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

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Abstract

Mass concentration levels and the inorganic chemical composition of PM_{10} (two fractions; $PM_{10-2.5}$ and $PM_{2.5}$) were determined during August 2003 and March 2004, in the centre of Athens, Greece. August 2003 monthly mean PM_{10} mass concentration, at 5 m above ground, was 56 $\mu g/m^3$ and the EU imposed daily limit of 50 $\mu g/m^3$ was exceeded on 16 occasions. The corresponding monthly mean for March 2004 was 92 $\mu g/m^3$ and the aforementioned daily limit was exceeded on 23 occasions. The PM_{10} ($PM_{10-2.5}$+$PM_{2.5}$) mass concentrations at 1.5 m above ground were found to be approximately 20% higher compared to the respective PM_{10} measured at 5 m. Consequently, for a realistic estimation of the exposure of citizens to particulate matter, PM_{10} sampling at a height of 1.5–3 m above ground, in the "breathing zone" 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 found to be the other major components of the same fraction. The above elements constitute the most important components of the fine fraction, together with the predominant sulphur. Toxic metals were found to be below the air quality limits and in lower concentrations compared to older studies, with the exception of Cu and V for which some increase was observed. Pb, in particular, appeared mostly in the fine fraction and in very low concentrations compared to studies dating more than a decade back. The major ions of the coarse fraction have been found to be Ca^{2+}, NO_3^- and Cl^-, while SO_4^{-2}, Ca^{2+} and NH_4^+ were the major ionic components of the fine fraction. The low molar ratio of NH_4^+/SO_4^{-2} indicated an ammonium-poor ambient air, where atmospheric ammonia is not sufficient to neutralize all acidity and the formation of NH_4NO_3 does not occur to a significant extend. Calcium predominated the coarse fraction and its good correlations with NO_3^- and SO_4^{-2} indicated its role as an important neutralizing agent of atmospheric acidity in this particle size range. In the fine fraction, both Ca^{2+} and NH_4^+ participate in the neutralizing processes with NH_4^+ being the major neutralizing agent of SO_4^{-2}. Chloride depletion from NaCl or $MgCl_2$

was not found to occur to a significant extend. 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 that may take place 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 the 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 quality in the EU 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 km^2 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 the major source of 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 taxies are diesel-powered. Other important causes of atmospheric pollution are considered to be industrial activity and winter-heating. Major heavy industries are located West and North West of the city, outside the valley.

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 some toxic metals in the PM (Scheff and Valiozis, 1990; Koliadima et al., 1998; Thomaidis et al., 2003; Manalis et al., 2005) and of some ionic species in $PM_{2.5}$ (Scheff and Valiozis, 1990; Siskos et al., 2001) 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 it is determining the mass concentration of PM_{10} as well as the concentrations of a series of gaseous pollutants, on a daily basis.

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 from the 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 Athens. Thirdly, the comparison of total particulate, metals and ions concentrations with previous studies for the city and 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. Lastly, the determination of the mechanisms through which the neutralization of atmospheric acidity takes place.

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 (≈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 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 BAPA), also equipped with a reflectometer for the determination of Black Carbon. In March 2004, a Differential Mobility Particle Sizer (DMPS, Neri Institute, Denmark) for the determination of ultra-fine particles concentrations and an Optical Particle Counter (OPC, LASAIR II 525, Particle Measuring Systems, USA) were added to the sampling equipment. 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 and a DMPS. The DSFU samplers' inlets in Athinas St. were set at a height of 1.5 m from the ground level and the OPC and DMPS inlets were set very near them. The Beta Attenuation Particle Analyzer inlet was set at a height of approximately 5 m from the ground level. In AEDA, the DSFU and DMPS sampling took place at a height of approximately 25 m above the street level.

Particles collected with the DSFUs were divided into two fractions; coarse, with an aerodynamic diameter between 2.5 μm and 10 μm (hereafter referred to as CPM), and fine, with an aerodynamic diameter smaller than 2.5 μm (hereafter referred to as FPM). Particles with an aerodynamic diameter greater than 10 μm, were trapped on a lightly greased pre-impactor surface, in the front part of the stack. Polycarbonate Membrane filters (Whatman) with a pore-diameter of 12 μm and 0.4 μm were used for the collection of CPM and FPM respectively. In order to avoid bounce-off phenomena, 12-μm 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 μg (Scaltec SBC22), before and after sampling, thus allowing the calculation of gravimetrical CPM and FPM concentrations. Prior to being weighed, filters were kept under stable environmental conditions (RH: ~20%, T=18°C) in vacuum desiccators for 24 h. 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, to record the within-a-day variability of the contributing sources emissions throughout the campaign. 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 (12 h) without air being sampled.

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 $y=0.988{\cdot}x-0.018$ ($R^2=0.97$). The relationship between the respective sampled masses of particulate matter, with the two samplers was found to be described by the equation: $y=0.965{\cdot}x+1.03$ ($R^2=0.96$).

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.

Meteorological data including wind speed and direction, relative humidity, temperature and solar radiation, as well as major urban gas-pollutants concentrations (O_3, $NO+NO_2$, 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) in Denmark (NERI) for identification and quantification of 24 metal species with an atomic number >12. 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, Democritus University of Thrace). In August 2003 ionic concentrations were not measured.

2.2.1 Elemental analysis

Elemental analysis was carried out by PIXE in accordance to the ISO 17025 standard (DANAK, Danish Accreditation no. 411). 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 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, H_2SO_4, HSO_4^- and NH_4^+).

2.2.2 Ions analysis

A Dionex Chromatograph (DX-500) 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 ($18.2 \cdot \mathrm{M}\Omega \cdot \mathrm{cm}^{-1}$) 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) different to the one of the calibration standards (Dionex). 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 $\leq$3%.

