Characterization of PM$_{10}$ Sources and Ambient Air Concentration Levels at Megalopolis City (Southern Greece) Located in the Vicinity of Lignite-Fired Plants

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ABSTRACT

PM$_{10}$ samples were collected in the area of Megalopolis City (Southern Greece) located in the vicinity of two lignite-fired power plants during an one-year long period (April 2009–March 2010). The samples were analysed for their BC and elemental concentrations (Ca, Fe, Ti, Mn, Cu, Zn, As, K, Cr, Ni) using a smoke reflectrometer and ED-XRF, respectively. The average PM$_{10}$ concentration was 21.6 ± 10 $\mu$g/m$^3$, while that of BC was 1.05 ± 0.55 $\mu$g/m$^3$. The concentrations of all the elements, except that of K, were significantly higher in the warm period compared to the cold period of the year, whereas the BC results presented the opposite trend. No statistically significant differences were found between mean PM$_{10}$ mass concentrations during the warm and cold periods. Source identification was attempted by EF calculations and by Condition Probability Function analysis relating the elemental concentrations to wind directions. The results show that soil/road dust re-suspension from opencast mines and unpaved roads, emissions from vehicle exhausts and mining activities, lignite combustion in the lignite-fired power plants and biomass burning, are the main sources of PM$_{10}$ in the air over Megalopolis City.

Keywords: Atmospheric particles; Seasonal variation; Enrichment factor; CPF.

INTRODUCTION

Atmospheric particles are of great concern due to their impacts on visibility, climate change and human health (Becker et al., 2005; Davidson et al., 2006; Brugge et al., 2007; Gaffney and Marley, 2009; Han et al., 2012). The impact on human health is mainly associated with inhalation of small sized particles of atmospheric aerosols. Specifically, a number of epidemiological and toxicological studies revealed a link between PM mass of coarse particles with diameter lower than 10 $\mu$m, (PM$_{10}$) and especially fine particles with diameter lower than 2.5 $\mu$m (PM$_{2.5}$) and a variety of adverse effects on human health, including both respiratory and cardiac diseases (Osornio-Vargas et al., 2003; Donaldson et al., 2005; Davidson et al., 2006; Neuberger et al., 2007; Bollati et al., 2010; Pakbin et al., 2010). However, recent epidemiological studies indicated that the relationship between inhalation of PM and adverse health effects cannot be solely explained by the PM$_{10}$ and PM$_{2.5}$ mass concentration levels. Other physical, chemical or biological properties play an important role on the effects of particulate matter on human health (Analitis et al., 2006; Ntziaschristos et al., 2007; Valavanidiset al., 2008). Several chemical components, including specific elements found in particulate matter, have been implicated in a variety of cardio-respiratory illnesses associated with exposure to urban air pollution (Salvida et al., 2002; Wellenious et al., 2003; Ntziaqhistos et al., 2007 and references therein; Hays et al., 2011). The biological mechanism triggered by the toxicity of certain PM elemental constituents is not yet well defined. For this purpose the elemental characterization of PM particles is of great importance. Elements in the coarse particles (PM$_{2.5-10}$) are mainly associated with natural sources (Eleftheriadis and Colbeck, 2001), whilst elements emitted from anthropogenic sources are associated with fine particles (PM$_{2.5}$) (Karanasiou et al., 2007). Chemical analysis of airborne particulate matter can also assist in source identification, since a number of sources can be characterized by their elemental composition.

The city of Megalopolis, Southern Greece, is located in the vicinity of two lignite-fired plants with 850 MW installed capacity and opencast mines (Fig. 1). It is well known that coal contains toxic trace elements in concentration, in some cases, higher than those in most sedimentary rocks (Seredin and Finkelman, 2008). During combustion, a considerable amount of toxic elements are released into the atmosphere as fly ash or vapors, while large amounts remain as bottom ash (Meij, 1995). The submicron fly ash particles, due to

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their high atmospheric mobility, can be transported over a wide range of distances and may constitute a potential hazard in the vicinity of the plant (Gaffney and Marley, 2009; Wang et al., 2011). In addition to stack emissions, coal use also results in fugitive dust emissions from mining and disposal of fly ash (Petaloti et al., 2006).

Bulk deposition studies, performed in the city of Megalopolis over a one-year period (February 1997–January 1998), revealed that the collected samples were enriched in As, Br, Mo, Se, Sb, U and Zn (Papaefthymiou, 2008). Arsenic, Mo, Sb, Se and U were also enriched in fly ash samples collected from the electrostatic filters of the power plant A (Papaefthymiou et al., 2007). It should be pointed out that, there are no other major industrial activities in the greater area.

