

## PAHS CONCENTRATION LEVELS IN THE AMBIENT AIR OF A SUBURBAN AREA IN ATHENS AND IN A RURAL AREA NEAR A TIMBER PROCESSING PLANT

**BAIRACHTARI K.<sup>1,2</sup>, SARAGA D.<sup>1</sup>, MOYSIADI A.<sup>3</sup>, VASILAKOS CH.<sup>1</sup> and MAGGOS T.<sup>1</sup>**

<sup>1</sup>Environmental Research Laboratory, INRASTES, NCSR "DEMOKRITOS", 15310 Aghia Paraskevi Attikis Athens, GREECE, <sup>2</sup>Hellenic Army Academy, Division of Physical Sciences & Applications, Vari, Greece, <sup>3</sup>Environmental Chemistry Laboratory, University of Athens Athens, Greece

E-mail: kyriaki@ipta.demokritos.gr

### ABSTRACT

PAHs have been recognized as a group of potential hazardous chemicals of environmental and health concern. It is well known that the major source of PAHs is human activities. Furthermore, creosote, the material used for wood preservatives, contains high quantities of PAHs. It is the purpose of the current study to investigate the PAHs concentration levels at two sites with different background and activities. More specifically, a rural area where a timber processing plant is operating and a suburban area of Athens where an intensive residential development occurred during the last years were studied.

Twenty six PAHs, among them B[a]A, B[b]F, B[k]F, B[a]P, Chr, D[ah]A and Ind which are considered to be possible human carcinogens, were identified and determined through GC-MS analysis. Comparing the results from the two sites, it is notable the significant effect of the timber processing plant in the concentration levels of PAHs in the ambient air of a "clean" area. As far as the suburban area is concerned, differences in concentrations of PAHs between winter and summer period is justified by the biomass and fossil fuel burning during the cold period.

**Keywords:** PAHs, ambient air suburban area, rural area, timber processing plant

### 1. Introduction

PAHs have been recognized as a group of potential hazardous chemicals of environmental and health concern and despite some natural sources (forest and prairie fires, volcanic eruptions), their occurrence is largely the result of anthropogenic emissions. PAHs are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood and the release of petroleum products [1, 2, 3]. They are also found in coal tar, crude oil, roofing tar, creosote etc [1]. Furthermore the creosote is the material used for wood preservatives and can lead to skin irritation and disease [4]. Among PAHs, benzo[a]pyrene (B[a]P) is notable for being the first chemical carcinogen to be discovered, and is often used as a marker for total exposure to carcinogenic PAHs, as the contribution of B[a]P to the total carcinogenic potential is high [1]. European Union has set an ambient limit value of 1 ng/m<sup>3</sup> of B[a]P in PM<sub>10</sub> fraction over a calendar year (Directive 2004/107/E). Phenanthrene is connected with the existence of motorways, railways and generally burning gasoline [2, 3]. B(a)P/B(ghi)P ratio can be used to indicate traffic emissions (0.5-0.6) or brown coal combustion (>1.25) [1].

The purpose of the current study is to compare the PAHs concentration levels at three sites with different background and activities. A rural area in northern Greece where a timber processing plant is operating, a suburban area in Athens (Spata - Koropi), close to the international airport of Athens surrounded by major highways and an urban background area about 12 km to the north from the center of Athens.

## 2. Experimental section

### 2.1. Sites description

#### 2.1.1. Rural area

At the rural area (Drama), the sampling was carried out during the winter period (29/10-2/11/2007) at two different sites in the surrounding area of the plant. Those sites were selected based on the potential routes of dispersion of pollutants from the wood storage sites of the timber processing plant under the prevailing atmospheric conditions. It is well known that timber plant used creosote as wood preservatives. Creosote is a mid-heavy distillate of coal tar and contains high quantities of PAHs [4]. Twelve air samples (n=12) were collected using *High Volume Samplers* (Tisch) for the determination of gas and particle-phase PAHs and *Low Volume Samplers* (Derenda) for the determination of PAHs in particulate matter (PM10).

#### 2.1.2. Suburban area

At the suburban area, the sampling was carried out at two sites in Spata (5-19/12/2013) and Koropi (17-30/06/2014 and 3-16/07/2014). Those sites are surrounded by major highways, the Athens International Airport and present intensive residential building construction trend. Twenty one (n=21) PM10 samples were collected during the winter period and eighteen (n=18) during the summer period using *Low Volume Samplers*.

#### 2.1.3. Urban background area (NCSR)

The monitoring site is located in the National Center for Scientific Research "DEMOKRITOS" (NCSR) and characterized as an urban background area. Nine samples (n=9) were collected using *High Volume Samplers* (Tisch) for the determination of gas and particle-phase PAHs.

