

Chemical characterization of the inorganic fraction of aerosols and mechanisms of the neutralization of atmospheric acidity in Athens, Greece

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Abstract. The PM_{10} mass concentration levels and inorganic chemical composition were determined on 12-h resolution sampling during August 2003 and March 2004, in the centre of Athens, Greece. The August 2003 campaign mean PM_{10} mass concentration, obtained by Beta Attenuation at 5 m above ground in Athinas Street, was $56 \mu\text{g m}^{-3}$ while the corresponding value for March 2004 was $92 \mu\text{g m}^{-3}$. In both campaigns the E.U. imposed daily limit of $50 \mu\text{g m}^{-3}$ was exceeded on several days. During the March campaign, in Athinas Street, additionally obtained DSFU- PM_{10} ($PM_{10-2.5}+PM_{2.5}$) gravimetric mass concentrations (mean: $121 \mu\text{g m}^{-3}$) in the “breathing zone”, at 1.5 m above ground were significantly higher compared to the respective mean PM_{10} mass concentrations obtained by the same method at 25 m above ground, in a second site (AEDA; mean: $86 \mu\text{g m}^{-3}$) also in the centre of the city. The above findings suggest that, for a realistic estimation of the exposure of citizens to particulate matter, PM_{10} sampling in the “breathing zone” (1.5–3 m above ground) is necessary. Such data are presented for the first time for the centre of Athens. In both campaigns, calcium was found to be the predominant component of the coarse fraction while crust-related aluminosilicates and iron were the other major components. The above elements constitute the most important components of the fine fraction, together with the predominant sulphur. All toxic metals were found in concentrations below the established air quality limits, and most of them in lower concentrations compared to older studies. Lead in particular, appeared mostly in the fine fraction and in very low concentrations compared to studies dating more than a decade back. The predominant ions of the coarse fraction have been found to be Ca^{2+} , NO_3^- , Na^+ and Cl^- , while SO_4^{2-} , Ca^{2+} and NH_4^+ were the major ionic components of the fine fraction. In the fine particles, a low molar ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ in-

dicated an ammonium-poor ambient air, and together with inter-ionic correlations suggested that atmospheric ammonia is the major neutralizing agent of sulfate, while being insufficient to neutralize it to full extent. The formation of NH_4NO_3 is therefore not favored and additional contribution to the neutralization of acidity has been shown to be provided by Ca^{2+} and Mg^{2+} . In the coarse particle fraction, the predominantly abundant Ca^{2+} has been found to correlate well with NO_3^- and SO_4^{2-} , indicating its role as important neutralizing agent in this particle size range. The proximity of the location under study to the sea explains the important concentrations of salts with marine origin like NaCl and MgCl_2 that were found in the coarse fraction, while chloride depletion in the gaseous phase was found to be limited to the fine particulate fraction. Total analyzed inorganic mass (elemental+ionic) was found to be ranging between approximately 25–33% of the total coarse particle mass and 35–42% of the total fine particle mass.

1 Introduction

The concentration levels, chemical composition and physical properties of urban aerosols depend on the nature of their emission sources, on their dispersion and on their subsequent chemical reactions in the atmosphere.

Throughout the last decades, a number of epidemiological studies have clearly demonstrated that aerosol pollution constitutes a potential hazard to citizens (Dockery and Pope, 1994; Touloumi et al., 1994; Katsouyanni et al., 1997; Katsouyanni et al., 2001; Pope III et al., 2002; Peng et al., 2005). In relation to this, special attention has been drawn on atmospheric pollution from particles in the “inhalable” size range, PM_{10} and their finer, “respirable” fraction, $PM_{2.5}$. The issue is of greater importance when it refers to largely populated urban environments, where often, high particulate pollution phenomena are observed. An integral part of improving air

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quality in the E.U. is the identification of the chemical composition and the principal sources of particulate pollutants, so as to permit the most effective, source-targeting, control strategies.

Athens, Greece, has an estimated population of 4 million inhabitants. The city is built in a 400 km² shallow valley, surrounded by moderate height hills to the north, west and east and the Saronikos Gulf to the south and south west. The hills surrounding the area are considered largely responsible for the poor dispersion conditions often observed in the city. Traffic is considered as a major source of anthropogenic atmospheric pollution in the area. The total number of vehicles circulating over the Greater Athens Area (GAA) exceeds 2 million. Of these, approximately 800 000 Light Duty Vehicles (LDV's) are non-catalytic, while ca. 100 000 Heavy Duty Vehicles (HDV's) and taxis are diesel-powered (Symeonidis, 2002). Other important causes of anthropogenic atmospheric pollution include industrial activity, as some of the country's major heavy industries are located right outside the valley, West and North West of the city, and domestic heating during the colder season.

Particulate matter pollution in Athens and the GAA has been the subject of several studies carried out during the past 20 years. Among the studied parameters is the fractionation and spatio-temporal variation of PM mass concentrations in GAA (Chaloulakou et al., 2003; Grivas et al., 2004), the concentrations of organic, elemental and inorganic carbon (Sillanpää and al., 2005) and some toxic metals in the PM (Scheff and Valiozis, 1990; Koliadima et al., 1998; Thomaidis et al., 2003; Manalis et al., 2005; Sillanpää et al., 2006) and of some ionic species in PM_{2.5} (Scheff and Valiozis, 1990; Siskos et al., 2001; Sillanpää et al., 2006) and in TSP (Eleftheriadis et al., 1998). In addition to the above, the monitoring network of the Ministry of Environment, Planning and Public Works, has been modernized and since 2000 the mass concentration of PM₁₀ as well as the concentrations of a series of gaseous pollutants, are determined on a daily basis, in a series of sites throughout the city.

While the aforementioned studies have aided in an understanding of the aerosol pollution in Athens, to a significant level, thorough knowledge of the chemical composition of the PM is still not existent. In addition to this, the governmental monitoring network and the aforementioned studies, in their entirety, have entailed aerosol sampling carried out at heights ranging from 7 to 25 m above ground. The present study aims to determine the concentrations and a more detailed inorganic chemical composition of the PM, not only at the aforementioned height levels, but also near the ground, in the "breathing zone" (Commission, 1999/30/EC), as this is indicative of the levels of pollution to which thousands of citizens, moving in the centre of the city, are exposed on a daily basis.

The detailed objectives of the present study are, firstly, the determination of the inorganic chemical composition "fingerprint" of fine and coarse particles in the centre of Athens.

Secondly, the comparison between the mass concentrations and chemical composition of coarse and fine particles collected near the ground and particles collected on a building roof, in the centre of the city. Thirdly, the comparison of total particulate matter, as well as metals and ions concentrations with the ones reported in previous studies for the city and in studies for other major urban centers of the world. Fourthly, the determination of the seasonal variation of mass concentration and chemical composition of the PM in the centre of Athens.

2 Experimental

2.1 Sampling

Aerosol sampling took place during two periods, the first between 7 and 27 August 2003 and the second between 8 and 28 March 2004. In both periods, sampling was carried out at a site located behind the Athens City Hall, in Athinas Street (\approx 12 000 vehicles/day) (38°02' N, 23°44' E). Athinas St. normally has a constant traffic load, largely due to the nearby Athens central market. At the time of the sampling periods, both in August 2003 and especially in March 2004, a series of construction activities were taking place at several points across Athinas St., due to the preparations for the Olympic Games of 2004. This resulted in a significant reduction of the traffic load. The sampling equipment on the first site consisted of a pair of Dichotomous Stack Filter Units (DSFU) (Luhana L. et al., 2001) for the collection of filter samples and a Particle Analyzer measuring mass concentration by use of Beta-Attenuation (FH62I-R, ESM-Thermo Andersen; hereafter referred to as BA), also equipped with a reflectometer for the determination of Black Carbon. Additional sampling during March took place on the roof of a governmental building (AEDA) also in downtown Athens. Blocks of 4 to 6-storey buildings dominate the location. The distance between the two sampling sites is approximately 700 m and their exact locations are shown in Fig. 1. Sampling at AEDA took place by means of 2 DSFUs. The DSFU samplers' inlets in Athinas St. were set at a height of 1.5 m above ground level. The Beta Attenuation Particle Analyzer inlet was set at a height of approximately 5 m from the ground level. In AEDA, the DSFU sampling took place at a height of approximately 25 m from the street level.

For the flow-control and measurement, four new 810C Mass-TraksTM (Full Model No.: 810C-CE-DR-2; SIERRA Instruments, Inc., Los Angeles, USA) were used. The devices have an accuracy of $\pm 1\%$ and a maximum systematic reading error of $\pm 0.2\%$. All four devices had been calibrated with air (calibration Method: Sierra Cal-Bench; Sierra Instruments) based on the US National Institute of Standards and Technology method). At the flow-rate of 6.0 L/min, that was employed during our campaigns, the 50% efficiency cut-off point is $10.1 \pm 0.5 \mu\text{m}$ for the DSFU pre-impactor,



Fig. 1. Map of Athens showing the sampling sites.

and $2.8 \pm 0.2 \mu\text{m}$ for the upper $12 \mu\text{m}$ filter (Luhana L. et al., 2001). As a result of this, particles collected were divided into two fractions; coarse, with an aerodynamic diameter between $2.8 \mu\text{m}$ and $10 \mu\text{m}$ (hereafter referred to as CPM), and fine, with an aerodynamic diameter smaller than $2.8 \mu\text{m}$ (hereafter referred to as FPM). Particles with an aerodynamic diameter greater than $10 \mu\text{m}$, were trapped on a lightly greased pre-impactor surface, in the front part of the stack. The flowrate was essentially constant, varying within approx. $\pm 2\%$, throughout the 12-h measurement sessions. For an estimation of the precision of the flow control/measurement in the pairs of DSFUs, the volumes of air sampled with each sampler were regressed to one another and the relationship between them was found to be $y=0.988x-0.018$ ($R^2=0.97$). The relationship between the respective sampled masses of particulate matter, with the two samplers was found to be described by the equation: $y=0.965x+1.03$ ($R^2=0.96$). Polycarbonate Membrane filters (Whatman) with a pore-diameter of $12 \mu\text{m}$ and $0.4 \mu\text{m}$ were used for the collection of CPM and FPM respectively. In order to avoid bounce-off phenomena, $12\text{-}\mu\text{m}$ filters were coated with a thin layer of Apiezon-L grease (Apiezon products, London, UK) (Harrison et al., 1996). All filters were weighed on a micro balance with an accuracy of $10 \mu\text{g}$ (Scaltec SBC22), before and after sampling, thus allowing the gravimetric determination of CPM and FPM mass concentrations. Prior weighing, filters were kept under stable environmental conditions (RH: $\sim 30\%$, $T=18^\circ\text{C}$) in vacuum desiccators for 24 hours. Every sampling day was divided into two periods; a morning period from 07:00 to 19:00 and an evening period from 19:00 to 07:00. Field blanks were collected at the beginning and the end of the sampling periods by placement of filters in the DSFU samplers for a complete sampling session with sampling pumps shut down.

Some FPM filters broke during the campaign, due to the vacuum behind them when they were overloaded. Moreover, in March 2004, during two weekends and a national holiday (25 March) access to the AEDA site, in the evening, was restricted due to the preparation of security measures for the then forthcoming Olympic Games. In those cases, as the change of filters in the evening was not possible, the sampling sessions in AEDA were necessarily 24-h long, which again resulted in the breaking of some FPM filters. The broken FPM filters have been excluded from the subsequent calculations and statistical analysis.

Meteorological data including wind speed and direction, relative humidity, temperature and solar radiation, as well as major urban gas-pollutants concentrations (O_3 , $\text{NO} + \text{NO}_2$, CO , SO_2), were obtained from the Hellenic Ministry of Environment. The meteorological stations were located in central parts of Athens, close to Athinas St. and AEDA.

2.2 Extraction and analysis

The use of two DSFUs in each of the sites, made it possible to obtain pairs of virtually equally loaded (“twin”) filters for every sampling session. One of the “twin” filters was analyzed by Proton Induced X-Ray Emission (PIXE) for identification and quantification of 24 metal species with an atomic number >12 , in the Department of Atmospheric Environment (NERI, Denmark) in accordance to the ISO 17025 standard (DANAK, Danish Accreditation no. 411, laboratory accredited for PIXE analysis). The second of the “twin” filters was analyzed for quantification of major anions (NO_3^- , PO_4^{3-} , SO_4^{2-} , Cl^-) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) in the water soluble fraction, by Ion Chromatography (IC), in the Laboratory of Atmospheric Pollution and Pollution Control Engineering (Department of Environmental Engineering,

Table 1. PIXE detection limits for ambient air samples on membrane filters of mixed cellulose esters (a.d.: area of deposit=13 cm²).

