PARTICULATE MATTER MEASUREMENTS AT AKROTIRI RESEARCH STATION, CRETE, GREECE

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EXTENDED ABSTRACT

Particulate matter measurements were performed at the Akrotiri research station on the island of Crete (Greece) using an 8-stages Andersen non-viable impactor. The main purpose of this work was to measure the ambient levels of PM₁₀ particulate matter and their concentrations of metals and ions in 9 different size bins.

The mean PM₁₀ concentration during the first measurement period was equal to 28.3 ± 12.4 μg/m³, whereas during the period of July 2008 was 41.6 ± 14.0 μg/m³. Moreover, mean concentrations of PM₃.₃ particulate matter were measured on the average equal to a 49 % and 45 % of PM₁₀, respectively. The measurements showed high concentration of nanoparticles (with aerodynamic diameter less than 0.9 μm), whereas the mass concentration peak was located at an aerodynamic diameter of 4 - 5 μm. Back trajectory analysis showed that during the measurement period winds were mainly originated from North-West direction.

Key words: particulate matter, metals, ions, PM₁₀.
1. INTRODUCTION

Particulate matter was measured at the rural site Akrotiri, on the island of Crete (Greece). The station, which has been established in the region of Akrotiri in 2003, is a typical urban background station. It is located 7 km away from the town of Chania (60000 inhabitants) at an elevation of 137 m from sea level. Only few measurements for airborne particles have been performed in the basin of East Mediterranean. The focus of the current study is on the PM ambient levels at the Akrotiri research station on the island of Crete, Greece.

Atmospheric aerosols play an important role in atmospheric chemistry, human health and climate, especially to the global mean radiative forcing in the climate system [1]. Investigations have shown that there is a strong correlation between aerosols, particularly fine and ultrafine particles, and health effects. Atmospheric aerosols contain hundreds of chemical species (organic compounds, metals, ions etc.). There have been many sampling efforts to measure aerosol size distributions in urban, rural, and remote sites around the world [2, 3]. However, only very few size distribution measurements have been performed in the Eastern Mediterranean.

In this paper, results on measurements of the ambient PM$_{10}$ fraction are presented and their chemical analysis in order to evaluate the concentration of metals and ions. The main purpose was to find the distribution of the particulate matter and chemical species to coarse, fine and ultrafine particles. In order to accomplish that a 9-stages sampler has been used, the non-viable Andersen impactor.

2. SITE DESCRIPTION AND METHODS

Two measurement campaigns took place at Akrotiri – Crete. The Akrotiri station is located 5 km at north-east (NE) direction from downtown Chania, a town with about 60000 habitants. It is a coastal site at an elevation of 137 m from sea level. The urban traffic from the city of Chania can affect the concentrations at the station only when the air masses arrive from the south-western directions. The station was established during 2002 and belongs to the Laboratory of Atmospheric Aerosols of the Department of Environmental Engineering of the Technical University of Crete [4].

An 8-stages non-viable Andersen impactor was used to collect particulate matter. The first campaign took place from August 10 to August 28, 2007 using GF filters (Grass Fiber) as substrate to collect atmospheric aerosols, and the second one was accomplished the period 9 – 19 July 2008 using QF filters (Quartz Fiber). GF and QF filters with 1.6 µm pore size and 81 mm diameter were used for the gravimetric sampler. On the whole, ten series of filters (each series consisted of 9 filters) were collected at each campaign. The duration of sampling for the eight series was 48 hours, whereas the last two samplings were 24 hours long. During the sample collection, ambient air was coming in with a flow rate equal to 28.3 L/min. However, in order to be accurate for the volume of air which had passed through the impactor, a dry gas meter was connected between Andersen impactor and the pump.

The Andersen sampler is a cascade impactor which consists of 9 stages (8 aluminium plates and one back-up stage) with aerodynamic diameter cutoff at 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, 0.4 µm and 0 µm. Before the analysis of samples, filters were dried before and after weighting, in a laboratory room with approximately constant temperature and relative humidity, for a 24-h period. A Sartorius balance with mass
resolution of 0.01 mg was used for the weighing of the filters, before and after the sampling. Chemical analysis was performed on GF and QF filters in order to evaluate the concentration of various metals (Fe, Cr, Cu, Ni and Pb) and ions (anions and cations).

