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MEASUREMENT OF DRY DEPOSITION AMOUNT OF PAHS IN ZONGULDAK REGION

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Abstract

Polyaromatic hydrocarbons (PAHs) consist of more than two unsubstituted benzene rings. They can be found in all media and some of them are cancerogenic. Polyaromatic hydrocarbons (PAHs) are formed during incomplete combustion of organic matter (i.e., coal, oil, gasoline, diesel fuel, garbage, and tobacco).
Increased concentrations of air pollutants caused by domestic heating, industrial activities, traffic and atmospheric transport in the city environments have been damaging air quality. Increased concentrations of air pollutants also cause health problems.
Zonguldak region has an important place in Turkey because of having large coal fields and coal production. However Catalagzı Thermal Power Plant , Eregli Steel Plant and usage of coal and wood in the region makes a potential input for PAHs in high concentrations.
In first stage of the study, calibration of PAH standards were made and PAH samples were collected periodically from 5 different sample collection points. In second stage of the study collected samples will be analysed.
This study will be a preliminary study for literature with measuring the concentration of dry deposition of PAHs. In addition, data obtained from the analyses will be used in preparing density map of PAH concentration and this will help us for detecting the effective source of pollutants.

***Key words**: domestic heating, dry deposition, industrial activities, PAHs, Zonguldak region.*

INTRODUCTION

Concentrations of particulate matter in the ambient air are typically composed of complex mixtures of chemical species, originating from a wide range of natural sources and human activities.
Among the organic compounds of anthropogenic origin, polycyclic aromatic hydrocarbons (PAHs) make up a significant group. Polycyclic aromatic hydrocarbons are a class of aromatic compounds found in ambient particulate matter and shown by several investigators to be carcinogenic and/or mutagenic.
PAHs are formed during incomplete combustion or pyrolysis of organic material and are related to the use of oil, gas, coal and wood in energy production. Other contributors to ambient air levels include indoor smoking and heating (WHO, 1987).
Lots of PAHs are in environment but 16 of them are at preferential list of EPA. They are acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(ah)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, phenanthrene and pyrene (EPA 2003).
High concentrations of atmospheric PAH exist in the urban environment, because of high domestic heating, vehicle density, industrial activities and dispersion of atmospheric pollutants.
Dry deposition is a major pathway for PAH transfers from air to land and water. Interest in atmospheric deposition has grown over the past decade because of concerns regarding the health effects resulting from the deposited material entering the environment.
In Turkey a few studies have been made about dry deposition of PAHs. One of them is about an industry region in Bursa province,

measuring the dry deposition flux of PAHs as 3300±5100 ngm^{-2} d^{-1} (Esen et al., 2007).
Again in 2007, in Izmir region a study was carried out about 15 PAHs, measuring for summer and winter periods. Results were given as 5792±3516 ngm^{-2} day^{-1} and 2650±1829 ngm^{-2} day^{-1} respectively for the season (Bozlaker et al., 2007).
Zonguldak province has hard coal deposits. There are two thermal power plants and one iron & steel plant in Zonguldak region. In addition to the industrial sources, domestic heating and increasing number of vehicles features air pollution studies in Zonguldak region. It is thought that PAHs concentrations can be high in this region but only one study about PAHs has been carried out at one point with an air sampler. PAH concentrations have been measured as 22.9 ngm^{-3} and 464 ngm^{-3} respectively for summer and winter periods (Akyuz and Cabuk, 2008).
Dry deposition in the region has not been studied and it will show the effective pollution sources.

MATERIALS AND METHODS

Sampling

To determine amount of PAH compounds, dry deposition sampling will be performed between July-August period with no rain. To avoid rain gush, sampling will be performed from 9 am to 9 pm everyday. Sampling period will be repeated every 5 day to get sufficient sample volume.
5 sampling points were determined between Kozlu and Çatalağzı, having distance approximately 20 km. Projected sampling points were given in Figure 1.