3 Results and discussion

Table 2 presents arithmetic means and standard deviations of the concentrations of elements measured in August 2003. Morning and evening values are presented separately as this may demonstrate, on a preliminary level, trends in the “within-a-day” variation of concentrations. Ionic species and gravimetrically determined PM were not measured during this campaign due to a technical problem. 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 b 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 traffic in downtown Athens was reduced due to the summer vacations. In relation to that, an increase in the measured BAPA-PM_{10} concentrations was observed towards the end of the month, after the end of the DSFU sampling, when the greatest percent of the population returned from vacations. On the other hand, during the campaign and throughout the year until the summer of 2004, construction work was taking place in the centre of the city. The meteorological conditions 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: 38.1°C) and low wind speed (daily mean: 2.7 km/h; min: 0.4 km/h).

Measured $BAPM_{10}$ concentrations shown in Table 2 (min: 38 $\mu g/m^3$; max: 90 $\mu g/m^3$) 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 PM_{10} values on the site exceeded on 16 occasions the E.U. imposed 24-h limit of 50 $\mu g/m^3$, which is not to be exceeded more than 35 times a year (limit to be met by January 2005). The predominant 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 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, predominant. 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). S and Zn 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, as well as the fact that the concentration of the latter has demonstrated an increase compared to older studies (Scheff and Valiozis, 1990). Both the above elements are traffic related. Pb is mainly found in FPM and its concentration in Athens has been greatly reduced in the last 20 years. Automotive fuel in Greece does no longer contain lead compounds. In this study, as well as in other recent studies with similar findings (Manalis et al., 2005), PM_{10} (CPM+FPM)

Pb is found to be significantly lower than the EU imposed annual limit of 500 ng/m^3, and lower by an order of magnitude or more, compared to measurements dating a decade back (Thomaidis et al., 2003). Arsenic concentration is almost double and Nickel slightly higher in the FPM, compared to the CPM, and their concentrations on the site were also found to be significantly lower than the EU proposed mean annual limits of 6 ng/m^3 and 20 ng/m^3 respectively. Mn 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. V 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 μg/m^3 (WHO, 2000). Ba and Cr are found at significantly higher levels in the CPM with the concentrations of the later to have increased significantly in the last decade.

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 mass concentrations, are shown in Tables 3 and 4, for Athinas St. and AEDA respectively. For Athinas St. BAPM$_{10}$ mass concentrations are also shown in Table 3. In this site at 1.5 m from the ground, the PM$_{10}$ (CPM+FPM) daily mean concentration was 121 μg/m^3 (daily max: 242 μg/m^3), with individual PM$_{10-2.5}$ and PM$_{2.5}$ concentrations being 80 and 40.5 μg/m^3 respectively. In the second site (AEDA), at 25 m from the ground, the respective daily mean concentration for the PM$_{10}$ was 86 μg/m^3 (daily max: 158 μg/m^3), with individual PM$_{10-2.5}$ and PM$_{2.5}$ concentrations being 55 and 32 μg/m^3 respectively. In Athinas St., at 5 m from the ground, the BAPM$_{10}$ daily mean concentration was 92 μg/m^3 (daily max: 133 μg/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%), 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).

The PM_{10} concentrations measured by BAPA ($BAPM_{10}$) at 5 m from the ground level, in Athinas St., are significantly lower than the gravimetrical DSFU-PM_{10} (calculated as the sum: CPM+FPM) concentrations measured at a height of 1.5 m from the ground level, 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 $BAPM_{10}$ and DSFU-PM_{10} shows that the morning mass concentrations are generally significantly higher than the evening ones. It is also shown that morning CPM mass concentrations are approximately 30% higher than the evening CPM concentrations, while the respective difference for the FPM fraction is approximately 22%. Roughly 35% of the particulate mass is found in FPM and 65% in CPM in Athinas St.

The DSFU-PM_{10} daily mean mass concentration in Athinas St. is significantly higher than the gravimetrical DSFU-PM_{10} daily mean measured in AEDA, at a height of approximately 25 m from the ground level. A comparison between the DSFU-PM_{10} in Athinas and the DSFU-PM_{10} in AEDA is shown in Table 6b and Fig. 4b. This comparison of the concentrations shows that the PM mass concentrations obtained at 25 m from the ground are significantly lower than the ones at 1.5 m from the ground. More specifically, the morning Athinas St. CPM mass concentrations are approximately 43% higher than the respective in AEDA. The difference for the morning FPM concentrations is approximately 28%. Respective evening differences are 26% and 17% for the CPM and FPM respectively. There is a significant increase in the CPM mass concentrations during the morning (07:00–19:00) in Athinas St., which could be attributed to the extensive contribution by construction, traffic and overall human activity. One may argue that this "morning-contribution", which, as discussed below, consists mainly of crust-related 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 two elevations, b) the respective discrepancies of the morning and evening

FPM concentrations, c) the discrepancy between the PM_{10} 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 b), shows that PM_{10} concentrations significantly increase the closer one gets to the ground, near the "breathing zone". This is in agreement with the findings of another study for Beijing (Chan et al., 2005).

