatus starting from the surface. Each time 3 cm thick snow layer was removed from top to bottom and four core samples were obtained. Each layer sample was analyzed separately by GC-MS. The vertical profiles of detected PAHs were shown in Figure 3.41. Top layer (1st layer) concentrations were usually higher than second layer except for Fl and Ph. Fl and Ph are lowest molecular weight PAHs. It is reasonable to assume that volatilisation losses are more pronounced for this two PAHs which might be the reason for lower surface concentrations of fluorene and phenanthrene. On the other hand, behavior of PAHs in snow is very complex considering partitioning, adsorption,volatilisation and solubilities, that is why a more detailed study is needed to explain the vertical behaviour of PAHs in snow.

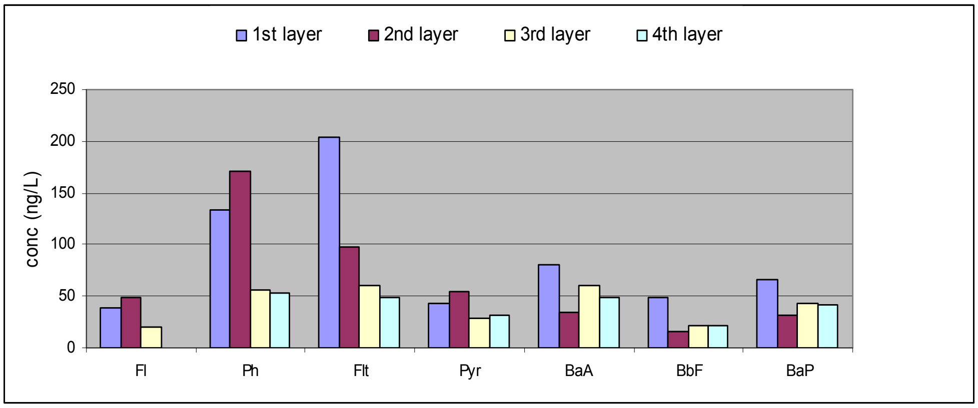


Figure 3.41 Verticle distribution of PAHs.

3.2.7. Flux calculations

Dry deposition of atmospheric particles to surfaces can be calculated using a variety of techniques including micrometeorological models, box models and the collection of dry deposition on inert or artificial foliage surfaces. The micrometeorological approaches are based on the measurements of vertical aerosol concentration gradients and vertical profiles of meteorological parameters (wind speed, humidity, temperature, air flow over the surface, etc.) are then used to estimate the deposition fluxes (Al-Momani et al.,)

The scarcity of dry deposition measurements results from the difficulty in constructing a representative surrogate surface. A surrogate surface can not accurately mimic a natural plant or lake surface. Nevertheless, surrogate collection devices has been deployed to estimate dry deposition to various ecosystems. Such devices include wet and dry collectors of various configurations, moss bags, glass fiber filters, Petri dishes, water surfaces, Frisbee shaped air foils and aluminum, glass, or Mylar plates coated with grease, glycerin, mineral oil or other material to prevent bounce-off. However, the difficulty is the extrapolation of deposition to surrogate surfaces to that experienced by natural surfaces (Franz et al., 1998).

Surrogate surface collectors have been commonly used for dry deposition measurements of PAHs since they are relatively easy to apply for field measurements. Water surfaces have been frequently used for dry deposition measurement, however there are difficulties maintaining constant water surface due to evaporation of water in the dry collector. Adsorption cartridges have been also used both for wet and dry deposition of PAHs, but it is very expensive to construct the whole system to measure effectively dry and wet deposition of PAHs (Lee et al., 2004).

In this work snow surface was used to measure dry deposition of PAHs in Ankara. PAH fluxes for each point were calculated using the sampler area, PAH concentration and time between two sampling periods. Average fluxes calculated were given in Table 3.11.. However it should be noted that the calculated fluxes are lower limit fluxes since fresh snow is not homogeneously distributed and limited number of fresh snow samples were collected.

Standard deviations of fluxes are very high like concentrations of PAHs indicating different sources of PAHs in different localities.

