

# **PARTICULATE MATTER SIZE DISTRIBUTION MEASUREMENTS AT AKROTIRI STATION, CRETE, GREECE**

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## **ABSTRACT**

Particulate matter, (PM), measurements were performed during the period 10.8.2007 – 28.8.2007 at the Akrotiri monitoring station on the island of Crete, Greece. The main purpose was to measure the ambient levels of PM<sub>10</sub> and their concentrations of metals and ions in 9 different size bins with aerodynamic diameter less than 10 µm. The mean PM<sub>10</sub> concentration during the measurement period was equal to  $28.27 \pm 12.42 \mu\text{g}/\text{m}^3$ , whereas the mean concentrations of the total measured ions and metals were  $8.31 \pm 2.07 \mu\text{g}/\text{m}^3$  and  $0.51 \pm 0.47 \mu\text{g}/\text{m}^3$  respectively. Moreover, the mean daily value of black carbon (BC) was  $0.69 \pm 0.22 \mu\text{g}/\text{m}^3$ .

## 1. INTRODUCTION

Aerosols are defined as suspensions of liquid or solid particles in a gas. Atmospheric aerosol particles range in size over more than four orders of magnitude, from freshly nucleated clusters containing a few molecules to cloud droplets and crustal dust particles up to tens of microns in size.

Atmospheric particles play an essential 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 correlation between PM, especially fine particles, and health effects.

Atmospheric aerosols contain hundreds of metals, ions, organic compounds and other chemical species. Research on the size distribution of aerosols has been intensified the last two decades, partially due to improved methodologies and advances in instrumentation technology. In the last years, however, the scientific focus is on the measurement of ultrafine particles, since a given mass of that size of particles has 100–1000 times more surface area than an equal mass of fine particles and approximately  $10^5$  times more surface area than an equal mass of coarse particles. Besides, the major part of the number size distribution remains in the ultrafine area.

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 we present results on measurements of the ambient PM<sub>10</sub> fraction and its chemical analysis in order to evaluate the concentration of metals and ions.

## 2. MATERIAL AND METHODS

The measurement campaign took place at Akrotiri – Crete (10-28/8/2007) a suburban area of the city of Chania. The Akrotiri station (35° 31' 48'' N, 24° 03' 36'' E) is located 5 km at north-east (NE) direction from downtown Chania, a town with about 60000 habitants. It is a coastal site (distance from the sea is 2 km from the northern and western directions, 3.3 km from the southern and 11.5 km from the eastward) 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 Andersen non-viable impactor was used to collect particulate matter from August 10 to August 28, 2007. On the whole, ten series of filters (each series consisted of 9 filters) were collected. 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 came 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 alluminium 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  $\mu\text{m}$  and 0  $\mu\text{m}$ . GF (Glass Fiber) filters with 1.6  $\mu\text{m}$  pore size and 81 mm diameter were used for the gravimetric sampler. Before the analysis of samples, filters used for particle collection were dried before and after weighting, in a laboratory room with approximately constant temperature and relative humidity, for a 24-h period.

The samples were transported from the sampling site in Petri dishes and equilibrated in the laboratory for 24 h minimum before weighting. To minimize the losses of chemical species from the collected particle matter, the samples were stored at  $-16^{\circ}\text{C}$  until use. Half of each filter was dedicated to Atomic Absorption Spectrometry (AAS) and the rest half to Ion Chromatography (IC) analysis. A percentage 10 % of the samples were also analyzed as blank filters. Blanks were analyzed using the same procedure used for samples.

Samples collected on the 8-filters on the alluminium plates and the back up filters of the cascade impactor, have been analyzed by AAS techniques, to determine their metals content and by IC to assess the concentrations of inions and cations. The 6 metals that were measured are: copper, chromium, iron, aluminium, lead and nickel. Furthermore, the ions measured are: sulphate, chloride, bromide, phosphate, oxalate, sodium, potassium, ammonium, calcium and magnesium.