In order to analyze metals, loaded GF filter samples were digested in an ultrasonic bath with 8 ml nano-pure water, 2 ml HCl and a small amount of HNO₃ (3 drops). Furthermore, loaded QF filters were digested with 5 ml HNO₃ (65 % v/v) and 5 ml nano-pure water in a microwave oven for 8 minutes. The determination of elements in atmospheric aerosols was conducted by Atomic Absorption Spectrometry (AAS) techniques (Fe with flame, and the rest of metals by the technique of graphite).

Moreover, the collected particulate matter from another piece of the filter, was extracted with 15 ml nano-pure water in an ultrasonic bath for 45 minutes. Extracts, after the addition of 150 μl CHCl₃ were stored in the fridge in temperature of 4°C and were further analyzed for the determination of the concentration of ions by Ion Chromatography (IC).

Finally, during August 2008 concurrent measurements were performed using a beta radiation attenuation monitor and a gravimetric sampler, in order to find the correlation between the two different sampling techniques.

3. RESULTS

3.1. Aerosol measurements

As it depicted from the next Table 1 the mean concentration for PM₁₀ and PM₃.₃ for the whole measuring time period was 28.3 ± 12.4 μg/m³, for August of 2007 were 14.5 ± 9.6 μg/m³, and 41.6±14.0 and for July of 2008, 19.2 ± 7.2. There is a variability of the PM₁₀ concentrations with concentrations ranging from 14.0 μg/m³ to 57.4 μg/m³ and from 21.3 μg/m³ to 66.4 μg/m³, for the first and second sampling, respectively. Moreover, there are some serious differences between the first and the second campaign. Mean concentration of PM₁₀ during the second one is higher that the mean value of PM₁₀ on GF filters. Indeed, during the first campaign the PM₁₀ concentration exceeded the 24-h limit value of 50 μg/m³ only once (10 - 28/8/2007), whereas for the second one (9 - 19/7/2008) two daily values are higher (and the rest eight lower) than the European PM₁₀ limit.

Table 1: Samplings of atmospheric airborne particles in the time period (a) 10/08/07 - 28/08/07, and (b) 09/07/08 - 19/07/08 at the Akrotiri research station.

<table>
<thead>
<tr>
<th>No. of sampling &amp; Type of filter</th>
<th>Date</th>
<th>Volume of air (m³)</th>
<th>PM₁₀ (μg/m³)</th>
<th>PM₃.₃ (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFF 1</td>
<td>10 - 12/08/07</td>
<td>80.9</td>
<td>17.0</td>
<td>7.0</td>
</tr>
<tr>
<td>GFF 2</td>
<td>12 - 14/08/07</td>
<td>96.2</td>
<td>24.7</td>
<td>7.8</td>
</tr>
<tr>
<td>GFF 3</td>
<td>14 - 16/08/07</td>
<td>96.3</td>
<td>14.0</td>
<td>7.4</td>
</tr>
<tr>
<td>GFF 4</td>
<td>16 - 18/08/07</td>
<td>96.3</td>
<td>23.9</td>
<td>13.2</td>
</tr>
<tr>
<td>GFF 5</td>
<td>18 - 20/08/07</td>
<td>96.0</td>
<td>28.3</td>
<td>16.4</td>
</tr>
<tr>
<td>GFF 6</td>
<td>20 - 22/08/07</td>
<td>95.7</td>
<td>21.1</td>
<td>10.1</td>
</tr>
<tr>
<td>GFF 7</td>
<td>22 - 24/08/07</td>
<td>94.0</td>
<td>57.4</td>
<td>39.9</td>
</tr>
<tr>
<td>GFF 8</td>
<td>24 - 26/08/07</td>
<td>96.4</td>
<td>39.0</td>
<td>15.0</td>
</tr>
<tr>
<td>GFF 9</td>
<td>26 - 27/08/07</td>
<td>46.7</td>
<td>26.5</td>
<td>12.4</td>
</tr>
<tr>
<td>GFF 10</td>
<td>27 - 28/08/07</td>
<td>46.7</td>
<td>30.9</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Mean values of GFFs 28.3 ± 12.4 14.5 ± 9.6
In the Figure 1 the daily averaged concentrations for PM are presented. The PM$_{3.3}$ fraction (the sum of the last 5 filters) constitutes the 32 - 70 % of the PM$_{10}$ during summer of 2007, and 30 - 60 % during the ten-days sampling of summer of 2008, with a mean value equal to 49 % in the first case and 45 % in the second one. Therefore, about half of the whole mass of PM$_{10}$ atmospheric particulate matter is in the form of fine particles with aerodynamic diameter less than 3.3 μm. In addition, the PM$_{3.3}$ levels are well correlated with the corresponding concentrations of PM$_{10}$ (R$^2$ (2007) = 0.88 and R$^2$ (2008) = 0.82).