In this study, a one year PM$_{10}$ sampling campaign was conducted in the city of Megalopolis. The annual average PM$_{10}$ mass concentration and the aerosol elemental concentrations are presented. Seasonal and wind direction variability were also investigated and the origin of the PM$_{10}$ concentrations was examined by means of Conditional Probability Function (CPF) analysis. In addition, the relative enrichment of the measured elements in comparison to crustal values was also evaluated.
MEASUREMENTS AND METHODS

Study Area
The Megalopolis Lignite Centre, located on the Peloponnese peninsula, Southern Greece, is one of the largest coal mining districts in the country with total mineable lignite reserves of about 434 Mt. The lignite deposits cover a total area of 40,000 m² and are exploited by the Greek Public Power Corporation since 1969 (Siavalas et al., 2009). Three opencast mines operate, namely from north to south the Kyparissia, Marathousa and Choremi fields (Fig. 1). The latter is the largest one, whereas the former, usually flooded, is only mined by conventional means and not by the use of bucket-wheel excavators and conveyor belts. Between Kyparissia and Marathousa fields the depleted and restored nowadays Thoknia field is located. Two lignite power plants are in operation in the Megalopolis Lignite Centre: the Megalopolis-A (Units I, II and III, 550 MW), which is in operation since the late 60s, and the Megalopolis-B (Unit IV, 300 MW) since the 90s. The stack height of Units I and II is 120 m, while the heights of units III and IV are 180 and 206 m, respectively (Papaefthymiou et al., 2005). The lignite deposit of the Megalopolis basin is of very low gross calorific value (16.9 MJ/kg on a dry basis) (Siavalas et al., 2007) and of high water content and ash yield (60% and 17%, respectively) (Papaefthymiou et al., 2007), reflecting its poor quality. At full load, the units consume about 22–25 × 10⁶ kg of pulverized lignite per day. Most of the produced fly ash is collected by electrostatic precipitators, which have a design collection efficiency of 99.6%, but considerable amounts of fly ash are still emitted to the atmosphere due to the large amounts of lignite required for electric power generation. The major amount of the fly ash, collected by the electrostatic filters, is stockpiled in open areas until its deposition in exhausted lignite mines, where fly ash layers are covered by soil layers (dump sites) or transferred away for other uses (e.g., as additive in cement production) (Papaefthymiou and Gouseti, 2008). Thus, fly ash might be suspended and transferred in the local atmosphere. In addition, fugitive dust from the mining process, emissions from the bucket-wheel excavators, vehicle traffic on unpaved roads, as well as transportation and deposition of lignite and fly ash are sources of particulate matter affecting the nearby area (Petaloti et al., 2006).

The city of Megalopolis, with 10,000 inhabitants, is located about 2.5 and 4 km NE to the lignite power plants A and B, respectively and about 1 to 2.5 km E and SE to the main opencast lignite mines Choremi and Marathousa, respectively (Fig. 1). The climate of Megalopolis is a transient-type Mediterranean to continental. The main volume of rainfalls is limited in the half-year period (October to March).

Aerosol Sampling
The PM₁₀ sampling campaign was performed during one year (April 2009–March 2010) in the city of Megalopolis. The monitoring station was within a self-contained, isobox located about 700 m from the city center (Fig. 1). The nearest road was a low traffic road located 30 m far from the sampling site, while the nearest trees were at a distance of 100 m of the sampling site. The wider area was free of high vegetation and surrounded by agricultural fields. The sampling was performed using a custom made air sampler. It consists of high capacity vacuum pump capable of maintaining constant flow through a critical orifice calibrated for 26 L/min. Samples are collected on membrane filters fitted within a filter holder. Before the filter holder a sampling inlet is fitted with a modified omnidirectional impaction head equivalent to the European Standard EN12341 (CEN, 1998) PM₁₀ inlet for the above nominal flow. A 5 mb resolution dial manometer is placed between the critical orifice and filter holder, in order to provide manual read outs of pressure drop differences between the beginning and the end of filter sampling and correct the mean sampled volume accordingly. The sampling inlet was approximately 3 m above the ground level. A total of 61 daily samples (37 onto quartz QMA-Whatman, and 24 onto Teflon filters) were collected during 9-day periods, covering both cold (November to March) and warm (April to October) periods. All filters were weighed before and after sampling to determine the collected PM₁₀ mass using a Sartorious PB211D microbalance (readability 0.1 µg). Before weighing, the filters were equilibrated for 24-h period inside a custom designed chamber with automated controls designed to maintain environmental conditions at a constant air temperature of 20°C and constant RH of 50%. To avoid static electricity interference the balance was equipped with a ²¹⁰Po static eliminator. The filters were loaded into clean polystyrene Petri dishes and transferred to the sampling site in the Megalopolis city. After sampling, the filters were kept in the same holders and returned to the same place for post-weighing using the procedure described earlier. As indicated in the study of Brown et al. (2006), even in closed Petri dishes the transportation could cause a change on the mass of the filter (significant to quartz filters, not significant to Teflon filters), this leading to false concentration results. To determine if that was a significant factor, blank pre-weighed (with the procedure previously described) filters were transferred to the sampling site and back to N.C.S.R “Demokritos” to be weighed under exactly the same conditions as the samples. The results indicated that no significant change in blank filters mass was occurred due to the transportation procedure.

