POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN FINE AND COARSE PARTICLES

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ABSTRACT
About 140 samplings of fine and coarse particles were gathered during the year 2006 in Kozani that represent an urban area surrounded by opencast coal mining. A low volume dichotomus sampler has been used to trap suspended particles. The filters used were teflon, which are ideal for analysis in the determination of PAHs. The determination of Polycyclic Aromatic Hydrocarbons (PAHs) has been carried out by the use of the analytic technique of large volume injection and gas chromatography – mass spectrometry (LVI - GC/MS). The extraction of substances has been made in a two stage procedure, firstly with agitation in a magnetic shaker and secondly by the use of ultrasonic bath. This technique has given high recoveries of PAHs, in short time intervals. The mean daily concentrations of fine particles varied from 4 to 48 µg m⁻³ and annual mean was 16 µg m⁻³. The mean daily concentrations of coarse particles respectively varied from 2 to 67 µg m⁻³ with 23 µg m⁻³ annual mean concentration. The \( \Sigma_{PAH} \) concentrations for fine samples were 4.80 ± 7.06 ng m⁻³ and for coarse samples were 1.36 ± 1.59 ng m⁻³. The mean \( \text{B[a]Py} \) concentration for fine particles was 0.38 ng m⁻³. Finally, diagnostic ratios were used to characterize and identify PAHs emission source in this study.

KEYWORDS: Fine, Coarse, PAHs, Suspended particles.

INTRODUCTION
In many studies significant correlation has been found between particulate matter PM fractions and health effects related to respiratory symptoms, while appear to cause cardiovascular effects. Particulate pollution is of outstanding importance in areas with open-pit mines because of its human health related effects (Glantz, 1993; Seaton et al., 1995). The mechanism of the distribution of airborne particulate matter (PM) into size fraction has become an increasing area of focus when examining the effects of particulate pollution (Triantafyllou et al., 2006a). Particle size distribution is important for human exposure and risk assessment, as well as for understanding the mechanisms of atmospheric processes. Particles with the size less than 10 µm (PM₁₀) have long been implicated in causing adverse health effects and increased mortality whereas fine (PM₂.₅) and ultrafine particles impose even higher risk (Crebelli et al., 1995; 1998; Pagano et al., 1996).
Over the past years PAHs have been found to be ubiquitous constituents of urban airborne particles and have become a major health concern mainly due to their well-known carcinogenic and mutagenic properties (De Raat, 1988; Oanh et al., 2002). PAHs are formed during incomplete combustion of organic materials such as fossil fuels, coke and woods. Residence time and removal mechanisms of PAHs in the atmosphere depend on their distribution among the particle size fractions.

Kozani is a heavily industrialized area in the northwestern part of Greece, which is characterized by complex topography. Within the basin, lignite Power stations (PS) operates with a total installed generating capacity of more than 4.7 GW. These PS contribute to about 57% of the total electrical energy produced in Greece. The lignite used by these power stations is mined in the nearby open-pit mines. Considerable amounts of pollutants are emitted from the PS stacks and mining activities (Triantafyllou et al., 2006a). The air quality around the area is monitored by a measurement stations network, which has been installed by the Greek Public Power Corporation. Specific atmospheric pollution measurements are also carried out by the Laboratory of Atmospheric Pollution and Environmental Physics of Technological Education Institute of West Macedonia (Triantafyllou et al., 2006b).

Several studies have been carried out and published on the atmospheric pollution in the greater area of Kozani in order to assess the air quality and the mechanism of pollutant dispersion and transportation (Triantafyllou et al., 2002). However, few studies focus on composition of particles and especially on PAH content (Evagelopoulos et al., 2006; Voutsa et al., 2004; Samara, 2005; Terzi and Samara, 2004; Kalaitzoglou et al., 2004).

The main objective of the present work was to study the seasonal variation of particulate PAHs in the urban atmosphere by considering their emission sources by using molecular diagnostic criteria.

