

Mass and chemical composition of size-segregated aerosols (PM₁, PM_{2.5}, PM₁₀) over Athens, Greece: local versus regional sources

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Abstract. To identify the relative contribution of local versus regional sources of particulate matter (PM) in the Greater Athens Area (GAA), simultaneous 24-h mass and chemical composition measurements of size segregated particulate matter (PM₁, PM_{2.5} and PM₁₀) were carried out from September 2005 to August 2006 at three locations: one urban (Goudi, Central Athens, “GOU”), one suburban (Lykovrissi, Athens, “LYK”) in the GAA and one at a regional background site (Finokalia, Crete, “FKL”).

The two stations in the GAA exceeded the EU-legislated PM₁₀ limit values, both in terms of annual average (59.0 and 53.6 μg m⁻³ for Lykovrissi and Goudi, respectively) and of 24-h value. High levels of PM_{2.5} and PM₁ were also found at both locations (23.5 and 18.6 for Lykovrissi, while 29.4 and 20.2 μg m⁻³ for Goudi, respectively).

Significant correlations were observed between the same PM fractions at both GAA sites indicating important spatial homogeneity within GAA. During the warm season (April to September), the PM₁ ratio between GAA and FKL ranged from 1.1 to 1.3. On the other hand this ratio was significantly higher (1.6–1.7) during the cold season (October to March) highlighting the role of long-range transport and local sources during the warm and cold seasons respectively. Regarding the coarse fraction no seasonal trend was observed for both GAA sites with their ratio (GAA site/FKL) being higher than 2 indicating significant contribution from local sources such as soil and/or road dust.

Chemical speciation data showed that on a yearly basis, ionic and crustal mass represent up to 67–70% of the gravimetrically determined mass for PM₁₀ samples in the GAA

and 67% for PM₁ samples in LYK. The unidentified mass might be attributed to organic matter (OM) and elemental carbon (EC), in agreement with the results reported by earlier studies in central Athens. At all sites, similar seasonal patterns were observed for nss-SO₄²⁻, a secondary compound, indicating significant contribution from regional sources in agreement with PM₁ observations.

The contribution of local sources at both GAA sites was also estimated by considering mass and chemical composition measurements at Finokalia as representative of the regional background. Particulate Organic Matter (POM) and EC, seemed to be the main contributor of the local PM mass within the GAA (up to 62% in PM₁). Dust from local sources contributed also significantly to the local PM₁₀ mass (up to 33%).

1 Introduction

The interest on aerosols has widely increased the last years due to their impact on air quality, human health and climate change. Legislation regarding air pollution, based on atmospheric particulate matter, is becoming gradually more stringent, as a result of the high levels of aerosols during intense episodes of either natural or anthropogenic origin. Such episodes could lead to the formation and accumulation of aerosol pollutants on regional or even continental scales since they can be associated with synoptic and mesoscale meteorological conditions (Querol et al., 2009).

The Greater Athens Area (GAA) is a quite densely populated region of 450 km² with a population that exceeds 4 million people and a massive number of registered vehicles in circulation (over 2.5 million, growing at a rate of 7% yearly).



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The majority of these vehicles is non-catalytic (0.8 million) or is powered by old technology diesel engines (0.2 million; Grivas et al., 2008). Long term monitoring of PM concentrations in the GAA (Chaloulakou et al., 2003, 2005; Grivas et al., 2004a, 2008) registered the occurrence of a significant number of PM₁₀ exceedances of the limits set by EU legislation (Directive 2008/50/EC) and point to the need for abatement strategies. The 2008/50/EC directive enacted a yearly limit value for PM₁₀ of 40 µg m⁻³ and a maximum authorized 24-h mean value of 50 µg m⁻³ that cannot be exceeded more than 35 days in a calendar year. However to propose such a strategy precise knowledge of PM sources is a prerequisite. For this reason the relative contribution of natural and anthropogenic sources and the role of local versus long range sources need to be determined. The EU directive specifically requires information for particles deriving from natural sources for the assessment of PM-related air quality, since EU recognizes the weakness of individual countries in reducing PM levels that are maintained by long range transport.

To address these critical issues for the GAA, mass and chemical composition of size segregated aerosols simultaneously collected at 3 locations, were analyzed: two sites in Athens, representing the urban and suburban environment (GOU; LYK) and a remote background site (FKL) for which previous studies (Mihalopoulos et al., 1997; Gerasopoulos et al., 2007; Koulouri et al., 2008b) documented its ability to represent the Eastern Mediterranean regional background.

2 Experimental

2.1 Sampling site

Simultaneous PM₁, PM_{2.5} and PM₁₀ sampling was conducted in the GAA, at both Lykovrissi (LYK) and Goudi (GOU) during the period September 2005–August 2006 (Fig. 1).

LYK, is a moderately populated municipality (4160 inhabitants per km²), in the northern part of the Greater Area of Athens, 10 km from the city center. The monitoring station lies within the premises of the National Agricultural Research Foundation, in an estate covered by small vineyards and unpaved roads. The site is in close vicinity (0.6 km) to the 8-lane A1 national road, part of the E75 international motorway, probably the most trafficked route within the Athens metro. A minor industrial zone is also located in close distance to the northeast (with the main activities being food production, secondary metal processing and manufacturing of appliances). The sampling height was 4 m above ground.

GOU is located downtown Athens (3 km from the city center), inside the campus of the Medical School of Athens and is influenced by traffic emissions. The distance from the nearest road is 10 m. The traffic volume on that road was estimated to be 14 000 mvh per day. A larger road with an



Fig. 1. Map indicating the location of the sampling sites referenced in the text.

estimated traffic volume of more than 40 000 mvh per day crosses at a distance of 30 m from the station. The area surrounding the site is mainly of residential and institutional land use, with the Medical School and three large hospitals in direct vicinity to the site. The sampling height was 4 m above ground. Details on the aforementioned sites can be found in Grivas et al. (2004b) and Grivas and Chaloulakou (2006).

Size-segregated aerosol samples were also collected at FKL, a regional background site located on Crete Island in the Eastern Mediterranean during the period July 2004–July 2006 (Fig. 1). FKL is situated 70 km northeast of Heraklion, the site characteristics and the prevailing meteorology can be found in Mihalopoulos et al. (1997), Gerasopoulos et al. (2007) and Theodosi et al. (2010a).

2.2 Sampling and analytical techniques

In the GAA, simultaneous 24-h PM₁, PM_{2.5}, and PM₁₀ measurements were conducted using Partisol (Thermo Fisher Scientific Inc., Waltham, MA US) low volume samplers (flow of 16.71 min⁻¹) with cyclonic separators for PM₁ at both sites and for PM_{2.5} at LYK, while Harvard impactors (Air Diagnostics and Engineering Inc., Naples, ME US, flow of 101 min⁻¹) were used for PM₁₀ at both sites and for PM_{2.5} at GOU. Particle mass was collected on pre-weighted Teflon-coated glass-fiber filters. Measurements were conducted on a regular basis of 1-sample every-3 days, collecting on average 10 samples per month for both sites and all three size fractions. Weighing is conducted using a microbalance with a reading precision of 1 µg (Sartorius M2P). Filters are equilibrated for at least 24-h at 40(±5) % relative humidity. At FKL aerosol samples were collected using a virtual impactor (VI; Loo and Cork, 1988) modified to divide particles into two size fractions: fine (aerodynamic particle diameter $D_a < 1.3$ µm, hereafter as PM₁) and coarse particles ($D_a > 1.3$ µm). The inlet situated before the VI has a cut-off size of 10 µm. The operational flow rate is 16.71 min⁻¹. Polytetrafluoroethylene (PTFE)

filters (Millipore Fluoropore; pore size 3.0 μm ; diameter 47 mm) were used in the VI sampler (henceforth PTFE-VI). Size resolved aerosol samples were collected, at a 1-every-3 days sampling frequency on a continuous basis. More details on sample collection can be found in Koulouri et al. (2008b). In addition, size resolved aerosol samples were also collected using a Small-Deposit-area low-volume-Impactor (SDI) (Maenhaut et al., 1996). The inlet preceding the SDI has a cut-off size (50 %) of 10 μm . The SDI has 12 collecting stages over the particle size range 0.041–10 μm with cut-offs at 0.041, 0.085, 0.138, 0.225, 0.346, 0.585, 0.762, 1.06, 1.66, 2.68, 4.08 and 8.39 μm . The average sampling time for both VI and SDI was 2 days (ranging from 1 up to 3 days). Both blank and field filter samples were conditioned at constant temperature (22 ± 3 °C) and relative humidity (40 ± 5 %), for at least 24 h prior to weighting, before and after sampling. These conditions were slightly different compared to the European norms EN12341 (1999), EN14907 (2005) requesting for 20 ± 1 °C and 50 ± 5 % RH. The experiment conditions applied in this work can introduce a small (less than 10 %) negative bias in measured concentrations when compliance with the EU limit values for PM is explored.

In total, 127 PM_1 , 127 $\text{PM}_{2.5}$ and 126 PM_{10} samples were collected at LYK, 114 PM_1 , 109 $\text{PM}_{2.5}$ and 107 PM_{10} samples at GOU and 90 aerosol samples at FKL for both VI and SDI. The filters were analyzed for water-soluble ions and elements. One quarter of each filter was extracted using 10 ml of nanopure water. The solutions obtained were analyzed by ion chromatography (IC) for anions (Cl^- , Br^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, MS^-) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). More details on the IC method are given by Bardouki et al. (2003). An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, *Thermo Electron X Series*) was applied to measure PM elemental concentrations (V, Cr, Mn, Fe, Ni, Cu, Cd and Pb) (Theodosi et al., 2010b).