Furthermore, the origin of the aerosols on the Akrotiri station was studied using the HYSPLIT4 Model the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA) [5, 6]. The 3-dimensional trajectories were computed for the coordinates 35.53N, 24.06E, which are the coordinates of the Akrotiri region, for 12:00 am for each day of measurements. The trajectories were 120h (5 days) long. Each trajectory was divided into five segments. Each segment was assigned to one of the eight sectors (north, north-east, east etc.). This analysis showed that in both cases (August 2007 and July 2008) winds from North – Northwest directions were dominated. This fact can explain the normal concentrations of PM$_{10}$ (absence of a Saharan dust episode). The air masses passed over the Mediterranean Sea for more than 48 hours prior to coming over the monitor station were filtered and finally arrived in Crete with low concentrations of particles. Hence, it can be supposed that particulate matter during the sampling periods is attributed to local emissions.
In Figure 2, where all the 48h or 24h values of 9-stages of the whole PM$_{10}$ are depicted, two main peaks are clearly evident. At aerodynamic diameter less than 1 μm, nanoparticles showed increased concentration, whereas a second mass concentration peak was observed at an aerodynamic diameter of about 4 μm for GF (August 2007) and 5 μm for QF filters (July 2008). These results are in agreement with recent research findings in the Aegean Sea. In the present work, a third maximum was observed, corresponding to the first two stages, where the impactor collected the largest atmospheric particles, with aerodynamic diameter larger than 5.8 μm.

**Figure 2**: Mass concentration distribution of Andersen impactor vs. aerodynamic mass diameter for (a) July 2007, and (b) August 2008.
Furthermore, during July 2008, from 09/07/2008 to 19/07/2008, continuous concurrent measurements of particulate matter (PM$_{10}$) were performed using a beta radiation attenuation monitor (FH 62 I-R) and a gravimetric sampler. The monitor used the radiometric dust measurement with two beam-compensation method for the continuous mass determination of the dust sample on the filter. Simultaneously, during the sampling, the accumulated particle mass on the filter was measured. The airflow rate was recorded on-line and regulated. A data logger was storing beta monitor data every 15 minutes. The daily averages were calculated after the extreme values of the beta attenuation monitor were removed. As it is depicted in Table 2, mean average concentrations of PM$_{10}$ were approximate (41.1 ± 11.1 μg/m$^3$ for beta monitor and 41.6 ± 14.0 μg/m$^3$ for the impactor), and moreover showed a fine Pearson'$^*$ coefficient ($r = 0.68$).

Table 2: Concurrent daily values with a beta monitor and a gravimetric sampler.

