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Chemical characterization of particulate matter (PM) and source apportionment study during winter and summer period for the city of Kozani, Greece

Invited Paper

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Abstract: Eordaia basin located in northwest of Greece, comprises an area which is characterized by intense energy related activities, including coal burning at four power plants and the associated mining operations. Air samples of inhalable (PM10) and respirable particles (PM2.5) were collected in cold and warm periods in 2010 at an urban background site of Kozani, the major city and capital of the region which is located close to the power plants. Particulate matter concentration, particle-bound polycyclic aromatic hydrocarbons and anionic species concentrations were determined using gravimetric, GC-MS in SIM mode and Ion Chromatography analysis, respectively. For the cold period, the mean PM10 and PM2.5 mass concentration was found to be 19.62 and 14.68 μg m^{-3}, respectively. Correspondingly, for the warm period, the mean PM10 and PM2.5 values were 35.29 and 25.75 μg m^{-3}, respectively. In general, the results indicated that the major sources of air pollution in Kozani are traffic, combustion from agricultural activities and lignite power plants emissions, contributing by different percentages to each particle fraction.

Keywords: *Particulate Matter • Polycyclic Aromatic Hydrocarbons • Ionic Species • Positive Matrix Factorization • Kozani*

1. Introduction

One of the major pollutants affecting air quality is particulate matter (PM) and especially PM10 and PM2.5 which have been re-regulated recently by the European Union [1]. Among their main chemical components, are polycyclic aromatic hydrocarbons (PAHs), trace elements and ionic species, many of which have been classified as potential human carcinogens and have received widespread interest in air pollution studies.

In Greece, most lignite deposits are located in the Florina–Ptolemais–Kozani basin, a large intensively exploited area, part of the West Macedonia region, in the north of the country. This area is exploited by

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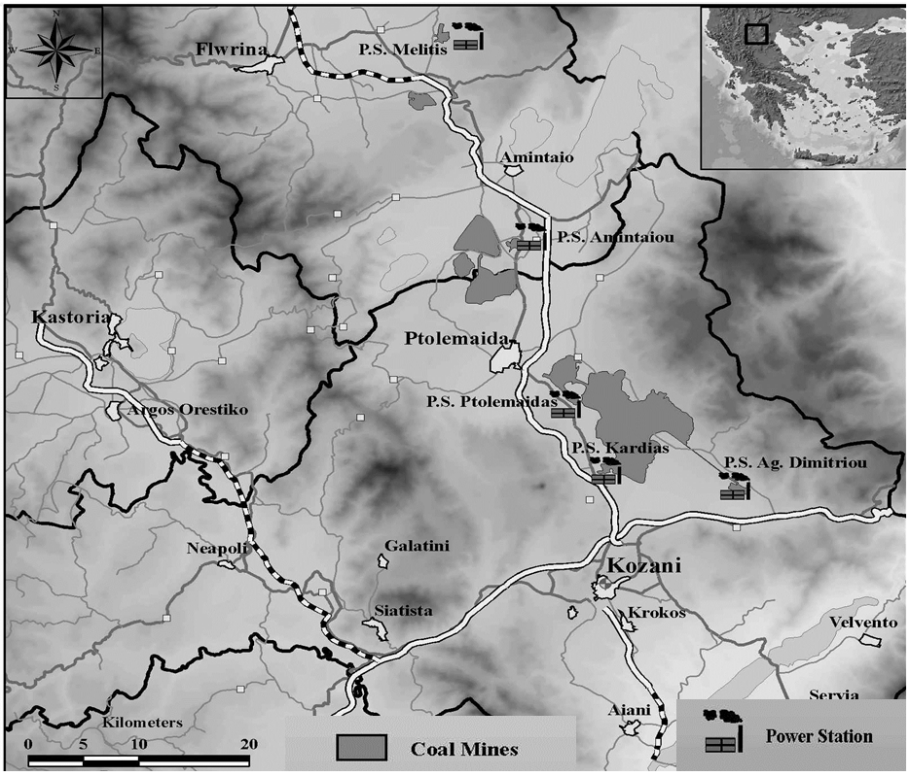

Figure 1. Map of the area of Eordea basin. The sampling site located at Kozani city.

open-cast mining and feeds nearby lignite-fired power stations. Although the lignite power stations use high performance filters to eliminate their exhausts, sometimes, the inhabitants report suffering from the high observed concentration levels of particulate matter. Several studies have been carried out demonstrating the levels of atmospheric pollution in the area of Kozani-Ptolemais basin and the impact of power plants [2-6]. As a consequence, a thorough study for estimating the contribution of the sources to the atmospheric particulate matter levels in the area attracts scientific interest. In addition to the experimental data, source apportionment methodology includes the application of receptor models using pollutant concentration measurements at a sampling site. To the best of our knowledge, there is only one source apportionment study using the Chemical Mass Balance approach for the West Macedonia area [2].