3 Results and discussion

3.1 Climatology of the studied regions

To better understand the PM variability along the three studied sites, seasonal variations of wind sectors at the GAA and FKL are reported in Fig. 2a–d. They are calculated from back trajectory analysis every 12 h, with the Hysplit Dispersion Model (Hybrid Single – Particle Lagrangian Integrated Trajectory; Draxler and Hess, 1998) using the location of air parcels 24 h before arrival at each site during the whole sampling period 2005–2006. Each wind sector covers a 90 degree sector centered on each direction (North, East, South, and West) similar to the approach used by Sciare et al. (2008). There is a very good agreement between the GAA and FKL in terms of air masses origin. On a yearly basis the

northern sector, which covers Central and Eastern Europe as well as part of the western Turkey is the most important, accounting for almost two thirds of the air masses arriving at both locations. During the warm period the contribution of this sector is almost identical in the GAA and FKL and results in almost identical PM levels (Fig. 2c). On the other hand during the cold period, this sector influences slightly more (about 20 %) the GAA than FKL, which in turn could also influence PM levels (see Sect. 3.2.3). Southern winds, responsible for Sahara dust events, are very frequent for both the GAA and FKL during spring and autumn, contributing up to 25 % of the prevailing air masses.

Grivas et al. (2004a) studied the spatial and temporal variation of PM_{10} mass concentrations within the GAA. They reported that Thrakomakedones (THR, Fig. 1), a remote suburb of Athens, situated 23 km North of the city center can be considered as a regional background location, due to the absence of primary sources affecting PM concentrations (Grivas et al., 2004a). Figure 3a, b reports the daily and monthly variability of mean PM_{10} levels at the GAA and FKL from May 2005 to October 2006, covering thus the studied period. Significant co variations between the PM_{10} recorded at two sites have been observed. The comparison of the monthly mean values of PM_{10} levels of the GAA and FKL reveals a significant correlation, slope of 1 with r^2 0.6, proving that FKL can be reasonably considered a background-reference site for the GAA.

3.2 PM mass concentrations

3.2.1 Atmospheric concentrations

The monthly mean observations of PM_1 , $\text{PM}_{2.5}$ and PM_{10} at the three stations are shown in Fig. 4a–c. The arithmetic mean and standard deviation of PM_1 , $\text{PM}_{2.5}$ and PM_{10} ($\mu\text{g m}^{-3}$) for the samples collected at the three locations are given in Table 1. PM_{10} particle concentrations reported for FKL refer to the aerosol samples collected using the VI. There was a noteworthy upward trend for PM_1 and $\text{PM}_{2.5}$ levels when moving from remote background to suburban and then to urban sites. On the contrary, for the PM_{10} fraction no pronounced difference was found between the GAA stations.

Annual mean PM_{10} values at both GAA sites ($53.6 \mu\text{g m}^{-3}$ at GOU and $59.0 \mu\text{g m}^{-3}$ at LYK), exceeded the limit value of $50 \mu\text{g m}^{-3}$ in 44 % and 51 % of the samples from GOU and LYK respectively. Even at the background station of FKL, with average PM_{10} of $37 \mu\text{g m}^{-3}$, the $50 \mu\text{g m}^{-3}$ value was exceeded 6 % during the year suggesting elevated background aerosol levels in the area under specific meteorological conditions.

The p-value statistical test was applied to check for similarities in PM fractions within the GAA. Statistically significant correlations were observed between the GAA stations for all PM fractions ($p = 1.6 \times 10^{-10}$, 6.7×10^{-10} and

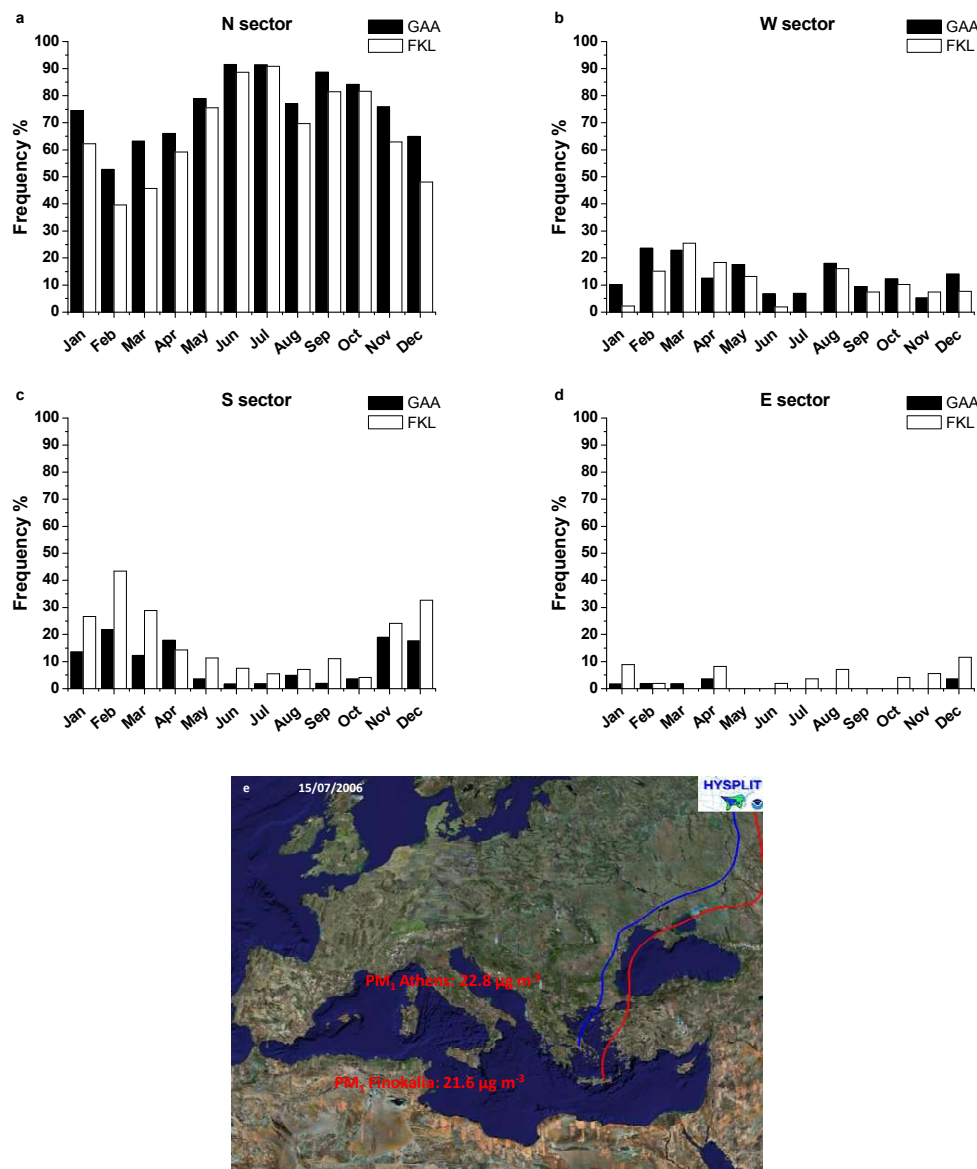


Fig. 2. Yearly-based wind direction occurrences for the 4 sectors (North; **a**, West; **b**, South; **c** and East; **d**) at GOU and FKL and a characteristic long range transport influence on PM₁ levels in the studied sites (**e**).

2.7×10^{-10} and $r^2 = 0.46$, 0.50 and 0.57 for PM₁, PM_{2.5} and PM₁₀ respectively) suggesting the existence of significant spatial homogeneity of PM within the GAA.

3.2.2 PM comparison between the different sites

The variability of the PM fractions is examined at the three locations. Strong correlations are observed between PM_{2.5} and PM₁₀ ($r = 0.63$) for both sites in GAA. The significant percentage of crustal elements content in PM_{2.5} (see Sect. 3.4) could be one of the factors responsible for this strong correlation. The PM_{2.5}/PM₁₀ ratios for the suburban, urban and remote background sites are 0.37, 0.56 and

0.58 respectively. The smaller ratio observed at LYK is relevant to the land use characteristics of the surrounding area (mainly unpaved roads and non built land), which favor the re-suspension of local soil particles, as demonstrated by the high nss-Ca²⁺ levels (see Sect. 3.3.3). The PM_{2.5}/PM₁₀ ratio observed for the central Athens site (GOU) is in agreement with the ratios reported by Chaloulakou et al. (2003, 2005) and Sillanpää et al. (2005) for measurements conducted at same-type locations (0.53 and 0.47 respectively).

On the other hand the plot between PM₁ and PM₁₀ present an important degree of scattering (Fig. 5). For instance at FKL the relation between PM₁ and PM₁₀ (Koulouri et al., 2008b) reveals the existence of two data subsets,

Table 1. Annual mean concentrations of PM fractions ($\mu\text{g m}^{-3}$) measured in Lykovrissi, Goudi and Finokalia from September 2005 to August 2006 and basic descriptive statistics.