$\mu\text{g/a.d.}$		$\mu\text{g/a.d.}$		$\mu\text{g/a.d.}$		$\mu\text{g/a.d.}$	
Al	1.9	Ti	0.02	Zn	0.05	Zr	0.005
Si	2.3	V	0.017	Ga	0.007	Mo	0.006
P	1.8	Cr	0.017	As	0.006	Cd	0.03
S	0.8	Mn	0.012	Se	0.002	Sn	0.04
Cl	0.6	Fe	0.14	Br	0.007	Sb	0.06
K	0.3	Ni	0.012	Rb	0.004	Ba	0.2
Ca	0.6	Cu	0.02	Sr	0.004	Pb	0.014

Democritus University of Thrace). In August 2003 ionic concentrations were not measured.

2.2.1 Elemental analysis

A calculation of the absolute standard deviation for each PIXE-analysed element is incorporated in the fit of the x-ray spectrum. The uncertainties and detection limits depend on the number of x-ray counts, the thickness of the filter material (due to the continuous spectral background), its purity and the matrix (interferences from neighbour spectral peaks). Table 1 shows detection limits for typical ambient air samples on mixed cellulose ester filters, using a proton radiation time of approximately 20 min per sample. The detection limit value is either the average standard deviation of the values in a series of blanks, or the standard deviation of the blank values, depending on which is the largest. PIXE detection limits are estimated as mass per area. The uncertainty of the integrated proton charge and fluctuations of the detector solid angle give rise to an additional standard deviation of 5%, which is geometrically added to the spectral uncertainty. The calibration is permanent and is regularly controlled. The calibration uncertainty for all elements is 7% on average and, as a result of the above, far from the detection limit the average accuracy is on average 9% for all elements (the geometric sum of 5% and 7%). For semi-thick samples, which need correction for x-ray self-absorption, a non-stratified (homogeneous) mixture of elements is assumed in the mass-per-area calculation. An extra uncertainty is included due to the possible stratification of the sample. Individual uncertainties have been calculated for every compound and every sample of the campaign. The PIXE analysis as a minimum includes the elements Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba, Pb, as well as others (e.g. P, I, W, Th) in the case they are present in significant amounts. The quantification of Cl is not considered very reliable, because a percentage of HCl is lost, during the PIXE analysis. The maximum possible loss of Cl is the equivalent quantity of sampled acidic compounds (organic acids, H₂SO₄, HSO₄⁻ and NH₄⁺).

2.2.2 Ions analysis

A DX-500 Chromatograph (Dionex Corp., Sunnyvale, CA, USA) with an AS-9HC column for anions and a CS12 column for cations were used for the ions analysis. An ASRS-Ultra II and a CSRS-Ultra suppressors, working in Auto-Recycle mode, were employed for the eluent suppression. All solid filter samples to be analyzed by IC were kept in a closet, under controlled room temperature (18°C) until the day of extraction. Extraction in Deionized Water (18.2 MΩ cm⁻¹) was done by 10-min vigorous shaking and 30-min ultrasonication and in batches of 20 filters. Three “laboratory blanks” were also prepared with every batch and analyzed together with field samples to check for potential in-laboratory contamination. All filter extracts were kept in freezer (-18°C) until analysis, when they were left to equilibrate with room temperature prior to being analyzed by Ion Chromatography. The detection limit for every compound was calculated as the blank signal plus 3 standard deviations (3σ) of the blank (Miller and Miller, 1993). Calibration accuracy was continuously monitored by analyses of calibration-verification standards; the uncertainty was at maximum 5%. The calibration verification standards were obtained from a commercial source (Alltech Associates, Inc., IL, USA) different to the one of the calibration standards (Dionex Corp., Sunnyvale, CA, USA). Reproducibility (precision) was calculated by 7 injections of a standard with concentrations approximately in the middle of the calibration range; the Relative Standard Deviation (RSD) was within 3% for all compounds of interest. To check for matrix effects, the standard additions method was carried out on every 10th sample and the discrepancy between measured and calculated value was equal or lower than 3%.

3 Results and discussion

Table 2 presents arithmetic means and standard deviations of the concentrations of metals measured in August 2003. Morning and evening values are presented separately as

Table 2. Morning and evening concentrations (ng/m^3) measured in Athinas St., in August 2003 (Mean \pm Standard Deviation); ^a Coarse Particulate Matter ($\text{PM}_{2.5-10}$); ^b Fine Particulate Matter ($\text{PM}_{2.5}$); ^c PM_{10} obtained by use of Beta Attenuation at a height of 5 m from ground level; gravimetric PM_{10} not determined during campaign.

	Athinas St.			
	CPM ^a ($n=35$)		FPM ^b ($n=30$)	
	Morning ($n=18$)	Evening ($n=17$)	Morning ($n=16$)	Evening ($n=14$)
Al	600 \pm 176	517 \pm 268	351 \pm 132	266 \pm 116
Si	1388 \pm 423	1186 \pm 741	544 \pm 248	356 \pm 154
S	344 \pm 221	301 \pm 155	4374 \pm 1992	4570 \pm 2260
Cl	129 \pm 96.0	114 \pm 87.6	43.4 \pm 24.4	31.3 \pm 11.5
K	317 \pm 96.6	292 \pm 183	351 \pm 98.7	339 \pm 95.0
Ca	5730 \pm 2321	4797 \pm 4428	1706 \pm 872	1074 \pm 4674
Ti	51.4 \pm 17.1	45.0 \pm 32.4	22.4 \pm 10.1	14.5 \pm 6.08
V	4.3 \pm 3.77	6.11 \pm 3.94	11.2 \pm 12.1	16.3 \pm 10.4
Cr	4.68 \pm 2.01	4.7 \pm 3.56	2.43 \pm 1.29	2.40 \pm 1.19
Mn	12.5 \pm 5.23	11.5 \pm 7.63	10.2 \pm 3.91	8.01 \pm 4.3
Fe	690 \pm 232	707 \pm 408	374 \pm 138	361 \pm 137
Ni	3.83 \pm 2.17	4.05 \pm 2.59	5.38 \pm 4.37	5.66 \pm 3.74
Cu	83.1 \pm 42.9	130 \pm 59.4	84.4 \pm 40.1	142.4 \pm 61.5
Zn	31.8 \pm 17.1	29.0 \pm 16.2	64.8 \pm 53.8	45.4 \pm 24.5
Ga	0.28 \pm 0.19	0.18 \pm 0.11	0.28 \pm 0.32	0.28 \pm 0.2
As	0.49 \pm 0.3	0.46 \pm 0.35	0.99 \pm 0.57	1 \pm 0.63
Se	0.05 \pm 0.12	0.03 \pm 0.08	1.11 \pm 0.75	0.99 \pm 0.46
Br	1.21 \pm 0.58	1.02 \pm 0.39	5.46 \pm 1.76	5.1 \pm 1.76
Rb	1.51 \pm 0.47	1.31 \pm 0.65	1.16 \pm 0.37	1.01 \pm 0.3
Sr	5.89 \pm 1.8	5.08 \pm 3.64	2.2 \pm 0.98	1.77 \pm 0.66
Zr	2.88 \pm 1.41	3.32 \pm 1.73	1.34 \pm 0.48	1.81 \pm 0.74
Sn	1.31 \pm 0.53	1.35 \pm 1.18	2.45 \pm 2.02	2.19 \pm 1.32
Ba	17.2 \pm 8.11	18.5 \pm 13.8	11.1 \pm 7.51	9.95 \pm 4.72
Pb	11.9 \pm 6.56	11.04 \pm 6.34	34.3 \pm 21.3	28.5 \pm 21.1
Total PM_{10}^c ($\mu\text{g}/\text{m}^3$)	Morning: 57 \pm 13; Evening: 55 \pm 19			

this may demonstrate, on a preliminary level, trends in the “within-a-day” variation of species concentrations. Ionic species and gravimetrically determined PM were not measured during this campaign due to a technical issue. In Tables 3 and 4, the March 2004 results are presented in a similar manner. The water soluble percentage column represents the ratio of the water soluble, ionic concentration to the respective elemental. Tables 5a and 5b present our campaigns total arithmetic means for elements and ions of major interest, next to respective results of previous studies carried out in Athens, in other cities of Greece and other urban centres of the world.

3.1 August 2003

3.1.1 Identification of major elements, distribution in the two fractions and comparison of concentrations with air quality limits

During the August 2003 campaign and throughout the year until the summer of 2004, construction work was taking place in the centre of the city. For a big part of August, traffic in downtown Athens was reduced due to the summer vacations. In relation to that, an increase in the measured BA- PM_{10} concentrations was observed towards the end of the month, after the end of the DSFU sampling, upon return of the greatest percent of the population. The meteorological conditions during this sampling period were typical of Athens in the middle of summer and were characterized by low relative humidity (daily mean: 42.7%; min: 24.0%), high temperatures (daily mean: 30.8°C; min: 24.1°C; max:

Table 3. Morning and evening concentrations (ng/m^3) measured in Athinas St., 1.5 m from the ground level, in March 2004 (Mean \pm Standard Deviation); ^a Coarse Particulate Matter ($\text{PM}_{2.5-10}$); ^b Fine Particulate Matter ($\text{PM}_{2.5}$); ^c PM_{10} obtained by use of Beta Attenuation at a height of 5 m from ground level; ^d Gravimetrically obtained, at a height of 1.5 m from the ground level.

Athinas St.								
	CPM ^a (<i>n</i> =37)				FPM ^b (<i>n</i> =29)			
	Morning (<i>n</i> =21)	% water soluble	Evening (<i>n</i> =16)	% water soluble	Morning (<i>n</i> =18)	% water soluble	Evening (<i>n</i> =11)	% water soluble
Al	671 \pm 519		655 \pm 359		372 \pm 450		305 \pm 257	
Si	1850 \pm 1415		1808 \pm 993		702 \pm 975		587 \pm 534	
SO ₄ ²⁻	1766 \pm 869		1958 \pm 795		6821 \pm 3060		6540 \pm 3438	
S	656 \pm 354		809 \pm 397		2876 \pm 1397		2556 \pm 1093	
S as SO ₄ ²⁻	586 \pm 290	89	653 \pm 265	81	2273 \pm 1020	79	2180 \pm 1146	85
Cl	1199 \pm 1160		1063 \pm 1027		204 \pm 419		163 \pm 183	
Cl ⁻	2474 \pm 1220		2917 \pm 812		381 \pm 251		267 \pm 255	
K	424 \pm 273		411 \pm 195		296 \pm 240		245 \pm 154	
K ⁺	177 \pm 68	42	197 \pm 150	48	145 \pm 66	49	145 \pm 57	59
Ca	15999 \pm 10731		15086 \pm 8087		3545 \pm 2107		3581 \pm 1588	
Ca ²⁺	12067 \pm 3597	75	11272 \pm 3553	75	3372 \pm 1193	95	3214 \pm 1630	90
Ti	115 \pm 97.3		136 \pm 73.5		42.6 \pm 50.9		74.1 \pm 58.4	
V	5.46 \pm 3.96		6.47 \pm 3.78		11.1 \pm 11.9		8.7 \pm 5.9	
Cr	8.56 \pm 5.46		8.25 \pm 4.17		2.59 \pm 2.63		2.76 \pm 1.58	
Mn	18.2 \pm 12.4		17.5 \pm 10.3		12.3 \pm 13.0		13.0 \pm 10.1	
Fe	1090 \pm 743		948 \pm 472		447 \pm 467		374 \pm 229	
Ni	5.46 \pm 5.36		4.81 \pm 2.29		4.47 \pm 4.1		4.33 \pm 3.32	
Cu	37.2 \pm 23.5		26.3 \pm 10.62		22.1 \pm 20.8		17.7 \pm 11.7	
Zn	52.9 \pm 34.5		75.5 \pm 42.9		76.4 \pm 68.9		118 \pm 113	
Ga	0.37 \pm 0.45		0.21 \pm 0.13		0.24 \pm 0.2		0.14 \pm 0.14	
As	0.73 \pm 0.47		0.92 \pm 0.35		1.58 \pm 0.48		1.72 \pm 0.3	
Se	0.15 \pm 0.17		0.16 \pm 0.12		0.59 \pm 0.49		0.49 \pm 0.23	
Br	3.99 \pm 2.38		3.52 \pm 2.11		7.39 \pm 0.48		6.73 \pm 3.58	
Rb	1.85 \pm 1.56		1.83 \pm 0.77		1.09 \pm 0.88		0.74 \pm 0.53	
Sr	15.2 \pm 12.2		22.2 \pm 16.9		4.93 \pm 5.32		5.38 \pm 6.98	
Zr	5.08 \pm 4.54		4.99 \pm 2.65		2.3 \pm 2.3		1.44 \pm 0.66	
Mo	2.25 \pm 1.43		1.38 \pm 0.64		1.87 \pm 1.32		1.31 \pm 0.61	
Sn	2.75 \pm 2.38		2.28 \pm 1.43		5.01 \pm 6.94		3.03 \pm 2.10	
Sb	4.84 \pm 3.76		2.86 \pm 1.63		3.25 \pm 3.26		1.88 \pm 1.31	
Ba	28.0 \pm 19.9		38.6 \pm 33.7		12.4 \pm 12.8		16.1 \pm 11.08	
Pb	21.4 \pm 23.2		14.86 \pm 9.86		53.9 \pm 66.6		31.0 \pm 15.4	
Na ⁺	835 \pm 464		735 \pm 580		294 \pm 242		235 \pm 87.5	
NH ₄ ⁺	158 \pm 99		267 \pm 126		1484 \pm 1246		1553 \pm 1014	
Mg ²⁺	277 \pm 133		327 \pm 173		109.3 \pm 44.8		110.2 \pm 44.0	
NO ₃ ⁻	2724 \pm 1836		2238 \pm 1219		410 \pm 228		276 \pm 172	
PM ^d ($\mu\text{g}/\text{m}^3$)	94.8 \pm 43.1		65.3 \pm 30.9		44.7 \pm 32.7		36.2 \pm 22.2	
Total PM ₁₀ ^c ($\mu\text{g}/\text{m}^3$)	(PM ₁₀ μm) Morning: 104.7 \pm 32.7; Evening: 78.5 \pm 32.3							

