WET DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS IN ANKARA

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ABSTRACT

Wet deposition samples were collected at Middle East Technical University campus, Ankara, between December 2000 and June 2002 by wet only sampler. Sampler was modified for the collection of samples for PAH analysis. Samples were in situ filtrated from glass fiber filter through a filtration apparatus in the field. Fifteen priority Polycyclic Aromatic Hydrocarbons (PAHs) were determined in both particulate and aqueous samples by Gas Chromotography-Mass Spectrometry in Selected Ion Monitoring mode.

Phenanthrene, fluoranthene, benzo (b+k) fluoranthene and pyrene were found to be major components in wet deposition samples. Seasonal variation of PAHs were observed having higher concentrations in winter period. Winter concentrations are found to be 2 times higher than summer due to increasing fossil fuel combustion. Wet deposition fluxes were calculated and found to be comparable with other urban sites in Europe.

Keywords: PAHs, wet deposition, deposition flux.

1. INTRODUCTION

Polycyclic Aromatic hydrocarbons (PAHs) represent a group of compounds which are regarded as persistent organic compounds in the environment. At ambient temperature, non volatile compounds (consisting of five or more rings) are condensed or adsorbed onto solid particles, medium volatility PAHs distributed betwen gas and the particle phase while the volatile compounds remain in the gas phase. Because of the long residence times of particles in atmosphere, PAHs can be used as tracers of anthropogenic activity [1,2].

It has been estimated that stationary sources contribute for approximately 90 % of total PAH emission, however in urban and suburban areas mobile sources have considerable contributions to the PAH emissions. The highest concentrations of atmospheric PAHs can be found in the urban environment, due to the increasing vehicular traffic and dispersion of the atmospheric pollutants. The risk associated with human exposure to atmospheric PAH is highest in the cities, considering the density of population [3].

Wet deposition of PAHs have been investigated by many researchers [4, 5, 6, 7, 8 ,9, 1]. Although wet and dry deposition of metals have been investigated in Turkey in detail [10, 11] there is no produced data about the deposition of PAHs. For the first time, atmospheric concentrations of PAHs via wet deposition was investigated in this study.

2. EXPERIMENTAL

2.1 Wet deposition sampling strategy

Wet deposition samples were collected in Middle East Technical University Campus in Ankara. 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.

Samples were collected by Andersen wet only sampler. Sampler originally consists of two polyethylene buckets placed in stainless steel cyclindirical containers and there is a humidity sensor which activates the lid so that wet bucket remains open only when precipitation occurs. Some modifications were done in the sampler for the measurement of PAHs. A 32 cm diameter glass funnel was placed in the wet bucket and collected samples were transferred to amber glass bottle through a filtration unit. Glass fiber filters (90 mm) were used for the in situ filtration of the samples. A schematic view of the sampler was shown in Figure 1.

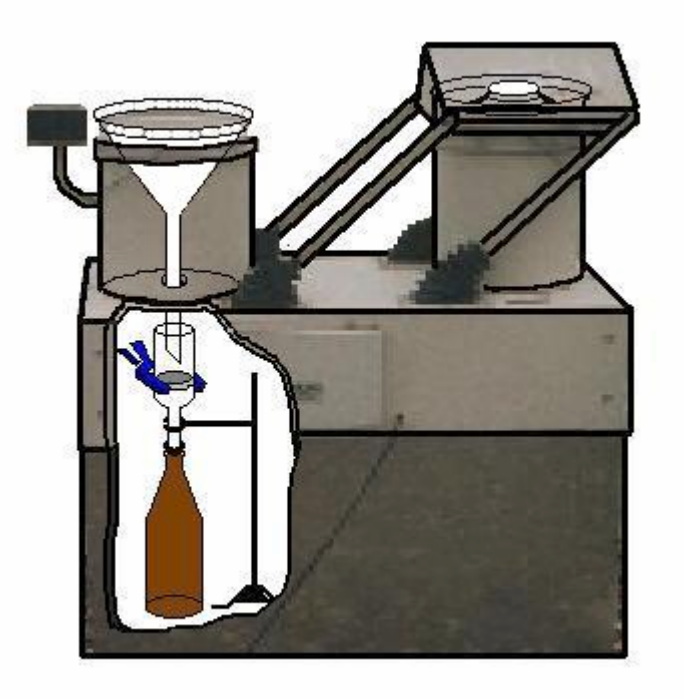

Figure 1. A picture of modified rain sampler

2.2. Preconcentration and analysis of the samples

Since amounts of PAHs are in the order of sub ppt, a preconcentration step is necessary before the analysis of samples. Two different kinds of extraction techniques were applied to samples. Filtered rain samples were extracted by Solid Phase Extraction by C18 disks and particles on glass fiber filters were extracted by ultrasonic extraction. Different solvents were used for both extractions to increase the recovery of PAHs. Deutorated surrogate standards (napthalane d8, acenapthene d10, phenanthrene d10, chrysene d12 and perylene d12) were added to samples prior to the extraction to calculate the recovery of PAHs.