Location		Average	Stdev	Median	Min	Max
This Study, Lykovrissi	PM ₁	18.6	9.1	16.9	3.1	58.9
	PM _{2.5}	23.5	10.8	21.8	4.6	71.2
	PM ₁₀	59.0	28.4	51.8	11.3	197.3
This Study, Goudi	PM ₁	20.2	7.4	18.7	8.2	43.8
	PM _{2.5}	29.4	10.3	28.4	11.5	67.7
	PM ₁₀	53.6	29.6	47.7	18.7	299.9
Koulouri et al., 2008a, b Finokalia	PM ₁	10.1	5.0	9.8	2.7	27.8
	PM _{2.5}	18.2	16.2	14.9	4.1	124.5
	PM ₁₀	37.0	54.2	24.3	13.7	307.5

corresponding to non-dust and dust events. Dust events were identified by air-mass trajectory analysis and are always associated with PM₁₀ values higher than $50 \mu\text{g m}^{-3}$, typical of dust transport from arid areas of Northern Africa (Gerasopoulos et al., 2007). The first subset has a slope of 0.90 suggesting the dominance of pollution particles, while the poorer correlation ($r = 0.49$) depicted the variability of submicron particle sources in the area. The second subset demonstrated higher PM₁₀ levels for the same order of PM₁ values (slope 9.6) as the non-dust case with a significant correlation ($r = 0.89$) related to transported dust.

As in FKL, PM₁/PM₁₀ ratios at the two GAA stations reveal also the existence of two data pairs corresponding to dust and non-dust events with PM₁/PM₁₀ ratios similar to those observed at FKL (1:1.1 to 1:2.1 for non-dust, and 1:11 to 1:5.8 for dust events, for Gou and LYK respectively). These results provide further support to the conclusion drawn by Gerasopoulos et al. (2007) and Querol et al. (2009) that in the Mediterranean due to high crustal content of PM, PM₁ rather than PM_{2.5}, monitoring can provide a more accurate estimation of the anthropogenic fraction. On that account, in the following discussion, fine and coarse fractions will correspond to PM₁ and PM₁₀₋₁ respectively.

3.2.3 Seasonal variation of PM fractions

The monthly mean variations of PM₁, PM_{2.5} and PM₁₀ at all sites are displayed in Fig. 4. Very high levels of PM₁₀ and PM_{2.5} are recorded in February and April at all locations, due to dust transport from North Africa. These events are so intense that they can influence the monthly mean PM levels in such extent that they can almost mask differences between urban and background sites (case of April 2006 for both PM₁₀ and PM_{2.5}). Note that the dust events were not visible in PM₁.

At all locations, the seasonal variation of PM fractions is examined after separation in warm (May to October) and cold season (November to April). During the warm season

the PM₁ ratio between the GAA and background site ranges from 1.1 to 1.3, whilst during the cold the ratio was significantly higher from 1.6 to 1.7. More intense anthropogenic activities in the GAA during the winter (e.g. heating), associated with a more shallow boundary layer, can be accounted for the difference during the cold season. Moreover differences in air masses origin could also be considered. For instance Gerasopoulos et al. (2011) suggested that Po Valley anthropogenic hotspot may significantly contribute to AOD levels above Athens during the winter period. On the other hand during the warm season, traffic related emissions are comparably less intense (this is a stable temporal pattern for the GAA; Stathopoulos and Karlaftis, 2001; Chaloulakou et al., 2005; Grivas et al., 2008) and the increased atmospheric turbulence favored ventilation of the GAA but also long range conditions.

Regarding the coarse fraction (PM₁₀₋₁) no seasonal trend is observed. Indeed the GOU/FKL ratio varies from 2.3 to 2.4 during the warm and cold season respectively. For LYK the corresponding values are 2.8 and 3.1, respectively. As discussed in Sect. 3.1.2 the higher LYK/FKL ratio is due to the higher coarse fraction at LYK location.

3.3 Ionic composition

3.3.1 Levels and size segregated distribution of water soluble ions

Annual average values of water soluble ions in PM₁, PM_{2.5} and PM₁₀ at the three studied locations are reported in Fig. 6a, b and c.

For FKL the water soluble ions levels and their size distribution are in agreement with those reported during previous years using other types of samplers (e.g. Bardouki et al., 2003; Sciare et al., 2008).

In the GAA, PM₁₀ and PM_{2.5}, levels of water soluble ions are in good agreement with the values reported in previous works conducted in Athens over shorter period (Sillanpää et

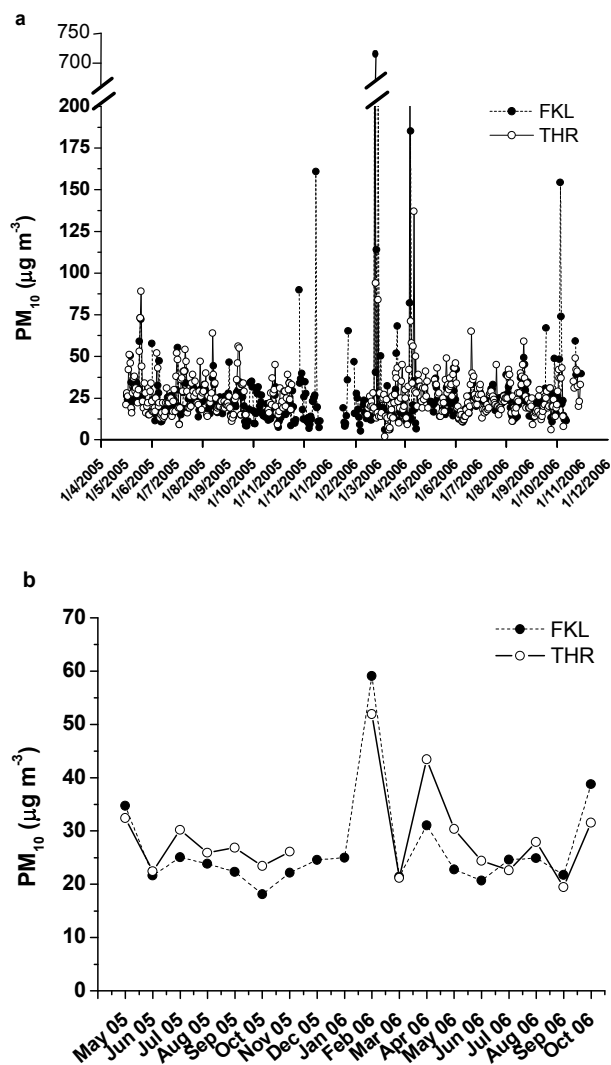


Fig. 3. Daily and monthly mean PM_{10} levels at the GAA and FKL from May 2005 to October 2006.

al., 2006; Karageorgos and Rapsomanikis, 2007, Table 2). For PM_1 , to our knowledge, this is the first time that water soluble ions are reported.

SO_4^{2-} in all PM fractions along with NO_3^- and Ca^{2+} mainly in coarse mode, have the higher contribution to the total ionic mass. In PM_1 , SO_4^{2-} and NO_3^- together account for about two thirds of the total ionic mass at both GAA stations, while for PM_{10} mass they account for 53 and 56% at LYK and GOU, respectively. The third most dominant ion particularly in PM_{10} , was Ca^{2+} with contribution of 30% at LYK and 23% at GOU.

The PM_1/PM_{10} ratios for all studied water soluble ions are shown in Fig. 6d. Water-soluble ions (Cl^- , Mg^{2+} and Ca^{2+}) are extensively found in the PM_{10-1} fraction (66–95% for LYK and 61–92% for GOU), as expected on the basis of their source and formation mechanism. The mass concentra-