Table 3.11. Summary statistics of Flux (ng/m^{2}day) measurements

	Average	Geometric Mean	Median	Std. Deviation	Minimum	Maximum
Fl	11.70	4.53	6.06	18.78	0.07	87.93
Phe	272.59	24.65	27.47	1207.68	1.18	6191.32
Flt	36.37	19.82	21.27	36.10	1.50	134.11
Pyr	25.60	14.63	20.73	22.09	0.14	78.98
BaA	12.03	7.73	6.62	11.63	0.81	48.82
Chr	10.00	6.36	6.48	9.12	0.18	40.48
B(b+k)F	29.16	12.58	13.19	42.16	0.47	185.93
BaP	14.01	8.68	8.47	17.42	0.84	99.18
Ind	18.18	5.17	9.36	25.32	0.11	100.85
DahA	5.89	2.81	3.29	6.27	0.05	19.99
BgP	18.68	10.47	13.22	19.64	1.49	72.70

It is not easy to compare our data with other studies since we calculated flux for each sampling point for a definite period of time (15 days) and took the average. On the other hand, most of the studies report the fluxes for a time series data. Second debate is the calculation of the flux, since some of the fluxes in the literature are calculated by considering dry deposition velocities. Dry deposition velocities also contain some uncertainties since they are calculated using models. Besides that there is no data produced using snow as a surrogate since in most cases, dry deposition plates, greased surfaces or water surfaces have been used for estimating dry deposition fluxes. Absorption of gas phase PAHs on greased surfaces was mentioned in the literature (Odabaşı et al.,1999). Absorption of gaseous semivolatiles increase the fluxes by plates. For that reason, studies performed using greased surfaces or plates for dry deposition measurements were not included in comparison. Our data is compared with similar studies in Figure.3.42