<table>
<thead>
<tr>
<th>Date</th>
<th>PM$_{10}$ of Beta radiation attenuation monitor (μg/m$^3$)</th>
<th>PM$_{10}$ of Andersen impactor(μg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>09-10/07/08</td>
<td>59.0</td>
<td>55.0</td>
</tr>
<tr>
<td>10-11/07/08</td>
<td>44.2</td>
<td>47.5</td>
</tr>
<tr>
<td>11-12/07/08</td>
<td>29.8</td>
<td>32.0</td>
</tr>
<tr>
<td>12-13/07/08</td>
<td>30.8</td>
<td>36.9</td>
</tr>
<tr>
<td>13-14/07/08</td>
<td>20.6</td>
<td>22.4</td>
</tr>
<tr>
<td>14-15/07/08</td>
<td>46.6</td>
<td>21.3</td>
</tr>
<tr>
<td>15-16/07/08</td>
<td>51.5</td>
<td>66.4</td>
</tr>
<tr>
<td>16-17/07/08</td>
<td>50.6</td>
<td>47.5</td>
</tr>
<tr>
<td>17-18/07/08</td>
<td>37.4</td>
<td>44.0</td>
</tr>
<tr>
<td>18-19/07/08</td>
<td>40.3</td>
<td>43.0</td>
</tr>
<tr>
<td>Mean values</td>
<td>41.1 ± 11.1</td>
<td>41.6 ± 14.0</td>
</tr>
</tbody>
</table>

3.2. Ions and metals concentrations

In Table 3, the results from the ion chromatography analysis are presented. In general, sulphate seem to be the most abundant anion (18.4 and 6.8 μg/m$^3$, in samplings of August 2007 and July 2008, respectively), whereas nitrates, sodiums and chlorides follow. The phosphates concentration values were extremely high in the QF samples, a result which was quite unusual. In general, high ions concentrations were observed in the area, and there is a need for more measurements to be performed, in order to determine the exact fluctuation of these concentrations. However, there have been cases, that high ion concentrations have been observed [7].

The sum of measured anions is about 6 times higher than the sum of cations in each stage in the first campaign, whereas only two times higher for the sampling period of July, 2008.

Table 3: Mean averaged concentrations of anions and cations in every filter (Tables (a) and (c)) and in every stage of the Andersen impactor (Tables (b) and (c)) (in ng/m$^3$).

<table>
<thead>
<tr>
<th>sampling</th>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>NO$_3^-$</th>
<th>PO$_4^{3-}$</th>
<th>SO$_4^{2-}$</th>
<th>C$_2$O$_4^{2-}$</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFF 1</td>
<td>2526.3</td>
<td>4.3</td>
<td>3261.5</td>
<td>0.0</td>
<td>9274.1</td>
<td>456.0</td>
<td>1661.7</td>
<td>364.3</td>
<td>264.7</td>
<td>109.8</td>
<td>410.9</td>
</tr>
<tr>
<td>GFF 2</td>
<td>3064.8</td>
<td>10.0</td>
<td>5077.2</td>
<td>0.0</td>
<td>14113.4</td>
<td>674.9</td>
<td>2470.2</td>
<td>261.7</td>
<td>224.3</td>
<td>120.3</td>
<td>193.0</td>
</tr>
<tr>
<td>GFF 3</td>
<td>1031.5</td>
<td>1.5</td>
<td>4318.9</td>
<td>0.0</td>
<td>25133.6</td>
<td>841.9</td>
<td>3691.6</td>
<td>699.7</td>
<td>613.1</td>
<td>88.6</td>
<td>294.3</td>
</tr>
<tr>
<td>GFF 4</td>
<td>2414.3</td>
<td>9.4</td>
<td>4771.9</td>
<td>57.6</td>
<td>20893.6</td>
<td>598.0</td>
<td>3412.5</td>
<td>533.2</td>
<td>616.4</td>
<td>92.8</td>
<td>340.5</td>
</tr>
<tr>
<td>GFF 5</td>
<td>1940.3</td>
<td>6.6</td>
<td>4410.3</td>
<td>31.2</td>
<td>23990.5</td>
<td>613.2</td>
<td>3786.6</td>
<td>1597.5</td>
<td>1084.3</td>
<td>107.4</td>
<td>823.8</td>
</tr>
<tr>
<td>GFF 6</td>
<td>2165.4</td>
<td>11.6</td>
<td>4394.9</td>
<td>15.1</td>
<td>13852.7</td>
<td>509.1</td>
<td>2832.4</td>
<td>596.5</td>
<td>592.8</td>
<td>69.7</td>
<td>237.8</td>
</tr>
<tr>
<td>GFF 7</td>
<td>3278.1</td>
<td>10.2</td>
<td>5703.8</td>
<td>13.7</td>
<td>27053.3</td>
<td>891.3</td>
<td>4485.0</td>
<td>1298.6</td>
<td>1652.2</td>
<td>137.1</td>
<td>858.2</td>
</tr>
<tr>
<td>GFF 8</td>
<td>9940.6</td>
<td>30.2</td>
<td>7631.0</td>
<td>46.8</td>
<td>15192.9</td>
<td>692.7</td>
<td>4838.4</td>
<td>410.6</td>
<td>444.4</td>
<td>364.4</td>
<td>926.1</td>
</tr>
<tr>
<td>GFF 9</td>
<td>5539.2</td>
<td>13.5</td>
<td>4707.7</td>
<td>0.0</td>
<td>15456.3</td>
<td>688.6</td>
<td>2910.4</td>
<td>487.6</td>
<td>248.3</td>
<td>128.9</td>
<td>630.1</td>
</tr>
<tr>
<td>GFF 10</td>
<td>5705.8</td>
<td>22.1</td>
<td>6420.4</td>
<td>0.0</td>
<td>19045.0</td>
<td>797.3</td>
<td>2668.0</td>
<td>548.6</td>
<td>145.0</td>
<td>193.7</td>
<td>7.2</td>
</tr>
</tbody>
</table>
Moreover, the atomic absorption spectrometry results are presented in Table 4. In general, the concentrations of anthropogenic elements (Cu, Cr, Pd and Ni) are low, as compared to the concentrations of Fe (crustal element). These results are in agreement with previous studies on the region of SE Mediterranean Sea [8, 9].