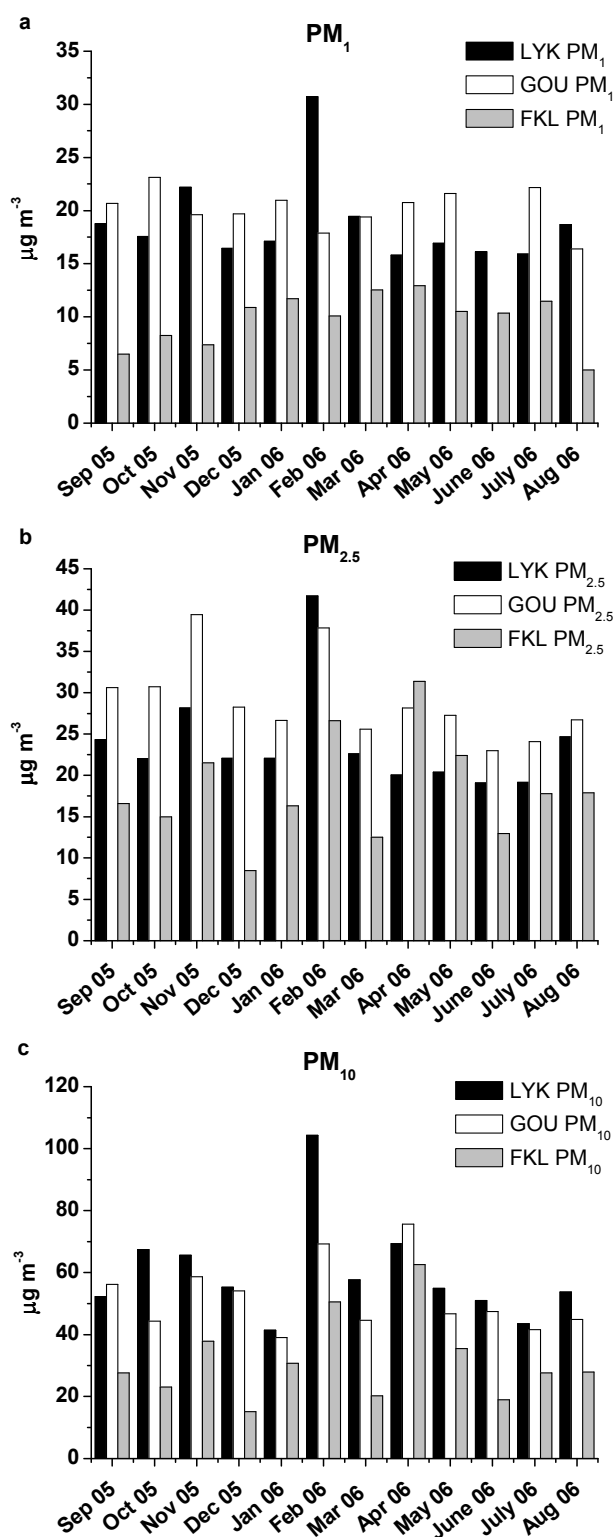
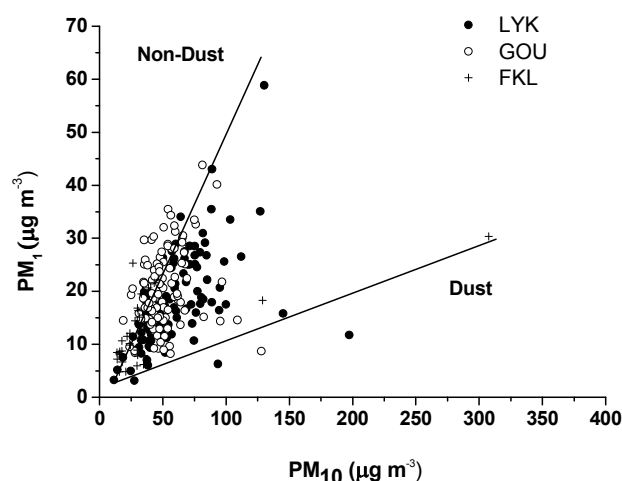


Fig. 4. Temporal variability of size segregated concentrations ($\mu g m^{-3}$) (a) PM_1 , (b) $PM_{2.5}$ and (c) PM_{10} for all three stations: LYK, GOU and FKL.

Table 2. Annual mean concentrations of ions (PM_{10} , $\text{PM}_{2.5}$ and PM_{10} ; $\mu\text{g m}^{-3}$) measured at Lykovrissi and Goudi from September 2005 to August 2006 and comparison with literature data.

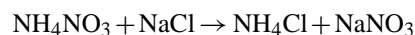
PM ($\mu\text{g m}^{-3}$)	Lykovrissi		Goudi		Finokalia	Karageorgos and Rapsomanikis, 2007	
	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	PM_{10}	$\text{PM}_{2.5}$	PM_{10}
Na^+	0.85	0.76	0.83	0.86	1.30	0.26	1.05
Cl^-	0.40	1.04	0.49	1.05	1.61	2.04	4.74
K^+	0.71	0.31	0.46	0.35	0.20	0.15	0.33
Mg^{2+}	0.07	0.18	0.05	0.17	0.19	0.11	0.41
NO_3^-	1.08	2.65	1.09	2.45	1.71	0.34	2.82
NH_4^+	0.79	0.42	0.92	0.41	1.42	1.52	1.71
SO_4^{2-}	6.08	7.03	5.79	6.32	5.42	6.68	8.54
$\text{C}_2\text{O}_4^{2-}$	0.37	0.44	0.32	0.39	0.15	–	–
Ca^{2+}	0.56	5.43	0.30	3.66	1.48	3.29	14.96

**Fig. 5.** $\text{PM}_1/\text{PM}_{10}$ ratios for all three stations during dust and non-dust events.

tions of oxalate ($\text{C}_2\text{O}_4^{2-}$) and non-sea salt sulfate (nss-SO_4^{2-} , estimated using Na^+ as a sea salt tracer) are mainly found in the fine mode (70–75 % and 72–88 %, respectively in the GAA).

Nitrate (NO_3^-) behaves differently at FKL and the GAA. At FKL on average, about 94 % of particulate nitrate (NO_3^-) is associated with coarse particles, strongly indicating that it is mainly chemically bounded with alkaline ions (Mamane and Gottlieb, 1992; Pakkanen et al., 1999). In GAA as in FKL, the most likely formation pathway for particulate nitrate (NO_3^-) in the coarse mode (60 % of the total nitrate) is the reaction of gaseous nitric acid or some other nitrogen compounds with sea salt and mineral dust particles (Metzger et al., 2006). In addition in the GAA, a significant portion of NO_3^- (about 30 %) was found in fine mode, indicating ammonium nitrate formation mainly for the winter period (see further Sect. 3.3.3 on NO_3^-).

For NH_4^+ it is interesting to note the lower values observed in PM_{10} compared to $\text{PM}_{2.5}$ and PM_1 . Similar behavior was observed by Viana et al. (2010) in Barcelona, another Mediterranean city, both in summer and winter in agreement with our observations. Volatilisation of NH_4Cl from the filter, formed by reaction of NH_4NO_3 and NaCl has been proposed to explain the NH_4^+ behavior:



Since sea salt (and NaCl) is mainly associated with coarse particles, this artefact is mainly expected for PM_{10} .

Such behavior is not seen at FKL, where temperatures are higher and observations do not indicate the presence of ammonium nitrate (Mihalopoulos et al., 1997).

3.3.2 Ionic balance

The ionic balance can be employed to determine potentially missing ionic species, which have not been measured using ion chromatography, such as CO_3^{2-} and H^+ . For this purpose, ionic balance was calculated both for the fine and coarse fractions of the aerosol particles for both GAA stations. Plots of total anions equivalents (eq m^{-3}) versus total cations equivalents for each size class are presented in Fig. 7a and b. The slope of the regression line for coarse particles indicated a value smaller than unity (slope = 0.2 to 0.4, $r = 0.61$ to 0.70), which may be due to the existence of CO_3^{2-} in this size fraction. In contrast, the slope of the regression line for the fine fraction is higher than unity (slope = 1.20 to 1.26; $r = 0.90$ to 0.92), which may be attributed to the presence of H^+ (not measured) in the aerosol samples. If this is the case, CO_3^{2-} is expected to associate with Ca^{2+} and H^+ with SO_4^{2-} in the coarse and fine fractions, respectively (Fig. 7c, d). A statistically significant correlation (slope = -0.77 to -0.82 ; $r = 0.89$ to 0.96) was found when Ca^{2+} concentrations were plotted versus the anions deficiency (sum cations

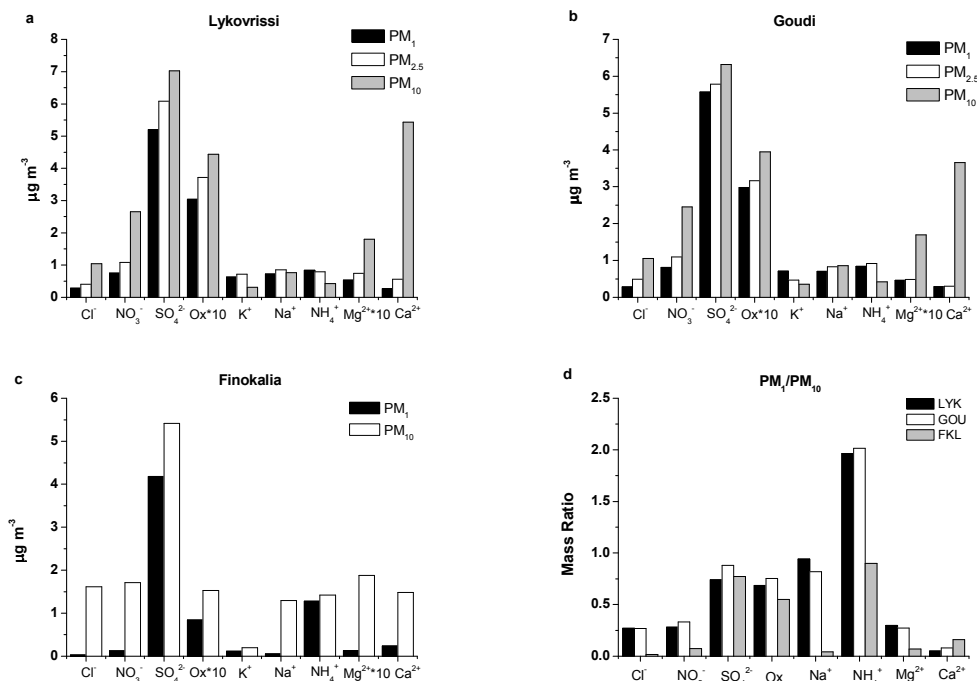


Fig. 6. Annual average concentrations ($\mu\text{g m}^{-3}$) of various ions for all three stations (a) LYK, (b) GOU, (c) FKL and (d) their PM₁/PM₁₀ mass ratios.

