

## **DRY DEPOSITION OF PAHs ON SNOW SURFACE**

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### **ABSTRACT**

Dry deposition of PAHs in Ankara was investigated using a sampling methodology developed in our laboratory. Snow surface was used as a surrogate surface for dry deposition. Ankara which is a typical urban city was divided into 56 2×2 km grids. Surface snow samples were collected from all grids right after a major snow event and 15 days later. There was no wet precipitation during two collection periods. Difference in concentrations of fresh and 15 days aged surface snow was due to dry deposition. An apparatus developed in our laboratory was used for sampling. Analytical methodologies for the pre-concentration and analysis of samples were optimized for snow samples. Gas chromatography-Mass Spectrometry was used as an analytical tool. Significant increase in concentrations of PAHs was observed at the end of 15 days due to dry deposition on snow surface. Snow is thus could be used as a surrogate surface for dry deposition of PAHs. Pollution maps were drawn for each PAH by Map Info GIS software. The major polluted zones are localities where low income families live and low quality coal used for domestic heating. Use of PAH ratios as markers of specific sources together with distribution maps indicated coal combustion and traffic emissions as the major sources.

Keywords: PAHs, dry deposition, snow

### **1. INTRODUCTION**

Polycyclic Aromatic hydrocarbons PAH can be formed in any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing C and H [1]. Major sources of PAHs include residential heating, open burning, coke and aluminum production, and motor vehicle exhaust [2].

PAHs are found in airborne particles and in the gaseous phase. In precipitation, they exist also as dissolved or suspended form. It is essential to measure both dry and wet deposition to assess the total atmospheric deposition of PAHs. Dry deposition results from the direct impaction on land and water of airborne gaseous and particulate PAHs. Airborne PAHs have relatively short life times in the atmosphere and they can not travel far from their sources [3,4]. However PAHs in wet deposition can travel far from their sources by clouds since cloud droplets may accumulate both gaseous and particulate PAHs [4].

Collection of wet deposition samples for PAH measurements are relatively easier than dry deposition. Wet deposition of hydrophobic organic compounds can be sampled on an event base but 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 [5, 6,7] 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 [8].

The objective of this study is to investigate suitability of snow surface for dry deposition of PAHs.

## 2. EXPERIMENTAL

### 2.1 Snow sampling strategy

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 which is located in North West of the city.

In order to assess the dry deposition of PAHs on snow surface, sampling area was divided into 2\*2 km grids. After defining sampling points, sampling periods were determined. The idea was to use snow surface as surrogate for dry deposition. Therefore two sampling campaigns were conducted in a definite period of time. Fresh snow samples were collected just after a major snow fall from certain grids to analyze the fresh snow PAH composition. Second sampling campaign was done after 15 days later from the first sampling campaign from all grids. During this 15 days period there was no other wet precipitation event occurred.

While collecting samples, special attention has been paid to collect surface snow samples from a definite depth without disturbing the surface. An apparatus which is made of stainless steel and developed in our laboratory was used to collect the snow (Figure 1). With that apparatus upper 3 cm snow layer on the tray was transferred to glass bottles by aluminum shovel. Collected snow corresponded to approximately 750 ml of snow melt water [9]. Collected samples were transferred to the laboratory and kept at dark and cold.

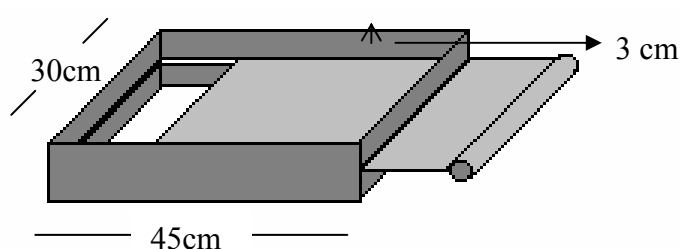


Figure 1. Sampling apparatus

### 2.2. Preconcentration and analysis of the samples

Preconcentration of PAHs is necessary prior to the analysis since amount of PAHs are very low (ng/L) in samples. Traditional extraction of liquids involve liquid liquid extraction (LLE). However large amounts of solvent is needed for the extraction of large number of samples. For that reason LLE has been largely replaced in past few years by SPE using a variety of sorbents [10,11]. In this study, Reversed Phase Solid Phase Extraction is preferred for preconcentration of PAHs from snow matrix. Octadecyl bonded silica disks were used for the

extraction of samples. Deuterated surrogate standards (acenaphthene d10, phenanthrene d10, chrysene d12 and perylene d12) were added to the melted snow samples prior to the extraction to calculate the recovery of PAHs. Extracted samples were analyzed by HP 6890 Gas Chromatograph- 5973 Mass Spectrometer. Instrumental conditions were optimised prior to the analysis and operating GC-MS conditions are shown in Table 1. Monitored PAHs are, Acenaphthylene (Acy), Acenaphthene (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) and Benzo(g,h,i)perylene (BgP).

Table 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

### 3. RESULTS AND DISCUSSION

#### 3.1. 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 major snowfall in December 3th, 2000, representing background concentrations before any dry depositon takes place over the snow surface. Concentration profiles of PAHs for one of the sampling points is shown in Figure 2.