Figure 1. Sampling points

Dry deposition samples will be collected with a stainless steel pot whose diameter and depth is 60.5 cm and 19 cm, respectively. There is a 20 cm long leading edge around the sampler to minimize air flow disruptions caused by shape of the collector as used in the previous studies (Vardar et al., 2004; Tasdemir and Esen, 2006; Esen et al., 2006).

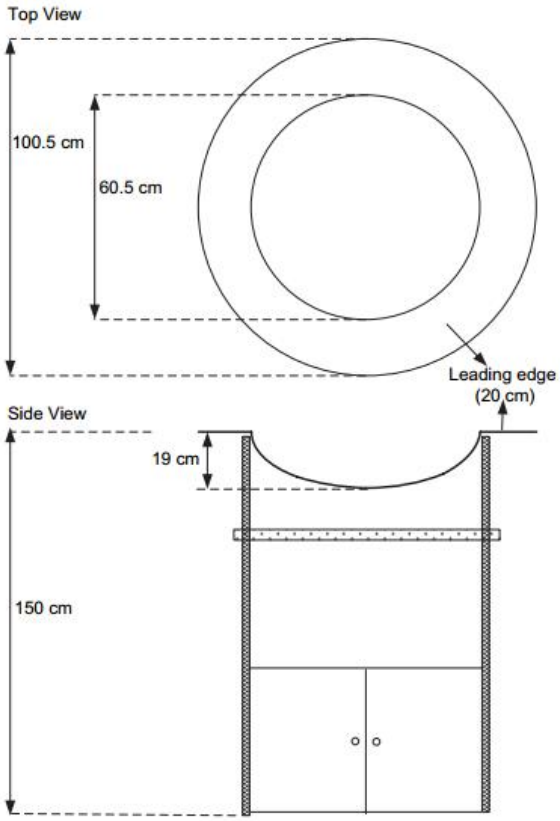

Figure 2. Side and top views of sampler

Extraction and analysis

At the end of each sampling period, the surface of bulk sampler is rinsed with DI water and MeOH sequentially and both of them is collected as a sample. The surface is then be wiped with a clean wiper and it is added into the sample. Samples are spiked with PAH surrogate standards and extracted with MEOH and DCM sequentially for 24 h for each solvent, respectively (Odabasi et al., 1999b; Tasdemir and Holsen, 2005; Tasdemir and Holsen, 2005; Esen, 2006). The MeOH and DCM extracts are combined and then concentrated to 5 ml with a rotary evaporator. Then the solvent is exchanged to HEX and

concentrated to 2 ml with a gentle stream of nitrogen.

Samples are spiked with PAH surrogate standards before extraction to determine analytical recovery efficiencies.

The collected samples are analysed for 15 individual PAHs: acenaphthalene (ACE), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthra cene (ANT), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP).

Samples will be analysed with Thermo Scientific TRACE™ Ultra gas chromatograph (GC) with flame ionization detector (FID) equipped with 30 m x 0.25 mm and 0.25 mm thickness TR5-MS column.

RESULTS AND DISCUSSIONS

Collected PAH samples will be analysed to determine sources and deposition fluxes into Zonguldak region. High and low concentrations of PAHs are being assumed with variations of sampling points. Points are considered for both industrial and urban sites. Traffic and atmospheric effects will also be remarked.

Due to lack of such a study in this region, effects of industry, domestic heating and traffic on human health will be discussed. Studies on dry deposition in the literature is given at Table 1 and Table 2.

In preliminary study, PAH calibration in GC was done with r^2 0,999169. Calibration curve and method procedure were given at Figure 3, 4. Peaks and calibration curve were given at Figure 5 and 6.

Table 1. Ambient air concentrations of individual PAHs in the combined gas and particle phases and comparison with measurements in the literature (ng m^{-3}) (Birgül et al., 2011).