MATERIALS AND METHODS

Sample collection

Particulate samples of fine and coarse particles were collected in the urban area of Kozani in Greece, for a period of one year (December 2005 to October 2006), every 6 days. The samples were collected by dichotomous sampler (Andersen Instruments Inc. Dichotomous Sampler) with a PM10 inlet probe and a PM2.5 virtual impactor to collect fine (PM2.5) and coarse (PM2.5-10) particles for gravimetric analysis. The samples were collected by passing air through 37 mm teflon PTFE filters. The technique for monitoring the size distribution of airborne aerosols with a dichotomous sampler is inertial impaction of particles into a void (virtual surface). The airflow for coarse particle sampling was 1.7 l min⁻¹, while that for fine particle sampling was 15 l min⁻¹, and the total airflow was 16.7 l min⁻¹.

Before sampling, the filters have been equilibrated to constant temperature (22°C± 3°C) and relative humidity (45%±5%) conditions and weighed. After sampling, the filters have been again equilibrated to the constant temperature and humidity conditions and again weighed. The concentration is calculated by dividing the weight of the particulate captured on the filter by the volume of air (at ambient conditions) that passed through the sampler. The flow rate is required to be maintained within 5% of 16.67 l min⁻¹ with a coefficient of variation of less than 2%.

Analytical procedures

Standard PAH Mixture containing 16 PAHs was used to identify the following compounds: Acenaphthene (Ace), Fluoranthen (Fl), Naphthalene (Np), Benzo(a)anthracene (B[a]An), Benzo(a)pyrene (B[a]Py), Benzo(b)fluoranthene (B[b]Fl), Benzo(k)fluoranthene (B[k]Fl), Chrysene (Chry), Acenaphthylene (Acn), Anthracene (An), Benzo(ghi)perylene (B[ghi]Pe), Fluorene (F), Phenanthrene (Ph), Dibenzo(a,h)anthracene (D[ah]An), Indeno(1,2,3-cd)pyrene (IPy), Pyrene (Py), plus benzo[e]pyrene B[e]Py which is frequently used as reference PAH. PAHs were recovered from filter according to procedures previously optimized (Evagelopoulos et al., 2008). Briefly PAHs are extracted quickly and in high portions by the use of ultrasonic bath, however, this may lead to partial PAH degradation when found in high concentration (Ping and Weavers, 2006). Thus, the teflon filters were separated from...
polypropylene ring with care in order to avoid loss of sample and then, they were extracted in a two stage procedure. First, they were purred in 50 ml liners with 5 ml hexane. The samples were placed in magnetic shaker for 30 min while heated below boiling temperature. At the second stage and after removing hexane extract, 5 ml hexane – acetone mixture (1:1) was added and the liner was placed in the supersonic chamber for 15 min. During both stages water freezer has been used for the condensation of the solvent in order to avoid loss of the low molecular weight substances.

The extracts then were transferred in conical 10 ml vials and the volume was reduced to 1 ml under ultra pure nitrate gas flow. The extract after addition of PAHs internal standard (mixture of Acenaphthene-d10, Chrysene-d12, 1,4-Dichlorobenzene–d4, Naphthalene-d8 and Pyrene-d12) was analyzed by Large Volume - Gas Chromatography / Mass Spectrometry (LVI-GC/MS) technique for the determination of PAHs content. The MS operated at Single Ion Monitoring (SIM) with three optimized ion groups and molecular ions, used for quantification. In some cases full scan mode (m/z 50-450) was employed in order to validate analysis results.

Recovery efficiencies (75-101%) were determined using the spiked method, as were the detection limits of each compound. In all analyses, a procedural blank was performed periodically to confirm that there was no contamination. The detection limits were estimated as three times the background noise (IUPAC criterion) and ranged from 0.025 to 0.333 ng ml⁻¹ for all analyzed compounds.

All glassware washed up by acetone and hexane prior use. The samples after centrifugation for the removal of solid endings were isolated from sunlight and stored in freezer (-20°C) until of their analysis.

RESULTS AND DISCUSSION

PAHs concentration levels

The mean daily concentrations of fine particles varied from 4 to 48 µg m⁻³ and annual mean was 16 µg m⁻³, which is higher than the limit (15 µg m⁻³) regulated in the United States, while lower from the annual limit (25 µg m⁻³) set by European Union. The mean daily concentrations of coarse particles respectively varied from 2 to 67 µg m⁻³ with 23 µg m⁻³ annual mean concentration.