AEDA DSFU-PM_{10} mass concentrations are very close to the respective PM_{10} values of other studies for the same period (Valavanidis et al., 2006), which also entailed measurements at a height of 25 m from the ground level, in a nearby to AEDA location. Daily CPM and FPM 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-PM_{10} are reasonably close to the results of other recent studies (Chaloulakou et al., 2005; Manalis et al., 2005), for the years 2001–2003 where measurements were again taken at building-storey levels, at approximately 7 m from the ground, or building-roof levels, approximately 25 m from the ground. The above support that PM_{10} concentrations appear 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 (5, 7 and 25 m) appear to be significantly higher for the heavier CPM and for daytime hours when 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 being predominant in the CPM and aluminosilicates being predominant. 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), 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 in the text. 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 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 difference between the two sites, though, is that in Athinas St., 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. As will be further discussed below, the ambient molar particulate ratio of NH_4^+/SO_4^{-2} has been found to be less than 1.5 ($NH_4^+/SO_4^{-2} \leq 1.35$), which 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). In addition to that, the reactions of $CaCO_3$, which in the Athenian atmosphere is existent in great excess, with HNO_3 and H_2SO_4 predominate over the reactions of NaCl with HNO_3 and H_2SO_4, as the first are significantly more rapid than the latter. As a result of this, chloride depletion, via formation of HCl and evaporation to the gaseous phase, has not occurred but to a very limited extend. The mean ratios of Cl^-/Na^+, which has been found to be $1.0 \leq Cl^-/Na^+ \leq 1.1$ (neq/m^3) for the FPM and $1.6 \leq Cl^-/Na^+ \leq 2.2$ (neq/m^3) for the CPM for the two sites, support the above conclusion.

Like with its elemental form, Ca^{2+} is predominantly found in the CPM, in which it is by far the most abundant compound. A relatively big percentage of it is probably found as $CaCO_3$ due to the calcitic nature of the crustal rock in Greece. Similar with Ca^{2+} bimodal distribution is observed for NO_3^- 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} is more than the respective in AEDA. The most of NH_4^+ 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 somewhere 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. mean concentrations in the two campaigns is shown in Tables 5a and b. For most major elements and ions, the March 2004 concentrations in Athinas St. appear in both fractions significantly elevated compared to the respective ones of August 2003. Ca concentrations in both fractions, in March are more than double 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, 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. 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. Sulphur, which is highly connected to fossil fuel burning, is significantly higher in August 2003 in Athinas. 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 b 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 presented 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 Na^+, which appears in higher concentrations than Madrid but lower than Barcelona. 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 SO_4^{-2} appears slightly lower and NO_3^- significantly lower than in past studies in Athens (Scheff and Valiozis, 1990), and Thessaloniki, Greece (Tsitouridou and Samara, 1993). The FPM SO_4^{-2}, on the other hand, is slightly higher than the values reported for Madrid, Barcelona and Ankara while the FPM NO_3^- 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 above calculations the mean individual masses of all compounds have been summed up. For the compounds that have been measured both in their elemental and ionic form though (e.g. Ca and Ca^{2+}), only the elemental has been used, with the exception of Cl/Cl^- for which the ionic 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 SO_4^{-2}. Due to its higher molecular weight, SO_4^{-2} constitutes higher mass concentrations than sulphur. As a result of this, the ionic SO_4^{-2} mass concentrations have been used in the pie 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 SO_4^{-2}. However, as the ratio [S as SO_4^{-2}]/[S] has been found to range from 75% to 95% and given the approximative 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 this 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 CO_3^- and OH^-, lighter elements that PIXE can not successfully analyze, 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),

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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 sum of nano-equivalent cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and the sum of nano-equivalent anions (Cl^-, NO_3^-, SO_4^{2-}) 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 largely due to the hydroxides, carbonates as well as carboxylic acids which are probably bound with the excessive amounts of Ca^{2+} and are not analyzable by our method.

Atmospheric ammonia, in its NH_4^+ form, is found predominantly in FPM with its CPM concentrations of NH_4^+ being very low. As a result of this, the quantities of NH_4^+ are insufficient to completely neutralize the atmospheric acidity, which is in agreement with older studies for Athens (Eleftheriadis et al., 1998), for other locations in Greece (Danalatos and Glavas, 1995), for other locations with similar crustal composition, in the eastern Mediterranean (Graham et al., 2004; Shaka and Saliba, 2004; Kouyoumdjian and Saliba, 2006), as well as for other parts of the world (Davis and Jixian, 2000; Pathak et al., 2004; Shaka and Saliba, 2004). Moreover, as stated above, the ambient molar particulate NH_4^+/SO_4^{-2} ratio has been found to be constantly less than 1.5. This indicates an ammonium–poor ambient air, where the existing NH_4^+, is insufficient to completely neutralize the available sulfate, existent as sulphuric acid, and the formation of NH_4NO_3 does not occur to a significant extend, since it would normally start only after sulfate was consumed (Seinfeld and Pandis, 1998; Pathak and Chan, 2005; Trebs et al., 2005).

Water soluble calcium, on the other hand, predominates the CPM and is a major component of the FPM. The above, as well as the good correlation between CPM Ca^{2+} and CPM NO_3^- and SO_4^{-2} (Tables 7a and b), indicate that calcium containing aerosols, originating from the calcium-rich soils in the region and the quick-lime extensively used in painting facades in Greece, are probably the most important neutralizing species in this fraction, on the surface of which acids like H_2SO_4 and HNO_3 react to form $Ca(NO_3)_2$ and $CaSO_4$. In the FPM fraction both Ca^{2+} and NH_4^+ appear to be important neutralizing agents of acidity. NH_4^+, which in this fraction is found in significant concentrations, correlates very well with SO_4^{-2} and is probably its major neutralizing agent, forming $(NH_4)_2SO_4$ and NH_4HSO_4. The respective correlations between FPM NO_3^- (Tables 7a and b), which in FPM is found in low concentrations, and FPM NH_4^+ are low, which, as has already been stated, is reasonable as the formation of NH_4NO_3 is not expected to occur to a significant extend. The FPM NO_3^-, on the other hand correlates well with Mg^{2+} and relatively well with Ca^{2+} which indicates that these two ions are its neutralizing species, forming $Mg(NO_3)_2$ and $Ca(NO_3)_2$. Strong correlations have been observed between Na^+ and Mg^{2+}, Na^+ and Cl^- and Mg^{2+} and Cl^-, which indicates the existence of NaCl and $MgCl_2$ salts. The above are in agreement with the aforementioned studies for Greece (Tsitouridou and Samara, 1993; Danalatos and Glavas, 1995; Eleftheriadis et al., 1998), for the eastern Mediterranean (Graham et al., 2004; Kouyoumdjian and Saliba, 2006), as well as for cities in Asia (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), 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 qualitative comparison indicates characteristic elemental and ionic peaks that are attributed to the geochemical characteristics of the area. 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). In addition to this, it is shown that with the exception of Zn, the traffic-related characteristic peaks are slightly higher for