Analysis of Elemental Composition
The concentration of black carbon (BC) in the collected filters was determined by optical analysis using a Smoke Reflectometer (Model 43 Smoke Stain Reflectometer, Diffusion Systems LTD). Calibration of the reflectometer is provided by the manufacturer. However, the mass concentration of reflectometer smoke is currently a parameter replaced by modern black or elemental carbon methods. In order to report results equivalent to these metrics a new calibration was established by parallel measurements of Teflon and quartz filter samples and real time monitoring of black carbon by a 7 wavelength aethalometer at the Demokritos GAW urban background site in Athens. An exponential relationship was established between black carbon mass concentration and reflectance response by the
Smoke reflectometer (Fig. 2). Due to the high uncertainty involved in all state of the art methods for the measurement of elemental or black carbon in atmospheric aerosol such comparison exercises are necessary to report results in a coherent manner (Eleftheriadis et al., 2009; Baumgardner et al., 2012). For simplicity we maintain here the term BC, although the term generally used for these BC mass concentrations based on optical methods is Equivalent Black Carbon (EBC). After the determination of BC, the same filters were used for elemental analyses.

Elemental composition of the collected PM\textsubscript{10} samples was determined by Energy Dispersive X-ray Fluorescence (ED-XRF) using an ED-XRF spectrometer custom built by the scientists of the Institute of Nuclear Physics in N.C.S.R. “Demokritos”. ED-XRF is a non destructive technique, commonly used for determination of elemental concentrations in PM samples (Niu et al., 2010). The measurements were performed in a Mo anode tube-secondary target XRF assembly. The experimental set-up consisted of a 3 kW generator (C3K5, Ital Structures), a four-window Mo anode X-ray tube (fine focus 12 d 0.4 mm\textsuperscript{2}, point focus 1.2 d 0.4 mm\textsuperscript{2}, Be window thickness 400 \(\mu\)m), an Si(Li) detector (3 mm crystal thickness, 30 mm\textsuperscript{2} area), having a resolution of 168 eV at the Mn-K peak, and a laboratory-made secondary target irradiation chamber (Zarkadas and Karydas, 2004). The ED-XRF analyses were conducted at the Institute of Nuclear Physics in N.C.S.R. “Demokritos”.

Calibration of the ED-XRF system was performed using the SRM NIST 2783 (Air Particulate on filter media). In total, the concentrations of 10 elements (K, Ca, Fe, Cu, Mn, Ni, Ti, Cr, As and Zn) were analyzed in the collected PM\textsubscript{10} samples. Detection limits for the Teflon filters were calculated as 24.0, 10.1, 1.1, 0.71, 1.51, 0.33, 7.7, 1.1, 0.03 and 0.37 ng/m\textsuperscript{3} for K, Ca, Fe, Cu, Mn, Ni, Ti, Cr, As and Zn, respectively. Chromium and Ni were determined only in the Teflon filters due to their relative high detection limits in the quartz filters. The measurement’s uncertainty was low (< 10% in both filter types) for K, Ca, Fe, Mn, Ti, Cu and Zn, but relatively high for As (30–40%). The measurement’s uncertainty for Cr and Ni in the Teflon filters was also low (< 10%). It should be noted that a number of elements (e.g., S, Ge, Si) were also detected in the ED-XRF spectra, but their concentrations are not presented due to their presence in a limited number of filters. Regarding the overall analytical strategy, the use of quartz filters adds an unnecessary source of uncertainty. As displayed above the calculated detection limits with the exception of K are at least doubled in the case of quartz filters. It was therefore decided to switch to PTFE filters when this became possible. From the analytical point of view the use of PTFE and Quartz fiber filters have been studied extensively with respect to reference analytical techniques (ICP-MS) for atmospheric aerosol particle loads by Yatkin et al. (2012). It was found that for most elements of relevance here (with the exception of Cr and V) quantitative results can be obtained for Quartz filters as well as PTFE filters, with the latter having the best performance regarding limit of quantification.

The same study conducted by Steinhoff et al. (2000) has also demonstrated the capacity of quantitative analysis for trace and earth elements on quartz filters.

**Enrichment Factor**

In order to have an indication on the sources of PM\textsubscript{10} in Megalopolis city, the enrichment factor (EF) of each element determined in the collected PM\textsubscript{10} samples was calculated according to the following equation (IAEA, 1992):

\[
EF = \frac{(X/C)_{PM10}}{(X/C)_{crust}}
\]

where X is the concentration of the element of interest and C is the concentration of a reference element, which is predominantly from natural origin and its mass is conserved. By convention, an EF < 5 is indicative of the elements’ crustal origin, due to some uncertainty related to natural variation of crustal composition. Elements with EF between 5 and 10 are considered as moderate enriched elements, that probably their concentrations were affected by anthropogenic emissions, whereas elements with EF > 10 as elements originated from anthropogenic sources. The EFs were calculated on the basis of Earth’s crust mean abundance of the elements given by Wedepohl (1995). In general, Al, Sc, or Fe is taken as reference element both in the sample and in the soil. In this study, Fe was used as reference crustal element, meaning that its presence in the examined samples is predominantly from natural origin.