The main objective of this study is to assess PM10 and PM2.5 concentration levels in the city of Kozani during a winter and a summer period, to characterize their chemical composition concerning PAHs and ionic species (NO_3^-, Cl^-, and SO_4^{2-}), to identify the main PM sources and estimate their contribution through both compositional analysis and a receptor model application, Positive Matrix Factorization (PMF).

2. Experimental procedure

2.1. Site description and sampling

Aerosol samples were collected during a winter (ten samples between December 2009 to January 2010) and summer period (ten samples on July 2010) from an urban background site of the city of Kozani. Kozani is the capital of the region of West Macedonia with about 48,000 inhabitants. The sampling site was at the roof of a building of the University of Western Macedonia (UOWM) which is located approximately 0.5 km away from the city center. The height of the building is about 9 meters above ground level, surrounded by residential buildings and very low traffic roads. The sampling site (40° 18' /21° 24') is located in Eordea basin in which four large lignite-burning power plants operate with their coal mines. The location of the power plants is north to northeast (N,NE) of the sampling site and approximately 10.5 km away (Fig. 1). 24-hour samples of suspended particulate matter were collected on 47 mm quartz fiber filters (Whatman), mounted in Low Volume Air Sampling Systems (Derenda LVS3.1/PMS3.1-15 and TCR TECORA BRAVO PM for PM2.5 and PM10 respectively). The air flow rate was 2.3 m^3 h^{-1} for 24 h of sampling beginning at 08:30 pm and the total sampled volume per filter was 55.2 m^3. Particle mass concentrations

Table 1. Mean concentration and standard deviation of PM10 and PM2.5 with mean meteorological parameters for the city of Kozani.

	N	PM10 ($\mu g\ m^{-3}$)	PM2.5 ($\mu g\ m^{-3}$)	T (°C)	RH (%)	Wind speed ($m\ s^{-1}$)
Cold period[a]	10	19.62 (±12.00)	14.68 (±8.39)	6.0	81	1.1
Warm period[b]	10	35.29 (±13.11)	25.75 (±11.19)	25.4	56	1.6

N: Number of samples
a: from 17-21 December 2009 and 11-15 January 2010
b: from 19-28 July 2010

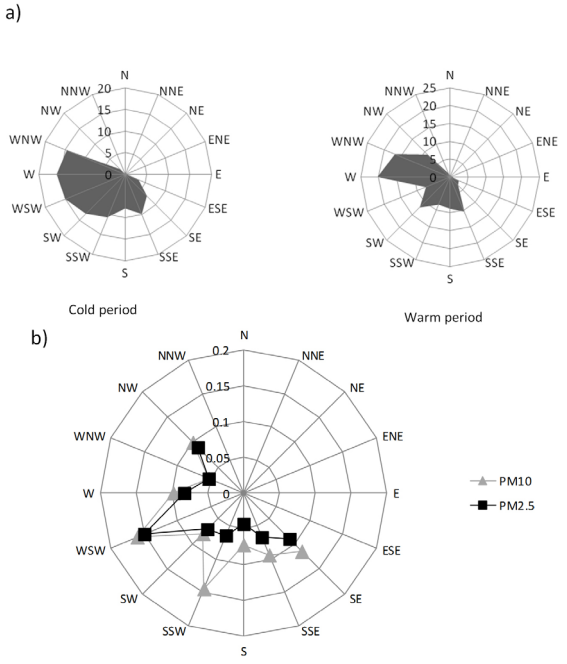

Figure 2. a) Prevailing wind direction during cold and warm period (in % frequency). b) Wind Rose diagrams between wind direction and the corresponding average PM10 and PM2.5 –B[α]P associating concentration (in ng m^{-3}) for all period.

were determined gravimetrically using an electronic microbalance (Mettler Toledo MX-5) with a resolution of 10^{-6} g, which was placed in a "weighting room". In order to create the appropriate conditions in the weighting room (T= 20±1°C, R= 50±5%), temperature and relative humidity were automatically controlled with the use of an air-conditioner operating on a continuous basis. Filters were left to the weighting room for 48-h before and after sampling according to EN 12347 [7]. After weighting, the samples were stored at -20°C prior to analysis and for no longer than two weeks prior to extraction.