Sampling site	Period	Phe	Ant	Flt	Pyr	BaA	Chr	BbF	BkF	BaP	IcdP	DahA	BghiP
Tainan, Taiwan	Mar-96	4.5	0.4	1.7	0.9	1.4	0.5	0.9	0.7	10.3	0.3	2.4	3.7
Seoul, Korea	Oct-98 Dec-99	16.4	2.7	8.1	12.5	2.6	3.6	4.8	2.5	3.5	0.5	3.2	
Gandy Bridge USA	Aug-02	15.7	0.5	5.9	2.4	0.05	0.5	0.1	0.02	0.01	0.04	0.01	0.1
Heraklion, Greece	Nov-00 Feb-02	20	3.3	4.9	6.6	1.1	3.1	1.5	1.8	1.2	2.5	0.1	3.4
BUTAL, Bursa Turkey	Aug-04 May-05	76.2	7	47.8	31.1	4.7	10.6	5.8	4.7	3.3	3.9	1.3	5.6
Singapore	Nov-06 Dec-06	7.2	2	5.6	7.3	0.5	0.9	1.2	0.2	0.5	0.8	0.07	1
BUTAL, Bursa Turkey	Sept-08 Jun-09	73.7	6.4	23.6	19.3	4.2	4.2	3.5	2.8	3.1	2.1	0.3	2.2

Chr/triphenylene

Table 2. Comparison of the dry deposition PAHs fluxes measurement (Pekey et al., 2007).

Location	Season	PAHs flux μg $m^{-2}day^{-1}$
Izmit Bay, Turkey	Summer	1.3
Seoul, Korea	Spring	5.5
Chicago, USA	Spring	6.9
Massachusetts Bay,USA	Summer	1.4
Tampa Bay, USA	Summer	0.6
Taichung, Taiwan	Urban	17.6
	Industrial	24.6