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![Reflectometer calibration curves for two type of filters.](image-url)
samples is considered as soil derived. The use of Fe as a crustal element was also based on the fact that its EF values were close to one in lignite and fly ash samples collected from the Megalopolis power plants (EF: 1.1 for both lignite and fly ash samples) (Papaefthymiou et al., 2007)

### Conditional Probability Function

To analyze point source impacts from various wind directions, the Conditional Probability Function (CPF) (Kim and Hopke, 2004) was calculated using the daily concentration of PM and BC, as well as the concentrations of the analyzed elements coupled with the wind direction. Nickel and Cr were excluded from the analysis, since they were detected only in the Teflon filters. Although the measurement uncertainty for As was high, it was included in the analysis, since it was detected in nearly all samples collected. It is also considered, along with Se, as a marker element for coal burning. Only the highest 25% of mass concentration measurements were used when the wind speed was equal or higher to 2 m/s. CPF is expressed mathematically by the following equation:

\[
CPF = \frac{m_{\Delta \theta}}{n_{\Delta \theta}}
\]

where \(m_{\Delta \theta}\) is the number of occurrence from wind sector \(\Delta \theta\), that exceeds the threshold criterion and \(n_{\Delta \theta}\) is the total number of data on the same wind sector. As mentioned above, calm winds (< 2 m/s) were excluded from the analysis and the threshold was set at the upper 25\(^{th}\) percentile. The sources are likely to be located in the direction that has high conditional probability values.

### Statistical Analysis

Statistical treatment of the data, including descriptive analysis, Kolmogorov-Smirnov normality test and correlation analysis was performed using the SPSS v.16 statistical software. One-way analysis of variance (ANOVA) test was also employed to the log transformed data set to check the wind sector effect on the elemental concentrations and the seasonal variations in the examined parameters during the cold (November to March) and warm (April to October) periods and their significance at the 0.05 level.

### RESULTS AND DISCUSSION

#### Meteorological Parameters

Meteorological parameters (wind speed, wind direction, temperature and relative humidity-RH\%) were recorded during the sampling period from a meteorological station located about 200 m far from the sampling station. Summary statistics of the measured meteorological parameters are shown in Table 1. It should be pointed out that, according to the employing one-way ANOVA test, the average temperature was significantly higher (\(P < 0.001\)) and the average RH\% was significantly lower (\(P = 0.01\)) during the warm period than that during the cold period. On the other hand, non significant variation between the two periods was found for wind speed (\(P = 0.952\)).

Fig. 3 presents the wind directions in the area during the sampling period. As shown in this figure, winds from NNE to ENE, WSW and WNW directions were prevailing, but also winds from ESE direction were also important.

#### PM\(_{10}\), BC and Elemental Concentrations

The Kolmogorov-Smirnov normality test applied to the data set revealed that the frequency distributions of PM\(_{10}\) mass and BC concentrations were normal (\(P = 0.757\) and \(P = 0.771\), respectively), whereas a log-normal distribution was derived for all elements determined (\(P < 0.05\)).

Descriptive statistics [arithmetic mean (AM), standard deviation (SD), geometric mean (GM), range] of PM\(_{10}\) mass, BC and elemental concentrations are presented in Table 2. This table also presents the mean values (AM) of the measured parameters according to seasons. As is apparent from this table, large variations in all measured parameters were observed, which could be attributed to fluctuations of the emission sources during the year and also to weather conditions that strongly affect the dispersion of the aerosol particles. The overall arithmetic mean of PM\(_{10}\) mass values during the sampling period was 21.6 \(\mu\)g/m\(^3\), with a standard deviation of 11 \(\mu\)g/m\(^3\). The highest PM\(_{10}\) value observed during this study was 53.3 \(\mu\)g/m\(^3\) on April 27, 2009. It is evident that the European Communities (EC) annual PM\(_{10}\) limit value of 40 \(\mu\)g/m\(^3\) and the 24-h PM\(_{10}\) limit value of 50 \(\mu\)g/m\(^3\) of no more than 35 occurrences per year were not exceeded (Directive 2008/50/EC). The highest PM\(_{10}\) mass concentrations in this study were observed between 24–28 of April and on May 15, 2009. To account for these elevated values the contribution of Saharan dust to PM has to be considered, when meteorological conditions allow the intrusion of air masses from North-African desert areas. The air mass trajectories at 1200 m above sea level (based on 150 h backward trajectory analysis, HYSPLIT developed by National Oceanic Atmospheric Administration) are shown in Fig. 4. It is apparent from this figure that the observed highest PM\(_{10}\) values could not be ascribed to Saharan dust from North Africa.

A similar study was conducted by Triantafyllou et al. (2006) in the Kozani-Polemiai basin (North-western Greece), a highly industrialized area where four lignite-fired power plants with 4 GW installed capacity are in operation close to one another. The data set showed that the frequency distributions of PM\(_{10}\) mass and BC concentrations were normal (\(P = 0.757\) and \(P = 0.771\), respectively), whereas a log-normal distribution was derived for all elements determined (\(P < 0.05\)).