2.2. Weather conditions

In Eordea basin the climate is continental Mediterranean characterized by quite low temperatures during winter time and high during summer time. The meteorological parameters were available from UOWM's weather monitoring station which is located at the same point as the sampling site. The measured parameters were temperature (°C), relative humidity (%), wind speed ($m\ s^{-1}$) and wind direction. The average values for the two sampling periods concerning temperature, relative humidity and wind speed are shown in Table 1, while the prevailing wind directions during sampling periods are shown in Fig. 2a.

2.3. Extraction and analysis of PAHs

After the determination of particulate concentration the filters were divided into two pieces. The methodology for extraction of PAHs from filter samples is described elsewhere [5]. Briefly, half of the filters were ultrasonic extracted twice with 40 mL of dichloromethane. The extracts concentrated to 5 mL and n-hexane (10 mL) was added twice and rotary evaporated until 2-3 mL of n-hexane remained. The n-hexane extract was transferred quantitatively to a pre-washed with dichloromethane column (25×0.9 cm i.d.) of silica gel topped with 0.5 g of anhydrous sodium sulphate. The PAH fraction was collected by eluting the column with 10 mL of a mixture of n-hexane-ethylacetate 9:1. The eluate was concentrated up to 2 mL and then was further concentrated up to 100 μL by the gently steam of pure nitrogen. All chemicals used were of analytical-reagent grade unless stated otherwise. Dichloromethane, n-hexane, ethylacetate and isooctane were purchased from Merck-Germany (SupraSolv for gas chromatography).

Extracts were analysed for PAHs using a DB-5MS capillary column (30 m, 0.25 mm I.D., 0.25 μm film thickness) by Agilent Technologies 6890N gas chromatograph coupled to a 5973 mass selective detector (GC-MSD) operated in the selected ion-monitoring mode (SIM). The final determination of the 2- to 6-ring PAHs was carried out according to the following parameters: carrier gas: Helium (1 mL min^{-1}, constant flow); temperature programme:

Table 2. Mean (min-max) particulate PAH concentrations at Kozani city (ng m^{-3}).

Compound	PM10		PM2.5	
	Cold period	Warm period	*Cold period*	Warm period
Naphthalene, Nap	*0.617 (0.143-1.449)*	0.040 (nd-0.150)	*0.279 (0.062-0.679)*	0.036 (nd-0.149)
Acenaphthylene, Ace	*0.012 (0.003-0.027)*	0.010 (nd-0.030)	*0.010 (nd-0.027)*	0.007 (nd-0.021)
Acenaphthene, A	*0.027 (nd-0.050)*	0.009 (nd-0.018)	*0.018 (nd-0.050)*	0.006 (nd-0.018)
Fluorene, Fl	*0.038 (0.012-0.070)*	0.034 (nd-0.160)	*0.035 (0.011-0.068)*	0.032 (nd-0.105)
Phenanthrene, Phe	*0.102 (0.026-0.226)*	0.188 (0.004-0.600)	*0.080 (0.026-0.124)*	0.149 (nd-0.448)
Anthracene, Ant	*0.006 (nd-0.025)*	0.030 (nd-0.146)	*0.006 (nd-0.024)*	0.016 (nd-0.069)
Fluoranthene, Flu	*0.162 (0.058-0.310)*	0.127 (0.008-0.660)	*0.149 (0.059-0.309)*	0.112 (0.012-0.661)
Pyrene, Pyr	*0.288 (0.073-0.954)*	0.309 (0.020-1.980)	*0.203 (0.070-0.422)*	0.230 (nd-1.963)
Benzo[a]anthracene, B[α]A	*0.138 (0.075-0.270)*	0.029 (0.005-0.135)	*0.124 (0.054-0.267)*	0.011 (nd-0.070)
Chrysene, Chr	*0.373 (0.173-0.810)*	0.118 (0.045-0.300)	*0.358 (0.174-0.771)*	0.087 (0.038-0.247)
Benzo[b]fluoranthene, B[b]F	*0.330 (0.127-0.620)*	0.304 (0.041-1.050)	*0.277 (0.134-0.594)*	0.194 (0.036-1.036)
Benzo[k]fluoranthene, B[k]F	*0.152 (0.076-0.260)*	0.153 (nd-0.500)	*0.134 (0.076-0.257)*	0.118 (nd-0.475)
Benzo[e]pyrene, B[e]P	*0.220 (0.129-0.430)*	0.199 (0.024-0.760)	*0.191 (0.108-0.427)*	0.124 (nd-0.584)
Benzo[a]pyrene, B[α]P	*0.123 (0.060-0.270)*	0.161 (0.014-0.825)	*0.097 (0.043-0.258)*	0.071 (nd-0.300)
Indeno[1,2,3-c,d]pyrene, InP	*0.282 (0.098-0.450)*	0.399 (0.027-1.997)	*0.176 (0.089-0.353)*	0.172 (nd-1.164)
Dibenzo[a,h]anthracene, DBA	*0.089 (nd-0.258)*	0.060 (nd-0.390)	*0.032 (nd-0.099)*	0.043 (nd-0.340)
Benzo[g,h,i]perylene, B[ghi]P	*0.364 (0.160-0.490)*	0.696 (0.043-3.202)	*0.260 (0.150-0.467)*	0.367 (0,035-2.757)
∑PAHs	*3.323*	2.865	*2.429*	1.774