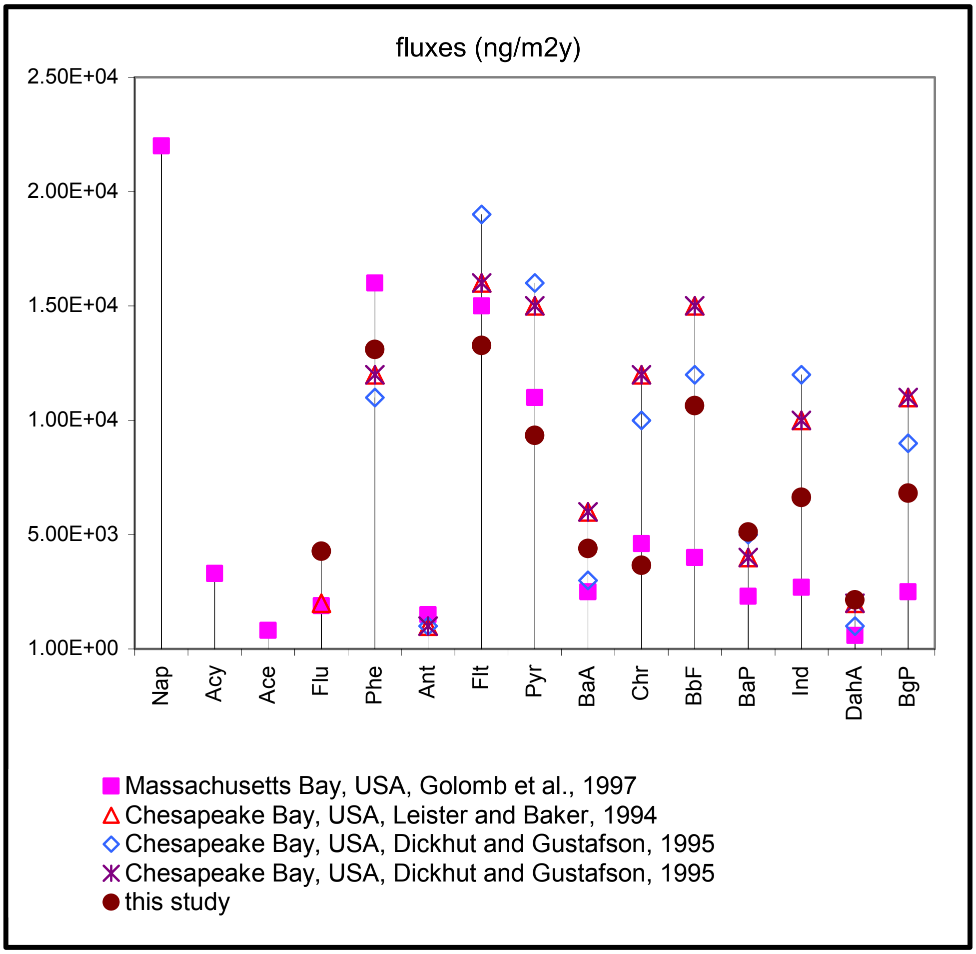


Figure 3.42. Comparison of our fluxes with literature

Usually fluxes of PAHs are comparable with other studies. Phe, Flt and Pyr, BaA fluxes are very close to other sites, however lower Fluxes for Chr, BaP, BbF, Ind and BgP were calculated for Ankara.

3.2.8. Hierarchical Cluster Analysis

Hierarchical cluster analysis was applied to data set of metals and PAHs together to observe the similarities of metal species and PAHs. Metal concentration data was provided by Onal (2004, unpublished data) for the same set of samples. Figure 3.43 represents the HCA results in the form of dendogram. The Average method was used to link the clusters. Species appearing in the same cluster are more like each other than species in other clusters.

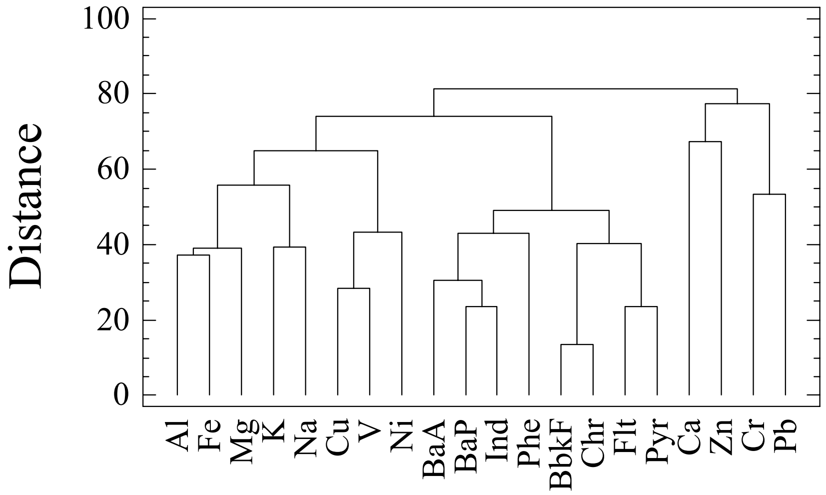


Figure 3.43. Hierarchical dendogram of PAHs and metals.

It is very clear that PAHs and metals are grouped together. 6 distinguished clusters are observed. Cluster 1:Al, Fe, Mg, K, Na, cluster 2: Cu, V, Ni, Cluster 3: BaA, BaP, Ind, Phe, Cluster 4: B(bk)F, Chr, Flt, Pyr, Cluster 5: Ca, Zn, Cluster 6: Cr, Pb.

3.2.9. Factor Analysis (FA)

Factor analysis were run to determine the sources of PAHs. Having data with metals and PAHs are very advantageous since sources of metals are well known than sources of PAHs. For instance Pb is a well known marker for tracing vehicle emissions. If any PAH exist in the same factor with Pb, one can say that major source of the PAH in this group is traffic emissions. Results of Factor analysis given in Table 3.12.