#### Table 1. Summary statistics of meteorological data concerning the PM\(_{10}\) sampling site.

<table>
<thead>
<tr>
<th>Wind Speed (km/h)</th>
<th>Relative Humidity (RH%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Range</td>
</tr>
<tr>
<td>Total</td>
<td>6</td>
<td>0–15</td>
</tr>
<tr>
<td>Warm</td>
<td>6</td>
<td>0–14</td>
</tr>
<tr>
<td>Cold</td>
<td>6</td>
<td>1–15</td>
</tr>
</tbody>
</table>
to residential areas. In this study, the mean PM$_{10}$ value for a 7 year period ranged from about 30 to 70 μg/m$^3$ for different sampling sites. The maximum mean daily concentration was observed in an area surrounded by open lignite mines. In the same area, fine fly ash particles have been also identified in large distances from their source (up to 30 km), whereas coarser can be observed mainly in the vicinity of the power plants (Iordanidis et al., 2007). In some cases fly ash (both coal combustion fly ash and industrial emission) can contribute up to 35.6% of the total PM$_{10}$ mass (Ni et al., 2012). The mean BC concentration was 1.05 μg/m$^3$ with a standard deviation of 0.57 μg/m$^3$ and ranged from 0.16 to 2.61 μg/m$^3$. These values are somewhat lower compared to BC concentrations (1.27 to 5.46 μg/m$^3$) measured by Tzima-Tsitouridou (2004) in TSP samples collected from 7 sampling sites in the Kozani-Ptolemais basin (North-western Greece). The above values are considered as typical values for urban sites. In general, black carbon consists of soot aggregates

![Wind rose](image1)

**Fig. 3.** Wind rose for the sampling period.

<table>
<thead>
<tr>
<th>AM</th>
<th>GM</th>
<th>S.D.</th>
<th>Range</th>
<th>Warm</th>
<th>Cold</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{10}$</td>
<td>21.6</td>
<td>18.3</td>
<td>11</td>
<td>1.0–53.3</td>
<td>22.9</td>
<td>19.5</td>
</tr>
<tr>
<td>BC</td>
<td>1.05</td>
<td>0.95</td>
<td>0.55</td>
<td>0.16–2.61</td>
<td>0.9</td>
<td>1.4</td>
</tr>
<tr>
<td>K</td>
<td>422</td>
<td>322</td>
<td>290</td>
<td>24.1–1400</td>
<td>374</td>
<td>492</td>
</tr>
<tr>
<td>Ca</td>
<td>805</td>
<td>542</td>
<td>670</td>
<td>40.8–3260</td>
<td>1080</td>
<td>406</td>
</tr>
<tr>
<td>Ti</td>
<td>46.6</td>
<td>28.8</td>
<td>53</td>
<td>&gt; DL–342</td>
<td>66.6</td>
<td>17.8</td>
</tr>
<tr>
<td>Cr</td>
<td>1.16</td>
<td>1.1</td>
<td>0.4</td>
<td>&gt; DL–3.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>11.4</td>
<td>6.6</td>
<td>12</td>
<td>1.53–69.7</td>
<td>16.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Fe</td>
<td>377</td>
<td>260</td>
<td>310</td>
<td>12.8–1570</td>
<td>506</td>
<td>191</td>
</tr>
<tr>
<td>Ni</td>
<td>0.93</td>
<td>0.8</td>
<td>0.5</td>
<td>&gt; DL–2.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>7.91</td>
<td>7.2</td>
<td>3.6</td>
<td>1.16–22.7</td>
<td>9.5</td>
<td>5.6</td>
</tr>
<tr>
<td>Zn</td>
<td>15.9</td>
<td>13.6</td>
<td>8.8</td>
<td>2.57–55.9</td>
<td>19.7</td>
<td>10.5</td>
</tr>
<tr>
<td>As</td>
<td>0.15</td>
<td>0.1</td>
<td>0.16</td>
<td>&gt; DL–1.1</td>
<td>0.20</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Table 2.** Descriptive statistics for PM$_{10}$ (in μg/m$^3$), BC and elemental concentrations (in ng/m$^3$), along with their arithmetic mean values in the warm and cold periods (DL: detection limit; N: number of measurements).

![Air mass trajectories](image2)

**Fig. 4.** Air mass trajectories passing over the sampling area on April 27 and May 15.
originating from combustion processes (Seinfeld and Pandis, 2006).

As shown in Table 2, 10 elements (K, Ca, Fe, Ti, As, Cu, Zn, Mn, Cr and Ni) were analyzed in the collected PM$_{10}$ samples using ED-XRF. It should be mentioned that, due to their high measurement uncertainty, the results for As, Cr and Ni are indicative. The annual arithmetic mean concentration of the analyzed elements was in a decreasing order as Ca > K > Fe > Ti > Zn > Mn > Cu > Ni > Cr > As. Determined elements accounted for about 9.2% and BC for 4.9% of the total PM$_{10}$ mass. Large aerosol mass including secondary inorganic aerosol and organic species is not accounted for. Concerning the current recommendations or regulations on air quality, the annual mean concentrations of As (0.15 ± 0.16 ng/m$^3$) and Mn (11.3 ± 11.7 ng/m$^3$) were much lower compared to the European annual target value of 6 ng/m$^3$ (Directive 2004/107/EC) and the WHO (2000) annual guideline value of 150 ng/m$^3$, respectively. The average concentration of Ni (in 24 PM$_{10}$ samples) was found to be 0.99 ± 0.7 ng/m$^3$, which is also much lower compared to the European annual target value of 20 ng/m$^3$ (Directive 2004/107/EC).