In order to analyze metals, loaded GFF filter samples were digested in an ultrasonic bath with 8 mL nano-pure water, 2 mL HCl and a small amount of  $\text{HNO}_3$  (3 drops). An atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) was used to determine the metals concentrations. For Fe and Al determination, acetylene – air flame was used as thermal energy source, whereas for Cu, Cr, Pb and Ni the graphite furnace mode was utilized. For each metal, a calibration curve was constructed with freshly prepared standards (the correlation coefficient  $r^2$ , for all curves was higher than 0.995). Each measurement was repeated three times for the construction of the calibration curve and two times for the samples.

Moreover, the second half of the filters was extracted by sonication in an ultrasonic bath in 15 mL of ultra-pure water for 45 minutes. Water-soluble ions were measured by ion chromatography (IC) at Environmental Chemical Processes Laboratory (ECPL), University of Crete, following the method described in details by Bardouki et al. (2003) [5]. Extracts, after the addition of 150  $\mu\text{L}$  chloroform ( $\text{CHCl}_3$ ) (as a biocide in the sample extracts), were stored at 4  $^{\circ}\text{C}$  and were further analyzed for the determination of the concentration of ions by Ion Chromatography within a week after extraction. A Dionex AS4A-SC column with ASRS-ultra-II suppressor in auto-suppression mode of operation was used for the analysis of anions, whereas for the cations a CS12-SC column was used with a CSRS-ultra-II suppressor.

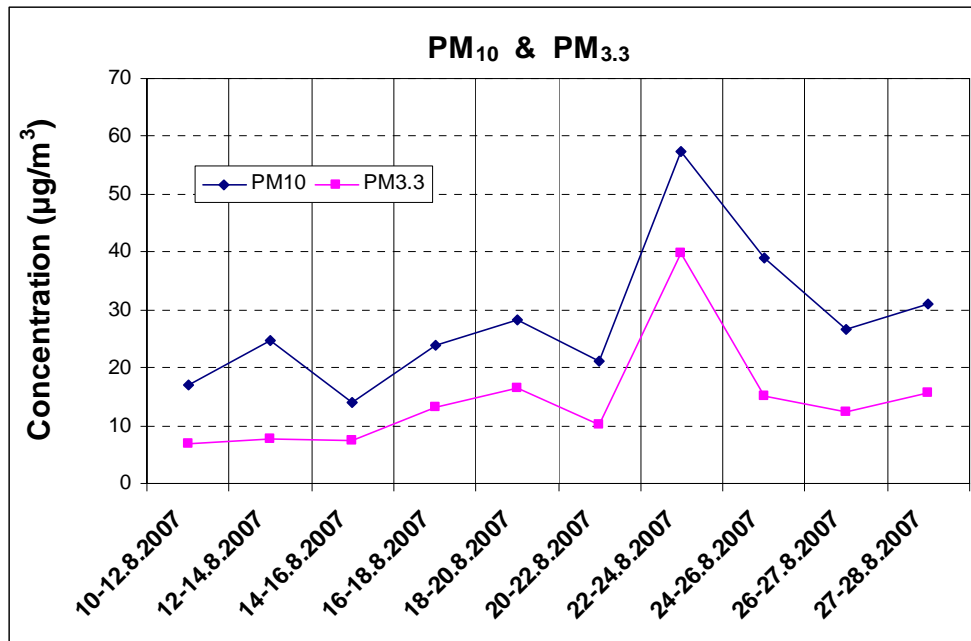
### 3. RESULTS AND DISCUSSION

In Table 1 information about the sampling is given.

**TABLE 1:** 24-h and 48-h samplings of atmospheric airborne particles in the time period 10/08/07-28/08/07 at the Akrotiri research station.