Table 4. Morning and evening concentrations (ng/m^3) measured in AEDA in March 2004, 24 m from the ground level (Mean \pm Standard Deviation); ^a Coarse Particulate Matter ($\text{PM}_{2.5-10}$); ^b Fine Particulate Matter ($\text{PM}_{2.5}$); ^c Gravimetrically obtained.

	AEDA							
	CPM ^a (<i>n</i> = 30)				FPM ^b (<i>n</i> = 20)			
	Morning (<i>n</i> =16)	% water soluble	Evening (<i>n</i> =14)	% water soluble	Morning (<i>n</i> =11)	% water soluble	Evening (<i>n</i> =9)	% water soluble
Al	411 \pm 211		428 \pm 284		320 \pm 174		273 \pm 174	
Si	1080 \pm 557		1070 \pm 682		463 \pm 347		415 \pm 284	
SO ₄ ²⁻	1092 \pm 442		1215 \pm 577		7140 \pm 5844		8086 \pm 7002	
S	476 \pm 166		535 \pm 442		3008 \pm 1924		2820 \pm 1604	
S as SO ₄ ²⁻	364 \pm 180	76	405 \pm 192	76	2380 \pm 1948	79	2645 \pm 2334	94
Cl	563 \pm 691		880 \pm 685		137 \pm 24.01		110 \pm 133	
Cl ⁻	1041 \pm 686		1436 \pm 1110		218 \pm 278	–	173 \pm 100	
K	234 \pm 115		245 \pm 148		291 \pm 139		307 \pm 152	
K ⁺	151 \pm 185	65	165 \pm 156	67	73.4 \pm 56.4	25	93.7 \pm 55.8	31
Ca	8050 \pm 4870		7007 \pm 4623		1728 \pm 946		1641 \pm 706	
Ca ²⁺	5753 \pm 2151	71	5491 \pm 2963	78	1375 \pm 947	80	1270 \pm 624	77
Ti	63.2 \pm 38.4		51.2 \pm 33.7		26.1 \pm 14.0		27.9 \pm 18.9	
V	4.07 \pm 2.74		4.75 \pm 2.85		9.32 \pm 5.82		16.42 \pm 8.91	
Cr	7.99 \pm 6.04		8.34 \pm 6.23		4.41 \pm 1.85		2.71 \pm 0.96	
Mn	12.6 \pm 7.34		13.1 \pm 9.18		13.7 \pm 4.46		9.64 \pm 3.8	
Fe	739 \pm 391		748 \pm 511		405 \pm 136		340 \pm 117	
Ni	3.76 \pm 2.47		3.62 \pm 3.07		5.06 \pm 3.23		5.64 \pm 2.21	
Cu	58.5 \pm 36.9		63.4 \pm 57.6		58.5 \pm 23.0		58.7 \pm 32.2	
Zn	36.3 \pm 22.3		31.63 \pm 21.7		73.4 \pm 75.5		53.5 \pm 27.9	
Ga	0.15 \pm 0.19		0.19 \pm 0.1		0.12 \pm 0.05		0.25 \pm 0.11	
As	0.45 \pm 0.28		0.52 \pm 0.35		0.73 \pm 0.27		0.57 \pm 0.1	
Se	0.09 \pm 0.07		0.09 \pm 0.05		0.63 \pm 0.4		0.81 \pm 0.33	
Br	2.12 \pm 1.68		2.67 \pm 1.29		6.81 \pm 1.84		7.8 \pm 2.15	
Rb	1.09 \pm 0.52		1.01 \pm 0.55		0.82 \pm 0.5		1.03 \pm 0.63	
Sr	6.95 \pm 3.93		6.51 \pm 3.49		2.77 \pm 1.38		2.45 \pm 1.18	
Zr	3.26 \pm 1.8		3.82 \pm 2.62		1.31 \pm 0.5		1.83 \pm 0.83	
Mo	2.61 \pm 1.59		3.79 \pm 2.12		4.56 \pm 1.51		5.17 \pm 3.17	
Sn	1.92 \pm 1.34		2.55 \pm 2.14		3.43 \pm 2.65		6.32 \pm 6.31	
Sb	3.4 \pm 2.58		5.19 \pm 2.74		3.1 \pm 1.0		3.05 \pm 1.78	
Ba	31 \pm 43.8		21.7 \pm 12.3		12.2 \pm 7.12		5.9 \pm 5.2	
Pb	16.6 \pm 13.2		25.5 \pm 27.69		37.2 \pm 27.2		27.2 \pm 89	
Na ⁺	553 \pm 391		709 \pm 412		286 \pm 305		206 \pm 205	
NH ₄ ⁺	126 \pm 123		198 \pm 167		1613 \pm 1731		1660 \pm 1706	
Mg ²⁺	193 \pm 110		234 \pm 111		85.7 \pm 74.6		80.9 \pm 43.8	
NO ₃ ⁻	1751 \pm 1353		2031 \pm 1421		350 \pm 408		168 \pm 129	
PM ^c ($\mu\text{g}/\text{m}^3$)	54.4 \pm 25.1		55.2 \pm 27.4		33.0 \pm 8.4		30.1 \pm 11.6	

38.1°C) and low wind speed (daily mean: 2.7 km/h; min: 0.4 km/h).

Measured BAPM₁₀ concentrations shown in Table 2 (morning: 57 \pm 13 $\mu\text{g m}^{-3}$; evening: 55 \pm 19 $\mu\text{g m}^{-3}$; min: 38 $\mu\text{g m}^{-3}$; max: 90 $\mu\text{g m}^{-3}$) are very close to the gravimetrically obtained ones reported for June–July of the same year, by another study (Sillanpää et al., 2006) and signify the

aerosol pollution problem in GAA, which has already been identified in other studies (Chaloulakou et al., 2003; Grivas et al., 2004; Manalis et al., 2005). Mean daily PM₁₀ values on the site exceeded on 11 days during the campaign the E.U. imposed 24-h limit of 50 $\mu\text{g m}^{-3}$, which is not to be exceeded more than 35 times a year (limit was to be met by January 2005).

Table 5a. Present study in comparison with literature values. Concentrations are shown in ng/m^3 unless otherwise stated. Sampling heights above ground are shown where declared. Date next to sampling location declares year of measurements, while date in parenthesis declares year of publication; (el): elemental concentration; (i): ionic concentration.

Element, (ng/m ³)	Current Study; Athinas St., August 2003, (1.5 m)	Current Study; Athinas St., March 2004, (1.5 m)	Current Study; AEDA, March 2004, (25m)	Thes/niki '99-'00 (Samara and Voutsas, 2004) (3.5 m)	Madrid 1999-'00 (Artunano et al., 2003)	Barcelona '99-'00 (Querol et al., 2001)	Milan, Dec '97-'Sep '98 (Marcazzan et al., 2001), winter;summer (3 m)	Helsinki '96-'97 (Pakkanen et al., 2001)	Vienna '99-'00 (Puxbaum et al., 2004), (3.4 m)	Budapest 1996, 1998-'99, (Salma et al., 2001)
CPM ($\mu\text{g}/\text{m}^3$)		80.1	54.8	39.7	47.7	49.8	110; 74	13.0	8.9	
Ca/Ca ²⁺	5264(el)	15543(el)/11670(i)	7529(el)/5622(i)		1920	2250	1550; 1280	480(el)/350(i)	540	610; 2780
Fe	699	1019	744	257	1930	890	2440; 1230	520	146	300; 2000
Al	559	663	420		1820 (as Al ₂ O ₃)	1220 (as Al ₂ O ₃)	1560; 1280	520		360; 1400
Cl/Cl-	122(el)	1131(el)/2696(i)	722(el)/1239(i)		380 (el)	1100 (el)		240(i)	100 (el)	50; 180
K/K+	305(el)	418(el)/187(i)	240(el)/158(i)		390 (el)	560 (el)	660; 300	200(el)/30(i)	80 (el)	160; 460
Zn	32	64	34	25	93	250	285; 140	7.9	13	10; 60
S	323	733	506				4100; 2640			280; 890
Si	1287	1829	1075		4560 (as SiO ₂)	2960 (as SiO ₂)	4390; 3930			990; 3820
Pb	11	18	21	15	118	149	310; 120	2	5.1	4; 40
As	0.48	0.83	0.49					0.21	0.28	
Cr	4.69	8.41	8.17	1.36	9	6	14; <10		0.39	
Ni	3.94	5.14	3.69	1.4	4	7	10; <6	0.79	0.4	
Cu	107	31.8	61.0	99.9	112	74	90; 45	6.2	7.9	
Mn	12.0	17.9	12.9	9.08		24			4.3	
V	5.21	5.97	4.41	2.96		13			0.53	
SO ₄ ⁻²		1862	1154		4380	6750		180	410	
NO ₃ ⁻		2481	1891		2090	5720		410	1300	
Mg/Mg ²⁺		302(i)	213(i)		250 (el)	290 (el)		130 (el)/31(i)	60 (el)	
Na/Na ⁺		785(i)	631(i)		310 (el)	940 (el)		300 (el)/290 (i)	120 (el)	
NH ₄ ⁺		192	162		1150	2710		10	300	

Table 5b. Present study in comparison with literature values. Concentrations are shown in ng/m^3 unless otherwise stated. Sampling heights above ground are shown where declared. Date next to sampling location declares year of measurements, while date in parenthesis declares year of publication; (el): elemental concentration; (i): ionic concentration.