### Seasonal Variation of the Analyzed Parameters

Fig. 5 shows bar plots for the seasonal distributions of PM$_{10}$ and BC concentrations. As shown in this figure (and also in Table 2), the mean PM$_{10}$ mass concentration was higher, whereas that of BC lower during the warm period than during the cold period. Fig. 6 shows the variability of elemental concentrations in the cold and warm periods. Chromium and Ni are not included in this figure due to the small number of measurements. The results show a marked seasonal trend, which is characterized by higher levels of the studied elements, except K, in the PM$_{10}$ during the warm period compared to that in the cold one. On the contrary, the mean K concentration was higher in the cold than that measured in the warm period. Potassium is a tracer of biomass burning and domestic heating. The significance of differences between the mean values of the examined parameters in the warm and cold periods of the year was tested by employing the one-way ANOVA procedure on the log transformed values. Results showed that, although a trend for higher PM$_{10}$ mass values during the warm period was observed, this trend was not significant (P = 0.190). Higher PM$_{10}$ mean mass values (but not statistically significant at the 0.05 level) in the warm (June–September) than in other two periods (November–February and March–May) were also found by Triadafyllou et al. (2006) in the Kozani-Ptolemais basin (North-western Greece). The mean BC concentration was significantly higher in the cold period with respect to that in the warm period (P < 0.001). Higher mean 24-h mean BC concentrations during the cold period as compared to those in the warm period were also reported by Diapouli et al. (2011) in three sampling sites in Athens (Greece) and also in other cities in the world (Tian et al., 2013). The mean concentration of all elements determined, except K, were significantly higher (P < 0.001) in the warm period than that in the cold one. As concerns K, the mean concentration was higher in the cold than in the warm period, but the difference in the mean seasonal concentrations was not statistically significant (P = 0.560). The elevated BC and K concentrations during the cold period might be related to the higher biomass and fossil fuels burning for heat during the cold period (Osan et al., 2002; Li et al., 2012). On the contrary, higher emissions of re-suspended soil/road dust particles and absence of particle’s precipitation, which is the main removal process, are expected during the dryer period of the year. Similar results have also been found in other Mediterranean areas (Gullu et al., 1998; Öztürk et al., 2012).

In addition, the higher concentrations of non-crustal elements during the warm period presumably suggest re-suspension of polluted road dust or influence of the opencast mines, the power plants and the open fly ash deposits present in the vicinity of the examined area. It should be mentioned that, the average temperature was significantly higher and the average RH% was significantly lower during the warm than in the cold period.

### Enrichment Factor

Table 3 presents the arithmetic mean, the SD and the range of the EFs for the elements detected in the PM$_{10}$ filters. As is apparent from this table, Cu and Zn were highly enriched in all PM$_{10}$ samples collected, meaning that these elements are released into the atmosphere by anthropogenic sources, such as traffic pollution and burning activities. Zinc is present in tire wear dust, as well as in tailpipe emissions due to its use in motor oil, and Cu is present in brake wear dust, diesel and petrol and coal combustion emissions (Yatin et al., 2000; Senarante and Shooter, 2004; Braga et al., 2005; Lopez et al., 2011). The average EF values of Ca and Ti in the PM$_{10}$ samples were lower than 5, indicating significant contribution from natural sources (soil or road dust re-suspension) (Huang et al., 2010). Potassium presented a moderate enrichment in about 20% of the samples. The origin of K is the soil, but also (at least in part) the ash from wood combustion and fields burning in spring and autumn (Osan et al., 2002). The presence of Mn in the collected particulate matter could be partially related to the fly ash emissions from the lignite power plants or to emissions from diesel and gasoline combustion (Kleeman et al., 2000). This is also supported by the fact that the EFs of Mn do not show a similar trend to the EFs of the soil-related elements Ti and Ca (Querol et al., 1998). The EF of As ranged from 1.2 to 60, with an average value of 8.0 ± 8.0. Release of As bearing particles from coal combustion facilities has been well documented by many researchers (Wang et al., 1999; Okada et al., 2008). It should also be mentioned that, lignite and fly ash samples collected from the Megalopolis power plant A, as well as bulk deposition samples collected from sites in the Megalopolis city were, among other elements, enriched in As (Papaefthymiou et al., 2007; Papaefthymiou, 2008). Although the measurement uncertainty of As with ED-XRF in the examined samples was relative high, its detection in all collected PM$_{10}$ samples is an indication of the impact of the lignite-fired power plants on the Megalopolis city atmosphere due to fly ash escaping from the stacks or to re-suspended surface soil/road dust containing deposited fly ash or lignite particles. The indicative enrichment
Fig. 5. Seasonal variability of PM$_{10}$ and BC concentrations.

Fig. 6. Elemental concentration’s variability between the cold and warm period.