No. of sampling	1	2	3	4	5	6	7	8	9	10
Type of filter & No. of series	GFF 21	GFF 22	GFF 23	GFF 24	GFF 25	GFF 26	GFF 27	GFF 28	GFF 29	GFF 30
Date	10-12/8	12-14/8	14-16/8	16-18/8	18-20/8	20-22/8	22-24/8	24-26/8	26-27/8	27-28/8
Volume of air ( $\text{m}^3$ )	80.86	96.17	96.33	96.28	96.02	95.66	93.95	96.36	46.73	46.73
$\text{PM}_{10}$ ( $\mu\text{g}/\text{m}^3$ )	16.96	24.65	14.04	23.89	28.29	21.12	57.42	38.98	26.49	30.92
$\text{PM}_{3.3}$ ( $\mu\text{g}/\text{m}^3$ )	6.99	7.80	7.41	13.23	16.43	10.11	39.91	15.01	12.43	15.73

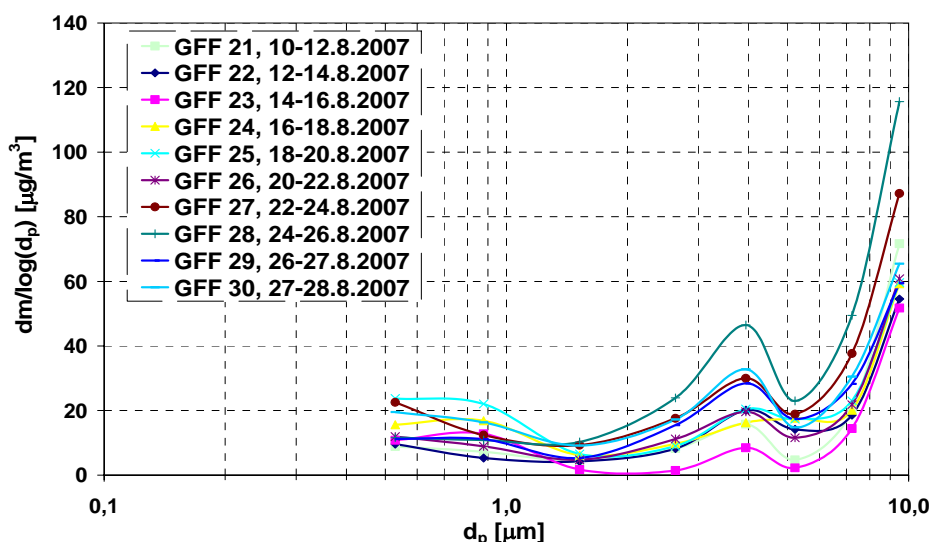
Furthermore, the two-days (or daily) averaged  $\text{PM}_{10}$  and  $\text{PM}_{3.3}$  (the sum of the last 5 filters) concentrations during the sampling period from 10/8/2007 to 28/8/2007 are presented in Figure 1. The mean concentration of  $\text{PM}_{10}$  for the whole measuring period was  $28.27 \pm 12.42 \mu\text{g}/\text{m}^3$ , whereas the corresponding value for  $\text{PM}_{3.3}$  particulate matter was  $14.51 \pm 9.59 \mu\text{g}/\text{m}^3$ . There is a variability of the  $\text{PM}_{10}$  concentrations with concentrations ranging from  $14.04 \mu\text{g}/\text{m}^3$  to  $57.42 \mu\text{g}/\text{m}^3$ .



**Figure 1:** 24h and 48h values of PM<sub>10</sub> and PM<sub>3.3</sub> concentrations.

As depicted in Figure 1, the PM<sub>10</sub> concentration exceeded the 24-h limit value of 50 µg/m<sup>3</sup> only once (22-24/8/2007), whereas for the rest of cases the concentrations are lower than the European PM<sub>10</sub> limit. Furthermore, the PM<sub>3.3</sub> fraction constitutes the 32 – 70 % of the PM<sub>10</sub>, with a mean value equal to 49 %. Therefore, about half of the whole mass of PM<sub>10</sub> atmospheric particulate matter is in the form of fine particles with aerodynamic diameter less than 3.3 µm. In addition, as the data in figure 1 show, the PM<sub>3.3</sub> levels are well correlated with the corresponding concentrations of PM<sub>10</sub> ( $R^2 = 0.88$ ).

In Figure 2, where all the 48h or 24h values of 9-stages of the whole PM<sub>10</sub> 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. 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.