nd: not detected

60°C (1 min), 60°C – 290°C (15°C min^{-1}) 290°C (15 min); injection volume: 1μL (splitless); injector temperature: 285°C.

The transfer line was held at 280°C and the identification - quantitation were based on calibration with standard PAHs solutions using the mass spectrometric parameters and on the basis of internal standard solution of deuterated PAHs (d8-Nap, d10-A, d10-Phe, d10-Chr, d10-Pyr, d12-B[*ghi*]P and d12-Perylene, for abbreviations see Table 2). The internal standard PAHs solutions were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and added prior to the analysis. The limit of detection (LOD) and limit of quantitation (LOQ) of the method were around 0.001 and 0.003 ng m^{-3}, respectively, for each PAH.

2.4. Extraction and analysis of ionic species

The second half of the filter was placed in an Erlenmeyer flask with 10 mL of ultra-pure water (Millipore Direct Q, resistivity 18.2 MΩ) and then treated in an ultrasonic bath for 30 min. The extract was then filtrated through 0.45 μm Nylon syringe filters and injected to a Metrohom 850 Professional, chromatographic system. The anions were determined using a Metrosep A Supp 5 250/4.0 mm column, with an eluent mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ and its flow rate during the analysis was equal to 0.7 mL min^{-1}. The ion chromatography injection volume was 20 μL, the run time was 30 min and the column temperature was kept to 30°C. The detection limits for Cl^-, NO_3^- and SO_4^{2-} were 0.01, 0.02 and 0.03 μg m^{-3} respectively. Field and laboratory blank were routinely analysed for both PAHs and anionic species and the results were subtracted from the sample values.

2.5. PMF model background

A widely used receptor model is Positive Matrix Factorization (PMF) which provides a flexible modeling approach using a set of data at a receptor site, to indentify the unknown sources and their profiles. PMF is a new variant factor analysis method and is described in detail by Paatero [8]. Only a brief description of the technique is given here. PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. The factor model can be written as

$$X = GF + E, \quad (1)$$

where X is the known $n \times m$ matrix of the m measured chemical species in n samples. G is an $n \times p$ matrix of the p sources contributions to the samples (time variations). F is a $p \times m$ matrix of source compositions (source profiles). Both G and F are factor matrices to be determined. E is defined as a residual matrix, *i.e.*, the difference between the measurement X and the model Y as a function of factors G and F.

$$e_{ij} = x_{ij} - y_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \, (i = 1,...,n; j = 1,...,m; k = 1,...,p) \quad (2)$$

The objective of PMF is to minimize the sum of the squares of the residuals weighted inversely with error estimates of the data points. Furthermore, PMF constrains all of the elements of G and F to be non-negative; meaning that sources cannot have negative species concentration ($f_{kj} \geq 0$) and samples cannot have a negative source contribution ($g_{ik} \geq 0$). The task of PMF analysis can thus be described as to minimize Q, which is defined as

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij} / s_{ij})^2 \quad (3)$$

with $f_{kj} \geq 0$; $g_{ik} \geq 0$ and s_{ij} is the error estimate for x_{ij}. The solution of Eq. 3 is obtained by a unique algorithm PMF2 in which both matrices, G and F, are adjusted in each iteration step. The process continues until convergence [8]. A critical step in PMF analysis is the determination of the number of factors. It is a fact that choosing too few factors may lead to non-well separated sources, whereas too many factors may essentially lead to a split up of a true source into two or more non-existing sources [9].