Element, (ng/m ³)	Current Study; Athinas St., August 2003, (1.5 m)	Current Study; Athinas St., March 2004, (1.5 m)	Current Study; AEDA, March 2004, (25 m)	Athens, 1984 (Valaoras et al., 1990), (summer; winter)	Athens, 1987 (Scheff and Valiozis, 1990), April-June (27 m)	Athens, 1995-'96 (Thomaidis et al., 2003), (25 m)	Thes/niki '99-'00 (Samara and Voutsas, 2004) (3.5 m)	Thes/niki '89-'90 (Tsitouridou et al., 1993) (3 m)	Madrid 1999-'00 (Artunano et al., 2003)	Barcelona '99-'00 (Querol et al., 2001)	Milan, Dec '97-'Sep '98 (Marcazzan et al., 2001), winter;summer (3 m)	Ankara, Feb and June 1993, (Yatin et al., 2000) (2 seasons)	Helsinki '96-'97 (Pakkanen et al., 2001)	Vienna '99-'00 (Puxbaum et al., 2004), (3.4 m)
FPM ($\mu\text{g}/\text{m}^3$)		40.5	31.6		80.7		66.5		34.1	35.0	70; 51		11.8	21.5
Ca/Ca ²⁺	1390(el)	3563(el)/3293(i)	1685(el)/1322(i)	1260; 770(el)	2610(el)			1178 (i)	660	510	80; 100		71(el)/53(i)	90
Fe	368	411	373	490; 300	1100		148.4		570	260	210; 170	103; 95	96	35
Al	309	339	297	130; 850	408				720 (as Al ₂ O ₃)	460 (as Al ₂ O ₃)	170; 250	88; 128	59	
Cl/Cl-	37 (el)	184(el)/324(i)	124(el)/196(i)	75; 450(el)	350(el)			2340(i)	420	590 (el)		42; 4.4	43(i)	120 (el)
K/K+	345(el)	271(el)/145(i)	299(el)/84(i)	160; 280(el)	428(el)				390	480 (el)	390; 135	128; 119	85(el)/67(i)	190 (el)
S	4472	2716	2914	970; 3100	4180						2980; 2280			
Si	450	645	439	410; 1110	1210				1820 (as SiO ₂)	1050 (as SiO ₂)	245; 700			
Zn	55	97	63	130; 210	273		520		59	178	145; 75	20; 9.6	14	22
Pb	31	42	32	610; 1100	699	190	32.2		99	130	190; 85	88; 59	5.8	17
As	1.00	1.65	0.65	34; 13		1.9						2.2; 0.63		0.66
Cr	2.42	2.68	3.56				1.1		2	6	5; <10	3.8; 2.5		0.4
Ni	5.52	4.40	5.35	21; 8.6	12	6.5	2.36		2	6	7; <6	4.5; 1.1	2	1.2
Cu	113	19.9	58.6	35; 26	51		148.5		41	52	21; 14		3.1	3.1
Mn	9.11	12.7	11.7	14	22		8.57			14				2.4
V	13.8	9.90	12.9	6.6			5.97			9				1.3
SO ₄ ⁻²		6681	7613		10 400			9750	3770	5750		10 488; 1993	2500	4200
NO ₃ ⁻		343	259		2000			1950	1330	4030		3298; 538	1600	2800
Mg/Mg ²⁺		110(i)	83(i)		132 (el)			70	90 (el)	80 (el)			25(el)/17(i)	20 (el)
Na/Na ⁺		265(i)	247(i)		369 (el)			1143	130 (el)	230 (el)		74; 32	170(el)/146(i)	70 (el)
NH ₄ ⁺		1519	1637					5190	1410	3180			1100	2200

In August 2003 the dominant element of the CPM is Ca. Other major elements in the fraction include Al, Si and Fe. Oxides of these compounds are found in crustal rock; hence a big part of their concentrations is probably related to dust/particle re-suspension. It is worth noting that their evening concentrations do not appear significantly lower compared to the morning ones. Other important components of this fraction are also S, K, Cu and Zn. The aforementioned elements are the most important components of the FPM fraction as well, with S being, in this case, the predominant element. The biggest part of Ca, Al, Si and Fe is found in the CPM, which is in agreement with other studies for the eastern Mediterranean (Graham et al., 2004; Kouyoumdjian and Saliba, 2006). Sulphur and zinc are higher in the FPM, and Cu is found on similar levels in both fractions. A “trend” of the prevalence of evening over morning values for FPM S and Cu in both fractions is worth mentioning. Lead is mainly found in FPM and its concentration in Athens has been greatly reduced in the last 20 years, as automotive fuel in Greece does no longer contain lead compounds. Arsenic concentration is almost double and Ni slightly higher in the FPM, compared to the CPM, and their concentrations on the site were also found to be significantly lower than the E.U. proposed mean annual limits of 6 ng m^{-3} and 20 ng m^{-3} respectively. Manganese is found on similar levels in both fractions and its concentrations are lower by an order of magnitude compared to the WHO-annual tolerance concentration of 150 ng m^{-3} . Vanadium is found mostly in the FPM with a trend for higher values in the evening and its concentrations have in all cases been by two orders of magnitude, or more, lower than the proposed 24-h threshold of $1 \mu\text{g m}^{-3}$ (WHO, 2000). Barium and Cr are found at significantly higher levels in the CPM with the concentrations of the later to have increased in the last decade, as is derived from the current and other recent studies (Manalis et al., 2005).

3.2 March 2004

3.2.1 The difference between 1.5 m and 25 m above ground for PM-mass and compound concentrations

For the March 2004 campaign gravimetrically measured CPM and FPM mean mass concentrations, calculated on a 12-h basis, are shown in Tables 3 and 4, for Athinas St. and AEDA respectively. For Athinas St. BAPM₁₀ mass concentrations are also shown in Table 3. In this site at 1.5 m from the ground, the PM₁₀ (CPM+FPM) campaign mean concentration was $121 \mu\text{g m}^{-3}$ (max: $242 \mu\text{g m}^{-3}$), with individual PM_{10–2.5} and PM_{2.5} concentrations being 80 and $40.5 \mu\text{g m}^{-3}$ respectively. In the second site (AEDA), at 25 m above ground, the respective campaign mean concentration for the PM₁₀ was $86 \mu\text{g m}^{-3}$ (max: $158 \mu\text{g m}^{-3}$), with individual PM_{10–2.5} and PM_{2.5} concentrations being 55 and $32 \mu\text{g m}^{-3}$ respectively. In Athinas St., at 5 m above ground, the BAPM₁₀ daily mean concentration was

$92 \mu\text{g m}^{-3}$ (daily max: $133 \mu\text{g m}^{-3}$). The meteorological conditions were again typical of the season for the city, with moderate relative humidity (daily mean: 63.4%; min: 49.2%; max: 79.1%), relatively high temperatures (daily mean: 14.6°C ; min: 10.8°C ; max: 17.9°C) and low wind speed (daily mean: 3.0 km/h; min: 1.6 km/h; max: 5.2 km/h).

A direct comparison of the Athinas St. and AEDA DSFU-PM₁₀ (calculated as the sum: CPM+FPM) carried out on a 12-h resolution basis shows that the PM₁₀ mass concentrations in the breathing zone, at a height of 1.5 m above ground are significantly higher than the ones at 25 m above ground (Table 6b and Fig. 4b). Additionally, morning CPM mass concentrations in Athinas St., are approximately 30% higher than the evening CPM concentrations, while the respective difference for the FPM fraction is approximately 22%. In the same site, roughly 35% of the particulate mass is found in FPM and 65% in CPM. Additionally, the morning Athinas St. CPM mass concentrations are approximately 43% higher than the respective ones in AEDA. The difference for the morning FPM concentrations is approximately 28%. Corresponding evening differences are 26% and 17% for the CPM and FPM respectively.

A series of studies have reported discrepancies between the PM mass concentrations obtained with continuous sampling methods such as TEOM or Beta Attenuation (BA) and filter-sampling with gravimetric quantification (Allen et al., 1997; Charron et al., 2004). Gravimetrically obtained PM mass concentrations are usually found to be higher than the corresponding concentrations obtained with the continuously monitoring methods. The main reason for this is the warming of the sampling line and filter, which results in the loss of semi-volatile compounds like NH_4NO_3 and water. However, it has also been found that the discrepancies in the results obtained with the different methods decrease with increasing ambient temperature and decreasing relative humidity (Charron et al., 2004). In a recent study (Gehrig et al., 2005), comparison of results obtained with Beta Attenuation and filter-samplers for two sites largely affected by mineral dust/soil showed a very close to unity BA-PM₁₀/Grav-PM₁₀ ratio (1.02 and 1.06). This confirms that the volatilisation losses, expected to occur due to the warming of the sampling line and filter at approx. $25\text{--}30^\circ\text{C}$ inside the BA, are not significant for traffic-(re)suspended mineral dust. In our study, in addition to the primary focus of directly comparing gravimetric PM mass concentrations obtained in the two sites, comparison of the PM masses obtained with the different methods and at different heights above ground in Athinas St., is considered applicable due to the following reasons. Firstly, Athinas St. has been a heavily influenced by soil/re-suspension site, with widespread construction activity taking place. Secondly, the weather conditions in the region during the campaign were characterized by relatively high temperatures and moderate-to-low relative humidities. Thirdly, as will be further discussed below, the region under study is an ammonium-poor environment where the formation of

Table 6a. Comparison between gravimetric DSFU-PM₁₀ (CPM+FPM), collected at a height of 1.5 m above ground and BA-PM₁₀ (obtained by use of Beta Attenuation), at a height of approx. 5 m from the ground level, in Athinas St., in March 2004.

	Gravimetric PM ₁₀ (CPM+FPM)	Beta Attenuation PM ₁₀
Mean±StDev	121±46	92±33
Median	137	93
Min	45	38
Max	242	165

Difference is significant at the 99% level, using student t-test.

Table 6b. Comparison between gravimetric DSFU-PM₁₀ (CPM+FPM), collected at a height of 1.5 m above ground in Athinas St. and the respective gravimetric PM₁₀, collected at a height of 25 m from ground level in AEDA, in March 2004.

	Gravimetric PM ₁₀ (CPM+FPM), Athinas	Gravimetric PM ₁₀ (CPM+FPM), AEDA
Mean±StDev	121±46 (CPM: 80.1; FPM: 40.5)	86±35 (CPM: 54.8; FPM: 31.6)
Median	137	84
Min	45	37
Max	242	158

Difference is significant at the 99% level, using student t-test.

semi-volatile NH₄NO₃ is not favoured. In light of the above, half-hourly PM₁₀ values obtained with BA (BAPM₁₀) were averaged over the respective 12-h periods corresponding to gravimetric (DSFU) sampling sessions and the BAPM₁₀ obtained at 5 m above ground were found to be significantly lower than the gravimetric DSFU-PM₁₀ concentrations obtained at 1.5 m above ground in the same site. Comparative results are shown in Table 6a. and Fig. 4a. Examination of the morning and evening values in Table 3, for BAPM₁₀ and DSFU-PM₁₀ shows that the morning mass concentrations are generally much higher than the evening ones.

The significant increase in the CPM mass concentrations during the “morning” session in Athinas St. could be attributed to the extensive contribution of construction, traffic and traffic-re-suspended soil/dust and overall human activity (e.g. large numbers of pedestrians). One may argue that this “morning-contribution”, which, as discussed below, consists mainly of crust-related species like calcium and aluminosilicate compounds, leads to an overestimation of the discrepancy in mass concentrations between the sites and elevations from ground. However, the examination of: a) the discrepancies of the evening CPM concentrations between the different sites and elevations above ground, b) the respective discrepancies of the morning and evening FPM concentrations, c) the discrepancy between the PM₁₀ at 1.5 m and at 5 m from the ground in Athinas St., and d) the discrepancy of the maximum concentrations for the three sampling points (Tables 6a and 6b), confirms that PM₁₀ concentrations significantly increase closer to the ground, near the “breathing zone”. This

is in agreement with the findings of another study for Beijing (Chan et al., 2005) and fundamental micrometeorological theory, and demonstrates the need for information on the PM mass concentrations in the “breathing-zone” for the centre of Athens.

The AEDA DSFU-PM₁₀ mass concentrations are very close to the respective PM₁₀ values reported by studies for the same period (Valavanidis et al., 2006), which also entailed measurements at a height of 25 m above ground level, in a nearby to AEDA location. Our campaign CPM and FPM mean mass concentrations as well as the distribution of PM mass between the two fractions in AEDA (~63% in the CPM and ~37% in the FPM) are also very close to the ones of the aforementioned study. In addition to the above, the AEDA DSFU-PM₁₀ are reasonably close to the results of other recent studies (Chaloulakou et al., 2005; Manalis et al., 2005), for the years 2001–2003, in which measurements were again taken at building-storey levels, at approximately 7m above ground, or building-roof levels, approximately 25 m above ground also in or near the centre of Athens. The above support the conclusion that PM₁₀ concentrations are significantly higher close to the ground, near the “breathing zone”, compared to the ones measured at higher elevations, which have been presented for the centre of the city to-date. The differences in mass concentrations between these elevations above ground appear to be significantly higher for the heavier CPM and for daytime hours when overall activity in the centre reaches its peak.