Table 1 gives the average total particle bound PAHs (ΣPAH) concentrations of airborne particles at the sampling site. Mean particulate PAHs concentrations (mean ± standard deviation) for fine samples were 4.80 ± 7.06 ng m⁻³ and for coarse samples were 1.36 ± 1.59 ng m⁻³. At warm period (15 April – 15 October) for fine samples concentrations were 2.62±5.60 ng m⁻³ and for coarse samples were 2.00±5.85 ng m⁻³. Finally, at cold period for fine samples concentrations were 8.88±9.00 ng m⁻³ and for coarse samples were 2.60±1.93 ng m⁻³.

These results indicate that the concentrations of airborne particulate PAHs varied seasonally and generally were decreasing with increasing temperature. The decrease in particulate PAH concentrations during warmer periods may be due to the temperature dependency of vapor pressure which controls particle/gas partitioning (Odabasi et al., 1999). In addition, the mean concentration of fine particulate PAHs was significantly higher than that measured in coarse, by a factor of 3.5.

PAHs emitted from combustion sources and thus emitted to atmosphere in gas phase or in fine particles. After the entrance to atmosphere they are cold and they unite or adsorbed into small particles. Those processes lead PAHs in higher concentrations to fine particles (Seinfeld, 1986).

Table 2 gives sixteen polyaromatic hydrocarbons with a molecular mass from 152 to 278 that were detected and quantified in the particulate phase of Kozani atmosphere. The most abundant PAHs in all samples were fluoranthene (0.53 ng m⁻³), pyrene (0.45 ng m⁻³), benzo[a]anthracene (0.41 ng m⁻³) and benzo[b]fluoranthene (0.57 ng m⁻³). B[a]Py concentration varied from 0.01 to 3.61 ng m⁻³ (average 0.38 ng m⁻³) (Table 2). That value exceeded the proposed annually averaged standard of 0.25 ng m⁻³ for B[a]Py in the United Kingdom, while lower from the target annual standard of 1ng m⁻³ set by European Union.
Table 1. Total Particulate PAHs Concentrations

<table>
<thead>
<tr>
<th></th>
<th>Fine (ng m⁻³)</th>
<th>Coarse (ng m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>4.80±7.06</td>
<td>1.36±1.59</td>
</tr>
<tr>
<td>Warm</td>
<td>2.62±5.60</td>
<td>2.00±5.85</td>
</tr>
<tr>
<td>Cold</td>
<td>8.88±9.00</td>
<td>2.60±1.93</td>
</tr>
</tbody>
</table>

All data represent mean ± SD.

Table 2. Mean concentration and SD of concentrations (ng m⁻³) for particulate PAHs in Kozani atmosphere

<table>
<thead>
<tr>
<th>PAH compounds</th>
<th>Fine (ng m⁻³)</th>
<th>Coarse (ng m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>SD</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.23</td>
<td>0.51</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.35</td>
<td>1.19</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.53</td>
<td>1.55</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.45</td>
<td>1.08</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.25</td>
<td>0.49</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>0.41</td>
<td>0.68</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>0.46</td>
<td>0.62</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>0.57</td>
<td>0.73</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>0.44</td>
<td>0.46</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.38</td>
<td>0.53</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>0.29</td>
<td>0.33</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.53</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Σ_{PAH} 4.80  7.06  1.36  1.59

PAHs concentrations have been reported for many different urban areas throughout the world (Odabasi et al., 1999; Kavouras et al., 1999; Tsapakis and Stephanou, 2004; Panther et al., 1999; Mantis et al., 2005; Chaloulakou et al., 2003). Direct comparison of PAH concentrations between various urban environments should be done with caution. Sampling methodology is a critical parameter affecting the comparison between the observed concentrations of PAHs in different sites (Tsapakis and Stephanou, 2004). In most published studies, collection of particulate phase of PAHs has been performed by using high volume air samplers and particles are trapped to glass fiber filters. In some cases underestimation of PAHs concentrations might have occurred due to reactions with atmospheric oxidants (especially ozone) and loss of most volatile compounds during sampling (Tsapakis and Stephanou, 2004).