Table 3.12.Varimax Rotated Factor Matrix

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Al		0.81				
Ca						0.74
Cr			0.84			
Cu				0.79		
Fe				0.61		
K		0.67	0.33			
Mg		0.81				
Na		0.49				
Ni				0.66		
Pb		0.48	0.48			0.27
V				0.92		
Zn						0.74
BaA	0.70				0.51	
BaP	0.86					
BbF	0.58		0.59			
Chr	0.35		0.76		0.30	
Flt	0.36		0.33		0.70	
Ind	0.86				0.30	
Phe	0.39				0.71	
Pyr			0.66		0.54	
Eigen value	5.68	3.13	2.33	1.49	1.24	1.00
Variance	28.4	15.6	11.7	7.44	6.19	5.04
Total variance						74.4

The majority of the data (74.4 %) was explained by 6 factors. Factor score maps (3.43, 3.44, 3.45, 3.46, 3.47, 3.48) were also drawn for each factor.

Factor scores indicate the weight of each factor in each sample. Factor 1, which explains 28.4 % of total variance is highly loaded with BaA, BaP, Ind and moderately loaded with B(b+k)F, Chr, Flt and Phe. Phe, Flt and high loadings of higher molecular weight PAHs are characteristic emissions of coal combustion (Duval and Friedlander, 1981., Harrison et al., 1996). However factor 1 is also highly loaded with Ind which is a typical marker for diesel emissions (Li et al., 1993) Based on the PAH profile, Factor 1 is assigned to represent coal

combustion and diesel emissions. Harrison et al. (1996) suggested that diesel emissions are similar to gasoline vehicle emissions but
may have a significant contribution from B(b+k) Fluoranthene. Since factor 1 is a combination of coal and diesel this trend is not observed. When the Figure 3.44 was examined, very good agreement in between the distribution of factor scores and composition of the factor is obtained. The part of the city with high density of the inter and intra city traffic, light industry and settlement area for low income families (gecekondu regions). For example around the Samsun, İstanbul and Eskisehir highway factor score density is the highest. These are the places with heavy diesel traffic. At the same time in these regions very low quality coal is burned for domestic heating. So our factor analysis solution clearly indicated source regions for diesel emission and coal burning.

Second factor represents surface soil which is highly loaded with Al, K, Mg, Na and Pb. The association of Pb which is an anthropogenic element is due to deposition of anthropogenic particles on the soil. Second factor is purely elemental composition and explains 15.6 % of the variance. There is no correlation of any measured PAHs in this factor. This result is also expected as PAHs are basically emitted from high temperature combustion sources. That is why PAHs are used to differentiate combustion sources from each other. But elemental composition help to easy identification of factors as a source category if there was not any elemental data (Al, Mg, k etc.,), we would not be able to identify a soil factor. As a matter of fact, for the identification of combustion factors elemental composition helps in a great extent. As it was mentioned previously PAH research is very new and there is not any international consensus about the composition of different combustion sources. One PAH could be used to explain more than one source. Another real physical limitation is overlapping of one source with another.

Both metals and PAHs contribute the third factor and explain 11.7 % of the total variance. Since Pb is a well known marker for traffic emissions, this factor represents traffic contribution. This is a different factor then the first factor which was explaining domestic coal burning and diesel emissions. Here we see the emissions from the cars which uses leaded gasoline. Among PAHs, B(b+k), Chr, Pyr appears with quite high loadings. Since third factor lack of B(b+k)F, mainly gasoline powered vehicles are represented in this factor. This observation is supported by the Factor score map shown in Figure 3.46. The density of the factor scores are high in the region of the city where the number of cars using unleaded gasoline is high.

Fourth factor represents fuel oil combustion. The typical oil combustion elements namely non-crustal V and Ni are loaded in this factor. The factor also includes Cu and Fe. Although in the last years natural is used in some parts of the city still oil burning is used for domestic purposes. Factor score densities on the map (Figure 3.47) shows the regions

Fifth factor lacks of any elemental source marker and highly loaded with Phe, Flt and BaA and moderately loaded with Pyr and Ind. Most of the Phe variance is explained in this factor suggesting that unburned fossil fuel is another source for pollution.

The last factor has loadings for only two elements Ca and Zn. There is no PAH associated with this factor. Zn imply that this factor is a representative of road dust. We have mentioned above that there is no good PAH marker for crustal contribution. But Ca has a soil component and Zn may come from tires and incineration. Since there is no big incinerator in Ankara and PAHs are not present in this factor, we identified the last factor as road dust or contaminated soil.

