

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN FINE AND COARSE PARTICLES

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EXTENDED ABSTRACT

Several epidemiological studies have shown an association between particulate air pollution and health effects. Suspended particulates appear to cause respiratory health effects and heart diseases. Particulate pollution is of exceptional importance in areas with open-pit mines because of its human health related effects.

Kozani is a heavy industrialized area in the northwestern part of Greece, which is characterized by complex topography. Within the basin, lignite 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. Dust emissions seem to be the most serious problem in the area, as the measured ambient concentrations of suspended particles are at high levels and exceed local and international standards.

The profile of fine (PM_{2.5}) and the coarse of (PM_{2.5-10}) particles in Kozani, with regard to PAHs was studied. These findings have taken into consideration the diagnostic ratios, correlation with air pollutants and with weather conditions, in investigating the sources of pollution in the region.

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 activities (e.g. resuspension) and tall stack raw lignite combustion activities (e.g. flying ash transfer). A low volume dichotomus sampler has been used to trap suspended particles. The filters used were teflo, which are ideal for analysis in the determination of PAHs. The determination of 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 by the combination of agitation with reflux solvent and bath of ultrasounds with reflux solvent. 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/m³ and annual mean was 16 µg/m³. The mean daily concentrations of coarse particles respectively varied from 2 to 67 µg/m³ with 23 µg/m³ annual mean concentration.

The Σ_{PAH} concentrations for fine samples were 4.80 ± 7.06 ng/m³ and for coarse samples were 1.36 ± 1.59 ng/m³. The mean B[a]Py concentration for fine particles was 0.38 ng/m³. Additionally, diagnostic ratio was used to characterize and identify PAHs emission source in this study.

KEYWORDS: Fine, Coarse, PAHs, Suspended particles.

1. INTRODUCTION

In many studies have been found significant correlation between particulate matter PM fractions and health effects related to respiratory symptoms. Particulate pollution is of outstanding importance in areas with open-pit mines because of its human health related effects [1,2]. 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 [3]. 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 (PM_{10}) have long been implicated in causing adverse health effects and increased mortality whereas fine ($\text{PM}_{2.5}$) and ultrafine particles impose even higher risk [4-6].

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 [8,9]. 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.

In the Kozani area lignite power stations produce the most percentage of the electrical energy produced in Greece. The lignite is mined in the nearby open-pit coal-mines and transported to the power stations. Considerable amounts of pollutants are emitted from the PS stacks and mining activities [3]. The air quality control 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 T.E.I of West Macedonia [10].

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 [11,12]. However, few studies focus on composition of particles and especially on PAH content [13-15]

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.

2. MATERIALS AND METHODS

2.1 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 with a PM_{10} inlet to collect particles in the PM_{10} size range for gravimetric analysis. The samples were collected by passing air through a 37 mm teflo PTFE filter. 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 1.7LPM (liter per min.), while that for fine particle sampling was 15LPM, and the total airflow was 16.7LPM.

Before sampling, the filters have been equilibrated to constant temperature and relative humidity 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 LPM with a coefficient of variation of less than 2%.

2.2 Analytical procedures

Standard PAH Mixture containing 16 PAHs was used to identify the following compounds: Acenaphthene (Ace), Fluoranthene (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 [16]. Briefly PAHs are extracted quickly and in high portions by the use of supersonic chambers, however, this may lead to partial PAH degradation when are found in high concentration. Thus, the teflo 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 purged in 50 ml liners with 5 ml hexane. The samples were placed in magnetic shaker for 30 min while heated below boiling temperature. In the second stage the extract was taken off by the addition of 5 ml hexane – acetone mixture (1:1) and then, the liner was placed in the supersonic chamber for 15 min. During both stages it has been used water freezer for the condensation of the solvent in order to avoid loss of the low molecular weight substances.

After cutting off filters end, the extracts 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 was analyzed by gas chromatography – mass spectrometry technique for the determination of polycyclic aromatic hydrocarbons (PAHs) content.

Recovery efficiencies 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.

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

3. RESULTS AND DISCUSSION

3.1 PAH concentration levels

The mean daily concentrations of fine particles varied from 4 to 48 $\mu\text{g}/\text{m}^3$ and annual mean was 16 $\mu\text{g}/\text{m}^3$, which is higher than the limit (15 $\mu\text{g}/\text{m}^3$) regulated in the United States [17]. The mean daily concentrations of coarse particles respectively varied from 2 to 67 $\mu\text{g}/\text{m}^3$ with 23 $\mu\text{g}/\text{m}^3$ annual mean concentration.

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

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 [18]. 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 [19].

Table 1. Total Particulate PAHs Concentrations of Airborne Particles

	Fine(ng/m^3)	Coarse(ng/m^3)
mean	4.80 \pm 7.06	1.36 \pm 1.59
warm	2.62 \pm 5.60	2.00 \pm 5.85
cold	8.88 \pm 9.00	2.60 \pm 1.93

All data represent mean \pm SD.