3. Results and discussion

3.1. PM10 and PM2.5 mass concentration

The average concentrations of PM10 and PM2.5 during the sampling periods are summarised in Table 1. For the cold period, the mean value of PM10 concentration was 19.62 μg m^{-3} with a standard deviation of ±12.00 μg m^{-3}. The range of the daily concentrations was between 7.33 and 50.28 μg m^{-3}. For the warm period, the average daily concentration was 35.29 μg m^{-3} (±13.11) with a range of 9.05 to 49.06 μg m^{-3}. According to the EU directive 2008/50/EC [1] the limit value for PM10 daily concentration of 50 μg m^{-3}, has been exceeded once (day with the maximum observed value). For PM2.5, the mean concentration value for the cold period was 14.68 μg m^{-3} (±8.39) and the values ranged between 6.12 and 37.10 μg m^{-3}, while the mean concentration for the warm period was found to be 25.75 μg m^{-3} (±11.19) and the daily concentrations varied between 7.18 and 37.06 μg m^{-3}. The maximum and minimum observed values for PM2.5 concentration during the sampling periods have been observed at the same days of the maximum and minimum values for PM10. This is probably due to the same origin of the corresponding particulate fractions and from the fact that for the minimum value most of the PM10 fraction consists from fine particles. It is worthy to mention that the annual limit value for PM2.5 according to the 2008 EU [1] directive will be 25 μg m^{-3} on 2015 and 20 μg m^{-3} on 2020.

PM2.5/PM10 concentration ratio has been calculated for examining the origin of different particle fractions. As found in previous studies [10 and reference therein], ratio values lower than 0.6 indicate contribution from re-suspended soil-dust, long distance dust transport (Sahara dust episodes), coal mining and processing industries and other mechanical activities. PM2.5/PM10 ratios for the present study were found to be 0.74±0.10 (mean value ± SD) for the whole sampling period while during the cold period the ratio was 0.75±0.12 (comparable with the value obtained in 2009, 0.79±0.11 [4]) and during the warm period was 0.72±0.09. The above values indicate significant contribution from secondary particulate formation of industrial, anthropogenic and combustion sources. Highest ratio values were noticed during the cold period as reported in similar studies [10,11]. The very good correlation factor (R^2) equal to 0.95 of the PM10 and PM2.5 suggesting that PM2.5 and PM10 come from similar sources.

3.2. Particulate PAHs concentration

In the current study 16 priority EPA-PAHs plus Benzo[*e*]pyrene were determined in PM10 and PM2.5 size fractions. Table 2 presents the mean, minimum and maximum concentrations values observed for the individual particle-bound PAHs. The mean total PAH concentration associated with PM10 was 2.86 ng m^{-3} for the warm period and 3.32 ng m^{-3} for the cold period. The corresponding values for PM2.5-bound PAHs were 1.77 ng m^{-3} and 2.43 ng m^{-3}. These values are in accordance with the values previously found in Kozani (3.61 ng m^{-3} concerning total suspended particles, 2.00 ng m^{-3} [12,4]) but in lower levels compared to the largest cities of Greece namely Athens [13] (32.9 ng m^{-3} in PM10) and Thessaloniki [14] (30.8 ng m^{-3} in PM10). Evagelopoulos *et al.* recently found [3] for PM10-bound PAHs concentration, the value of 7.6 ng m^{-3} which is slightly higher than that found in the present study due to the different location of the sampling point (close to traffic roads, 3 m above ground). It is commonly observed that higher molecular weight PAHs are often associated with particulates while low molecular

weight compounds tend to be more concentrated in the vapour phase. Also airborne particle PAHs increase with decreasing temperature. These trends were also observed in our study.

The polycyclic aromatic hydrocarbon with the highest concentration for PM10 and PM2.5 is benzo[*g,h,i*]perylene followed by benzo[*b*]fluoranthene and chrysene for the cold period. For the warm period, indeno[1,2,3-*c*,*d*]pyrene and pyrene were among the most abundant PAHs. Taking into account the PAH profiles associated with emission sources [15], it appears that, cyclopentan[c,d]pyrene-dibenzo[*a,h*]anthracene and phenanthrene-fluorene-pyrene are identified as markers for power plant and coal combustion sources, respectively. Additionally, InP and B[*ghi*]P are usually considered to be indicators of traffic emissions [16]. As it is shown in Table 2, in the present study, the species related to power plants and coal combustion are not the predominant ones among PAH compounds except for the case of pyrene, which during the warm period was the third most abundant component of PM10, while the traffic emission markers are present. Finally, the mean value for benzo[*α*]pyrene, was 0.142 ng m^{-3} which is lower than the EU yearly limit value of 1 ng m^{-3} [17] for PM10-bound particles. The maximum measured value was 0.825 ng m^{-3}, which was comparable to this limit value. In Fig. 2a is presented the average B[α]P concentration for both particulate fraction against the prevailing wind direction. It clearly showed that the wind direction plays an important role to the B[α]P concentration.