Similar PAHs concentrations, with those at present work, have been reported before for the area of Kozani (Voutsas et al., 2004; Terzi et al., 2004; Kalaitzoglou et al., 2004). Moreover, these values are comparable to those found in Athens (Mantis et al., 2005) and lower (2 to 4 times) than those found in Thessaloniki (Manoli et al., 2004).

Diagnostic ratios of PAHs
Diagnostic ratios for PAHs, such as BF₅/B[ghi]Pe, FI/(FI+Py), IPy/(B[ghi]Pe+IPy), B[a]A/(B[a]An+Chry), B[e]Py/B[a]Py and C_{PAH}/Σ_{PAH} are presented at Table 3. The PAH ratios
have been used as confirmation indicators of the source that emits the pollution into the urban atmosphere in many studies (Kavouras et al., 1999; Tsapakis and Stephanou, 2004; Mantis et al., 2005). However, they should be used with caution because often is difficult to discriminate between different sources, moreover they can be altered due to the reactivity of some PAHs species with other atmospheric species, such as NOx, O3, etc. (Mantis et al., 2005). The ratios of total concentration of nine combustion PAHs to the total concentration of PAH ($\text{CPAH}/\Sigma \text{PAH}$) were determined by Rogge (Rogge et al., 1993) for noncatalyst (0.41), catalyst-equipped (0.51) automobiles and for heavy-duty diesel trucks (0.3). The ratio of $\text{CPAH}/\Sigma \text{PAH}$ was 0.85–0.93 in this study, which was much higher than any of the above ratios, but it was well consistent with the results of Kavouras et al. (0.78±0.16) (Kavouras et al., 1999). Emissions from lignite power stations may be the reason for such high ratio values.

The mean $\text{Fl}/(\text{Fl+Py})$ ratio for cold period 0.50 for fine and 0.46 for coarse particles, which was similar to that for oil combustion. At warm period the ratio was lower and similar with that for automobiles emissions (0.43 and 0.39 respectively) (Rogge et al., 1993).

The BF$_{s}$/B[ghi]Pe ratio proposed (Cretney et al., 1985), for use in discriminating automobiles (0.21–0.28) from domestic fires (2.6–14 in coal/wood soot). In present work the BF$_{s}$/B[ghi]Pe ratios are characteristic of coal combustion.

The literature reported value for IPy/(IPy+B[ghi]Pe) were 0.18, 0.37 and 0.56, for cars, diesel vehicles, and coal combustion, respectively (Grimmer et al., 1983). The ratios in this study ranges 0.31-0.37, which was comparable to that for diesel emissions indicated the discrepancy of traffic influence.

B[e]Py/B[a]Py ratio might be affected by the strong reactivity in the atmosphere since B[a]Py was easily decomposed by light and oxidants. The B[a]Py has half-life of 5.3 h under simulated sunlight conditions, while B[e]Py is relatively more stable to photolysis with a half-life of 21.1 h (Panther et al., 1999). Finally, the B[a]An/B[a]An + Chry ratio values was characteristic of a faster decay of B[a]An in comparison to the more stable isomer Chry. Those ratios indicating possible transport of PAHs from a distant source.

### Table 3. Molecular diagnostic ratios of PAH concentrations of fine and coarse particles

<table>
<thead>
<tr>
<th>Ratios/period</th>
<th>Mean</th>
<th>Cold</th>
<th>Warm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fine</td>
<td>coarse</td>
<td>fine</td>
</tr>
<tr>
<td>BF$_{s}$/B[ghi]Pe</td>
<td>4.84</td>
<td>3.73</td>
<td>8.39</td>
</tr>
<tr>
<td>IPy/(IPy+B[ghi]Pe)</td>
<td>0.35</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>B[a]An/(B[a]An+Chry)</td>
<td>0.64</td>
<td>0.62</td>
<td>0.64</td>
</tr>
<tr>
<td>Fl/(Fl+Py)</td>
<td>0.46</td>
<td>0.43</td>
<td>0.50</td>
</tr>
<tr>
<td>B[e]Py/B[a]Py</td>
<td>1.74</td>
<td>3.12</td>
<td>1.30</td>
</tr>
<tr>
<td>C$_{PAH}$/\Sigma \text{PAH}$</td>
<td>0.91</td>
<td>0.83</td>
<td>0.93</td>
</tr>
</tbody>
</table>