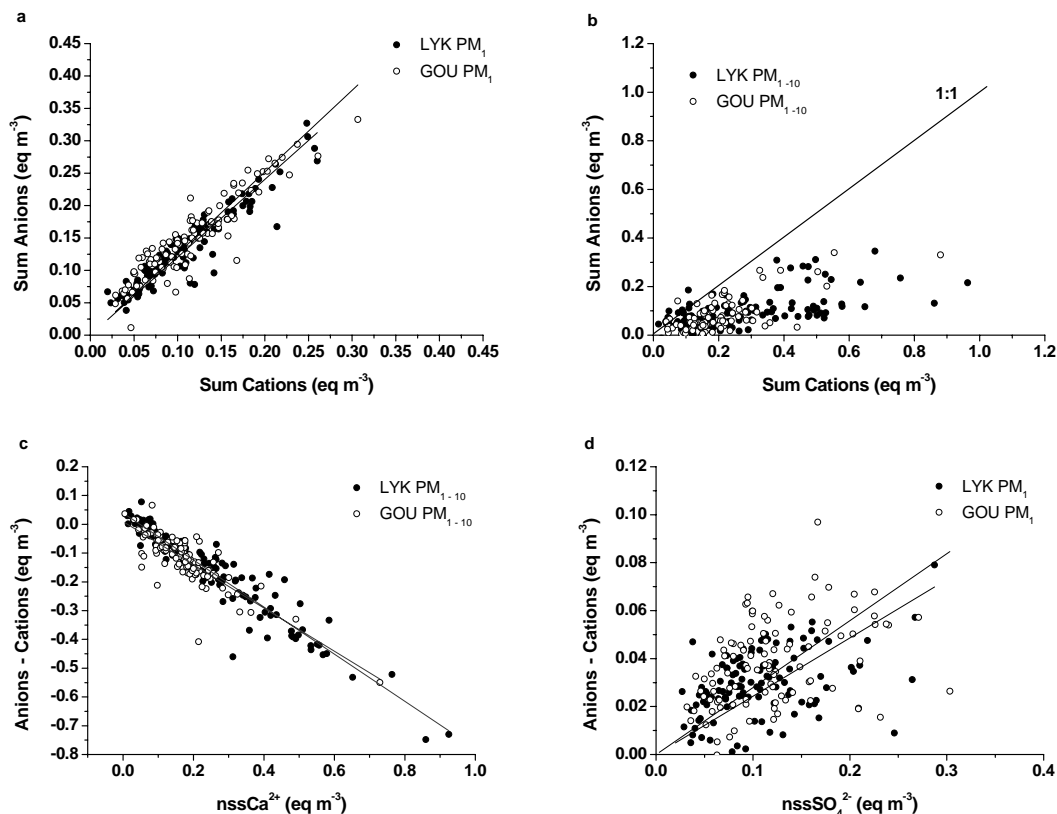


Fig. 7. Ionic balance (eq m^{-3}) for both GAA stations for (a) fine and (b) PM₁₀ fractions. Anions deficiency versus nssCa²⁺ in PM₁₀ samples (c) and nssSO₄²⁻ in PM₁ samples (d).

– sum anions, in eq m^{-3}), indicating that CO_3^{2-} is most probably the missing anion in the coarse aerosol fraction. Similar findings for the ionic balance in coarse particles were reported by Karageorgos and Rapsomanikis (2007) for a site in central Athens. Silanpää et al. (2005) also identified carbonate associated with Ca^{2+} , as an important constituent of coarse PM in the atmosphere of GAA.

A significant correlation is also found between SO_4^{2-} and the cation deficiency in the fine fraction, indicating possible association of H^+ with SO_4^{2-} in both sites. Indeed nss- SO_4^{2-} neutralization by NH_4^+ was incomplete throughout the year with NH_4^+ versus nss- SO_4^{2-} slope being below unity (varying from 0.69 to 0.73 during warm and cold periods respectively), suggesting that 27–31 % of SO_4^{2-} could be associated with H^+ . If ammonium nitrate formation during the cold period is considered, then neutralisation of nss- SO_4^{2-} by NH_4^+ is even smaller (0.61 instead on 0.73). Similar temporal pattern for H^+ in fine particles was also reported by Siskos et al. (2001) based on one year of measurements in central Athens. However acidification in the GAA is higher when compared to FKL by almost a factor of 2 to 3 (0.15 in FKL versus 0.35 to 0.39 in GAA) which could have possible implications on secondary organic aerosol (SOA) formation. Indeed laboratory studies suggest that heterogeneous acid-catalyzed reactions in the particle phase are important mechanisms for SOA formation and that particle acidity has an impact on SOA yield (Hallquist et al., 2009). Thus the exact role of acidity in SOA production in GAA atmosphere needs further investigation.

3.3.3 Temporal variability of the main ionic species

As mentioned, the three main ions observed in all locations are SO_4^{2-} , NO_3^- and Ca^{2+} . These ions represent three different major sources categories: secondary particle formation processes (SO_4^{2-}), primary anthropogenic sources related to fuel combustion and vehicular circulation (NO_x) and finally natural sources producing geological particles (Ca^{2+}), respectively. A very similar monthly distribution pattern is observed for SO_4^{2-} and NO_3^- and to a lesser extent in the case of Ca^{2+} in the GAA (Fig. 8). High spatial homogeneity for sulfate and nitrate is indicated by the significant correlations with slopes close to 1, as stated below. Local sources of crustal particles at LYK could account for slope smaller than 1 observed for nss- Ca^{2+} . Indeed for the PM_{10} fraction, the correlations (r) between LYK and GOU were 0.93 for SO_4^{2-} with slope of 1.1, while 0.81 for NO_3^- with slope of 1.0. For PM_{10} the correlations (r) were 0.94 for SO_4^{2-} with slope of 0.9 and 0.81 with slope of 0.9 for NO_3^- . Whilst for Ca^{2+} the slope was 0.6 and the correlation was weaker ($r = 0.54$).

The temporal variability for each one of the main ions is presented below.

Non-sea-salt sulfate (nss- SO_4^{2-}): nss- SO_4^{2-} presents a prominent peak in winter (only in GAA) and summer (in all

sites; Fig. 8a). The summer peak could be related to enhanced photochemistry, lack of precipitation, low air mass renovation at regional scale or the increment of the summer mixing layer depth favouring the regional mixing of polluted air masses (Mihalopoulos et al., 2007). Note also that during summer air masses are almost exclusively originating from Central/Eastern Europe which bring higher levels of SO_2 than the rest of the wind sectors (Kouvarakis et al., 2002a; Sciare et al., 2003). Sulfate has also natural sources, namely oxidation of marine emitted dimethylsulfide (DMS), peaking also during summer time (Kouvarakis and Mihalopoulos, 2002).

The secondary maxima of SO_4^{2-} concentration commonly recorded during the winter could concur with the anticyclonic pollution episodes as also indicated by the high nitrate levels (Querol et al., 2009).

In the case of nss- SO_4^{2-} there is a clear decreasing gradient from urban to suburban and to natural sites (5.3, 5.0 and $4.2 \mu\text{g m}^{-3}$ in PM_{10} for GOU, LYK and FKL, respectively). In addition a clear seasonal variation is observed in the GAA/FKL ratio regarding nss- SO_4^{2-} at both GAA sites. Indeed during the warm season the GAA/FKL nss- SO_4^{2-} ratio ranges between 1.1–1.25, indicating that sulfur levels above Greece are largely controlled by long-range transport and processes evolving at a large spatial scale. On the other hand during winter the GAA/FKL nss- SO_4^{2-} ratio significantly increases ranging from 1.4–1.5. This behavior indicates significant contribution from local anthropogenic sources (combustion of sulfur-rich diesel for domestic heating) within the GAA during the cold-season.

Nitrate (NO_3^-): as expected higher contributions of nitrate are found at the urban and suburban sites compared to the background site due to the presence of local sources of NO_x in conjunction with thermodynamic conditions producing stable ammonium nitrate (PM_{10} : 2.7, 2.5 and $1.7 \mu\text{g m}^{-3}$; PM_{10} : 0.8, 0.8 and $0.1 \mu\text{g m}^{-3}$, for LYK, GOU and FKL respectively; Fig. 8c, d). In the GAA, NO_3^- presents strong seasonal variability in both PM_{10} and PM_{10} , with higher values during colder months, which, as in the case of SO_4^{2-} , are likely to originate from local pollution sources and especially vehicular traffic. On the contrary, no clear seasonal trend is observed at FKL. The summer minimum of NO_3^- in the GAA, which is more prominent in the fine mode, is due to instable ammonium nitrate formation during that period (Harrison and Pio, 1983; Querol et al., 2004). No ammonium nitrate formation occurs during the warm season due to high temperature in agreement with Eleftheriadis et al. (1998). As reported previously, the nitrate partitioning over the fine and coarse fractions is quite variable and on average, about 94 % of particulate nitrate was associated with coarse particles at FKL and 69–72 % at GOU and LYK. In the GAA yet again a clear seasonal trend is evident for nitrate partitioning with the lowest values in winter (down to 50 % in January) due to ammonium nitrate formation.