The diagnostic ratio between individual compounds is a way to investigate the potential emission sources of polycyclic aromatic hydrocarbons. Table 3 presents the diagnostic ratio for both PM10 and PM2.5-bound PAHs for both sampling periods. The mean Fl/(Fl+Pyr) ratio for the PM10 bound PAHs was approximately 0.3 for both periods, denoting that combustion sources are predominant in Kozani [18]. Literature review for the same ratio also reveals that values higher than 0.5 denote diesel combustion as a source while values lower than 0.5 indicate gasoline combustion as a possible source [19]. In our study the Fl/(Fl+Pyr) ratio for both PM fractions were below 0.5.

On the other side, B[α]A/Chr, B[b]F/B[k]F and InP/B[ghi]P ratios have been found to indicate coal/coke combustion when they correspond to 1.0-1.3, 3.8-4.2 and 1.0-1.2 values, respectively. In our study, different values were found for these ratios as shown in Table 3. Especially for B[α]A/Chr ratio, traffic source-origin is estimated (0.28-1.2 for gasoline and 0.17-0.36 for diesel engines according to literature values). The values found in the present work in all PM cases fall in both ranges (Table 3). InP/(InP+B[ghi]P) ratio values in the present study ranged between 0.32 and 0.44, being similar to the values estimated for gasoline and diesel engine emissions (0.44 and 0.35-0.70 respectively) rather than coal burning (0.56) as reported elsewhere [20]. Furthermore, B[e]P/(B[*e*]P+B[α]P) ratio which also represents gasoline emission has been found [15] to vary between 0.6-0.8 or 0.57-0.63, and in our study this ratio ranged between 0.55 and 0.66.

B[b]F+B[k]F/B[ghi]P ratio is usually used to distinguish motor vehicles (when ratio values range between 0.21-0.28) from domestic coal/wood fire (when ratio values range between 2.6-14). In this study, the ratio values indicated lay more to motor vehicles origin (0.66, 0.85) especially during the warm period while for the cold period ratio values were noticed to be higher and more closely to the coal/wood domestic fire (1.33 for PM10-associated PAHs and 1.59 for PM2.5-associated PAHs). The above findings did not allow us to draw a safe conclusion for the particular diagnostic ratio. Another diagnostic ratio that is used to identify the sources of PAHs is Flu/Pyr, with values close to 1.4 characterizing coal combustion, values close to 1 characterizing wood combustion, and values close to 0.6 characterizing vehicular sources [19]. In our study, this ratio did not exceed 0.73, suggesting vehicular a possible, additional PAH source.

3.3. Anionic constituents of particulate matter

Table 4 presents the average concentration values of the sulfate, nitrate and chloride anions of the PM10 and PM2.5 aerosol fractions for the two sampling periods. Results show higher concentrations for SO_4^{2-} during the summer time for both PM10 and PM2.5 fractions, probably due to the higher oxidation rate of SO_2 during summer. The opposite is observed for NO_3^- which shows higher levels during the winter period. Querol et al. also detected for the Barcelona metropolitan area high concentrations of NO_3^- in winter than in summer time due to a) low thermal stability of NH_4NO_3 and b) high winter NO levels [21]. For the chloride anionic species, higher concentration levels are observed during winter, probably due to the usage of salt on the icy roads. Present data reveal comparable values with those measured during previous studies at Kozani city, as well as other semi-rural or rural sites across the Mediterranean region [4,22,23]. Fig. 3 demonstrates the relative percentage of the measured particulate-bound anions for the corresponding sampling periods. The anion with the largest percentage was sulfate, constituting 61% and 60% of the total measured anions for PM10 and PM2.5, respectively during the cold period, while for the warm period the above percentages rise to 76% for PM10 and

Table 3. Diagnostic ratios of PM10 and PM2.5-bound PAHs concentration.

	PM10		PM2.5	
	Cold period	Warm period	*Cold period*	Warm period
InP/B[ghi]P	*0.78*	0.57	*0.68*	0.47
Pyr/B[a]P	*2.34*	1.91	*2.10*	3.23
Flu/Pyr	*0.56*	0.41	*0.73*	0.49
B[α]A/Chr	*0.37*	0.25	*0.34*	0.13
B[b]F/B[k]F	*2.17*	1.99	*2.06*	1.64
InP/InP+B[ghi]P	*0.44*	0.36	*0.40*	0.32
Flu/Flu+Pyr	*0.36*	0.29	*0.42*	0.33
B[e]P/B[e]P+B[α]P	*0.64*	0.55	*0.66*	0.64
B[b]F+B[k]F/B[ghi]P	*1.33*	0.66	*1.59*	0.85

Table 4. Mean (min-max) concentrations of anionic components in PM10 and PM2.5 in winter and summer time at the sampling site (in $\mu g\ m^{-3}$).