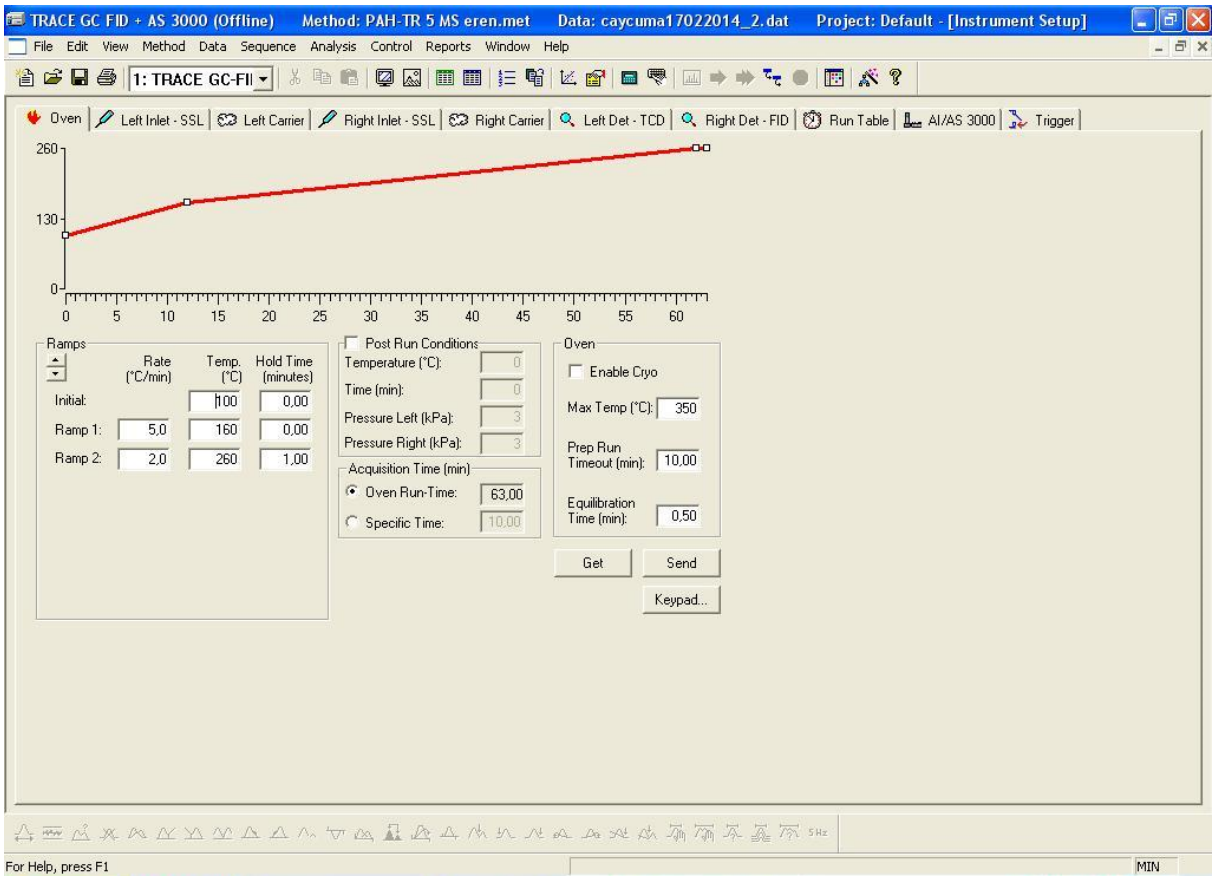

Figure 3. PAHs- GC method information-1

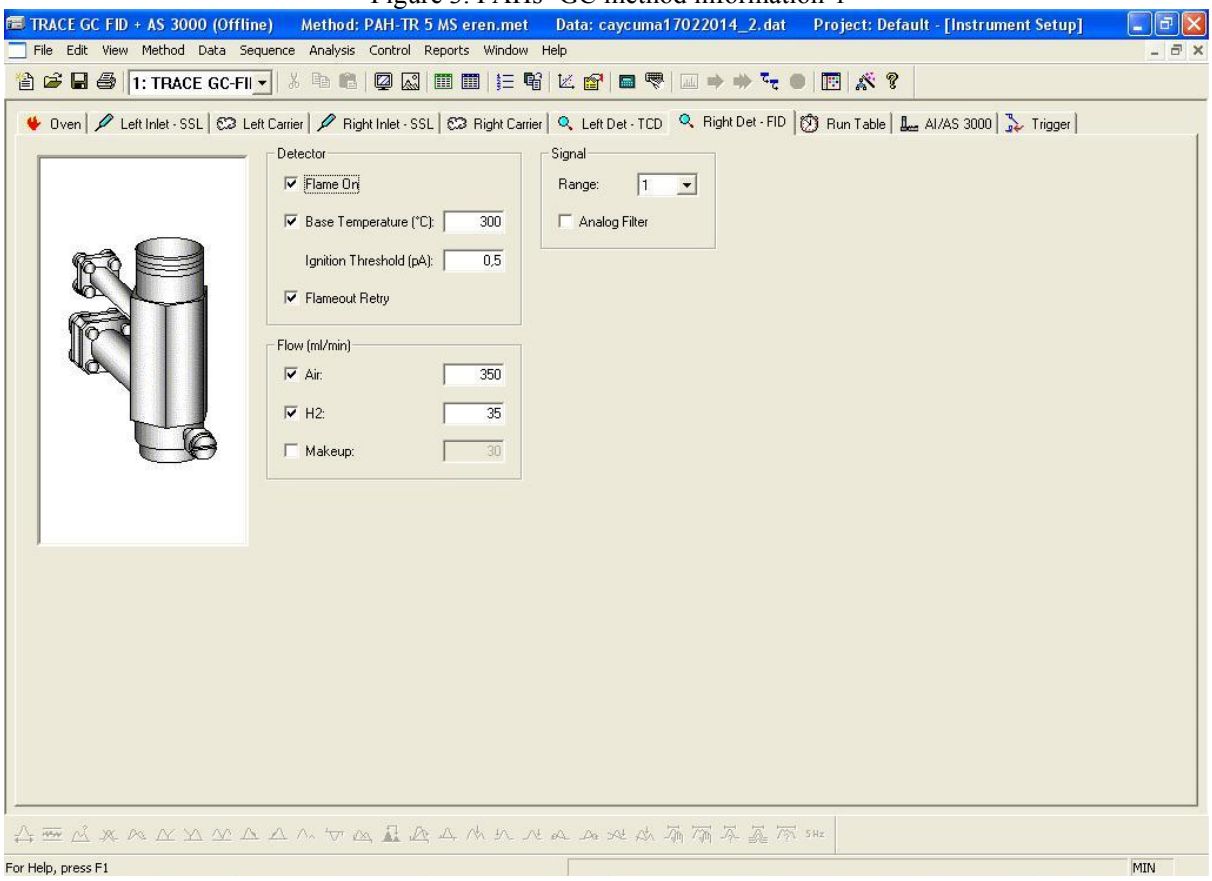

Figure 4. PAHs- GC method information-2

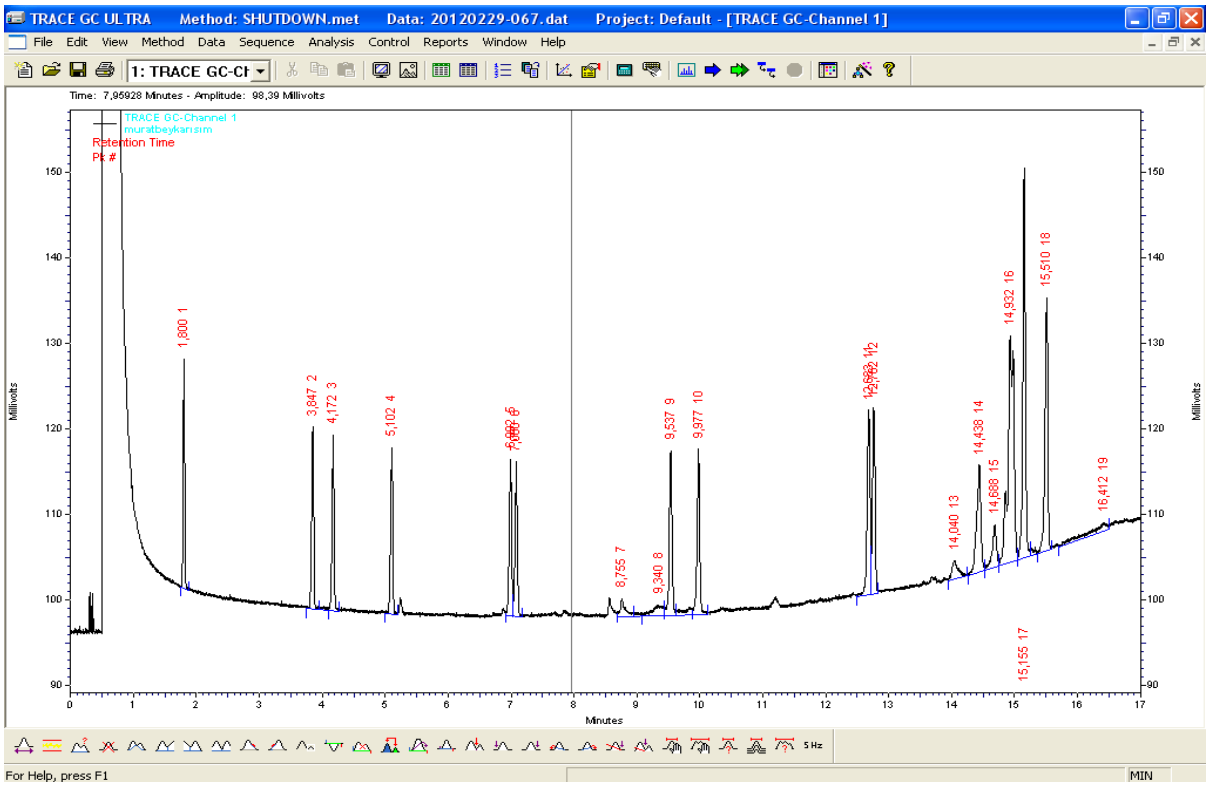

Figure 5. PAH Peaks

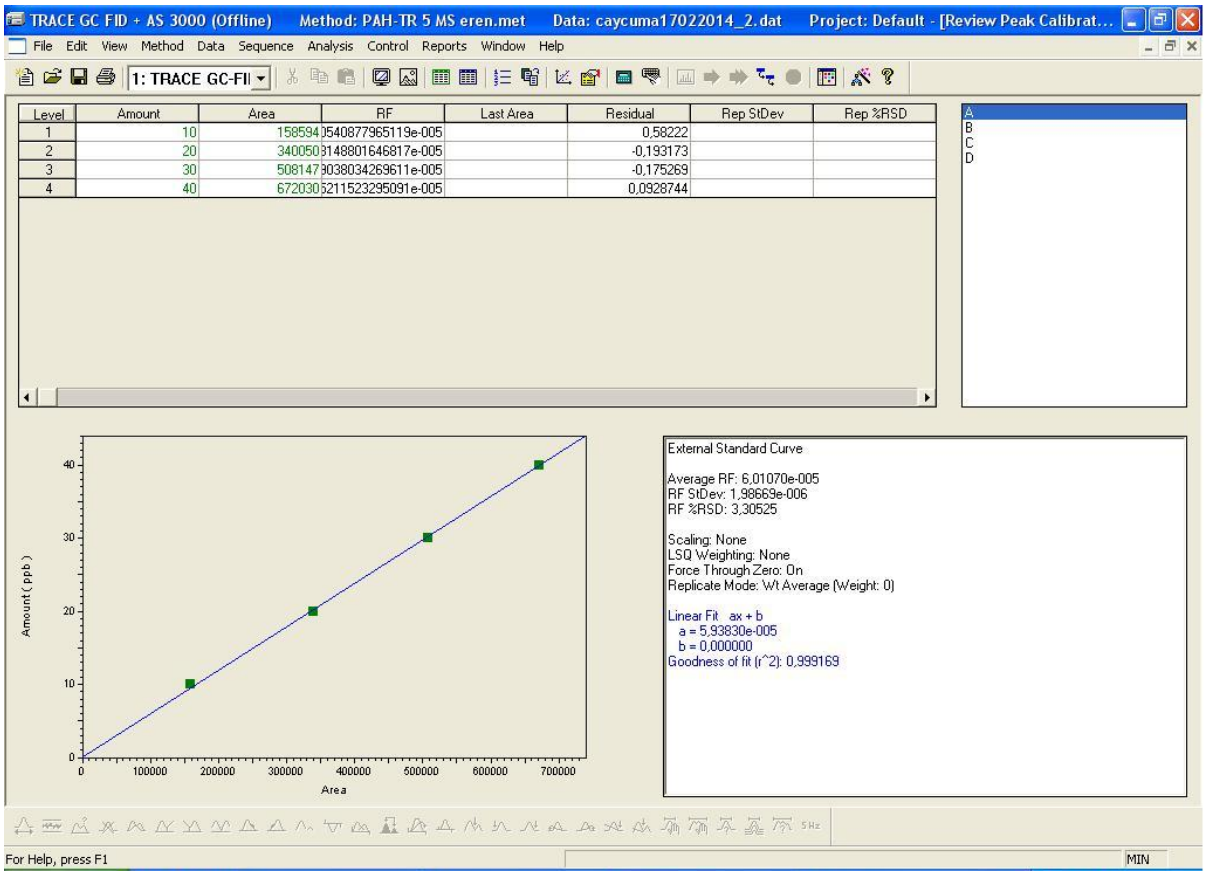

Figure 6. PAHs- GC method calibration curve

CONCLUSIONS

In previous study, particle associated PAHs through active air sampling has been measured in Zonguldak region at one point. Total concentration of PM10-associated PAHs were found as 492.4 ngm^{-3} in winter and 26.0 ngm^{-3}in summer times (Akyuz and Cabuk, 2009).

In this study, calibrations of PAHs were made in the first stage. In the second stage, dry deposition samplers will be used for measurement of PAHs deposition. With results of the projects, important data about PAHs will be obtained and sources of PAHs will be identified. We will have information about how PAH emissions disperse and deposits in Zonguldak region.

Potential exposures to PAHs may be assessed and results will help us to evaluate the degree of intake of PAHs into the human body.

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