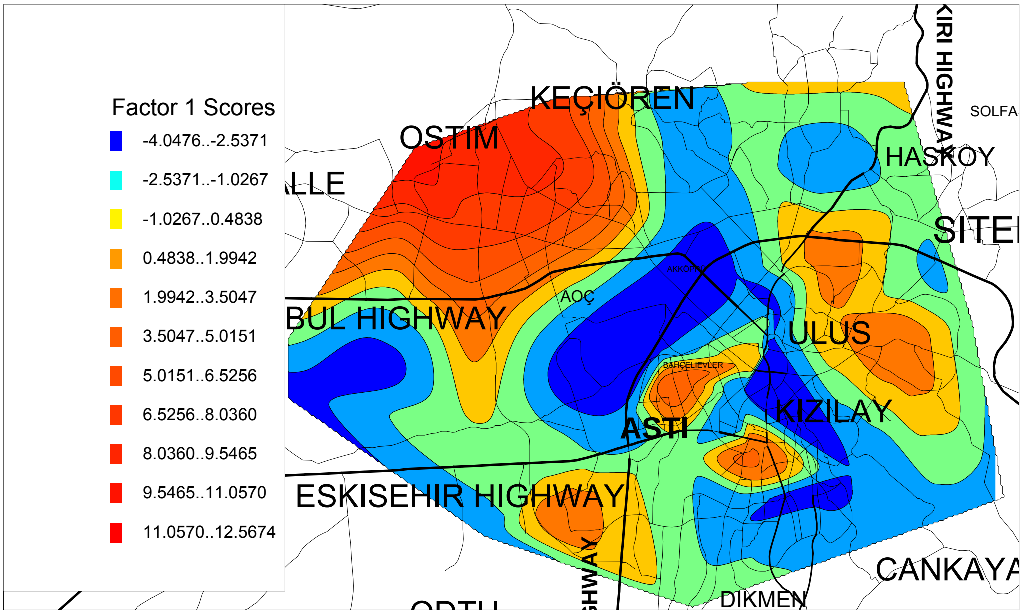


Figure 3.44. Factor score map of 1st Factor

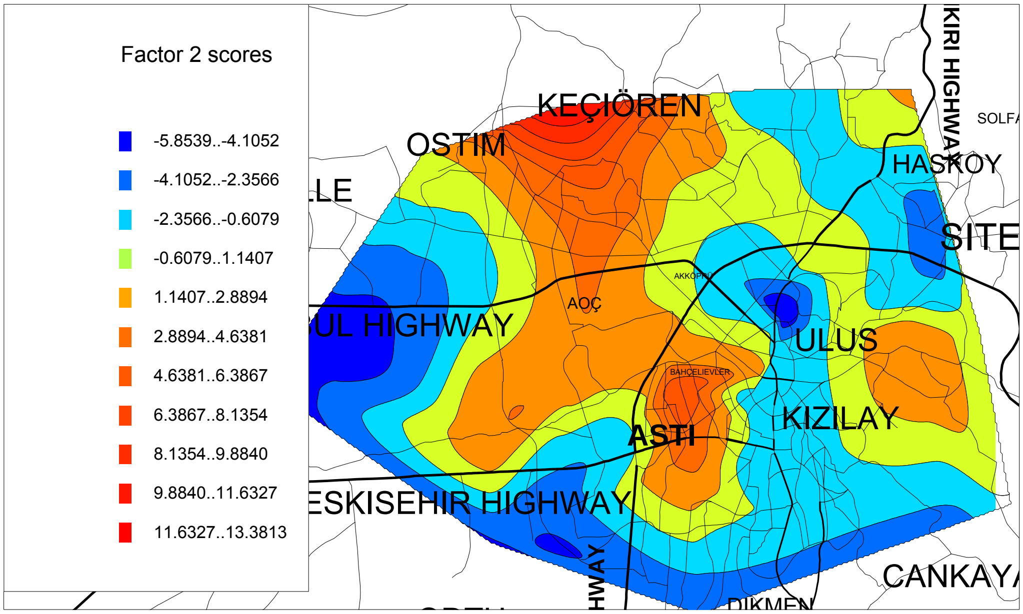


Figure 3.45. Factor score map of 2nd Factor

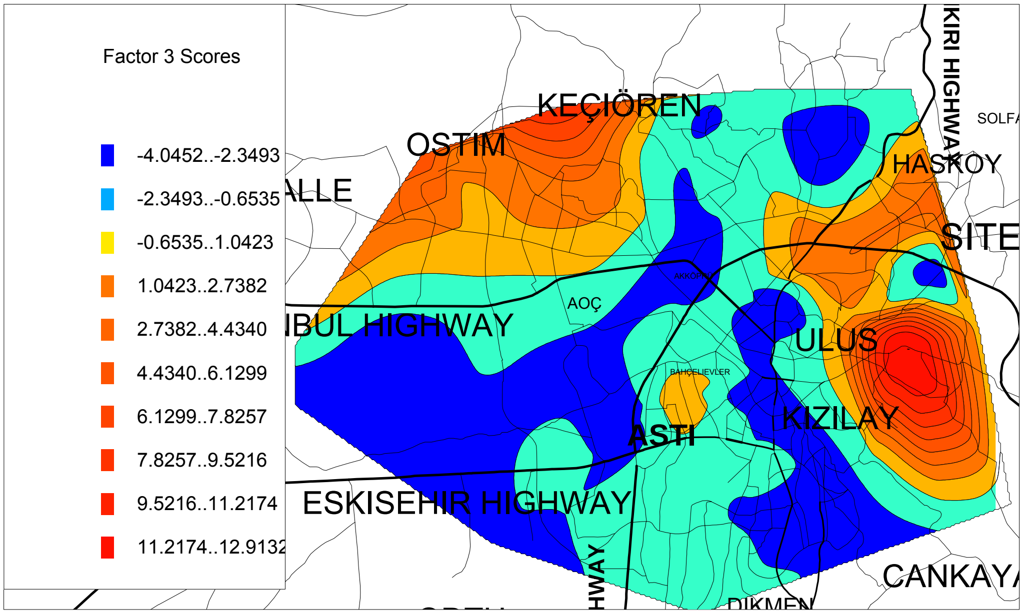


Figure 3.46. Factor score map of 3rd Factor

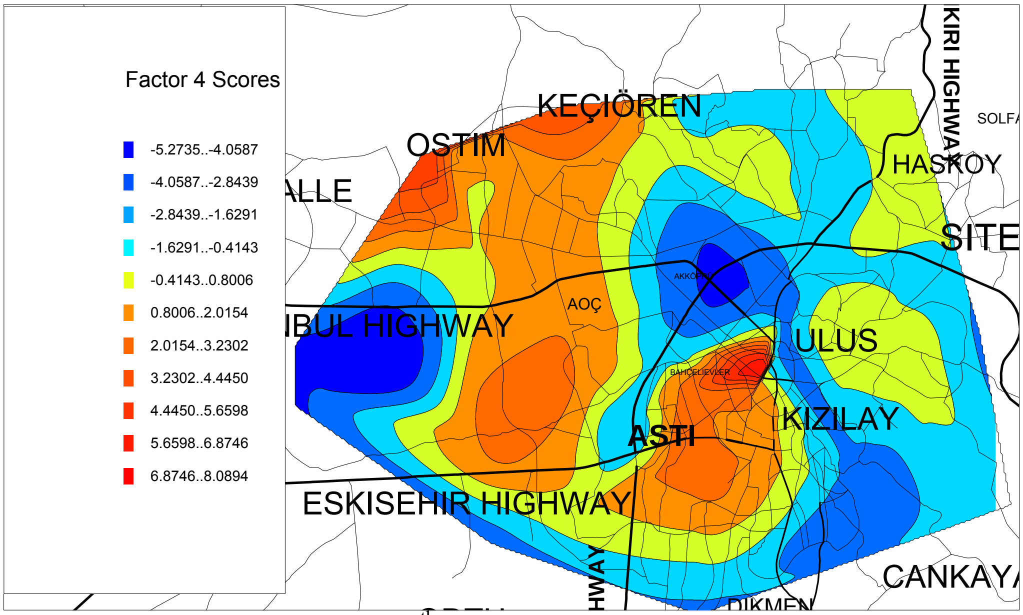


Figure 3.47. Factor score map of 4th Factor

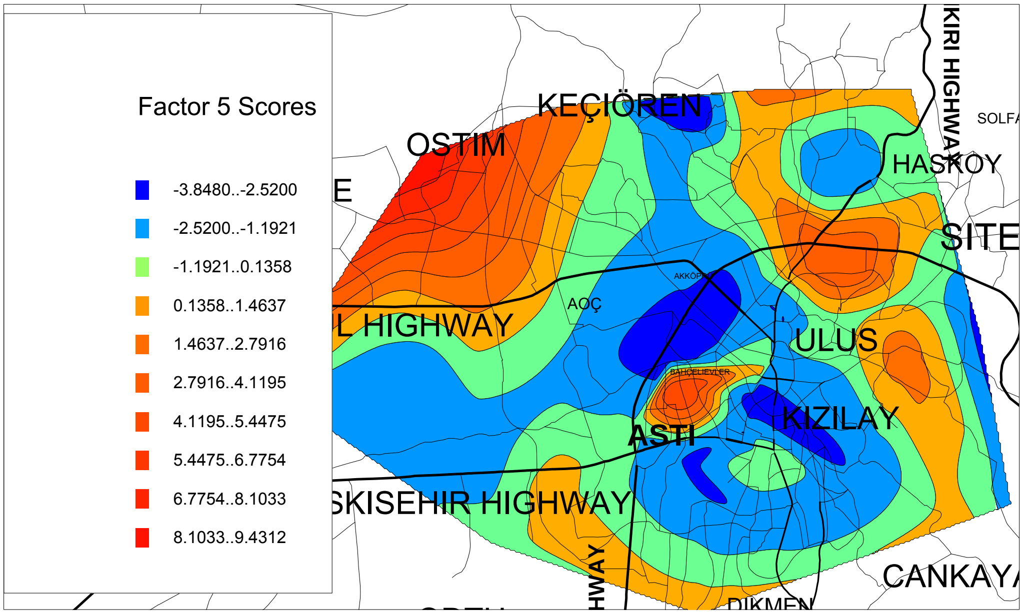


Figure 3.48. Factor score map of 5th Factor

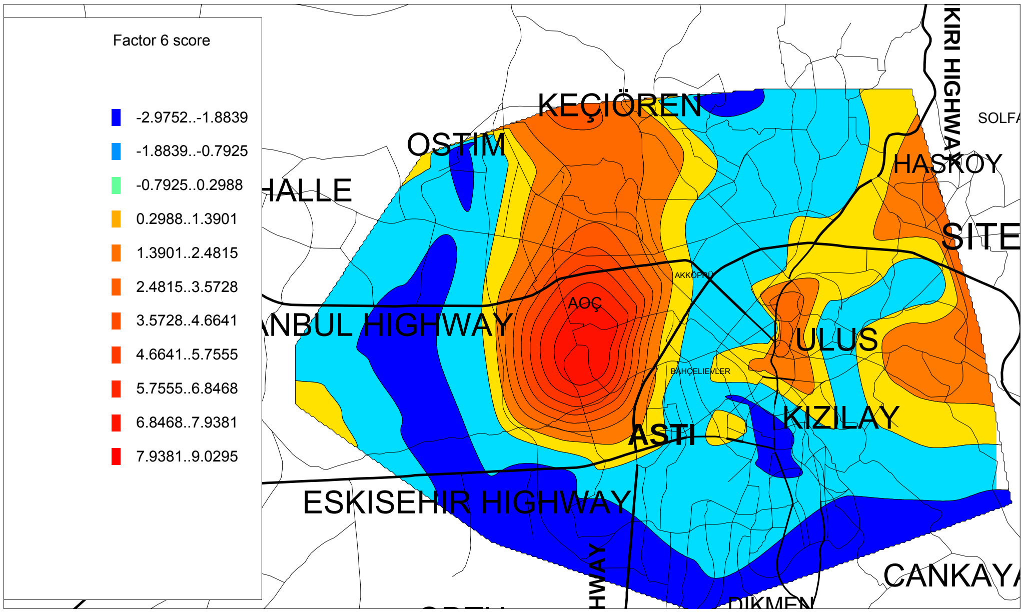


Figure 3.49. Factor score map of 6th factor

CHAPTER IV

CONCLUSIONS

A comprehensive study was performed to investigate the wet and dry deposition of PAHs in Ankara. Rain is sampled at one point for wet deposition and snow surface was used as a surrogate for dry deposition of PAHs. It was possible to determine the concentrations of 12 PAHs in both wet and dry deposition samples.

Solid Phase Extraction (SPE) and ultrasonic extraction techniques were used for the trace enrichment of PAHs from samples. Different solvents were tried to improve the recovery of PAHs from filter samples and 2 hr DCM extraction resulted in higher recoveries. Different