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

PAH compound	Fine(ng/m^3)		Coarse(ng/m^3)	
	mean	SD	mean	SD
Acenaphthylene	0.23	0.51	0.06	0.08
Acenaphthylene	0.10	0.16	0.06	0.08
Fluorene	0.07	0.11	0.05	0.05
Phenanthrene	0.35	1.19	0.17	0.45
Anthracene	0.06	0.19	0.05	0.17
Fluoranthene	0.53	1.55	0.14	0.29
Pyrene	0.45	1.08	0.15	0.22
Chrysene	0.25	0.49	0.06	0.09
Benzo[a]anthracene	0.41	0.68	0.10	0.13
Benzo[k]fluoranthene	0.46	0.62	0.11	0.11
Benzo[b]fluoranthene	0.57	0.73	0.16	0.20
Benzo[e]pyrene	0.44	0.46	0.13	0.17
Benzo[a]pyrene	0.38	0.53	0.11	0.18
Indeno[1,2,3-cd]pyrene	0.29	0.33	0.07	0.12
Dibenzo(a,h)anthracene	0.09	0.14	0.06	0.14
Benzo[ghi]perylene	0.53	0.56	0.11	0.12
Σ_{PAH}	4.80	7.06	1.36	1.59

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 exceed the proposed annually averaged standard of 0.25 ng/m^3 , for B[a]Py in the United Kingdom.

PAHs concentrations have been reported for many different urban areas throughout the world [18,20-24]. 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 [21]. 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 [21].

Similar PAHs concentrations, with those at present work, have been reported before for the area of Kozani [25,26]. Moreover, these values are comparable to those found in Athens [23] and lower (2 to 4 times) than those found in Thessaloniki [27].

3.2 Diagnostic ratios of PAHs

Diagnostic ratios for PAHs, such as $BFs/B[ghi]Pe$, $FI/(FI+Py)$, $IPy/(B[ghi]Pe+IPy)$, $B[a]A/(B[a]An+Chry)$, $B[e]Py/B[a]Py$ 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 [20,21,23]. 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 NO_x , O_3 , etc. [23]. The ratios of total concentration of nine combustion PAHs to the total concentration of PAH (C_{PAH}/Σ_{PAH}) were determined by Rogge et al. [30] for noncatalyst (0.41), catalyst-equipped (0.51) automobiles and for heavy-duty diesel trucks (0.3). The ratio of C_{PAH}/Σ_{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) [20]. Emissions from lignite power stations may be the reason for such high ratio values.

The mean $FI/(FI+Py)$ 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) [30].

The $BFs/B[ghi]Pe$ ratio proposed [28], for use in discriminating automobiles (0.21–0.28) from domestic fires (2.6–14 in coal/wood soot). In present work the $BFs/B[ghi]Pe$ 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 [29]. 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 [22]. 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

ratios\period	mean		cold		warm	
	Fine	coarse	fine	coarse	fine	coarse
$BFs/B[ghi]Pe$	4.84	3.73	8.39	3.24	1.36	4.14
$IPy/(IPy+B[ghi]Pe)$	0.35	0.34	0.37	0.34	0.31	0.32
$B[a]An/(B[a]An+Chry)$	0.64	0.62	0.64	0.61	0.64	0.61
$FI/(FI+Py)$	0.46	0.43	0.50	0.46	0.43	0.39
$B[e]Py/B[a]Py$	1.74	3.12	1.30	2.36	2.16	4.40
C_{PAH}/Σ_{PAH}	0.91	0.83	0.93	0.85	0.90	0.83

C_{PAH} : $FI + Py + B[a]An + Chry + B[e]Py + BFs + B[a]Py + B[ghi]Py + IPy$

BFs : $B[b]Fl + B[k]Fl$

3.3 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 (NO₂) and sulfur dioxide (SO₂) were measured in the same area at the same time period. The correlation coefficients (Pearson) with Σ_{PAH} are displayed in Table 3.

Positive correlations were found between PAH concentration and SO₂, CO, NO, NO₂ concentration and negative correlations were found between PAH concentration and O₃ 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 level 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 [23]. 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 [23].

Negative correlation was found for solar radiation and temperature due to faster degradation of PAHs with higher solar radiation. Additionally, a negative relation of Σ_{PAH} with wind speed showed that the PAHs emissions are not originating from long distance sources [24].

Table 4. Pearson correlation coefficients for Σ_{PAH} and meteorological parameters and ambient air pollutants

	Σ_{PAH} - fine	Σ_{PAH} -coarse
SO₂	0.62	0.40
NO	0.42	0.28
NO₂	0.43	0.32
O₃	-0.36	-0.11
CO	0.61	0.34
Temperature	-0.50	-0.24
Solar Radiation	-0.36	-0.15
Wind Speed	-0.13	-0.08

4. CONCLUSIONS

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/m³, respectively. All of the total individual PAHs concentrations in fine were higher than coarse. The mean B[a]Py concentration was 0.38 ng/m³ and was exceeded the proposed annually averaged standard of 0.25 ng/m³ in the United Kingdom.

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.

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