3.2.2 Identification of major elements and ions, distribution in the two fractions and comparison of concentrations with air quality limits

Following the above findings, individual element and ions concentrations have been examined for similar discrepancies between sampling sites and heights. For both sites, and both fractions, major components of the PM are the same as in the previous campaign, with Ca and aluminosilicates being predominant in the CPM. In the FPM, in AEDA S is the most abundant element, while near the ground, in Athinas St. site, Ca dominates this fraction also, with concentrations significantly higher than the ones of AEDA. Previous publications have mentioned the existence of great amounts of Ca in the atmosphere of locations in Greece (Danalatos and Glavas, 1995), and in Athens, in particular (Scheff and Valiozis, 1990; Sillanpää et al., 2006), as well as other eastern Mediterranean sites (Graham et al., 2004; Kouyoumdjian and Saliba, 2006). The CPM concentrations of Ca, Al, Si, Fe and Ti are higher in Athinas St. A similar phenomenon is observed for the respective FPM concentrations of these compounds, with the exception of Fe and Al for which FPM Athinas St. concentrations do not differ much from the ones in AEDA. It is worth mentioning that, during this campaign, Cu was almost equally distributed in the two fractions, while its concentrations are lower than in the previous campaign, especially in Athinas St. site. Traffic in Athinas St. might have not been further reduced during the March 2004 campaign, compared to August 2003, hence the Cu seasonal variation has raised questions on the extend to which Cu in downtown Athens is solely related to traffic and whether significant parts of it have been connected with other emission sources as well. As expected, the greater part of Pb is found in the FPM fraction and its concentration remains very low compared to the air quality limit and results of older studies. Moreover, in both fractions the Pb concentration between the two sites does not differ significantly. Nickel concentrations do not differ much between the two sites and are generally equally distributed in the CPM and FPM in Athinas St., while its concentrations appear slightly higher in FPM than in CPM in the AEDA site. Arsenic concentrations, on the other hand, appear higher in Athinas St., while in both sites FPM values prevail over CPM. However, both As and Ni are found in concentrations much lower than the air quality limits, mentioned earlier. Mn is another compound found in higher concentrations in Athinas St. Its CPM values are higher than in the respective FPM in Athinas St., while in AEDA it is equally distributed in both fractions. Its levels remain at low levels compared to the pre-mentioned air quality threshold. FPM V is again prevalent over CPM; AEDA values are higher than Athinas St. in the first fraction, while the reverse happens for the latter fraction. Ba and Cr concentrations are higher in the CPM than in the FPM with their values being similar in the two sites. A slight difference between the two sites, though, is that in Athinas, a trend for

their morning values to be higher than their evening values is observed, while in AEDA the reverse is true, with the exception of CPM Cr for which morning and evening values are almost equal.

3.2.3 March 2004 – ionic concentrations

A known issue when sampling particulate matter for latter analysis of ionic species is the sampling artefacts which may occur, particularly for ammonium, sulfate, nitrate and chloride. The ambient molar particulate ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ has been found to be less than 1.5 ($\text{NH}_4^+/\text{SO}_4^{2-} \leq 1.35$), which, as will be further discussed below, is indicative of an ammonium-poor atmosphere, where formation and consequent evaporation of NH_4NO_3 is not favoured (Seinfeld and Pandis, 1998; Pathak et al., 2004; Trebs et al., 2005). The absorption of SO_2 on particles collected on filters, which could lead to sulfate artefacts, has been found to be negligible for ammonium poor environments (Pathak et al., 2004). This is considered applicable in the present study, given the moderate-to-low SO_2 concentrations obtained at two sites nearest to ours during the March campaign ($29 \mu\text{g m}^{-3}$ in Patision and $22 \mu\text{g m}^{-3}$ in Aristotelous; PERPA; Hellenic Ministry of Environment). Furthermore, the reaction of CPM CaCO_3 , with HNO_3 and H_2SO_4 predominates over the reactions of particulate NaCl with HNO_3 and H_2SO_4 . As a result of this, chloride depletion, via formation of HCl and evaporation to the gaseous phase, is negligible for the CPM fraction, where the largest percentages of particulate Cl^- and Na^+ have been observed and Ca^{2+} is by far the most predominant ion. Their nano-equivalent ratio has been found to range between $1.6 \leq \text{Cl}^-/\text{Na}^+ \leq 2.2$ for the two sites, supporting the above conclusion. Chloride depletion was found to occur in the fine fraction, and the percentage of depleted FPM- Cl^- , calculated in accordance to (Holland, 1984; Yao et al., 2001), has been found to be approximately 33% for Athinas St. and 55% for the AEDA site. However, on three sampling occasions when the concentrations of the rest of the species were not especially high, high FPM concentrations of Cl^- and Na^+ were obtained, with a molar ratio of Cl^-/Na^+ well above 1. The retrospective determination of the origin of those high values is beyond the scope of the current study.

Like with its elemental form, Ca^{2+} is predominantly found in the CPM, in which it is by far the most abundant element. A relatively big percentage of it is probably found as CaCO_3 due to the calcitic nature of the crustal rock in Greece which is supported by the results of a recent study (Sillanpää et al., 2005). Similar with Ca^{2+} unimodal distribution is observed for NO_3^- , Cl^- and Na^+ , as they are mainly found in the CPM. For all of these ions, Athinas St. concentrations are higher than AEDA, for both fractions with the exception of FPM Na^+ for which concentrations in the two sites are relatively close. The dominant compound in FPM is SO_4^{2-} , which in this fraction is found in slightly higher concentrations in AEDA. At the same time Athinas St. CPM SO_4^{2-}

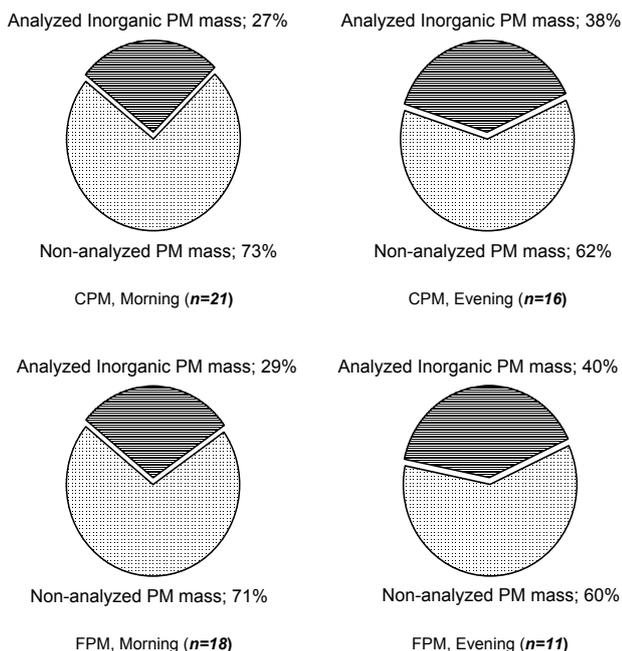


Fig. 2. Total analyzed inorganic versus total collected PM₁₀ mass concentration, in the FPM and CPM fractions, for morning and evening, in Athinas St. site, at 1.5 m above ground, in March 2004.

is more than the respective in AEDA. The most of NH₄⁺ is found in the FPM fraction with AEDA values being slightly higher than the ones of Athinas St. A tendency for slightly higher concentrations of the compound in the evening for both fractions is also observed. Lastly, Athinas St. Cl⁻ is in both fractions higher than the respective in AEDA with CPM values being more than double in the first site compared to the second.

The ratio of water soluble (ionic) concentration over the total elemental concentration has been calculated. Slightly higher than 70% of the CPM Ca appears to be water-soluble in both sites. In the FPM, this percentage for Athinas St is near 90% while in AEDA it appears lower, around 80%. The greatest percentage of S is also water-soluble in both sites and both fractions, with the CPM ratios ranging from 75% to 85% and the FPM ones from 79% to 94%. Similar findings have been reported for other locations in the eastern Mediterranean (Graham et al., 2004). In Athinas St., for both fractions, on average 50% of K⁺ appears to be water soluble, while in AEDA the respective percentages are 60% in the CPM and 30% in the FPM.

3.3 Seasonal variation; comparison between August 2003 and March 2004; comparison with other studies in Athens and in other cities

A direct comparison of Athinas St. campaign mean concentrations is shown in Table 5a and 5b. For most major elements and ions, the March 2004 concentrations in Athinas

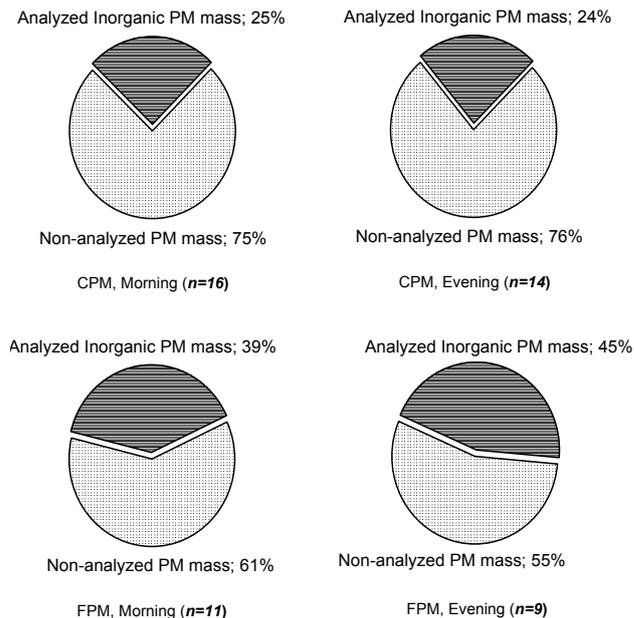


Fig. 3. Total analyzed inorganic versus total collected PM₁₀ mass concentration, in the FPM and CPM fractions, for morning and evening, in AEDA site, at 25 m above ground, in March 2004.

St. appear in both fractions significantly elevated compared to the respective ones of August 2003. For example, Ca concentrations are in both fractions more than double in March compared to August. Two exceptions to the above are observed. The first is Al for which only a small increase is observed in March, for both fractions. The second is S, the greatest percent of which is found as sulphate, which appears higher in the CPM in March but significantly lower in the FPM compared to August. CPM S, Si, Mn, Cr, Pb and Zn are also higher in March, while, as mentioned above, the reverse is true for Cu. An increase in the concentration of the latter has been recently reported compared to the late 80's (Manalis et al., 2005). Such an increase was seen in the August campaign, when in Athinas St FPM Cu mean concentration has more than doubled compared to the one reported by Scheff and Valiozis (1990), but not during the March campaign. During the March campaign, AEDA Cu concentrations were found to be only slightly higher to the ones reported by Scheff and Valiozis (1990). The respective March 2004 Athinas St. concentration was lower than the one obtained in the August 2003 campaign in the same site, lower than the one obtained in AEDA in the same campaign, and lower than the one reported by Scheff and Valiozis (1990). It can thus be derived, that Cu-enrichment sources during the August 2003 were less active or influencing the Athinas St site during March 2004, which is to be further researched. A similar seasonal pattern is observed for higher in August and overall high sulphur concentrations. Significant contribution to the sulphur-concentrations is believed to be due to the

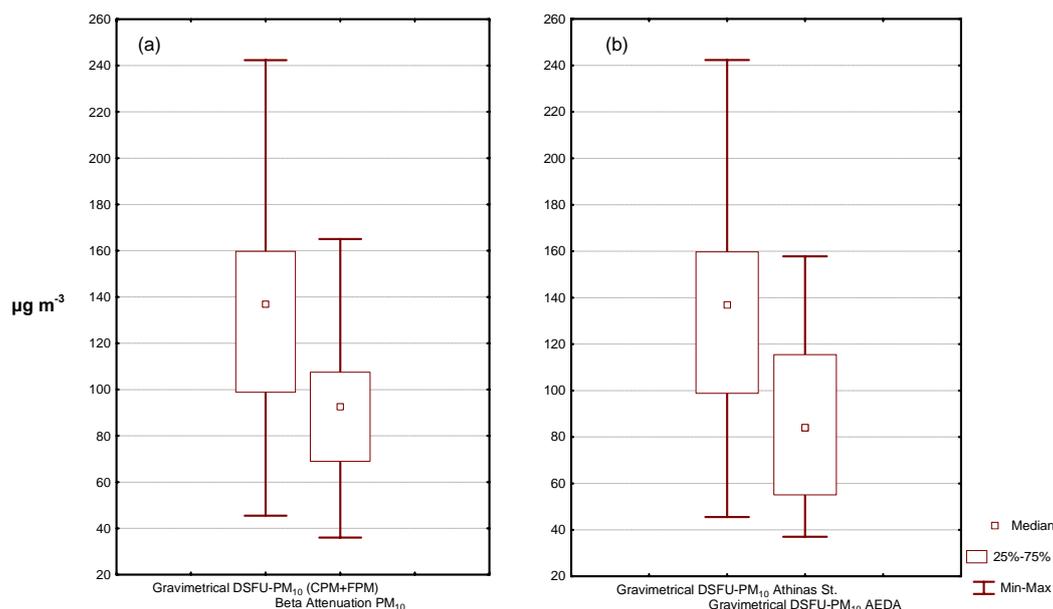


Fig. 4. (a) Comparative graph of the gravimetric DSFU-PM₁₀ (calculated as the sum of CPM+FPM) collected at a height of 1.5 m above ground and BA-PM₁₀ (obtained by Beta Attenuation) collected at 5 m above ground, in Athinas St., in March 2004; (b) Comparative graph of the gravimetric DSFU-PM₁₀ collected at a height of 1.5 m above ground in Athinas St., and the respective gravimetric DSFU-PM₁₀ at a height of approx. 25 m above ground in AEDA.

high sulphur-content of diesel for road-transport in Greece (Kalligeros et al., 2001; Commission, 2005), in addition to the major contribution by fossil-fuel combustion for domestic heating during the March 2004. In this study, as well as in other recent studies with similar findings (Manalis et al., 2005), PM₁₀ (CPM+FPM) Pb is found to be significantly lower than the E.U. imposed annual limit of 500 ng/m³, and lower by an order of magnitude or more, compared to measurements dating a decade back (Thomaidis et al., 2003). On the other hand, in March, CPM Vanadium remains on the same levels with the previous campaign. Similar is the case for the FPM values of the above compounds, as they also appear higher in March 2004, with the aforementioned exception of sulphur. In a similar manner, FPM Cu and V have also been found at higher concentrations during the August 2003 campaign.