combination of solvents were experimented for SPE and conditioning with DCM and methanol and elution with DCM was found to be optimum for the preconcentration of PAHs from rain matrix. Surrogate standards were used to calculate the recoveries of PAHs. The range of recoveries were in between 60-100 %. Gas Chromatography-Mass Spectrometry used in Selected Ion Monitoring Mode (SIM) provided high analytical capacity for the analysis of samples. Quantitative analysis of PAHs were performed by monitoring 1 target and 2 qualifier ions were monitored. PAHs in snow samples were quantified using external calibration method while internal standard calibration method was used for the rain samples.

Phe, Flt, Pyr and B(b+k)F were found to be dominant PAHs in wet deposition samples. Concentrations of PAHs in wet deposition samples were higher than other stations in Europe. All the measured PAHs showed temporal variations with high winter concentrations. Approximately 2 fold higher concentrations of PAHs were observed in winter period. PAH concentrations were inversely related with ambient temperature. Lower ambient air temperatures are characterized by higher PAH emissions. Concentrations of PAHs were inversely related with surface wind speed. Wind sector analyses revealed NE and SE as the major wind direction for observed high concentrations. 46 % of the PAHs comes from NE sector, 28 percent from SW and 26 percent from both NE and SW sectors.

Annual wet deposition fluxes of Phe, Flt, Pyr and B(b+k)F were found to be higher than other PAHs. Calculated PAH fluxes in Ankara are usually lower than industrial sites and comparable with similar urban sites in Europe.
Concentration ratios are used as markers for different sources, revealed motor vehicles and coal combustion as major source contributing cources. Factor analysis solution provided categories and composition of contributing sources. It was possible to explain 72.3 % of the total variance in Factor analyses. Three identified sources are, i) coal combustion, ii) traffic and iii) unburned fossil fuel and natural gas combustion.

Developed sampling strategy for dry deposition was very successful. It was possible to identify PAH composition of dry deposition. Local PAH pollution at different sites of the city successfully evaluated. Major polluted sites were NE and SW parts of the city which are Ostim, Sentepe, Mamak and Altındağ. Dry deposition of PAHs was comparable with similar sites. Concentration ratio calculations indicated that major sources of pollution are traffic and coal combustion. Ratio maps clearly indicated the sites where traffic emissions are higher. PAH fluxes were calculated using snow surface and comparable values obtained with similar sites. Factor analysis revealed 5 source categories explaining 74.4 % of the variance. Following factors were identified in FA; coal, soil, traffic, oil, road dust and a mix pyrolytic source.

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VITA

Eftade O.Gaga was born in Üsküdar, İstanbul on December 12, 1972. She received her B.S. degree in Chemistry from the Middle East Technical University in June 1995. She received her M.Sc. Degree in Chemistry Department in 1997. She worked as a teaching assistant in Chemistry Department from August 1995 to February 2004. Her main areas of interest are atmospheric pollution and environmental chemistry.