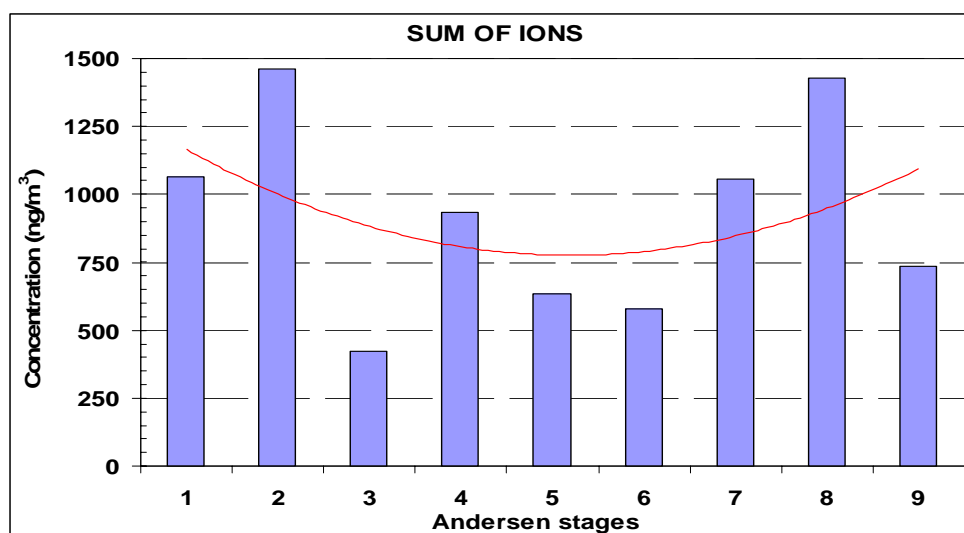
**Figure 2:** Mass concentration distribution of Andersen impactor vs. aerodynamic mass diameter.

Furthermore, black carbon data (BC), (Aethalometer, Magee Scientific), were collected during the sampling period. The mean daily value of BC was  $691.2 \pm 222.0 \text{ ng}/\text{m}^3$  (data not shown).

In Table 2, the results from the ion chromatography analysis are presented. In general, sulphate seem to be the most abundant anion ( $4631.32 \text{ ng}/\text{m}^3$ ), whereas nitrates and chlorides follow with mean concentrations of  $1275.15 \text{ ng}/\text{m}^3$  and  $939.84 \text{ ng}/\text{m}^3$ , respectively. The sum of 6 measured anions is 4 – 14 times higher than the sum of 5 cations in each stage. Besides, as it can be seen in Figure 3, atmospheric aerosols with a moderate aerodynamic diameter have lower concentrations of ions.

**TABLE 2:** Mean averaged concentrations of inions and cations (in  $\text{ng}/\text{m}^3$ ).

Stages	$\text{Cl}^-$	$\text{Br}^-$	$\text{NO}_3^-$	$\text{PO}_4^{3-}$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
1	274.95	0.35	195.87	0.88	405.25	11.25	125.81	7.61	20.23	2.93	19.90
2	360.71	0.36	353.69	1.33	456.24	16.98	168.06	6.41	27.42	11.21	60.30
3	56.79	0.17	72.70	1.05	257.70	6.74	15.05	4.67	2.78	1.45	5.08
4	138.30	0.23	291.17	0.00	323.07	17.29	130.60	4.22	0.89	6.37	20.62
5	62.56	0.21	204.45	0.43	279.58	19.84	55.64	4.83	0.45	3.02	3.00
6	33.18	0.25	112.65	0.00	353.26	23.99	45.82	5.45	0.00	2.42	0.64
7	0.75	0.42	20.14	0.42	847.56	22.76	87.03	37.57	34.07	2.20	4.12
8	1.23	0.60	12.74	0.00	1108.05	28.39	123.87	88.90	54.63	2.46	5.47
9	11.37	0.43	11.74	0.00	600.61	22.84	65.81	10.90	5.98	3.48	0.67
total	939.84	3.02	1275.15	4.11	4631.32	170.08	817.69	170.56	146.45	35.54	119.8



**Figure 3:** Total ions concentration in 9 stages of Andersen impactor.

Moreover, in Table 3 the results from the atomic absorption spectrometry are presented. In general, the concentrations of anthropogenic elements (Cu, Cr, Pd and Ni) are low, as compared to the concentrations of Fe and Al (crustal elements). These results are in agreement with previous studies on the region of SE Mediterranean Sea [7].