AEDA, indicating slightly stronger influence of traffic for this site. From the respective ionic ratios (Figs. 7a and b) it can be derived that a big part of Cl^- is found as NaCl coming from the sea and that, especially in the CPM, an influence by some additional non-marine source of Cl^- is probably also present. The Mg^{2+}/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 the sea. The SO_4^{-2}/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 (Yaaqub et al., 1991), suggests the existence of anthropogenic sources contributing to SO_4^{-2} conncentrations. Lastly, the calcium enrichment is again obvious as the ratio Ca^{2+}/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. In August 2003, when a large portion of the population was absent and the traffic in the city was significantly reduced, the PM_{10} mass concentration (obtained by Beta Attenuation) was, on average, 56 μg/m^3 at a height of 5 m from the ground, in Athinas St. In the second season, in March 2004, aerosol sampling took place at two sites. The first was the same with the August 2003 campaign in Athinas St., where aerosol sampling took place both at 5 m from the ground and at 1.5 m from the ground, near the "breathing zone", as defined by the EU (Commission, 1999/30/EC). Additional sampling, during this campaign, took place in a second site on the roof of a governmental building (AEDA), at a height of 25 m from the ground, also in the centre of the city. The PM_{10} ($PM_{10-2.5}$+$PM_{2.5}$) mass concentrations at 1.5 m from the ground in Athinas were found to be approximately 20% higher compared to respective PM_{10} measured at 5 m from the ground in the same site. In addition to this, the $PM_{2.5}$ mass concentrations at 1.5 m from the ground in Athinas St. were found to be approximately 22% higher than the respective concentrations at 25 m from the ground in AEDA. For the heavier $PM_{10-2.5}$ this discrepancy was even higher, as the mass concentrations at 1.5 from the ground were found to be approximately 30% higher than the respective concentrations at 25 m. There is an obvious significant contribution to the CPM mass concentrations during the day in Athinas St., which can be attributed to construction, traffic and overall human activity. This "morning-contribution", which consists mainly of crust-related calcium and aluminosilicate compounds, may lead to an overestimation of the difference between the morning values in the two sites and elevations, raising it to a 43% for the CPM. However, examination of the evening CPM and the morning and evening FPM concentrations, as well as the $PM_{\leq 10}$ at 1.5 and at 5 m from the ground in Athinas St., shows that PM concentrations significantly increase the closer one gets to the ground, near the "breathing zone". As a result of the above it becomes evident that for a realistic estimation of the exposure of citizens to particulate matter, in the centre of Athens on a daily basis, $PM_{\leq 10}$ at a height of 1.5–3 m from ground, in the "breathing zone", are 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 compound in the coarse fraction, appearing in very high concentrations. Its elevated 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. Crust-related aluminosilicates and iron have also been found to be major components of the coarse fraction, while the above elements constitute the most important components of the fine fraction, together with the predominant, in this fraction, S. 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 observed. Pb, in particular, appears mostly in the fine fraction and in very low concentrations compared to studies dating more than a decade back.

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. The low molar ratio of NH_4^+/SO_4^{-2} has indicated an ammonium-poor ambient air, where atmospheric ammonia is not sufficient to neutralize all acidity and the formation of NH_4NO_3 does not occur to a significant extend. Calcium, on the other hand, predominates the coarse fraction and its good correlations with coarse NO_3^- and SO_4^{-2} indicate that calcium-containing aerosols are probably major neutralizing species in this fraction, on the surface of which acids like HNO_3 and H_2SO_4 react to form $Ca(NO_3)_2$ and $CaSO_4$. In the fine fraction both Ca^{2+} and NH_4^+ play the role of the neutralizing agents. The very good correlation between NH_4^+ and SO_4^{-2} indicate that the first is the major neutralizing agent of the latter. The respective correlations between NH_4^+ and NO_3^- are low which agrees with the fact that the formation of NH_4NO_3 is not favoured. Strong correlations have been observed between Na^+ and Mg^{2+}, Na^+ and Cl^- and Mg^{2+} and Cl^-, which indicates the existence of NaCl and $MgCl_2$ salts. These findings are in agreement with studies for other locations in Greece, in eastern Mediterranean as well as for some locations in Asia.

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 of them, morning concentrations prevailed only slightly over the evening concentrations, when most traffic and construction activity in the city was reduced. At the same time for some other species like Cl^-, NO_3^- and NH_4^+, as well as some elements originating from human activities, evening values appear slightly higher over morning ones. The above 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 be ranging between approximately 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 carbon, organics and polymers, which usually constitute more than 50% of the urban aerosol mass.

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Table 1. PIXE detection limits for ambient air samples on membrane filters of mixed cellulose esters (a.d.: area of deposit=13 cm^2).