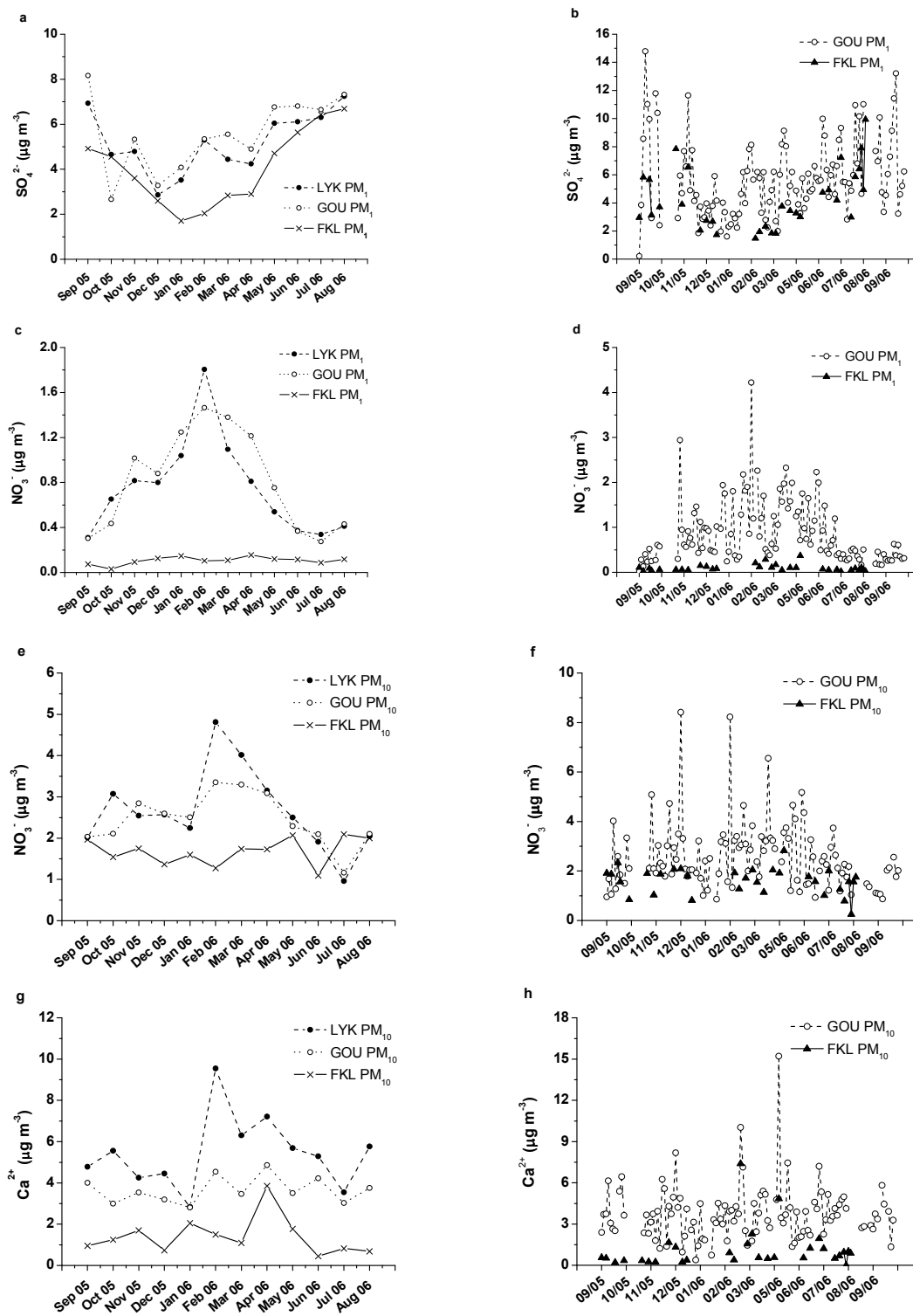


Fig. 8. Seasonal (a, c, e, g, i, k and m) and daily (b, d, f, h, j, l and n) variations ($\mu\text{g m}^{-3}$) for SO_4^{2-} , NO_3^- , Ca^{2+} , $\text{C}_2\text{O}_4^{2-}$ and K^+ in PM_{10} and for NO_3^- and Na^+ in PM_{10} samples.

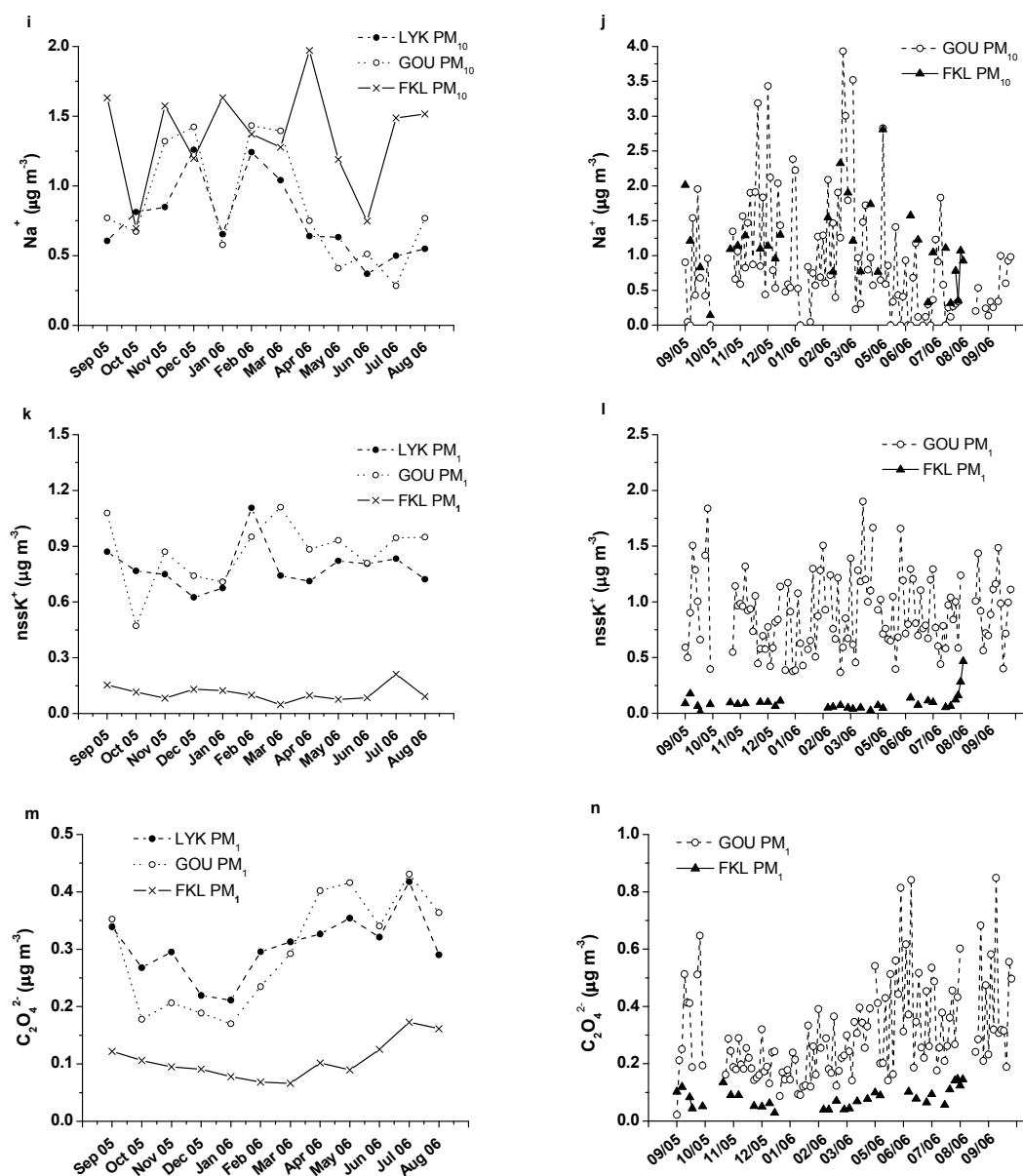


Fig. 8. Continued.

By comparing the NO_3^- levels in PM_{10} , the difference between GAA and FKL minimized during the warm season (2.1 and $1.8 \mu\text{g m}^{-3}$, respectively). On the other hand local anthropogenic sources within the GAA dominates during the cold season as for PM_{10} the GAA/FKL ratio is reaching values up to 2. Similar trend also existed for NO_3^- in the PM_1 fraction. However the GAA/FKL ratio during winter was much pronounced and reached values as high as 8 that is almost double the factor of 4–5 during the warm season. This observation is in agreement with ammonium nitrate formation in the GAA during winter.

Non-sea-salt calcium (nss-Ca^{2+}): nss-Ca^{2+} is considered as an effective tracer of crustal sources in the area (Sciare

et al., 2005; Vrekoussis et al., 2005). Despite the vicinity of FKL to N. Africa, nss-Ca^{2+} levels in PM_{10} were significantly higher at the GAA sites compared to background one (up to 3.5 times higher; Fig. 8g). Additional sources of nss-Ca^{2+} in the GAA such as dust resuspension from traffic and/or local activities (case of PM_{10} at LYK) can explain this trend. By plotting nss-Ca^{2+} as a function of coarse mass for all sites although a significant correlation is obtained from all sites (r^2 of 0.67–81), the slopes differ significantly ranging from 0.03 at FKL to 0.12 at LYK and GOU, respectively. Considering that all nss-Ca^{2+} at FKL is due to regional dust, the remaining part for the GAA could be explained by “local dust”, most probably soil dust and car/road abrasion. Thus

local sources in the GAA can account for almost 75 % of the observed nss-Ca^{2+} . The temporal variation of Ca^{2+} concentrations in GAA reveal higher levels during the warm season (Fig. 8d), when prevailing weather conditions (reduced relative humidity, leading to the drying up of surfaces) favor road dust resuspension (Nicholson and Branson, 1990). “Local dust” can significantly influence atmospheric chemistry with GAA. Indeed field and laboratory studies indicated that mineral dust particles can serve as reaction surfaces for different species, including those of man-made origin (Mamane and Gottlieb, 1992; Koçak et al., 2007). Gaseous species such as SO_2 , N_2O_5 , HNO_3 and O_3 can react with mineral dust particles (Mamane and Gottlieb, 1992; Dentener et al., 1996) and result in the modification of optical properties, size distributions and chemical composition of the aerosols (Kouvarakis et al., 2002b; Vrekoussis et al., 2005).