Table 3. Enrichment factor values (EF) for elements determined in the PM$_{10}$ samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>AM ± SD</th>
<th>Range</th>
<th>Element</th>
<th>Average ± SD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.9 ± 1.8</td>
<td>0.2–8.0</td>
<td>Cu</td>
<td>71 ± 63</td>
<td>22–339</td>
</tr>
<tr>
<td>Ca</td>
<td>2.3 ± 0.8</td>
<td>1.0–5.7</td>
<td>Ni</td>
<td>8.6 ± 13</td>
<td>0.8–79</td>
</tr>
<tr>
<td>Ti</td>
<td>1.3 ± 0.8</td>
<td>0.3–5.9</td>
<td>Cr</td>
<td>10 ± 16</td>
<td>1.1–112</td>
</tr>
<tr>
<td>Mn</td>
<td>2.2 ± 2.9</td>
<td>0.4–24</td>
<td>As</td>
<td>8.0 ± 8.0</td>
<td>1.2–60</td>
</tr>
<tr>
<td>Zn</td>
<td>36 ± 25</td>
<td>13–151</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
factors of Cr and Ni ranged between 1.1–112 and 0.8–79, respectively, showing a possible enrichment in some days of the year.

The EF results obtained in this study confirm observations made by other researchers (Samara et al., 1990; Reimann and de Caritat, 2000) that they are largely dependent on particle size: elements associated with coarse particles show lower EF values, whereas anthropogenic elements that are distributed mostly in fine particles show high EF values. It is also well established that elements from anthropogenic sources, found mainly in the fine particles, can reach deeply in the alveolar region in the lungs and might increase respiratory symptoms (Karanasiou et al., 2007; Ny and Lee, 2011).

**Correlation Coefficients**

The results for the binary Spearman correlation coefficients of daily PM$_{10}$, BC and elements studied are reported in Table 4. The correlation between PM$_{10}$ mass values and BC in the collected PM$_{10}$ samples is shown in Fig. 7. Results show that, the PM$_{10}$ exhibited moderate, but significant positive correlation with BC (at the 0.01 level), whereas moderate positive significant correlations (at the 0.01 level) were also observed between BC-K and PM$_{10}$-K, suggesting possibly common origin or/and behavior between the correlated species.

In addition, weak (R $\leq$ 0.4) but significant positive correlations between PM$_{10}$ mass and elemental concentrations were found for all elements, except for Fe, K, and Ca, which presented moderate (R = 0.4–0.6) significant correlations with PM$_{10}$ mass. Binary strong (R $>$ 0.8) positive correlations were also observed between the crustal elements Fe, Ca, Ti, Mn, which should be considered as soil-derived. It is worth mentioned that K presented also significant positive, but weak correlation with the anthropogenic element Zn, indicating a mixed source of K. As is also shown in this table, the binary correlation coefficients between the anthropogenic elements As, Cu, and Zn are high. The observed significant and positive correlations between pollution derived elements (As, Cu, Zn) and crustal elements (Fe, Mn, Ti, Ca) indicate that part of the atmospheric concentrations of the anthropogenic elements can be accounted for by the re-suspension of soil/road dust enriched in these elements, which are originated mainly from traffic pollution and coal combustion.

### Conditional Probability Function

EF analysis results indicated that particulate matter (PM$_{10}$) in the city of Megalopolis could be attributed to both natural and anthropogenic sources. To further elucidate the local source impacts on particulate matter in the area under study, we conducted the Conditional Probability Function (CPF) analysis to our data. CPF analysis using the measured wind direction and wind speed gives information on the source impacts from various wind directions. The sources are likely to be located in the directions that have high conditional probability values. It should be pointed out that the CPF analysis may present slightly higher values obtained for the southwest sector, due to the relatively few samples for that particular wind direction (Lee and Hopke, 2006).

CPF plots for PM$_{10}$ (Fig. 8) shows that their sources have higher probability to be located north, northeast, northwest, and southwest from the sampling station. The source located at north and northeast can be identified as the city of Megalopolis. The sampling station is located relatively close to the city and thus due to the city’s large area it would be wrong to regard it as a point source. Southwest of the sampling station is the location of the lignite-fired power plants along with the Marathousa lignite mine and southwest the location of the Choremi lignite mine. We could say that, due to the absence of any other source located in these directions, the identification of the power plant, the mining process and the city of Megalopolis as major PM sources on the area is almost certain. CPF for black carbon identifies the city of Megalopolis and the Choremi lignite mine as its main sources. City’s contribution to BC levels can be attributed to wood burning and traffic, while Choremi mine’s contribution comes from diesel emissions from the bucket-wheel excavators and the heavy track used for fly ash and lignite transportation. These CPF plots interpret the significant correlations found between PM$_{10}$ and BC. The CPF plots shown in Fig. 9 indicate similar local sources for Mn, Ti, Ca, Fe, K, and Cu with somewhat different strengths. The concentrations of these elements, but K, were the highest on days with winds from southwest direction, following by winds from west directions. In addition, influence on the

### Table 4. Spearman correlation coefficients between all determined parameters (except Cr and Ni) in the collected PM$_{10}$ samples.