In addition to the seasonal variation in the concentrations, in Tables 5a and 5b a comparison of values measured during the current study with the ones of previous studies in Athens and other cities is shown. The CPM Ca concentrations appear significantly higher than the values recently reported for Madrid, Barcelona and Milan which also have elevated calcium concentrations. For other metals of crustal origin such as Fe, Al and Si, as well as some of the toxic metals such as Cr, Pb, Zn and Mn, values are on the same levels or lower to the values for the abovementioned cities. Similar is the case for most ionic species in most fractions, with the exception of marine related Na⁺ and Cl⁻, which appears in higher concen-

trations than Madrid but lower than Barcelona. In general, for most species concentrations in the CPM fraction are generally significantly higher than the ones reported for other cities to the North of Europe, like Vienna, Helsinki and Budapest.

In the FPM, the calcium concentrations are generally close to the ones measured in Athens in the 80's. The August '03 S concentrations appear very close to the ones presented in an older study (Scheff and Valiozis, 1990), which entailed measurements in the late spring and early summer. In this fraction, most other metals of crustal origin appear in lower concentrations than the ones of the previous studies, and generally close to the ones for the aforementioned Mediterranean cities. FPM SO₄²⁻ appears slightly lower and NO₃⁻ significantly lower than in past studies in Athens (Scheff and Valiozis, 1990), and Thessaloniki, Greece (Tsitouridou and Samara, 1993). The FPM SO₄²⁻, on the other hand, is slightly higher than the values reported for Madrid, Barcelona and Ankara while the FPM NO₃⁻ appears significantly lower than the respective concentrations for these cities.

3.4 Analyzed inorganic versus total particulate mass

In Figs. 2 and 3 the analyzed inorganic mass against the total sampled particulate mass is presented separately for morning and evening, for both sites and both fractions. For the pertinent calculations the mean individual masses of all compounds have been summed up. For the compounds that have

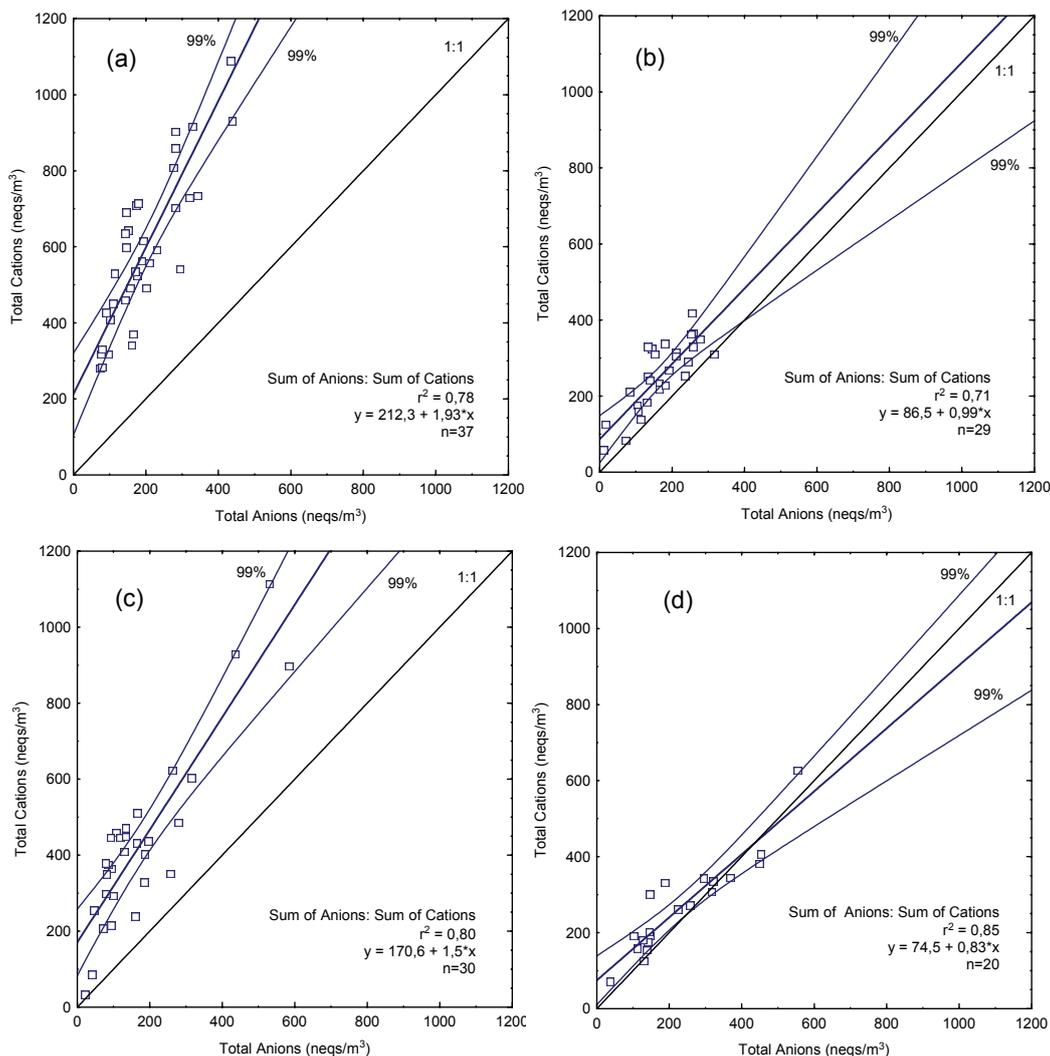


Fig. 5. Ionic balances for both fractions in the two sites. From top left to lower right: (a) Athinas St. CPM, and (b) FPM; (c) AEDA CPM, and (d) FPM.

been measured both in their elemental and ionic form (e.g. Ca and Ca²⁺), the elemental has been used, with the exception of Cl/Cl⁻ for which the ionic form has been used, due to the aforementioned issue of losses of Cl in the PIXE analysis. Moreover, sulphur has been determined in its elemental form and as SO₄²⁻. Due to its higher molecular weight, SO₄²⁻ constitutes higher mass concentrations than sulphur. As a result of this, the ionic SO₄²⁻ mass concentrations have been used in the pie-chart calculations instead of the elemental S. This slightly underestimates the sulphur “contribution” to the slice of known chemical composition in the pies, as it takes into account only the part of sulphur that is found as SO₄²⁻. However, as the ratio [S as SO₄²⁻]/[S] has been found to range from 75% to 95% and given the approximate character of this calculation, this underestimation is not considered very important.

Analyzed CPM mass ranges from 24% to 27% of the total CPM mass, with the exception of Athinas St. in the evening where the respective percent appears significantly higher (38%). While further examination of the contributing sources is needed, on a preliminary level the elevated values in the evening CPM in Athinas St. may be related to the fact that, while CPM mass is significantly lower than in the morning CPM, the calcium concentrations, both elemental and ionic, remain at very high levels. The analyzed FPM mass ranges from 39% to 45% of the total FPM mass, with the exception of Athinas St. in the morning where this percentage appears lower at approximately 29%. Ions such as CO₃⁻ which has been recently identified in great amounts in the Athens atmosphere (Sillanpää et al., 2005), OH⁻, lighter elements that PIXE can not successfully analyze, strongly bound water that remains at the low RH of the weighing

Table 7. The correlation coefficients (r^2) between the major inorganic anions and the respective cations for a) Athinas St.; b) for AEDA.

a)																	
Athinas St.	CPM									FPM							
	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻		Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Na ⁺	1								Na ⁺	1							
NH ₄ ⁺	.45	1							NH ₄ ⁺	.32	1						
K ⁺	.18	.01	1						K ⁺	.16	.44	1					
Mg ²⁺	.81	.36	.00	1					Mg ²⁺	.76	.24	.02	1				
Ca ²⁺	.19	.00	.06	.44	1				Ca ²⁺	.07	.12	.00	.35	1			
Cl ⁻	.92	.32	.56	.74	.22	1			Cl ⁻	.76	.31	.23	.56	.09	1		
SO ₄ ²⁻	.24	.20	.17	.14	.53	.04	1		SO ₄ ²⁻	.16	.72	.36	.05	.19	.20	1	
NO ₃ ⁻	.04	.00	.00	.13	.47	.05	.44	1	NO ₃ ⁻	.35	.19	.05	.54	.42	.08	.02	1

b)																	
AEDA	CPM									FPM							
	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻		Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Na ⁺	1								Na ⁺	1							
NH ₄ ⁺	.74	1							NH ₄ ⁺	.00	1						
K ⁺	.01	.00	1						K ⁺	.00	.00	1					
Mg ²⁺	.85	.51	.00	1					Mg ²⁺	.64	.02	.00	1				
Ca ²⁺	.01	.09	.00	.23	1				Ca ²⁺	.22	.00	.07	.38	1			
Cl ⁻	.94	.66	.10	.92	.01	1			Cl ⁻	.85	.02	.00	.92	.28	1		
SO ₄ ²⁻	.25	.44	.00	.32	.54	.20	1		SO ₄ ²⁻	.04	.80	.11	.14	.21	.12	1	
NO ₃ ⁻	.00	.00	.01	.03	.45	.00	.18	1	NO ₃ ⁻	.34	.08	.01	.77	.47	.40	.30	1

chamber (Harrison et al., 2003) other mineral compounds (including bound oxygen and nitrogen), as well as carbon, organics and polymers, are believed to constitute the biggest percentage of the unknown part of the PM. According to recent studies (D'Alessandro et al., 2003), these compounds usually constitute more than 50% of the urban aerosol mass.

3.5 Ionic balances and neutralization of atmospheric acidity

Strong correlations between the nano-equivalent sum of cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and the nano-equivalent sum of anions (Cl⁻, NO₃⁻, SO₄²⁻) have been found for both sites and both fractions (Fig. 5). However, as can be seen in the ionic balance plots, a clear deficit of anions is observed in the CPM while in the FPM the anion/cation ratio is close to 1. The anionic deficit in the CPM is probably due to the carbonates, hydroxides, as well as carboxylic acids which are probably bound with the excessive amounts of Ca²⁺ and are not analyzable by our method.

Atmospheric ammonia, in its NH₄⁺ form, is predominantly found in FPM whilst the CPM is NH₄⁺-poor. As has been previously stated, the ambient molar particulate NH₄⁺/SO₄²⁻ ratio has been found to be less than 1.5, which is indicative of an ammonium-poor aerosol system, where the existing NH₄⁺ is insufficient to completely neutralize the available sulphuric acid and the formation of NH₄NO₃ is not favoured (Seinfeld and Pandis, 1998 and references therein; Pathak and

Chan, 2005; Trebs et al., 2005). The correlations between NH₄⁺ and SO₄²⁻ (Tables 7a and b) indeed suggest that in the fine particles, NH₄⁺ is an important neutralizing agent of sulphuric acid forming salts like NH₄HSO₄, (NH₄)₃(SO₄)₂ and (NH₄)₂SO₄. In addition to this, and as expected, the respective correlations for NH₄⁺ and NO₃⁻ are low, in agreement with the prediction that formation of NH₄NO₃ is not expected to occur to a significant extent. The relatively little NO₃⁻ in the fine fraction, correlates well with Mg²⁺ and relatively well with Ca²⁺ which is indicative of formation of salts like Mg(NO₃)₂ and Ca(NO₃)₂.