	μg/a.d.		μg/a.d.		μg/a.d.		μg/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

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 2. Morning and evening concentrations (ng/m^3) measured in Athinas St., in August 2003 (Mean±Standard Deviation); [a] Coarse Particulate Matter (PM$_{2.5-10}$); [b] Fine Particulate Matter (PM$_{2.5}$); [c] PM$_{10}$ obtained by use of Beta Attenuation at a height of 5 m from ground level; gravimetrical 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±176	517±268	351±132	266±116
Si	1388±423	1186±741	544±248	356±154
S	344±221	301±155	4374±1992	4570±2260
Cl	129±96.0	114±87.6	43.4±24.4	31.3±11.5
K	317±96.6	292±183	351±98.7	339±95.0
Ca	5730±2321	4797±4428	1706±872	1074±4674
Ti	51.4±17.1	45.0±32.4	22.4±10.1	14.5±6.08
V	4.3±3.77	6.11±3.94	11.2±12.1	16.3±10.4
Cr	4.68±2.01	4.7±3.56	2.43±1.29	2.40±1.19
Mn	12.5±5.23	11.5±7.63	10.2±3.91	8.01±4.3
Fe	690±232	707±408	374±138	361±137
Ni	3.83±2.17	4.05±2.59	5.38±4.37	5.66±3.74
Cu	83.1±42.9	130±59.4	84.4±40.1	142.4±61.5
Zn	31.8±17.1	29.0±16.2	64.8±53.8	45.4±24.5
Ga	0.28±0.19	0.18±0.11	0.28±0.32	0.28±0.2
As	0.49±0.3	0.46±0.35	0.99±0.57	1±0.63
Se	0.05±0.12	0.03±0.08	1.11±0.75	0.99±0.46
Br	1.21±0.58	1.02±0.39	5.46±1.76	5.1±1.76
Rb	1.51±0.47	1.31±0.65	1.16±0.37	1.01±0.3
Sr	5.89±1.8	5.08±3.64	2.2±0.98	1.77±0.66
Zr	2.88±1.41	3.32±1.73	1.34±0.48	1.81±0.74
Sn	1.31±0.53	1.35±1.18	2.45±2.02	2.19±1.32
Ba	17.2±8.11	18.5±13.8	11.1±7.51	9.95±4.72
Pb	11.9±6.56	11.04±6.34	34.3±21.3	28.5±21.1
Total PM$_{10}^{c}$ (μg/m^3)	Morning: 57±13; Evening: 55±19			

Table 3. Morning and evening concentrations (ng/m^3) measured in Athinas St., 1.5 m from the ground level, in March 2004 (Mean±Standard Deviation); [a] Coarse Particulate Matter (PM$_{2.5-10}$); [b] Fine Particulate Matter (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 (*n*=37)				FPM^b (*n*=29)			
	Morning (*n*=21)	% water soluble	Evening (*n*=16)	% water soluble	Morning (*n*=18)	% water soluble	Evening (*n*=11)	% water soluble
Al	671±519		655±359		372±450		305±257	
Si	1850±1415		1808±993		702±975		587±534	
SO_4^{2-}	1766±869		1958±795		6821±3060		6540±3438	
S	656±354		809±397		2876±1397		2556±1093	
S as SO_4^{-2}	586±290	89	653±265	81	2273±1020	79	2180±1146	85
Cl	1199±1160		1063±1027		204±419		163±183	
Cl^-	2474±1220		2917±812		381±251		267±255	
K	424±273		411±195		296±240		245±154	
K^+	177±68	42	197±150	48	145±66	49	145±57	59
Ca	15999±10731		15086±8087		3545±2107		3581±1588	
Ca^{2+}	12067±3597	75	11272±3553	75	3372±1193	95	3214±1630	90
Ti	115±97.3		136±73.5		42.6±50.9		74.1±58.4	
V	5.46±3.96		6.47±3.78		11.1±11.9		8.7±5.9	
Cr	8.56±5.46		8.25±4.17		2.59±2.63		2.76±1.58	
Mn	18.2±12.4		17.5±10.3		12.3±13.0		13.0±10.1	
Fe	1090±743		948±472		447±467		374±229	
Ni	5.46±5.36		4.81±2.29		4.47±4.1		4.33±3.32	
Cu	37.2±23.5		26.3±10.62		22.1±20.8		17.7±11.7	
Zn	52.9±34.5		75.5±42.9		76.4±68.9		118±113	
Ga	0.37±0.45		0.21±0.13		0.24±0.2		0.14±0.14	
As	0.73±0.47		0.92±0.35		1.58±0.48		1.72±0.3	
Se	0.15±0.17		0.16±0.12		0.59±0.49		0.49±0.23	
Br	3.99±2.38		3.52±2.11		7.39±0.48		6.73±3.58	
Rb	1.85±1.56		1.83±0.77		1.09±0.88		0.74±0.53	
Sr	15.2±12.2		22.2±16.9		4.93±5.32		5.38±6.98	
Zr	5.08±4.54		4.99±2.65		2.3±2.3		1.44±0.66	
Mo	2.25±1.43		1.38±0.64		1.87±1.32		1.31±0.61	
Sn	2.75±2.38		2.28±1.43		5.01±6.94		3.03±2.10	
Sb	4.84±3.76		2.86±1.63		3.25±3.26		1.88±1.31	
Ba	28.0±19.9		38.6±33.7		12.4±12.8		16.1±11.08	
Pb	21.4±23.2		14.86±9.86		53.9±66.6		31.0±15.4	
Na^+	835±464		735±580		294±242		235±87.5	
NH_4^+	158±99		267±126		1484±1246		1553±1014	
Mg^{2+}	277±133		327±173		109.3±44.8		110.2±44.0	
NO_3^-	2724±1836		2238±1219		410±228		276±172	
PM^d (μg/m^3)	94.8±43.1		65.3±30.9		44.7±32.7		36.2±22.2	
Total PM$_{10}^c$ (μg/m^3)	(PM$_{10}$$\mu$m) Morning: 104.7±32.7; Evening: 78.5±32.3							