	PM10 (N=10)		PM2.5 (N=10)	
	Cold period	Warm period	*Cold period*	Warm period
Cl^-	0.12 (0.07-0.19)	0.07 (0.03-0.13)	0.07 (0.03-0.12)	0.03 (0.02-0.05)
NO_3^-	1.64 (0.56-3.89)	1.39 (1.12-1.77)	1.41 (0.46-3.39)	0.78 (0.61-0.96)
SO_4^{2-}	2.71 (0.83-8.38)	4.60 (1.45-8.88)	2.25 (1.15-6.52)	3.89 (1.35-8.05)

83% for PM2.5. Anionic soluble species measured for cold period comprise on average 22.8% and 25.4% of the PM10 and PM2.5 mass concentration, respectively. The contribution of anionic species during the warm period to the mass of PM10 and PM2.5 fall to 17.2% and 18.2%, respectively. This means that there is a significant part of aerosol associated with the formation of secondary inorganic particles.

3.4. PMF results

In the frame of this study, PMF model was applied in selected measured species: Benzo[*b*]fluoranthene, Benzo[*k*]fluoranthene, Benzo[*e*]pyrene, Benzo[*α*]pyrene, Indeno[1,2,3-*c,d*]pyrene, Dibenzo[*a,h*]anthracene, Benzo[*g,h,i*]perylene, Cl^-, NO_3^- and SO_4^{2-}. Lighter PAHs were excluded from the analysis for avoiding analytical error amplification. As mentioned before, a critical step in PMF analysis is the determination of the number of factors which correspond to potential particle sources. In this work, the number of factors which was examined ranged from three to nine, although a number between three and five seemed more appropriate. Analysis of the goodness of fit variable Q, can be used to help determine the optimal number of factors. Assuming that reasonable estimates of the individual data point uncertainties are available, then fitting each value should add one to the sum, and the theoretical value of Q should be equal to

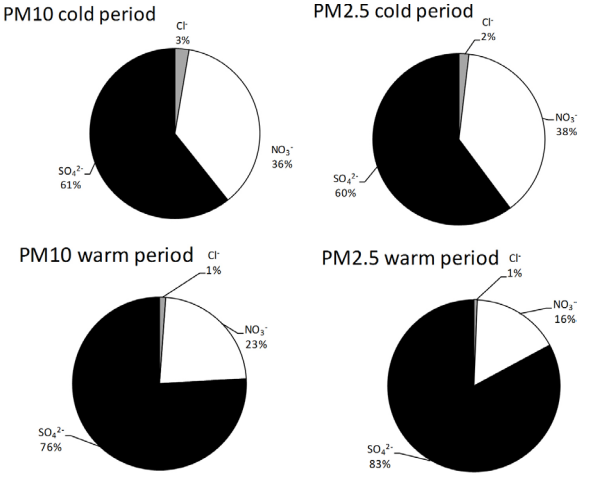

Figure 3. Relative contributions (in %) of anionic species measured in PM 2.5 and PM10 during sampling periods.

the number of data points in the data set. However, the resulting solutions also have to make physical sense within the system being studied [24]. On the basis of this analysis, *four factors* were chosen for both PM2.5 and PM10 data sets.

In particular, in both PM fractions, the first factor was related to the seven PAHs included in the analysis (by 28-42%) implying combustion-source origin. Additionally, a reasonable percentage of SO_4^{2-} (25% for