BF$_{s}$: B[b]Fl + B[k]Fl

\Sigma \text{PAH}$: Total PAH concentration

### Correlation of PAHs with air pollution and meteorological parameters

Meteorological parameters (temperature, wind speed and solar radiation) as well as the concentrations of other atmospheric pollutants such as ozone (O$_3$), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO$_2$) and sulfur dioxide (SO$_2$) were measured in the same area at the same time period. The correlation coefficients (Pearson) with $\Sigma \text{PAH}$ are displayed in Table 3.

Positive correlations were found between PAH concentration and SO$_2$, CO, NO, NO$_2$ concentration and negative correlations were found between PAH concentration and O$_3$ concentration, temperature and solar radiation.

The total concentration of particulate PAHs for fine particles was strongly correlated with sulfur dioxide ($R=0.62$ and $P=0.005$). Sulfur dioxide, in the urban environment, was mainly emitted from domestic central heating and from power plants. PAHs are also emitted from the
same sources. This might be the reason of the positive correlation between the two factors. In addition PAHs concentration was positively correlated with CO and NO concentration. CO and NO are primary pollutants and their concentrations levels are dominated by traffic. PAHs are also emitted by engine exhaust.

Negative correlation was found between O₃ concentration and particulate PAH concentration while positive correlation was found between NO₂ concentration and particulate PAH. The negative correlation with O₃ and the positive correlation with NO₂ has also been reported for other locations (Mantis et al., 2004). These relations are possibly due to the secondary NO₂ and O₃ formation, where time, dilution and environmental factors play an important role in dispersing the contaminants in the ambient atmosphere (Panther et al., 1999).

Negative correlation was found for solar radiation and temperature due to faster degradation of PAHs with higher solar radiation. Additionally, a negative relation of ΣPAH with wind speed showed that the PAHs emissions are not originating from long distance sources (Chaloulakou et al., 2004).

<table>
<thead>
<tr>
<th></th>
<th>ΣPAH-fine</th>
<th>ΣPAH-coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>0.62</td>
<td>0.40</td>
</tr>
<tr>
<td>NO</td>
<td>0.42</td>
<td>0.28</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>O₃</td>
<td>-0.36</td>
<td>-0.11</td>
</tr>
<tr>
<td>CO</td>
<td>0.61</td>
<td>0.34</td>
</tr>
<tr>
<td>Temperature</td>
<td>-0.50</td>
<td>-0.24</td>
</tr>
<tr>
<td>Solar Radiation</td>
<td>-0.36</td>
<td>-0.15</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>-0.13</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

CONCLUSIONS
The mean daily concentrations of fine particles varied from 4 to 48 µg m⁻³ and annual mean was 16 µg m⁻³, higher than the annual arithmetic mean of 15 µg m⁻³ established by the United States and lower from the annual limit (25 µg m⁻³) set by European Union. The mean daily concentrations of coarse particles respectively varied from 2 to 67 µg m⁻³ with 23 µg m⁻³ annual mean concentration.

The average fine and coarse ambient air particle-bound PAHs concentrations at Kozani sampling site were found to be 4.80 and 1.36 ng m⁻³ respectively. All of the total individual PAHs concentrations in fine were higher than coarse. The mean B[a]Py concentration was 0.38 ng m⁻³ and exceeded the proposed annually averaged standard of 0.25 ng m⁻³ in the United Kingdom, while it was lower from the target annual standard of 1 ng m⁻³ set by European Union.

Based on the diagnostic ratios the result showed that oil and or coal burning was the possible major PAHs pollutant sources. Besides, comparison with diagnostic ratios, the influences of vehicle exhaust was become an important factor for PAHs concentrations.

The positive and negative correlation from PAHs analysis showed that PAHs are emitted locally and their concentration is varied by the presents of other pollutants in the atmosphere and the meteorological conditions.

REFERENCES