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀◀ | ▶▶
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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

	AEDA							
	CPM^a (n = 30)				FPM^b (n = 20)			
	Morning (n=16)	% water soluble	Evening (n=14)	% water soluble	Morning (n=11)	% water soluble	Evening (n=9)	% water soluble
Al	411±211		428±284		320±174		273±174	
Si	1080±557		1070±682		463±347		415±284	
SO_4^{2-}	1092±442		1215±577		7140±5844		8086±7002	
S	476±166		535±442		3008±1924		2820±1604	
S as SO_4^{2-}	364±180	76	405±192	76	2380±1948	79	2645±2334	94
Cl	563±691		880±685		137±24.01		110±133	
Cl^-	1041±686		1436±1110		218±278	–	173±100	
K	234±115		245±148		291±139		307±152	
K^+	151±185	65	165±156	67	73.4±56.4	25	93.7±55.8	31
Ca	8050±4870		7007±4623		1728±946		1641±706	
Ca^{2+}	5753±2151	71	5491±2963	78	1375±947	80	1270±624	77
Ti	63.2±38.4		51.2±33.7		26.1±14.0		27.9±18.9	
V	4.07±2.74		4.75±2.85		9.32±5.82		16.42±8.91	
Cr	7.99±6.04		8.34±6.23		4.41±1.85		2.71±0.96	
Mn	12.6±7.34		13.1±9.18		13.7±4.46		9.64±3.8	
Fe	739±391		748±511		405±136		340±117	
Ni	3.76±2.47		3.62±3.07		5.06±3.23		5.64±2.21	
Cu	58.5±36.9		63.4±57.6		58.5±23.0		58.7±32.2	
Zn	36.3±22.3		31.63±21.7		73.4±75.5		53.5±27.9	
Ga	0.15±0.19		0.19±0.1		0.12±0.05		0.25±0.11	
As	0.45±0.28		0.52±0.35		0.73±0.27		0.57±0.1	
Se	0.09±0.07		0.09±0.05		0.63±0.4		0.81±0.33	
Br	2.12±1.68		2.67±1.29		6.81±1.84		7.8±2.15	
Rb	1.09±0.52		1.01±0.55		0.82±0.5		1.03±0.63	
Sr	6.95±3.93		6.51±3.49		2.77±1.38		2.45±1.18	
Zr	3.26±1.8		3.82±2.62		1.31±0.5		1.83±0.83	
Mo	2.61±1.59		3.79±2.12		4.56±1.51		5.17±3.17	
Sn	1.92±1.34		2.55±2.14		3.43±2.65		6.32±6.31	
Sb	3.4±2.58		5.19±2.74		3.1±1.0		3.05±1.78	
Ba	31±43.8		21.7±12.3		12.2±7.12		5.9±5.2	
Pb	16.6±13.2		25.5±27.69		37.2±27.2		27.2±89	
Na^+	553±391		709±412		286±305		206±205	
NH_4^+	126±123		198±167		1613±1731		1660±1706	
Mg^{2+}	193±110		234±111		85.7±74.6		80.9±43.8	
NO_3^-	1751±1353		2031±1421		350±408		168±129	
PM^c (μg/m^3)	54.4±25.1		55.2±27.4		33.0±8.4		30.1±11.6	

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/m3)	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 Voutsa, 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 ($\mu g/m^3$)		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 Al2O3)	1220 (as Al2O3)	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 SiO2)	2960 (as SiO2)	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/m3)	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 Voutsa, 2004) (3.5 m)	Thes/niki '89–90 (Tsitouridou et al., 1993) (3 m)	Madrid 1999-'00 (Artinano 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 (μg/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 Al2O3)	460 (as Al2O3)	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 SiO2)	1050 (as SiO2)	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

Table 6a. Comparison between gravimetrical DSFU-PM$_{10}$ (CPM+FPM), collected at a height of 1.5 m above ground and BA-PM$_{10}$ (obtained by use of Beta Attenuation), at a height of approx. 5 m from the ground level, in Athinas St., in March 2004.

	Gravimetrical 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 gravimetrical DSFU-PM_{10} (CPM+FPM), collected at a height of 1.5 m above ground in Athinas St. and the respective gravimetrical PM_{10}, collected at a height of 25 m from ground level in AEDA, in March 2004.

	Gravimetrical PM_{10} (CPM+FPM), Athinas	Gravimetrical 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.