Water-soluble ionic calcium is by far the most abundant specie in the CPM fraction. Hence, the good correlation between CPM Ca²⁺ and CPM NO₃⁻ and SO₄²⁻ (Tables 7a and b), suggests that calcium-containing aerosols, originating from the calcium-rich soils in the region as well as the quick-lime extensively used in painting facades in Greece, are probably the most important neutralizing species in the coarse fraction, on the surface of which acids like H₂SO₄ and HNO₃ react to form Ca(NO₃)₂ and CaSO₄. Lastly, strong correlations observed between Na⁺ and Cl⁻ and Mg²⁺ and Cl⁻, for both fractions, indicate the presence of NaCl and MgCl₂ salts, the biggest percentage of which is found in the coarse fraction. The above are in agreement with aforementioned studies in Greece (Tsitouridou and Samara, 1993; Danalatos and Glavas, 1995; Eleftheriadis et al., 1998), in other locations with similar crustal composition, in the East-

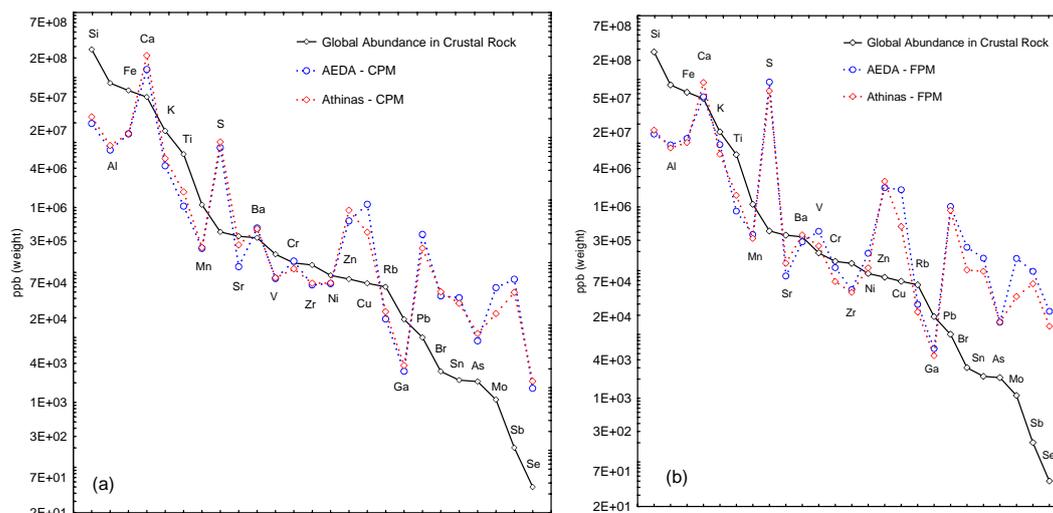


Fig. 6. Elemental chemical composition in the two sites (Athinas St. and AEDA) for (a) CPM and (b) FPM, plotted together with the average global abundance of elements in crustal rock as a reference.

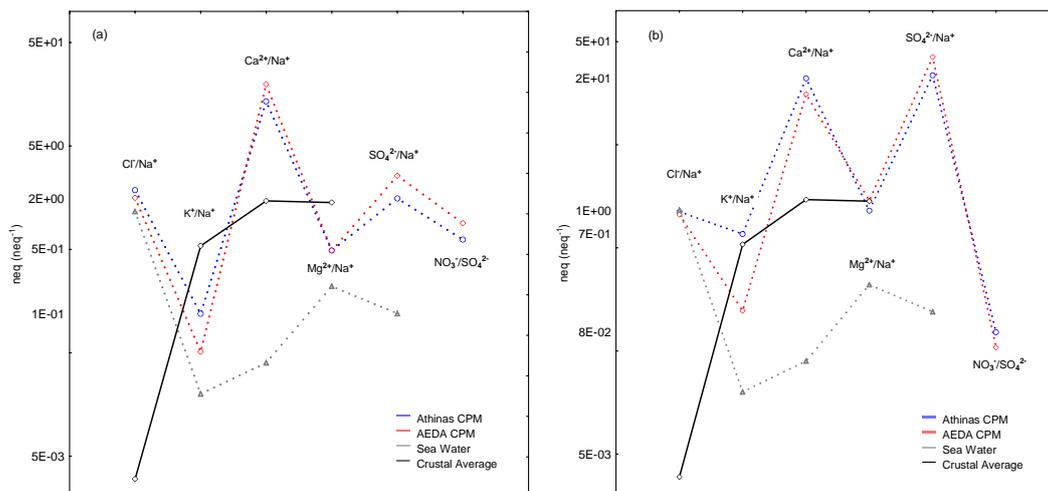


Fig. 7. Ionic concentration ratios in the two sites (Athinas St. and AEDA) for (a) CPM and (b) FPM, plotted together with the sea-water and crustal global averages.

ern Mediterranean (Graham et al., 2004; Kouyoumdjian and Saliba, 2006), as well as in other parts of the world (Davis and Jixian, 2000; Pathak et al., 2004; Xie et al., 2005).

3.6 An attempt to establish the fingerprint of inorganic aerosol pollution

In an attempt to graphically establish the fingerprint of the elemental composition of PM_{10} aerosol in Athens, we compare our findings with globally averaged crustal composition (Fyfe, 1974; Mason and Moore, 1982; www.webelements.com), in Figs. 6a and b and in Figs. 7a and b. Although quantitative comparisons are not possible since there exist no data on the pristine Athenian PM_{10} composition, this qualita-

tive comparison indicates characteristic elemental and ionic peaks that are attributed to the geochemical characteristics of the area, as well as the nature of human activity. For example, one could note Ca enrichment and Ga, Sr and Zr deficit. It could also be argued that S, Zn, Cu, Pb, Sn, Mo, As and Sb peaks can be attributed to fossil fuel burning and to traffic related emissions (tyres, catalysts and brakes). The extensive construction activity in the centre of the city at the time has probably contributed to a significant extend, to the aforementioned Ca enrichment, especially nearer to the ground and the construction works in Athinas St. In addition to this, it is shown that with the exception of Zn, the characteristic automotive traffic/exhaust-emitted elemental peaks are slightly higher for AEDA, which lies nearby an important cross-road

with high diesel-burning taxi circulation and a nearby diesel-burning city-bus station, indicating slightly stronger influence of traffic/vehicle-exhaust pollution for this site. From the respective ionic ratios it can be derived that a big part of Cl^- is found as NaCl originating from sea-spray. In the CPM, an influence by some additional non-marine source of Cl^- is probably also present. The $\text{Mg}^{2+}/\text{Na}^+$ ratio appears very close to the crustal average for the FPM fraction, which might be indicative of dust contributions in this fraction. The same ratio appears close to the sea-water average for the CPM fraction which is in accordance to the aforementioned finding that a big part of CPM Mg^{2+} is found as MgCl_2 originating from sea spray. The $\text{SO}_4^{2-}/\text{Na}^+$ ratio for both CPM and FPM appears significantly higher than the one of the sea-water which, given the fact that the earth's crust is a negligible source of sulfates (Yaqub et al., 1991), suggests the existence of anthropogenic sources contributing to SO_4^{2-} concentrations. Lastly, the calcium enrichment is again obvious as the ratio $\text{Ca}^{2+}/\text{Na}^+$ is much higher than the one of the crustal average.

4 Conclusions

Aerosol sampling took place, on a 12-h time-resolution basis, in the centre of Athens, Greece, during two 20-day periods, in August 2003 and March 2004. The August 2003 campaign mean PM_{10} mass concentration, obtained by Beta Attenuation at 5 m above ground in Athinas Street, was $56 \mu\text{g m}^{-3}$ while the corresponding value for March 2004 was $92 \mu\text{g m}^{-3}$. In both campaigns the E.U. imposed daily limit of $50 \mu\text{g m}^{-3}$ was exceeded on several occasions. During the March campaign, in Athinas Street, additionally obtained DSFU- PM_{10} ($\text{PM}_{10-2.5} + \text{PM}_{2.5}$) gravimetric mass concentrations (mean: $121 \mu\text{g m}^{-3}$) in the "breathing zone", at 1.5 m above ground were significantly higher compared to the respective mean PM_{10} mass concentrations obtained by the same method at 25 m above ground, in a second site (AEDA; mean: $86 \mu\text{g m}^{-3}$) also in the centre of the city. For the fine particulate matter the Athinas St. concentrations were on average 22% higher than the respective AEDA ones, while for the coarse fraction, this discrepancy was even higher, reaching 30%. The significantly higher particulate mass concentrations close to the ground were mainly due to crust-related calcium and aluminosilicate compounds and were related to a significant extend to construction as well as dust/soil re-suspension by traffic and overall human activity. PM_{10} mass concentration measurements near ground level, in the "breathing zone", are presented for the first time for the centre of Athens and, it is shown that, for a realistic estimation of the exposure of citizens to particulate matter in the centre of the city, knowledge of PM_{10} levels within the "breathing zone" is necessary.

The simultaneous sampling with a pair of DSFUs allowed for the determination of ionic and elemental concentrations.

Calcium has been found to be the predominant element in the coarse fraction, appearing in very high concentrations compared to the ones reported for other cities. Its extremely elevated near-ground concentrations have been probably connected with the extensive construction works that were taking place in the centre of the city for the Olympic Games of 2004, as well as the calcitic rocks that predominate the geology of the region. Crust-related aluminosilicates and iron have also been found to be major components of the coarse and fine fraction and sulfur has been predominant in the fine fraction. Toxic metals have been found to be well below the air quality limits and reduced compared to older studies, with the exception of Cu and V for which some increase has been recently observed. Pb, in particular, appears mostly in the fine fraction and in very low concentrations compared to studies dating more than a decade ago.

In the coarse fraction, major ions have been found to be Ca^{2+} and NO_3^- , while SO_4^{2-} , Ca^{2+} and NH_4^+ were the major ionic components of the fine fraction. An important deficiency of anions has been found in the coarse fraction and is assumed to be due to the existence of great amounts of CO_3^- , as has been verified by another recent study, and OH^- ; both species are not analyzed by our method. The low molar ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ has indicated an ammonium-poor ambient air, where atmospheric ammonia is consumed with sulfate without sufficing its neutralization to full extend and the formation of NH_4NO_3 is therefore not favoured. The high correlations between NH_4^+ and SO_4^{2-} indeed suggested that in the fine particles, NH_4^+ is an important neutralizing agent of sulphuric acid forming salts like NH_4HSO_4 , $(\text{NH}_4)_3(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$. In addition to this, and as expected, the respective correlations for NH_4^+ and NO_3^- have been found low, in agreement with the prediction that formation of NH_4NO_3 does not occur to a significant extend. The relatively little fine-fraction NO_3^- correlates considerably well with Mg^{2+} and Ca^{2+} which indicates the formation of salts like $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$. Water-soluble ionic calcium is by far the most abundant specie in the coarse fraction. Hence, the good correlation between Ca^{2+} with NO_3^- and SO_4^{2-} suggests that calcium-containing aerosols, originating from the calcium-rich soils in the region as well as the quick-lime extensively used in painting facades in Greece, are probably the most important neutralizing species in the coarse fraction, on the surface of which acids like H_2SO_4 and HNO_3 react to form $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 . Strong correlations have been observed between Na^+ and Mg^{2+} , Na^+ and Cl^- and Mg^{2+} and Cl^- , which indicates the existence of marine-related NaCl and MgCl_2 .

Morning and evening means have been calculated and presented separately, as this may demonstrate trends in the "within-a-day" variation of elements and ionic species concentrations. For many days, morning concentrations were slightly higher than the evening concentrations, when most traffic and construction activity in the city was reduced.

However, on some occasions and for some species like Na, Cl^- and NO_3^- in the coarse fraction and SO_4^{2-} and NH_4^+ in the fine fraction, as well as some elements, evening values were slightly higher over morning ones. This might be indicative of the trapping of near-surface aerosols under a shallow atmospheric boundary layer during the night. Total analyzed inorganic mass (elemental+ionic) has been found to range between 25–33% of the total coarse particle mass and 35–42% of the total fine particle mass. The unknown part is believed to include major ions (CO_3^- , OH^-), lighter elements and other mineral compounds (with bound oxygen and nitrogen), as well as strongly bound water, carbon, organics and polymers, which usually constitute more than 50% of the urban aerosol mass.