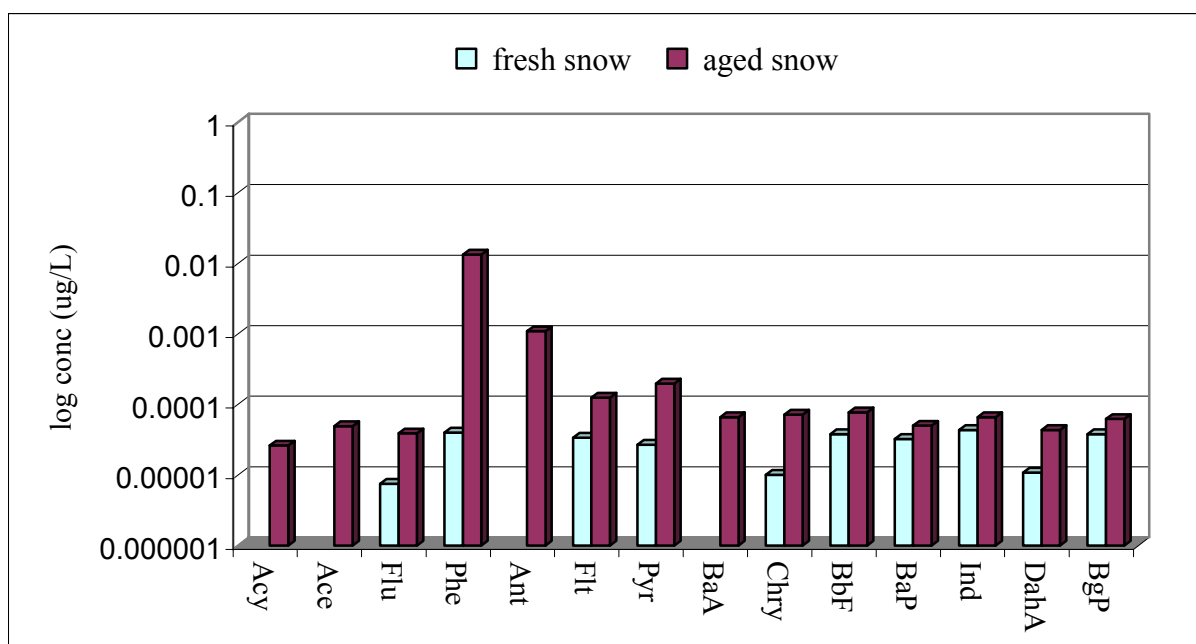


Figure 2. Concentration changes of PAHs in between two sampling campaigns

As it is clear from the Figure 2 that concentrations of PAHs increased at the end of 15 days period. Since there were not any wet deposition event in this period, observed PAH concentrations are only due to dry deposited pollutants on snow surface. In Figure 2, some of the PAHs were not detected in fresh snow samples due to very low concentrations.

### 3.2. 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.. 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. Among the measured PAHs, map prepared for Flt was shown in Figure 3. Usually similar pollution patterns were observed for all measured PAHs as expected because of their common sources.

Concentrations of all PAHs, except for BaP are high on the east of Ankara, without any exception, concentrations of all PAHs are high in the northwest of the study area, which includes Ostim industrialized district. 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. 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 as compared to cost of natural gas.

Another polluted site lies on the North East of the city. Some of these districts are the areas populated with high income families. 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. 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 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.

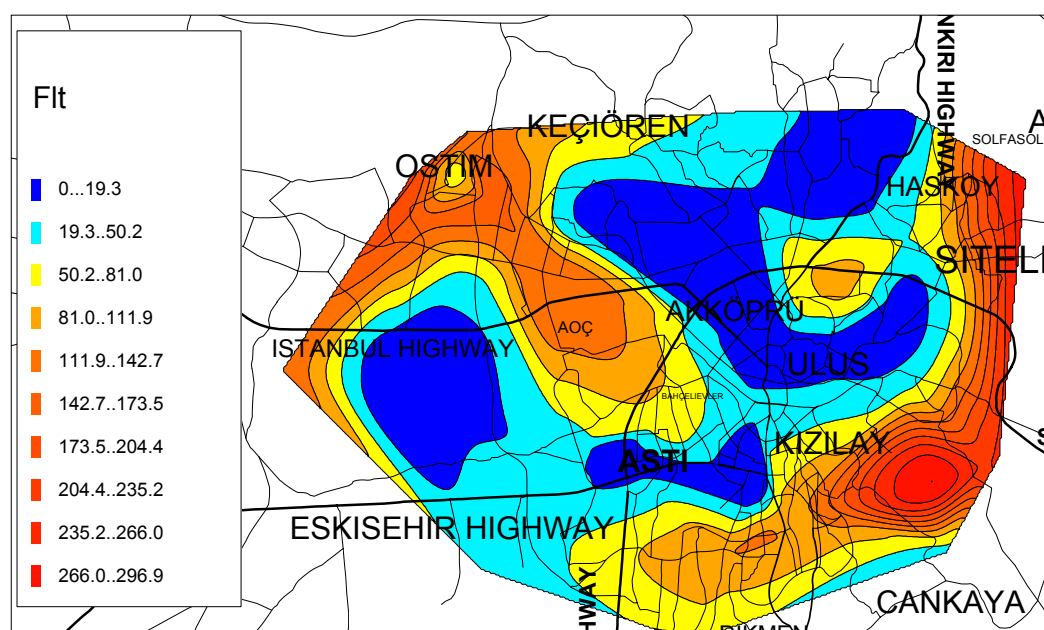


Figure 3. Pollution map of Flt.

### 3.3. Use of PAH ratios for source identification

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. There are different PAH ratios that are being used to differentiate between traffic and combustion sources [12, 13, 14]. 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 [13]. 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 main source of observed PAH in the atmosphere. These two ratios were calculated for each sampling point. As a result of ratio calculations, it was observed that main pollution sources are traffic emissions in congested parts of the city and coal combustion in residential sites where low income families live.

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