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

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

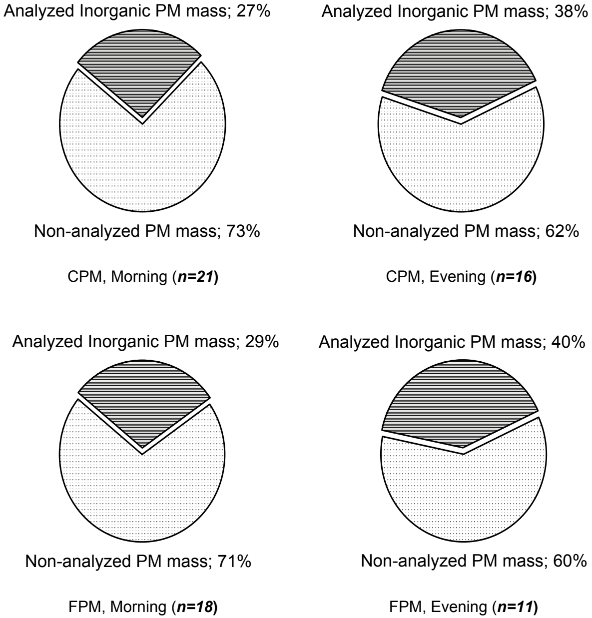
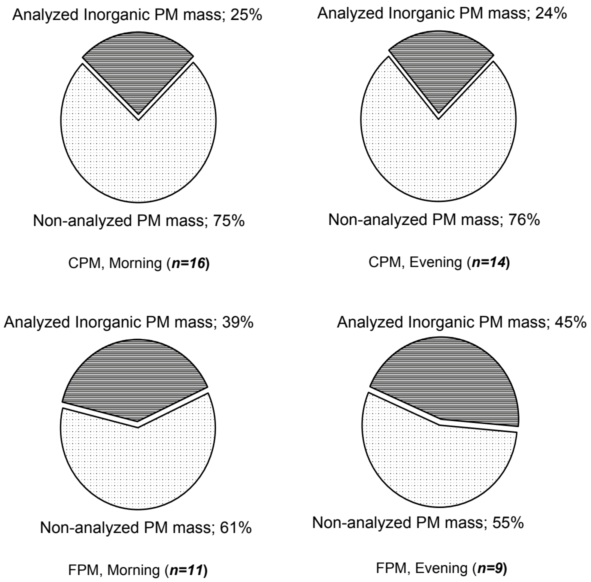


Fig. 2. Total analyzed inorganic versus total collected PM_{10} mass concentration, in the FPM and CPM fractions, for morning and evening, in Athinas St. site, at 1.5 m above ground, in March 2004.



CPM, Morning (***n=16***)

CPM, Evening (***n=14***)

FPM, Morning (***n=11***)

FPM, Evening (***n=9***)

Fig. 3. Total analyzed inorganic versus total collected PM_{10} mass concentration, in the FPM and CPM fractions, for morning and evening, in AEDA site, at 25 m above ground, in March 2004.

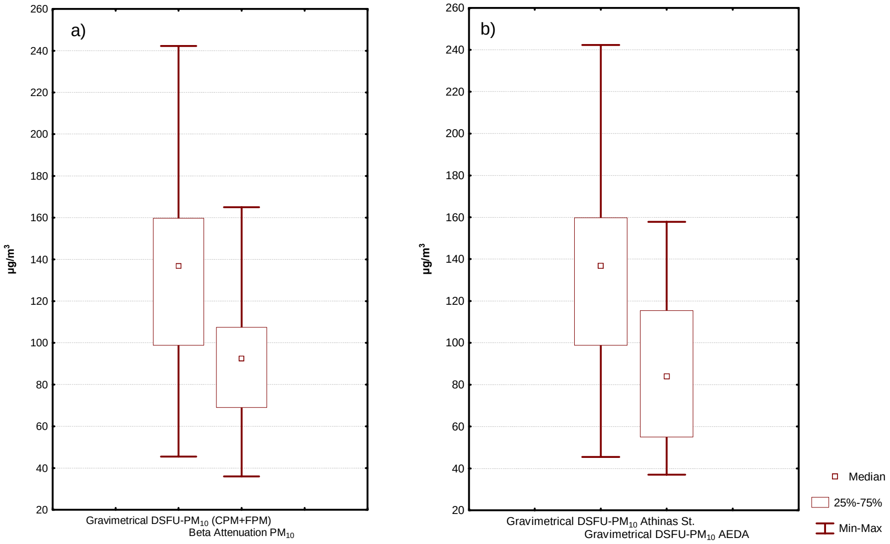


Fig. 4. **(a)** Comparative graph of the gravimetrical DSFU-PM_{10} (calculated as the sum of CPM+FPM) collected at a height of 1.5 m above ground and BA-PM_{10} (obtained by Beta Attenuation) collected at 5 m above ground, in Athinas St., in March 2004; **(b)** Comparative graph of the gravimetrical DSFU-PM10 collected at a height of 1.5 m above ground in Athinas St., and the respective gravimetrical DSFU-PM10 at a height of approx. 25 m above ground in AEDA.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀▌ | ▶▌
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