Other ions: Fig. 8i–n present the seasonal variation of Na^+ , non-sea-salt potassium (nss-K^+) and oxalate ($\text{C}_2\text{O}_4^{2-}$) at the three sites. Na^+ and nss-K^+ can be used as tracers of sea-salt and of biomass burning influences, respectively. $\text{C}_2\text{O}_4^{2-}$ has multiple sources such as biomass burning and multiphase oxidation of volatile organic compounds (VOC; Myriokefalitakis et al., 2011). For nss-K^+ and $\text{C}_2\text{O}_4^{2-}$ higher values are observed at GAA compared to FKL (5 and 3 times, respectively) highlighting the importance of local sources, including biomass burning and VOC emissions. At all locations $\text{C}_2\text{O}_4^{2-}$ presents a summer maximum due to enhanced photochemistry and increased VOC emissions (especially isoprene and terpenes). For nss-K^+ although a double peak can be seen at FKL due to regional biomass burning activities (Sciare et al., 2008), no clear seasonal variation exists in GAA. Most probably intense local sources of nss-K^+ mask any regional signal. Finally for Na^+ the slightly higher values at FKL, especially during summer, are due to the vicinity to the sea shore and the high wind speeds occurring in the area. In GAA sea-salt contribution calculated based on Na^+ observations (sea salt = $3.27 \times [\text{Na}]$) accounts for about $2.5 \mu\text{g m}^{-3}$ that is 4–5 % of PM_{10} mass.

3.4 Atmospheric concentration of trace metals

Trace metals were analyzed in PM_{10} samples collected at FKL, LYK and GOU and as well as in the PM_1 fraction sampled at FKL and LYK and can be used as tracers of specific sources such as Earth’s crust, combustion etc. The annual average concentrations of all studied metals are presented in Table 3 and Fig. 9a. In general, the levels of the studied trace metals in PM_{10} are in good agreement with values reported for Athens (Manalis et al., 2005; Karegeorgos and Rapsomanikis, 2007; Karanasiou et al., 2007). Lead concentrations have further reduced through the years (2001 to 2006), since non-catalyst equipped vehicles are gradually removed from circulation. For PM_1 , to our knowledge, this is the first time that trace metals are reported. It is therefore interesting to analyze their size distribution.

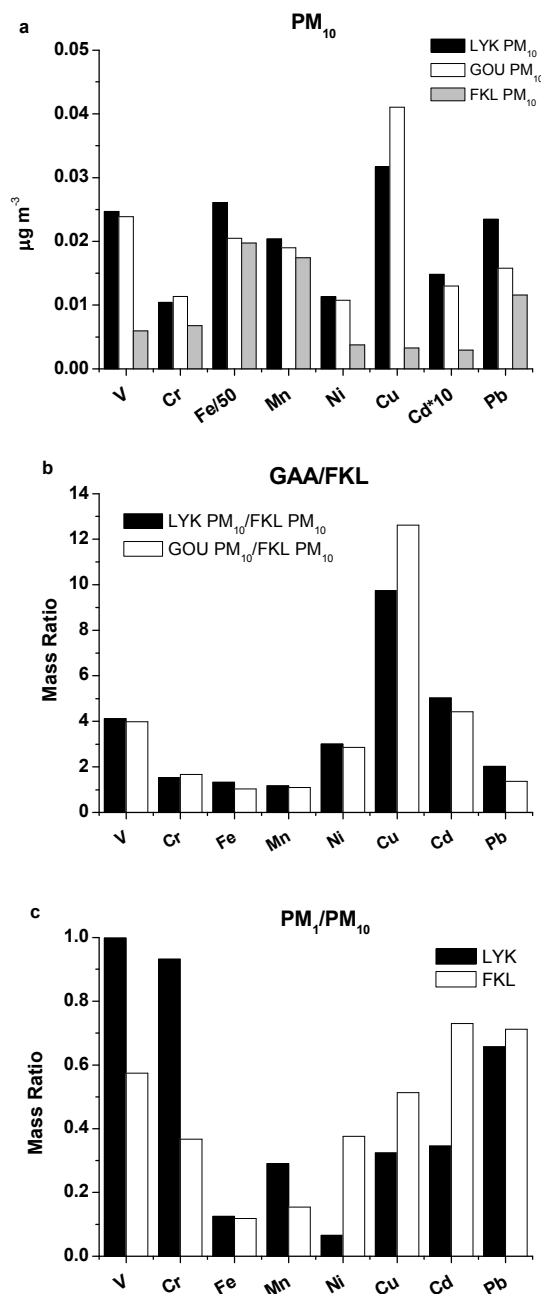


Fig. 9. Annual average concentrations ($\mu\text{g m}^{-3}$) of the studied metals for the three stations (a) in PM_{10} , (b) GAA/FKL mass ratio and (c) $\text{PM}_1/\text{PM}_{10}$ mass ratio.

The $\text{PM}_1/\text{PM}_{10}$ ratios of trace metal concentrations are shown in Fig. 9b. The majority of the measured trace metals are found in the coarse mode (ratios lower than 0.5) as in the case of the crust originated trace metals (e.g. Fe and Mn). Only Cr, V and Pb, especially in the GAA, are confined in the fine mode, this is indicative of anthropogenic sources origin. Generally and apart from Cr, the distribution of metals in the GAA presents similarities with that observed at FKL.

Table 3. Annual mean concentrations of metals ($\mu\text{g m}^{-3}$) measured at Lykovrissi (PM_{10} and PM_{10}) and Goudi (PM_{10}) from September 2005 to August 2006 and comparison with literature data.

PM ($\mu\text{g m}^{-3}$)	Karageorgos and					
	Lykovrissi PM_{10}	Goudi PM_{10}	Finokalia PM_{10}	Rapsomanikis (2007) PM_{10}	Manalis et al. (2005)	
					PM_{10} GAA (urban area)	PM_{10} GAA (THR)
V	0.025	0.024	0.006	0.016–0.019	0.010	0.004
Cr	0.010	0.011	0.007	0.007–0.011	0.013	0.010
Fe	1.304	1.024	0.987	1.067–1.430	–	–
Mn	0.020	0.019	0.017	0.021–0.031	0.019	0.004
Ni	0.011	0.011	0.004	0.009–0.010	0.011	0.009
Cu	0.032	0.041	0.003	0.052–0.220	0.052	0.013
Cd	0.001	0.001	0.000	–	0.003	0.002
Pb	0.023	0.016	0.012	0.042–0.060	0.047	0.025

Figure 9c depicts the ratios of the levels of trace metals in PM_{10} measured in the GAA during this work to those reported at FKL. Based on the GAA/FKL ratio metals can be divided into two categories: those having a ratio below 2 and those above. A ratio lower than 2 or even closer to 1 is calculated for Fe, Mn and Pb. Long range transport from arid Sahara represented the main source of Fe and Mn. Trajectory analysis confirmed our assumption since the above trace metals present the highest values in air masses originating from that area. Pb is also associated with transport from the Southern sector as it has been used as additive in gasoline in some North African countries.

On the other hand V, Ni, Cd and especially Cu appear to have a local origin since the GAA/FKL ratio is higher to 2. Stationary combustion of fossil fuels for V, Ni and Cd and cars vehicular circulation for Cu (Weckwerth, 2001) are considered as the main sources of the above metals. This is also confirmed by the lack of correlation between these elements within the GAA suggesting significant contribution from local rather regional sources.

3.5 Chemical mass closure

Chemical composition is defined by three main classes: Dust, Ionic Mass (IM) and “unidentified”, the later accounting mainly for elemental carbon (EC) and organic matter (OM). IM is the sum of the anions and cations measured. Dust levels are calculated using Fe or Mn as indicator of crustal material assuming an upper crust relative ratio as described by Guieu et al. (2002) and Wedepohl (1995). Both estimations gave comparable results for dust within 20%. Figure 10 presents the chemical mass closure on a monthly basis for PM_{10} fraction in LYK and GOU, respectively.

In total, crustal elements can account for 36–46% of PM_{10} mass (depending on the element used and location) in both GAA sites, with maximum during the transition period (spring and autumn). This high percentage is related to the frequent occurrence of Saharan dust transport to the eastern Mediterranean during transition season (Kalivitis et al., 2007 and references therein) and to “local” dust, due to soil dust and car/road abrasion. Regional dust levels derived from the measurements at FKL estimated to be of the order of $10 \mu\text{g m}^{-3}$ (Querol et al., 2009). Thus “local” dust accounts for 13–18 $\mu\text{g m}^{-3}$, i.e. 20–28% of the PM_{10} levels recorded in GAA. According to the Directive 2008/50/EC, contributions of natural source can be subtracted to daily overall PM_{10} concentrations when calculating the number of exceedances. By deducing the regional dust levels the number of exceedances significantly decreases both in LYK (39% from 51%) and GOU (22% from 44%).