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References

- Artunano, B., Salvador, P., Alonso, D. G., Querol, X., and Alastuey, A.: Anthropogenic and natural influence on the PM_{10} and $\text{PM}_{2.5}$ aerosol in Madrid (Spain). Analysis of high concentration episodes, *Environ. Pollut.*, 125, 453–465, 2003.
- Chaloulakou, A., Kassomenos, P., Spyrellis, N., Demokritou, P., and Koutrakis, P.: Measurements of PM_{10} and $\text{PM}_{2.5}$ particle concentrations in Athens, Greece, *Atmos. Environ.*, 37, 649–660, 2003.
- Chaloulakou, A., Kassomenos, P., Grivas, G., and Spyrellis, N.: Particulate matter and black smoke concentration levels in central Athens, Greece, *Environ. Int.*, 31, 651–659, 2005.
- Chan, C. Y., Xu, X. D., Li, Y. S., Wong, K. H., Ding, G. A., Chan, L. Y., and Cheng, X. H.: Characteristics of vertical profiles and sources of $\text{PM}_{2.5}$, PM_{10} and carbonaceous species in Beijing, *Atmos. Environ.*, 39, 5113–5124, 2005.
- Charron, A., Harrison, R. M., Moorcroft, S., Booker, J.: Quantitative interpretation of divergence between PM_{10} and $\text{PM}_{2.5}$ mass measurement by TEOM and gravimetric (Partisol) instruments, *Atmos. Environ.*, 38(3), 415–423, 2004.
- Commission, E.: 1999/30/EC. Relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, Official Journal of the European Communities, L 163/41–60, 1999.
- Commission, E.: Quality of petrol and diesel fuel used for road transport in the European Union (Reporting year 2003), Report from the Commission, COM(2005), Brussels, 2.3.2005, COM(2005) 69 final, 2005.
- D' Alessandro, A., Lucarelli, F., Mando, P. A., Marazzan, G., Nava, S., Prati, P., Valli, G., Vecchi, R., and Zucchiatti, A.: Hourly elemental composition and sources identification of fine and coarse particulate matter in four Italian towns, *Aerosol Sci.*, 34, 243–259, 2003.
- Danalatos, D. and Glavas, S.: Atmospheric nitric acid concentrations in a Mediterranean site, Patras, Greece, *Atmos. Environ.*, 29, 1849–1852, 1995.
- Davis, B. L. and Jixian, G.: Airborne particulate study in five cities of China, *Atmos. Environ.*, 34, 2703–2711, 2000.
- Dockery, D. W. and Pope, C. A.: Acute respiratory effects of particulate air pollution, *Ann. Rev. Publ. Health*, 15, 107–132, 1994.
- Eleftheriadis, K., Balis, D., Ziomas, I. C., Colbeck, I., and Manalis, N.: Atmospheric aerosol and gaseous species in Athens, Greece, *Atmos. Environ.*, 32, 2183–2191, 1998.
- Fyfe, W. S.: *Geochemistry*, Oxford University Press, 1974.
- Graham, B., Falkovich, A. H., Rudich, Y., Maenhaut, W., Guyon, P., and Andreae, M.: Local and regional contributions to the atmospheric aerosol over Tel Aviv, Israel: a case study using elemental, ionic and organic tracers, *Atmos. Environ.*, 38, 1593–1604, 2004.
- Grivas, G., Chaloulakou, A., Samara, C., and Spyrellis, N.: Spatial and temporal variation of PM_{10} mass concentrations within the Greater Area of Athens, Greece, *Water, Air Soil Pollut.*, 158, 357–371, 2004.
- Harrison, R. M., Smith, D. J. T., and Luhana, L.: Source Apportionment of Atmospheric Polycyclic Aromatic Hydrocarbons Collected from an urban location in Birmingham, UK, *Environ. Sci. Technol.*, 30, 825–832, 1996.
- Harrison, R. M., Jones, A. M., Lawrence, R., G.: A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites, *Atmos. Environ.*, 37, 4927–4933, 2003.
- Katsouyanni, K., Touloumi, G., Spix, C., Schwartz, J., Balducci, F., Medina, S., Rossi, G., Wojtyniak, B., Sunyer, J., Bacharova, L., Schouten, P., Ponka, A., and Andersen, H. R.: Short term effects on ambient air sulphur dioxide and particulate matter on mortality in 12 European cities: results from time series data from the APHEA project, *British Medical Journal*, 314(7095), 1658–1663, 1997.
- Katsouyanni, K., Touloumi, G., Samoli, E., Gryparis, A., Le Tertre, A., Monopoli, Y. Y., and Tossi, G.: Confounding and effect modification in the short-term effects of ambient particles on total mortality: results from 29 European cities within the APHEA2 project, *Epidemiology*, 12, 521–531, 2001.
- Koliadima, A., Athanasopoulou, A., and Karaiskakis, G.: Particulate matter in the air of the cities of Athens and Patras (Greece): particle size distributions and elemental concentrations, *Aerosol Sci. Technol.*, 28, 292–300, 1998.
- Kouyoumdjian, H. and Saliba, N. A.: Mass concentration and ion composition of coarse and fine particles in an urban area in Beirut: effect of calcium carbonate on the absorption of nitric and sulfuric acids and the depletion of chloride, *Atmos. Chem. Phys.*, 6, 1865–1877, 2006, <http://www.atmos-chem-phys.net/6/1865/2006/>.
- Luhana, L., H. Mao, and Sokhi, R. S.: Laboratory and field evaluation of UH Dichotomous Stacked Filter Units (DSFU), *Univer-*

- sity of Hertfordshire, SAPPHERE Report (EVK4-2001-00192), 2001.
- Manalis, N., Grivas, G., Protonotarios, V., Moutsatsou, A., Samara, C., and Chaloulakou, A.: Toxic metal content of particulate matter (PM₁₀), within the Greater Area of Athens, *Chemosphere*, 60, 557–566, 2005.
- Marazzan, G. M., Vaccaro, S., Valli, G., and Vecchi, R.: Characterisation of PM₁₀ and PM_{2.5} particulate matter in the ambient air of Milan (Italy), *Atmos. Environ.*, 35, 4639–4650, 2001.
- Miller, J. C. and Miller, J. N.: *Statistics for Analytical Chemistry*, Ellis Horwood PTR Prentice Hall, England, 1993.
- Pakkanen, T. A., Loukkola, K., Korhonen, C. H., Aurela, M., Mäkelä, T., Hillamo, R. E., Aarnio, P., Koskentalo, T., Kousa, A., and Maenhaut, W.: Sources and chemical composition of atmospheric fine and coarse particles in the Helsinki area, *Atmos. Environ.*, 35, 5381–5391, 2001.
- Pathak, R. K., Louie, P. K. K., and Chan, C. K.: Characteristics of aerosol acidity in Hong Kong, *Atmos. Environ.*, 38, 2965–2974, 2004.
- Pathak, R. K. and Chan, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers, *Atmos. Environ.*, 39, 1597–1607, 2005.
- Peng, R. D., Dominici, F., Pastor-Barriuso, R., Zeger, S. L., and Samet, J. M.: Seasonal analyses of air pollution and mortality in 100 US, *Am. J. Epidemiol.*, 161, 585–594, 2005.
- Pope III, C. A., Burnett, R. T., Thun, M. J., Cale, E. E., Krewski, D., Ito, K., and Thurston, G. D.: Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution, *J. Am. Medical Assoc.*, 287, 1132–1141, 2002.
- Puxbaum, H., Gomiscek, B., Kalina, M., Bauer, H., Salam, A., Stopper, S., Preining, O., and Hauck, H.: A dual site study of PM_{2.5} and PM₁₀ aerosol chemistry in the larger region of Vienna, Austria, *Atmos. Environ.*, 38, 3949–3958, 2004.
- Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C. R., Cots, N., Massague, G., and Puig, O.: PM₁₀ and PM_{2.5} source apportionment in the Barcelona Metropolitan area, Catalonia, Spain, *Atmos. Environ.*, 35, 6407–6419, 2001.
- Salma, I., Maenhaut, W., Zemplén-Papp, E., and Zaray, G.: Comprehensive characterization of atmospheric aerosols in Budapest, Hungary: physicochemical properties of inorganic species, *Atmos. Environ.*, 35, 4367–4378, 2001.
- Scheff, P. A. and Valiozis, C.: Characterization and source identification of respirable particulate matter in Athens, *Atmos. Environ.*, 24A, 203–211, 1990.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From air pollution to climate change*, John Wiley & Sons, 1998.
- Shaka, H. and Saliba, N. A.: Concentration measurements and chemical composition of PM_{10–2.5} and PM_{2.5} at a coastal site in Beirut, Lebanon, *Atmos. Environ.*, 38, 523–531, 2004.
- Sillanpää, M., Hillamo, R., Saarikoski, S., Frey, A., Pennanen, A., Makkonen, U., Spolnik, Z., Van Grieken, R., Branis, M., Brunekreef, B., Chalbot, M., Kuhlbusch, T., Sunyer, J., Kerminen, V., Kulmalak, M., Salonen, R. O.: Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe, *Atmos. Chem. Phys.*, 5, 2869–2879, 2005, <http://www.atmos-chem-phys.net/5/2869/2005/>.
- Sillanpää, M., Frey, A., Hillamo, R., Pennanen, A. S., and Salonen, R. O.: Chemical composition and mass closure of particulate matter at six urban sites in Europe, *Atmos. Environ.*, 40, S212–S223, 2006.
- Siskos, P., Bakeas, E., Lioli, I., Smirnioudi, V. N., and Koutrakis, P.: Chemical characterization of PM_{2.5} aerosols in Athens – Greece, *Environ. Technol.*, 22, 687–695, 2001.
- Thomaidis, N. S., Bakeas, E., and Siskos, P.: Characterization of lead, cadmium, arsenic and nickel in PM_{2.5} particles in the Athens atmosphere, Greece, *Chemosphere*, 52, 959–966, 2003.
- Symeonidis, P.: Study of atmospheric pollution and its sources by use of GIS, PhD Thesis (in Greek), Aristotle University of Thessaloniki, 2002.
- Touloumi, G., Pocock, S. J., Katsouyanni, K., and Trichopoulos, D.: Short term effects of air pollution on daily mortality in Athens. A time series analysis, *Int. J. Epidemiol.*, 23, 957–967, 1994.
- Trebs, I., Metzger, S., Meixner, F. X., Helas, G., Hoffer, A., Rudich, Y., Falkovich, A. H., Moura, M. A. L., Da Silva Jr., R. S., Artaxo, P., Slanina, J., and Andreae, M.: The NH₄⁺-NO₃⁻-Cl⁻-SO₄⁻²-H₂O aerosol system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids?, *J. Geophys. Res.*, 110, 1–18, 2005.
- Tsitouridou, R. and Samara, C.: First results of acidic and alkaline constituents determination in air particulates of Thessaloniki, Greece, *Atmos. Environ.*, 27B, 313–319, 1993.
- Valavanidis, A., Fiotakis, K., Vlahogianni, T., Bakeas, E. B., Triantafyllaki, S., Paraskevopoulou, V., and Dassenakis, M.: Characterization of atmospheric particulates, particle-bound transition metals and polycyclic aromatic hydrocarbons of urban air in the centre of Athens (Greece), *Chemosphere*, 2006.
- WHO: *Air Quality Guidelines*, 2nd ed., WHO Regional Office for Europe, Copenhagen, Denmark, 2000.
- Xie, R. K., Seip, H. M., Leinum, J. R., Winje, T., and Xiao, J. S.: Chemical characterization of individual particles (PM₁₀) from ambient air in Guiyang City, China, *Sci. Total Environ.*, 343, 261–272, 2005.
- Yaaqub, R. R., Davis, T. D., Jickells, T. D., and Miller, J. M.: Trace elements in daily collected aerosols at a site in southeast England, *Atmos. Environ.*, 25A, 985–996, 1991.
- Yatin, M., Tuncel, S., Aras, N. K., Olmez, I., Aygun, S., and Tuncel, G.: Atmospheric trace elements in Ankara, Turkey: 1. factors affecting chemical composition of fine particles, *Atmos. Environ.*, 34, 1305–1318, 2000.