<table>
<thead>
<tr>
<th></th>
<th>PM$_{10}$</th>
<th>BC</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{10}$</td>
<td>1</td>
<td>.523**</td>
<td>.571**</td>
<td>.423**</td>
<td>.305**</td>
<td>.345**</td>
<td>.443**</td>
<td>.242</td>
<td>.393**</td>
<td>.327**</td>
</tr>
<tr>
<td>BC</td>
<td>1</td>
<td>.536**</td>
<td>.001</td>
<td>.052</td>
<td>.089</td>
<td>.023</td>
<td>.157</td>
<td>.038</td>
<td>.080</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>.459**</td>
<td>.339**</td>
<td>.250</td>
<td>.453**</td>
<td>.250</td>
<td>.371**</td>
<td>.222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>.880**</td>
<td>.804**</td>
<td>.902**</td>
<td>.693**</td>
<td>.757**</td>
<td>.637**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1</td>
<td>.816**</td>
<td>.865**</td>
<td>.797**</td>
<td>.738**</td>
<td>.711**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1</td>
<td>.837**</td>
<td>.832**</td>
<td>.853**</td>
<td>.747**</td>
<td>.736**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>.765**</td>
<td>.853**</td>
<td>.747**</td>
<td>.736**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>.742**</td>
<td>.736**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>.727**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level; * Correlation is significant at the 0.05 level.
concentrations of the above elements had winds from northeast directions and to a lesser extent from north winds. On the contrary, the CPF analysis for K identifies north winds as the influential direction resulting in high concentrations, with the west-southwest directions being less important. The Zn concentrations were also highest on days with southwest and north wind directions, whereas west winds had also a relatively weak influence. These results suggest common sources of all elements determined, explaining the significant correlations found between crustal and anthropogenic elements.

To determine whether wind directions (N, NE, E, ES, S, SW, W, WN) were significant factors for PM$_{10}$, BC and elemental concentrations, one-way ANOVA test was employed on their concentration data. Although statistical analysis showed that the concentration of Ca, Ti, Mn, Fe, Cu, Zn and As were higher from west and southwest wind directions when compared to all other wind sectors, the differences were statistically significant only for Zn, Cu and As, indicating as major sources the emissions from the bucket-wheel excavators and the heavy tracks used for fly ash and lignite transportation. As concerns PM$_{10}$ concentrations, wind direction was not found significant at the 0.05 level, meaning that all sources had more or less the same influence. BC and K presented the highest concentrations from northeast wind direction, but only for BC the mean concentration from northeast direction, where the city of Megalopolis is located, was significantly higher compared to mean concentrations of other wind directions (e.g. west, southwest).

It seems from the above results that the contribution of the lignite-fired power plants’ stack emissions on the particulate matter in the Megalopolis city atmosphere was lower compared to all other sources. Similar results have been also found by Samara (2005) in a lignite burning electricity producing area in Western Greece.

Further studies are needed to identify the role of the
Fig. 9. CPF plots for K, Fe, Ti, Ca, Mn, Zn and Cu.
lignite power plants on the actual sources that may significantly affect the ambient air concentration levels in the city of Megalopolis.

CONCLUSIONS

The PM$_{10}$, BC and elemental concentrations of Ca, Ti, Mn, Fe, Cu, Zn, K, As, Cr and Ni were determined in the ambient air of the Megalopolis city (southern Greece), located in the vicinity of two lignite-fired plants, during a one-year sampling campaign. The mean PM$_{10}$ mass concentration was 21.6 ± 11 μg/m$^3$, whereas that of BC 1.05 ± 0.55 μg/m$^3$. Statistical analysis indicated that season was a significant factor for all elements analyzed, except K, and that their concentrations were significantly higher in the warm than in the cold period, whereas BC concentration was significantly higher in the cold period than that in the warm period. On the contrary, non-significant seasonal variations were found for PM$_{10}$ mass and K concentrations.

Zinc and Cu were the most enriched elements in all PM$_{10}$ samples collected, revealing their anthropogenic origin, whereas Ca and Ti were not enriched indicating crustal origin. Potassium and Mn presented moderate enrichment, meaning that a portion of these elements probably originates from anthropogenic sources. Although the measurement’s uncertainty of As was relative high, it was found enriched in nearly all PM$_{10}$ samples collected originating mainly from fossil fuels combustion.

The binary Spearman correlation coefficients results for PM$_{10}$, BC and elemental concentrations are in consistency with the Conditional Probability Function plots, revealing that the major sources of the particulate matter were the soil/road dust re-suspension from the opencast mines and unpaved roads, emissions from vehicular traffic and mining activities, the lignite-fired power plants and biomass burning. Concentrations of the anthropogenic elements Zn, Cu and As were significantly higher from west and southwest compared to all other wind directions identifying the mining activities in the two opencast mines as their major sources, whilst BC and K presented the highest concentrations from northeast wind direction identifying emissions from the city of Megalopolis as their major sources. Non significant wind effect was found for PM$_{10}$ concentration.

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