Table 4: Mean averaged concentrations of metals in every stage and the total concentration of metals (in ng/m$^3$).

<table>
<thead>
<tr>
<th>Stages</th>
<th>Cu</th>
<th>Cr</th>
<th>Fe</th>
<th>Pb</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>25.1</td>
<td>343.6</td>
<td>15.0</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>19.7</td>
<td>345.7</td>
<td>12.1</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>8.4</td>
<td>249.2</td>
<td>5.8</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>2.4</td>
<td>233.4</td>
<td>5.8</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>2.1</td>
<td>239.8</td>
<td>5.9</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>2.2</td>
<td>243.8</td>
<td>6.5</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>1.3</td>
<td>211.5</td>
<td>6.4</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>0.8</td>
<td>193.6</td>
<td>5.3</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>0.4</td>
<td>293.4</td>
<td>6.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Total</td>
<td>4.8</td>
<td>64.4</td>
<td>2254.0</td>
<td>69.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>
A good Pearson correlation has been shown between PM$_{10}$ and PM$_{3.3}$ levels and concentration of Fe (0.72 and 0.75, respectively), and between PM$_{3.3}$ and concentration of Pb ($r = 0.84$) (data not shown).

4. CONCLUSIONS

Particulate matter measurements were performed at the Akrotiri research station on the island of Crete, Greece. Gravimetric analysis of samples has shown PM$_{10}$ values lower than the European Union limit of 50 $\mu$g/m$^3$, except in one case in August 2007, and twice in July 2008, with values ranged from 14.0 $\mu$g/m$^3$ to 57.4 $\mu$g/m$^3$ and from 21.3 $\mu$g/m$^3$ to 66.4 $\mu$g/m$^3$, for the first and second sampling, respectively. The size distribution had a bimodal shape, with mass mean diameters at 0.8 and 4 $\mu$m, and 0.8 and 5 $\mu$m, respectively.

Furthermore, the chemical composition of aerosols was determined by the size of resolved aerosol samples. Ions have shown very high concentrations in all 9 stages, especially in sulphate, sodium, chloride, nitrate and phosphate ions. Finally, crustal metals as Fe, have shown higher concentrations than anthropogenic elements, since the Akrotiri station is situated in a suburban, non industrial area.

REFERENCES