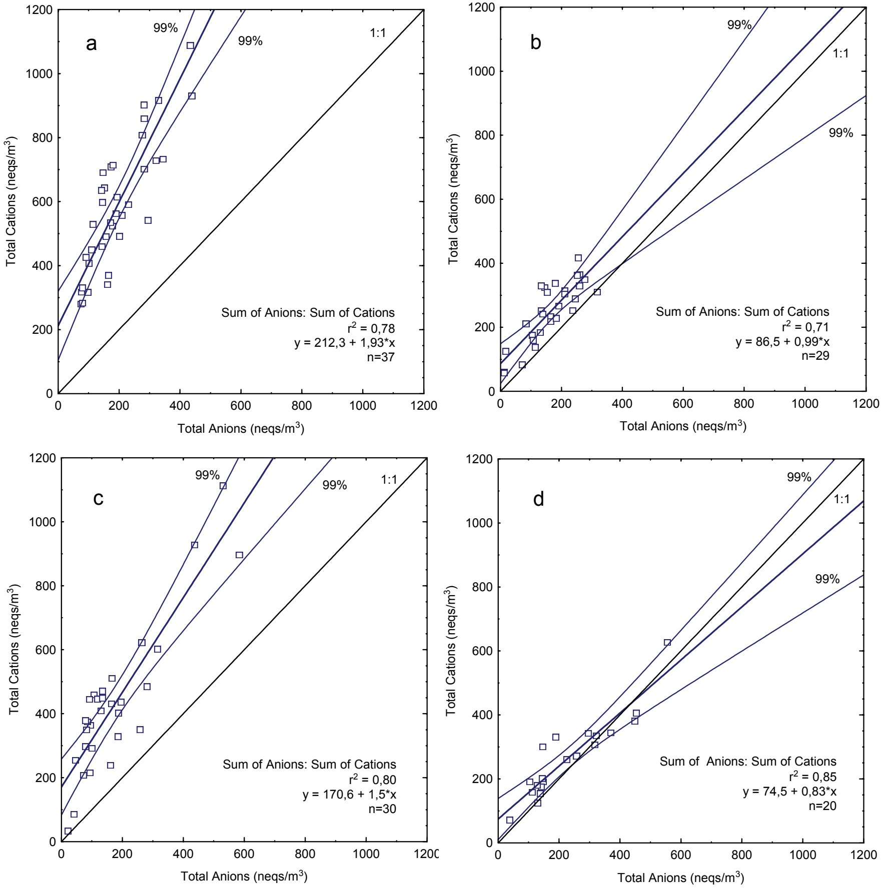


Fig. 5. Ionic balances for both fractions in the two sites. From top left to lower right: **(a)** Athinas St. CPM, and **(b)** FPM; **(c)** AEDA CPM, and **(d)** FPM.

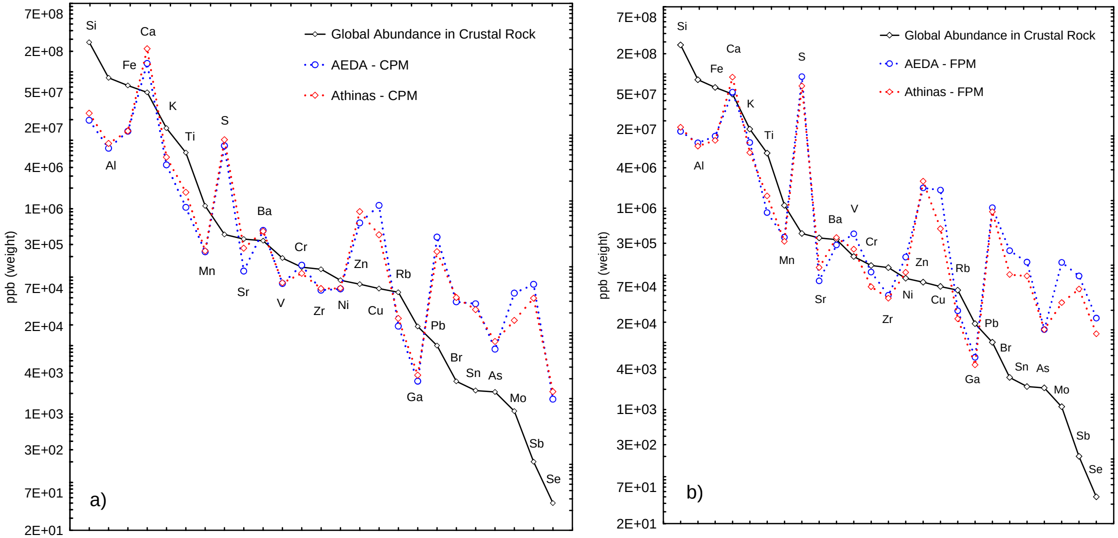


Fig. 6. Elemental chemical composition in the two sites (Athinas St. and AEDA) for **(a)** CPM and **(b)** FPM, plotted together with the average global abundance of elements in crustal rock as a reference.

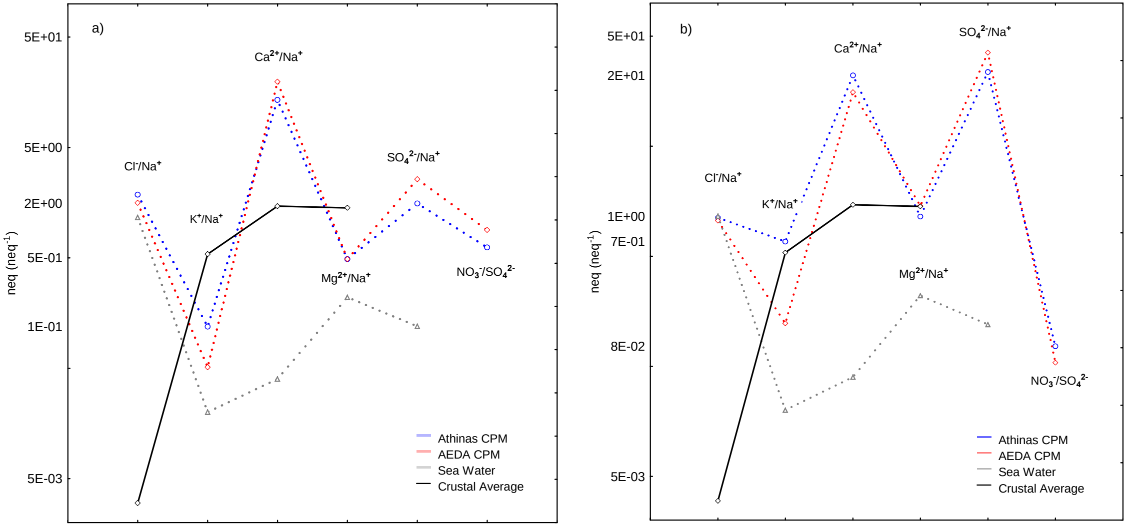


Fig. 7. Ionic concentration ratios in the two sites (Athinas St. and AEDA) for **(a)** CPM and **(b)** FPM, plotted together with the sea-water and crustal global averages.