### 2.2. Sample preparation

The analytical procedure for the determination PAHs in atmospheric samples, which follows the ISO 12884:2000, is briefly described below:

After sampling, adsorbents and filters were extracted in a Soxhlet extractor, using cyclohexane. Before the extraction, deuterated PAHs (d8-Nap, d10-A, d10-Phe, d10-Chr, d10-Pyr, d12-B[ghi]P and d12-Perylene) were added as internal standards to monitor recovery. Ambient air extracts were concentrated in a rotary evaporator, loaded onto activated silica gel column chromatography and eluted with n-hexane and n-hexane/dichloromethane (3:2). PAHs fraction was concentrated under a gentle steam of nitrogen and an aliquot was analyzed by gas chromatography-mass spectrometric analysis (GC/MS).

### 2.3. Apparatus and analytical procedure

Agilent Technologies 7890A GC System, 5975 C inertXL EI/CI MS Detector, provided with 7683B autosampler, is used for PAHs determination and quantitation in air samples. Twenty six PAHs were detected, including a group of suspected carcinogens PAHs.

The detection limits (LOD) range from 0.62 to 4.11 pg for the air samples. The uncertainty ranges from 6% to 21% for the air samples (in accordance with the international standard, uncertainty should be at least +/-50%). The precision ranges from 1.5% to 8.2% for the air samples (in accordance with the international standard, precision should be at least +/-25%).

## 3. Results and discussion

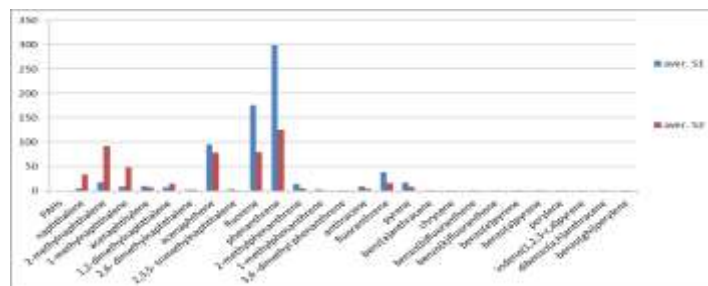
### 3.1. PAHs concentration in TSP and in PM10 at timber processing plant

The concentration of ΣPAHs in TSP, ranged from 227 ng/m<sup>3</sup> to 809 ng/m<sup>3</sup>, with an average value of 613 ng/m<sup>3</sup>. The most abundant components were phenanthrene with an average concentration of 212 ng/m<sup>3</sup>, fluorene 127 ng/m<sup>3</sup>, fluoranthrene 26.6 ng/m<sup>3</sup> and acenaphthene 86.6 ng/m<sup>3</sup>.

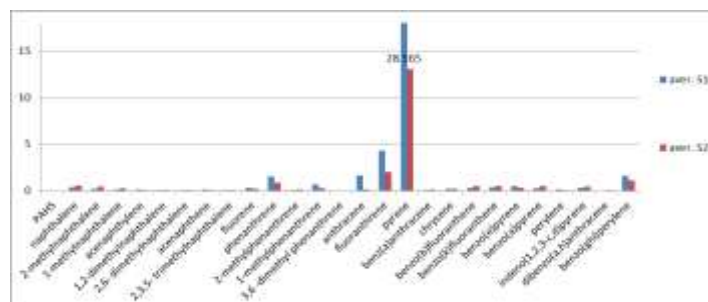
The average concentration of possible human carcinogens PAHs according EPA and IARC [(BaA), (Chr), (BaP), (BbF), (BkF), (DBA), (IP)] was 2.95 ng/m<sup>3</sup>. Among them, benzo(b)fluoranthrene presents the highest concentration and dibenzo(a,h)anthracene the lowest. The average concentration of benzo[a]pyrene was 0.34 ng/m<sup>3</sup>.

At site 1, the average concentration of  $\Sigma$ PAHs in TSP, was found to be higher than that at site 2 (Fig. 1). This difference is likely due to the weather conditions, particularly to the wind direction and due to the fact that, site 1 was closer to the timber processing plant. The effect of weather conditions is confirmed by the fact that at the same day, the highest concentration of  $\Sigma$ PAH was observed at site 1 (B) and the lowest at site 2 (B).

The average concentration of  $\Sigma$ PAHs in PM<sub>10</sub>, was 32.62 ng/m<sup>3</sup> while the average concentration of probable human carcinogens  $\Sigma$ PAHs [(BaA), (Chr), (BaP), (BbF), (BkF), (DBA), (IP)] was 1.93 ng/m<sup>3</sup>. Among them, benzo(b)fluoranthrene has the highest concentration and dibenzo(a,h)anthracene the lowest. Benzo[a]pyrene concentration did not exceed the target value of 1 ng/m<sup>3</sup>, in both sites and sampling days (average value 0.36 ng/m<sup>3</sup>). The average concentration of  $\Sigma$ PAHs in PM<sub>10</sub> at site 1, was found to be higher than that at site 2 (Fig. 2). This difference is likely due to the wind direction. In addition, site 1 was closer to the timber processing plant. In the second day of sampling, the concentration of  $\Sigma$ PAHs in PM<sub>10</sub> was much higher than that of the first day.