IM, mainly secondary aerosol contribution (nss-SO_4^{2-} , NO_3^- and NH_4^+) shows lower contributions that minimizes in winter and sharply increased from winter to summer. On a yearly basis, ionic composition, accounts for about 23–25% of the total mass at both GAA sites. On average ionic mass plus crustal mass represent 70% and 67% of the gravimetrically determined mass for PM_{10} samples in LYK and GOU respectively, whilst 67% for PM_{10} samples in LYK. The unidentified mass (30–33% in PM_{10}) might be attributed to OM, EC which was not measured and accounted for the remaining of the PM_{10} mass (Koulouri et al., 2008b). This percentage is in very good agreement with results reported by earlier studies in central Athens. Prosmiris et al. (2004) have accounted the contribution of elemental and organic carbon to PM_{10} at 43% at Goudi. Sillanpää et al. (2005, 2006) estimated POM contribution to PM at about 35 and 25% for $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ respectively. Grivas et al. (2007) calculated the contribution of the sum of POM and EC to $\text{PM}_{2.5}$ at 31% for central Athens. Pateraki et al. (2011) measured aerosol chemical composition in $\text{PM}_{2.5}$ and PM_{10} samples

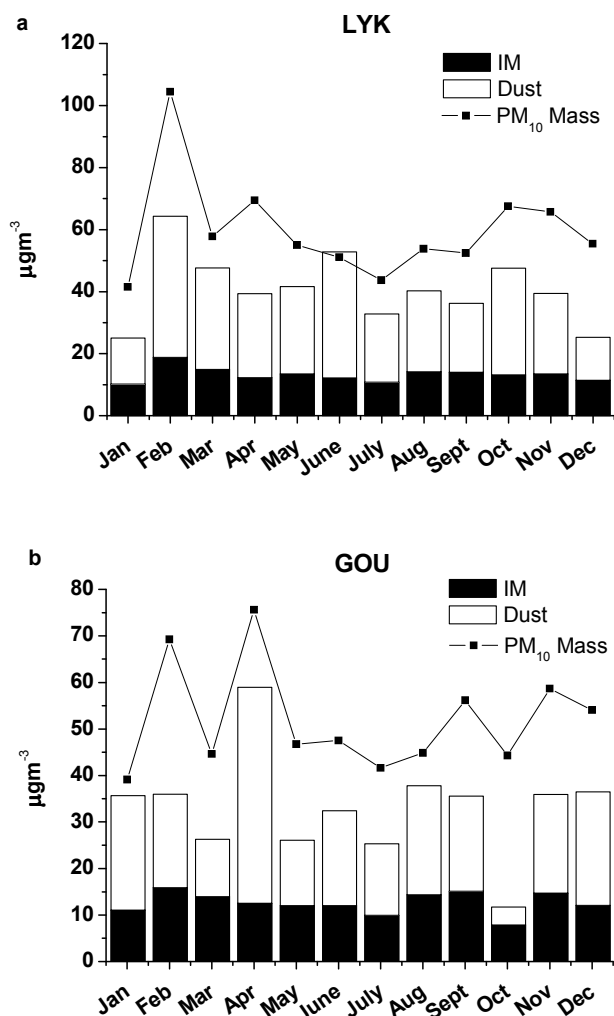


Fig. 10. Mass Closure (Ionic Mass and Dust) versus measured PM₁₀: (a) LYK and (b) GOU.

collected in 3 locations around Athens in summer and winter in 2008. POM and EC accounted for 32 and 37 % of the PM_{2.5} and PM₁ mass respectively in agreement with our conclusions reported in the present manuscript.

3.6 Local versus regional contribution to PM mass

By considering mass and chemical composition measurements at FKL as representative of the regional background, the contribution of local sources at both GAA sites can be estimated for both PM₁ and PM₁₀ fractions. The results are presented in Fig. 11. In this figure two columns are presented for each GAA site for both PM₁ and PM₁₀ fractions. The first column corresponds to PM regional background (FKL) and the second to the local sources (PM_{GAA} – PM_{FKL}). As expected dust from local sources (wind dust and car abrasion) contribute significantly to the local PM₁₀ mass (up to 33 % of

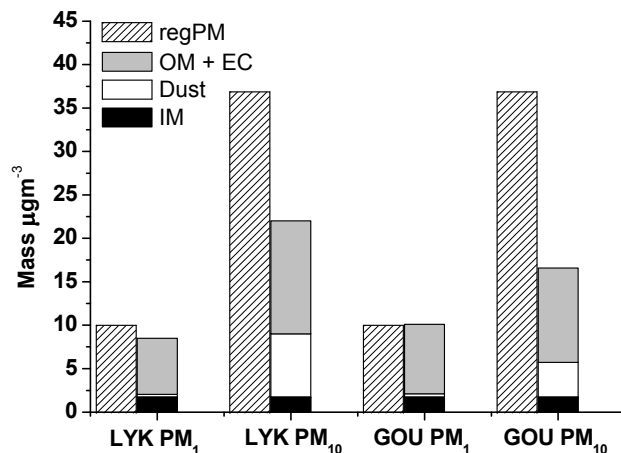


Fig. 11. Relative contribution of regional and local sources to PM levels in GAA. Regional PM (regPM) corresponds to PM measurements at FKL.

PM mass). The contribution of IM ranges from around 10 % in local PM₁₀ to 20 % in local PM₁).

Carbonaceous material (POM and EC) seems to be the main contributor of the missing local PM mass (up to 79 % in PM₁). Simultaneous organic and elemental carbon measurements performed during winter and summer of 2008 in various locations around the GAA and at FKL as background site confirmed the above conclusion (Pateraki et al., 2011 and Mihalopoulos, unpublished data).

4 Conclusions

The chemical composition of size-segregated aerosols (PM₁, PM_{2.5} and PM₁₀) was determined at three sites: remote background FKL, suburban LYK and urban GOU from September 2005 to August 2006 in order to identify the major factors controlling levels and chemical composition of aerosols in GAA and to evaluate the role of local versus regional sources.

Although our sampling covered only the one third of the year, the EU annual limit value of 40 µg m⁻³ for PM₁₀ was exceeded at both urban and suburban sites in GAA and frequent exceedances of the 24-h limit value of 50 µg m⁻³ (more than the allowed limit of 35) were recorded at all GAA locations. The respective percentages for PM₁₀ concentrations over 40 µg m⁻³ were 72 % and 79 % for LYK and GOU.

Simultaneous measurements of PM₁ and PM₁₀ can highlight natural contributions, since PM₁ is closely related to anthropogenic aerosol and thus better represent the anthropogenic particle fraction. For air quality monitoring policy our results imply that PM₁ would be a better indicator for fine/anthropogenic aerosols and should be also continuously monitored. Atmospheric Chemical Speciation Monitor (ACSM) could be used for continuous PM₁ chemical

composition measurements with a relatively low measurement uncertainty for such small mass fraction.

During the warm season there is no significant difference in PM₁ and sulfur between urban and natural locations, highlighting the role of long-range transport. On the other hand local anthropogenic sources dominated during the cold season.

Regarding the coarse fraction a significant contribution from soil was found in urban locations all over the year. The difference in the slope of Ca²⁺ versus PM between rural and urban locations indicated that about 1/3 is of natural origin suggesting traffic-related aerosol sources at both sites in Athens in addition to the regional background of FKL Regional dust levels derived from the measurements at FKL estimated to be of the order of 10 µg m⁻³. By deducing the regional dust levels the number of exceedances significantly decreases both in LYK (39 % from 51 %) and GOU (22 % from 44 %).

Chemical speciation data showed that PM in the GAA was characterized by relatively constant contribution of ionic mass, 23–25 % of the PM₁₀ mass, with SO₄²⁻ and NO₃⁻ as the dominant ionic species. Crustal material was accounted for almost half of the mass contribution (46 %), with a maximum during the transition period (spring and autumn). On a yearly basis, ionic and crustal mass represent 70 % and 67 % of the gravimetrically determined mass for PM₁₀ samples in LYK and GOU, respectively. The unidentified mass might be attributed to OM and EC, in agreement with the results reported by earlier studies in central Athens.

The contribution of local sources at both GAA sites was also estimated by considering mass and chemical composition measurements at FKL as representative of the regional background. Carbonaceous material (POM and EC) seemed to be the main contributor of the local PM mass (up to 79 % in PM₁). Dust from local sources (mainly car abrasion/road dust) contributed significantly to the local PM₁₀ mass (up to 33 %). The contribution of local IM ranged from around 10 % in PM₁₀ to 20 % in PM₁ given the role of regional sources on the measured SO₄²⁻ and NO₃⁻ levels.

Note however that our sampling only covers 1/3 of the year and it can only serve as an indicator for PM₁₀ annual concentration in the GAA. Continuous and long term measurements of PM₁ and PM₁₀ fractions both in the GAA and an urban background site (FKL or THR) associated with complete chemical composition (ionic mass, dust and carbonaceous material) are clearly needed to accurately investigate the relative contributions of natural/anthropogenic sources in the GAA and check the efficiency of abatement strategies. This approach should be also applied to other Mediterranean megacities such as Istanbul and Cairo to better assess the role of these hot spots in the atmospheric quality and climate of the Eastern Mediterranean.

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