SPE extractions were performed using standard filtration apparatus purchased from Millipore. Disks were wetted first with 10 ml of dichloro methane and then methanol. After disk conditioning sample was eluted and PAHs on disk is collected with 2 portions of dichloro methane. Collected eluate volume was reduced under gentle stream of nitrogen prior to analysis. Glass fiber filters were extracted in ultrasonic bath using dichloro methane for 2 hours. Analysis were performed by using HP 6890 Gas Chromatograph- 5973 Mass Spectrometer. Instrumental conditions were optimised prior to the analysis. Analysis were performed in Selected Ion Monitoring mode. 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.

3. RESULTS AND DISCUSSION

3.1. Overwiev of the produced data set

In this work PAHs were determined in wet deposition samples in Ankara for the first time. Ankara, capital of Turkey, is a typical urban city with a population of 4.5 Million. There are no major industrial activities but some small plants has been settled down in North East of the city.

Concentrations of PAHs were determined in both aqueous and particle phase and reported values are summation of two concentrations. 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.

Basic statistical calculations were performed for the data set and presented in Table 1. The goodness of the fit was then tested using Kolmogorov-Smirnov (K-S DN) statistics. Result of the test indicated lognormal distribution for all the measured PAHs. Among the measured PAHs, highest concentrations were obtained for Phe followed by Flt, B(b+k)F and Pyr.

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

	Size	Average	Std. Dev.	Median	Geo.mean
Acy	52	18.3	20.6	9.77	11.2
Flu	57	66.4	68.7	43.8	43.2
Phe	59	196	171	140	138
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

3.2. Monthly and Seasonal Variations of PAHs

Monthly volume weighted average concentrations of PAHs were given in Figure 2. 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. 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 2 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.

We have investigated the seasonal concentrations of PAHs in Figure 3. 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.

Seasonal variation of PAHs investigated by researchers [12, 13, 7]. 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. In this study similar PAH pattern was observed having approximately 2 times higher concentrations in winter.