**Figure 1:** Average concentrations of PAHs (ng/m<sup>3</sup>) in TSP, at the two sampling sites



**Figure 2:** Average Concentration of PAHs (ng/m<sup>3</sup>) in PM<sub>10</sub>, at the two sampling sites

### 3.2. Suburban area in Attica

In the case of the suburban area, on summer period (Koropi), the concentration of PAHs in PM<sub>10</sub> ranged from 7.48 ng/m<sup>3</sup> to 22.4 ng/m<sup>3</sup>. The average concentration was 14.7 ng/m<sup>3</sup>, while the average concentration of probable human carcinogens PAHs was 0.30 ng/m<sup>3</sup>. Among them, chrysene presented the highest concentration. Benzo[a]pyrene concentration did not exceed the target value of 1 ng/m<sup>3</sup> (90.0 ng/m<sup>3</sup>).

During winter period (Spata), the average concentration of PAHs in PM<sub>10</sub>, was 95.6 ng/m<sup>3</sup> while during the summer period was 14.7 ng/m<sup>3</sup>. The most abundant components were phenanthrene, fluorine, fluoranthrene and pyrene. It is evident that the levels of PAHs in winter are much higher than those in summer mainly due to the central heating (fossil fuels) and biomass burning (Fig. 3). The average concentration of probable human carcinogens PAHs during winter and summer period was 9.04 ng/m<sup>3</sup> and 0.30 ng/m<sup>3</sup> respectively. Among them, chrysene demonstrated the highest concentration. Benzo[a]pyrene exceeded the target value in 8 out of 21 sampling days. The highest benzo[a]pyrene concentration was observed during winter period, ranging from 0.11 to 6.26 ng/m<sup>3</sup> with an average concentration of 1.20 ng/m<sup>3</sup>.



photochemical decomposition due to high sunshine and convert PAHs into other forms such as nitro-PAH [1].

However the biomass burning origin of PAHs during the winter period, is reinforced by the B(a)P/B(ghi)P ratio. The latter indicates traffic emission sources when ranged from 0.5 to 0.6 or brown coal combustion when the value is higher than 1.25 [1]. In our study, the above ratio during the winter period was 1.26 while the corresponding value during summer was 0.40.

#### 4. Conclusions

Comparing the results from the rural and the urban background area in TSP, the significant effect of the timber processing plant in the concentration levels of PAHs in the ambient air of a “clean” area can be noticed. Although the concentration of volatile PAHs in TSP is high, benzo(a)pyrene (bounded to particles) concentration was at low level in TSP following the PAHs composition of creosote content.

As far as the suburban area is concerned, differences in concentrations of PAHs in PM10 between winter and summer period is justified by the biomass and fossil fuels burning during cold period. The latter is confirmed by the B(a)P/B(ghi)P ratio which in winter period was 1.26, indicating brown coal combustion.

Furthermore, independently of the season, the levels of phenanthrene are higher than any other PAH's measured, indicating motorways, railways and generally burning gasoline sources

Finally, concentration of benzo[a]pyrene in PM10, ranged from 0.11 to 6.26 ng/m<sup>3</sup> with an average concentration of 1.20 ng/m<sup>3</sup> in winter period, exceeded the target value of EU Directive defined at 1 ng/m<sup>3</sup>. In summer period, benzo[a]pyrene concentration did not exceed the target value.

#### ACKNOWLEDGEMENTS

Financial support from the EnTeC FP7 Capacities programme (REGPOT-2012-2013-1, FP7, ID: 316173), is kindly acknowledged.

#### REFERENCES

1. Ravindra K., Sokhi R., Grieken R (2008), Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors, and regulation”, *Atmospheric Environment* **42** 2895-2921, Science Direct.
2. Noth Elizabeth M., S. Katharine Hammond, Gregory S. Biging, Ira B. Tager (2013), Mapping and modeling airborne urban phenanthrene distribution using vegetation biomonitors, *Atmospheric Environment*, Volume **77**, 518–524.
3. Hwang H.M., T. L. Wade (2008), Aerial Distribution, Temperature-dependent Seasonal Variation and Sources of Polycyclic Aromatic Hydrocarbons in Pine Needles from the Houston Metropolitan Area, Texas, USA, *Journal of Environmental Science and Health – Part A, Toxic/ Hazardous Substances and Environmental Engineering*, Volume **43**, Issue 11, 1243-1251.
4. Yoshiaki Ikarashi, Masa-aki Kaniwa, Toshie Tsuchiya (2005), Monitoring of PAHs and water extractable phenols in creosotes and creosote-treated woods made and procurable in Japan, *Chemosphere* **60**, 1279-1287.
5. Hu J., C.Q. Liu, G.P. Zhang, Y.L. Zhang (2012), Seasonal Variation and Source Apportionment of PAHs in TSP in the atmosphere of Guiyang, Southwest China, *Atmospheric Research*, Volume **118**, 271-279