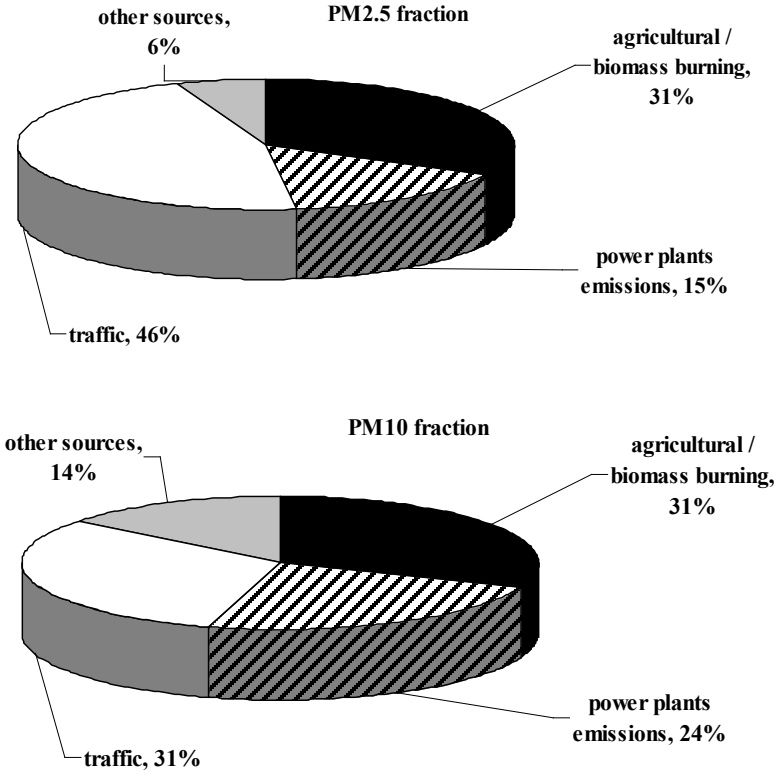

Figure 4. % percentages of sources contribution to PM2.5 and PM10 fractions.

PM2.5 and 28% for PM10) is also associated with this factor, leading to a correspondence with agricultural or biomass burning sources. The factors variation during both seasons amplifies the previous assumption as combustion during agricultural activities is not seasonal. Factor 2 is significantly associated with dibenzo[a,h] anthracene (42% for PM2.5 and 44% for PM10), implying power plants origin as mentioned previously [15]. NO_3^- and SO_4^{2-} ions are also related to this factor (32-36%). Factor 3 is highly associated with traffic markers as indeno[1,2,3-*cd*]pyrene (38% in PM2.5 and 34% in PM10), benzo[*g,h,i*]perylene (44% in PM2.5 and 39% in PM10) [16]. High percentages of NO_3^- and SO_4^{2-} ions also correspond to this factor (34-45%), amplifying the assumption for vehicles exhausts origin. Finally, a fourth factor is associated with Cl^- (28% in both fractions), benzo[*e*]pyrene (23-24%) and in a lower rate, to the other included PAHs.

Taking into consideration the fact that the four factors do not present a seasonal variation, four non-seasonal sources can be identified: agricultural/biomass burning activities, power plants emissions, traffic and a group of other, unidentified mixed sources. The % percentages of each group of sources to both PM fractions are presented in Fig. 4. The traffic-related source presents higher percentage for the fine fraction (PM2.5) while the opposite happens for power plants emissions (higher contribution in PM10).

Finally, a point for consideration is the kind of source-markers which should be included for identifying the separate combustion sources. Organic and elemental carbon and specific elemental data should be included in a further future study. Also, the a priori knowledge of the local sources profiles could be helpful in the application of a receptor model.

4. Conclusions

PM10 and PM2.5 samples were collected in the city of Kozani during the cold and warm period of 2010. Apart from the mass concentration determination, the samples were analyzed for particle bound PAHs and anionic components. The concentration of particulate matter during the cold period for the city of Kozani was found to vary between 7.3 and 50.3 μg m^{-3} for PM10 and between 6.1 and 37.1 μg m^{-3} for PM2.5. Concentration during warm period was higher, ranging between 9.0 and 49.0 μg m^{-3}, and between 7.1 and 37.0 μg m^{-3} for PM10 and PM2.5, respectively. The sum of mean

values for the sampling period of the 16 PAHs+BeP was 3.09 and 2.10 ng m^{-3} for PM10 and PM2.5, respectively. Concerning the whole sampling period the polycyclic aromatic compound with the highest concentration measured was benzo[*g,h,i*]perylene. The most abundant PAH found for the cold period was Chr followed by B[ghi]P and B[b]F, while for the warm period the most abundant PAH was B[ghi]P followed by InP and Pyr, which are known as carcinogenic. The mean value for Benzo[*α*]pyrene 0.142 ng m^{-3} for PM10-bound was lower in relation to the EU limit value of 1ng m^{-3}. The most predominant anionic species was SO_4^{2-} with an average concentration of 3.66 μg m^{-3} and 3.07 μg m^{-3} for PM10 and PM2.5, respectively, representing the 73% of the measured anionic species for PM2.5 and 69% for PM10 during the whole sampling period.

Based on the diagnostic ratios and marker compounds for PAHs and ionic species, it is concluded that during the particular sampling periods, the predominant source of airborne particulate pollution in the city of Kozani seems to be the urban pollution (including vehicular emissions and domestic heating), rather than the lignite power plants. Positive Matrix Factorization resulted in a relatively congruent conclusion, indicating traffic and agricultural/biomass burning as the predominant sources for both PM fractions, followed by power plants emissions source (however, in PM10, the three percentages are almost equivalent).

Finally, due to the small amount of data in the area, conclusions are preliminary. Studies for further research are under way in order to investigate the impact of industrialisation of the area on the quality of the air.

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