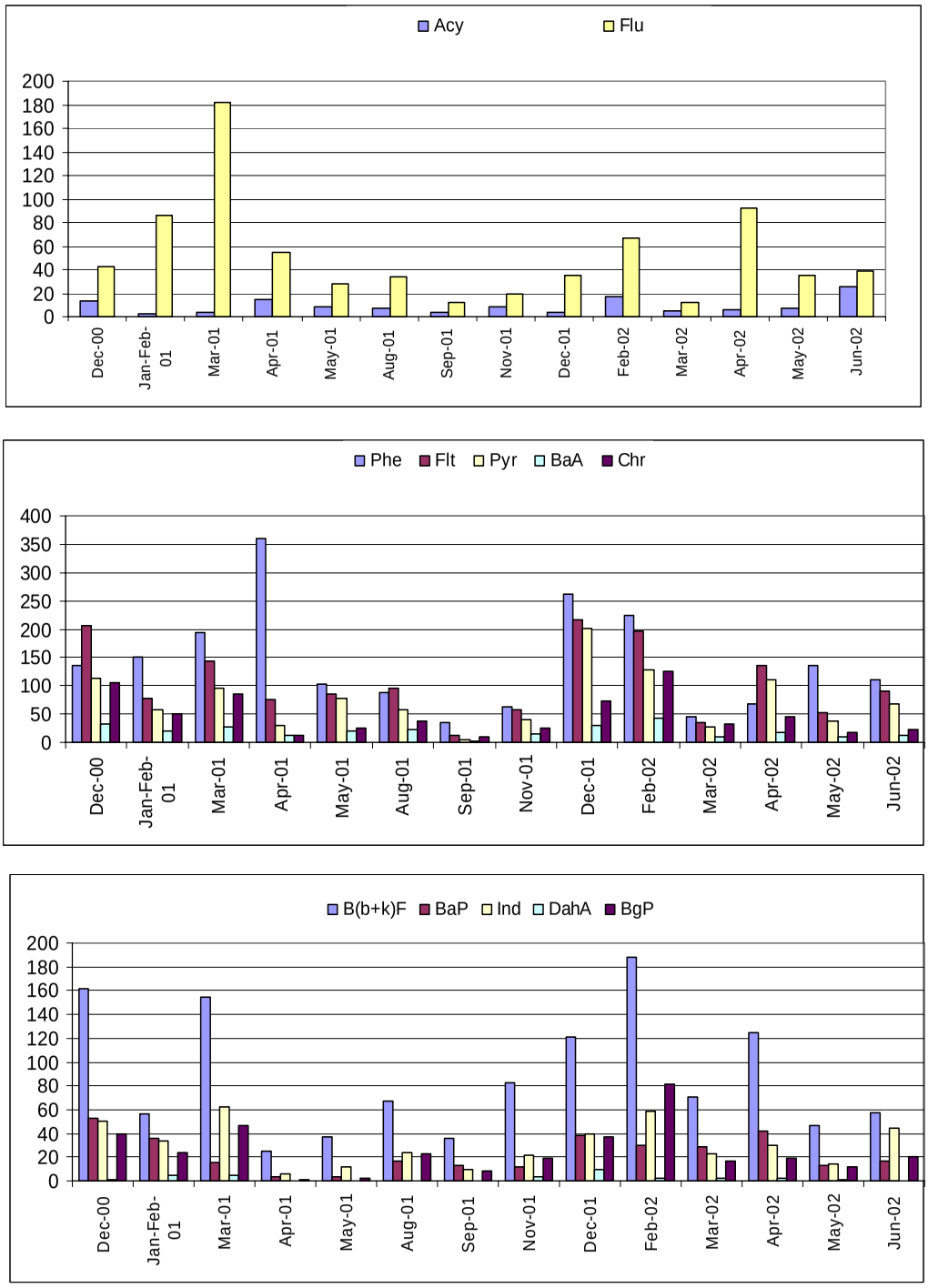

Figure 2. Monthly volume weighted averages of measured PAHs

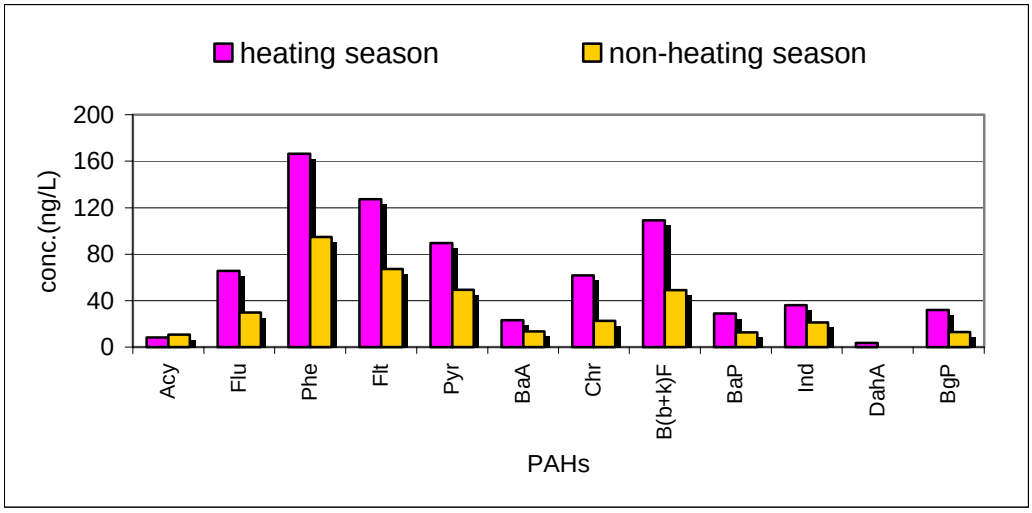

Figure 3. Seasonal behavior of PAHs

Annual wet deposition fluxes were calculated . We compared the annual wet deposition flux of total PAHs with Paris [8]. Annual flux of total PAHs was reported as 234 μg/m^2 in Paris while it was 213 μg/m^2 for our data. Bulk deposition fluxes of total PAHs were reported as in the range of 74.7-393.6 μg/m^2 in Northern Greece [7] and it was 334.8 μg/m^2 for Swedish west coast [14].

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