**TABLE 3:** Mean averaged concentrations of metals (in ng/m<sup>3</sup>).

Stages	Cu	Cr	Fe	Al	Pb	Ni
1	0.40	0.05	52.35	20.50	0.38	0.00
2	0.96	0.09	18.21	57.82	0.29	0.00
3	0.55	0.00	4.95	8.92	1.02	0.00
4	0.03	0.00	2.08	7.52	0.42	0.00
5	0.00	0.00	1.86	129.43	0.63	0.00
6	0.05	0.00	0.00	23.46	0.68	0.00
7	0.25	0.00	36.71	50.26	0.59	0.00
8	0.00	0.00	1.86	45.16	0.44	0.60
9	0.00	0.00	6.80	34.42	0.77	3.03
total	2.24	0.14	124.82	377.49	5.22	3.63

## CONCLUSIONS

Particulate matter measurements were performed at the Akrotiri research station on the island of Crete, Greece. Gravimetric analysis of samples showed PM<sub>10</sub> values lower than the European Union limit of 50 µg/m<sup>3</sup> (except one day) with values ranged between 14.04 and 57.42 µg/m<sup>3</sup>. The size distribution had a bimodal shape, with mass mean diameters at 0.8 and

4  $\mu\text{m}$ , respectively. Furthermore, the chemical composition of aerosols was determined in the size resolved aerosol samples. Ions are concentrated in ultrafine and coarse particles. Finally, crustal metals showed higher concentrations than anthropogenic elements since the Akrotiri station is situated in a suburban, non industrial area.

## REFERENCES

1. Novakov T. and Penner J.E. (1993) "Large contribution of organic aerosols to cloud-condensation nuclei concentrations" **Nature**, Vol. 365, pp. 823 – 826.
2. Morawska L., Jayarantne E.R., Mengersen K. and Thomas S. (2002) "Differences in airborne particle and gaseous concentrations in urban air between weekdays and weekends" **Atmospheric Environment** Vol. 36, pp. 4375–4383.
3. Stanier C.O., A.Y. Khlystov and S.N Pandis. (2004) "Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS)" **Atmospheric Environment** Vol. 38, pp. 3275–3284.
4. Lazaridis M., Dzumbova L., Kopanakis I., Ondracek J., Glytsos T., Aleksandropoulou V., Voulgarakis A., Katsivela E., Mihalopoulos N. and Eleftheriadis K. (2007) "PM<sub>10</sub> and PM<sub>2.5</sub> levels in the Eastern Mediterranean (Akrotiri Research Station, Crete, Greece)" **Water Air & Soil Pollution**, doi: 10.1007/s11270-007-9558-y.
5. Bardouki H., Liakakou H., Economou C., Sciare J., Smolik J., Zdimal V., Eleftheriadis K., Lazaridis M., Dye C. and Mihalopoulos N. (2003) "Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter" **Atmospheric Environment**, Vol. 37, pp. 195–208.
6. Eleftheriadis K., I. Colbeck, C. Housiadas, M. Lazaridis, N. Mihalopoulos, C. Mitsakou, J. Smolik, V. Zdimal (2006) "Size distribution, composition and origin of the submicron aerosol in the marine boundary layer during the eastern Mediterranean "SUB-AERO" experiment" **Atmospheric Environment** Vol. 40, pp. 6245–6260.
7. Smolik J., Zdimal V., Schwarz J., Lazaridis M., Havranek V., Eleftheriadis K., Mihalopoulos N., Bryant C., Colbeck I., (2003) "Size resolved mass concentration and elemental composition of atmospheric aerosols over the Eastern Mediterranean area" **Atmospheric Chemistry and Physics**, Vol. 3, pp. 2207–2216.