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Mass and chemical composition of size-segregated aerosols (PM_1, $PM_{2.5}$, PM_{10}) 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 mass and chemical composition measurements of size segregated particulate matter (PM: PM_1, $PM_{2.5}$ and PM_{10}) were carried out from September 2005 to August 2006 at three locations: one urban (Goudi, Central Athens) and one suburban (Lykovrissi, Athens) in GAA and the third in a regional background site (Finokalia, Crete).

The two stations in GAA exceeded the EU-legislated PM_{10} limit values, both in terms of annual average (59.0 and 53.6 $\mu g\,m^{-3}$ for Lykovrissi and Goudi, respectively) and of 24-h value, while the concentration levels at the remote site of Finokalia indicated an elevated background. High levels of $PM_{2.5}$ and PM_1 were also found at all locations (23.5 and 18.6 for Lykovrissi, while 29.4 and 20.2 $\mu g\,m^{-3}$ for Goudi, respectively).

Significant correlations were observed between same PM fractions at both GAA sites indicating important spatial homogeneity within GAA. During the warm season, the PM_1 ratio between the GAA and the background site ranged from 1.1 to 1.3. On the other hand this ratio was significantly higher (1.6–1.7) during the cold season highlighting the role of long-range transport and local sources during the warm and cold seasons respectively. Similar seasonal and geographical patterns were observed for nss-SO_4^{2-}, a secondary compound characteristic of regional sources, confirming the above hypothesis.

Regarding the coarse fraction no such seasonal trend was observed for both GAA sites with their ratio (GAA site/Finokalia) being higher than 2 indicating significant contribution from local sources such as road dust and/or constructions as confirmed by Ca^{2+} measurements.

Chemical speciation data showed that on a yearly basis, ionic and crustal mass represent up to 78% of the gravimetrically determined mass for PM_{10} samples in GAA. The unidentified mass might be attributed to organic carbon (OC) and elemental carbon (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 Finokalia as representative of the regional background. Carbonaceous material, Particulate Organic Matter (POM) and EC, seemed to be the main contributor of the local PM mass within GAA (up to 62% in PM_1). Dust from local sources (mainly resuspension) contributed also significantly to the local PM_{10} mass (up to 33%).

1 Introduction

The interest on aerosols 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 (PM) 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 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).

Long term monitoring of PM concentrations in the Greater Athens Area (GAA; Chaloulakou et al., 2003, 2005; Grivas et al., 2004a, 2008a) registered the occurence of a significant number of PM exceedances above the limits set by EU legislation and point to the need for abatement strategies. However to propose such strategy precise knowledge of PM sources is a prerequisite. For this the relative contribution of natural and anthropogenic sources and the role of local versus long range sources need to be determined. The EU directive (2008/50/EC) 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 and a natural background site (Finokalia, Crete) 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 PM_1, $PM_{2.5}$ and PM_{10} sampling was conducted in the GAA, at Lykovrissi and Goudi during the period September 2005–August 2006. Lykovrissi (LYK), is a residential suburban site at the Northern part of GAA, affected by primary emission sources and particle transport from the southern part of the GAA basin. Goudi (GOU) is an urban roadside located in the center of GAA and it is affected by heavy traffic-related activities. Details on the sites characteristics can be found in Grivas et al. (2004b) and Grivas and Chaloulakou (2006).

Size-segregated aerosol samples were also collected at Finokalia (FKL), a regional background site located on Crete Island in the Eastern Mediterranean during the period July 2004–July 2006. 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 GAA, simultaneous 24-h PM_1, $PM_{2.5}$, and PM_{10} measurements were conducted using Partisol low volume samplers with cyclonic separators for PM_1 at both sites and for $PM_{2.5}$ at LYK, while Harvard impactors were used for PM_{10} 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 one sample every-3 days, collecting on average 10 samples per month for both sites and all three size fractions.

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 $D_a < 1.3\,\mu$m, hereafter as PM_1) and coarse particles ($D_a > 1.3\,\mu$m). The inlet situated before the VI has a cut-off size of 10 µm. Polytetrafluoroethylene (PTFE) filters (Millipore Fluoropore; pore size 3.0 µm; diameter 47 mm) were used in the VI sampler (henceforth PTFE-VI). 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 preceeding the SDI has a cut-off size 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.

In total, 127 PM_1, 127 $PM_{2.5}$ and 126 PM_{10} samples were collected at LYK, 114 PM_1, 109 $PM_{2.5}$ 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-}, $C_2O_4^{2-}$, 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 PM mass concentrations

3.1.1 Levels

The monthly mean observations of PM_1, $PM_{2.5}$ and PM_{10} at the three stations are shown in Figs. 1a–c. The arithmetic mean and standard deviation of PM_1, $PM_{2.5}$ and PM_{10} ($\mu g\,m^{-3}$) for the samples collected at the three locations are given in Table 1. There was a noteworthy upward trend for PM_1 and $PM_{2.5}$ levels when moving from natural 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 ($53.6\,\mu g\,m^{-3}$ and $59.0\,\mu g\,m^{-3}$ at GOU and LYK), exceeded the limit value of $50\,\mu g\,m^{-3}$ in 44% and 51% of the samples from GOU and LYK respectively. Even at the background station of FKL, with average PM_{10} of $37\,\mu g\,m^{-3}$, the $50\,\mu g\,m^{-3}$ value was exceeded 6% during the year suggesting elevated background aerosol levels in the area under specific meteorological conditions.

Statistically significant correlations were observed between the GAA stations for all PM fractions ($p = 1.6 \times 10^{-10}$, 6.7×10^{-10} and 2.7×10^{-10} for PM_1, $PM_{2.5}$ and PM_{10} respectively) indicating the existence of significant spatial homogeneity of PM within the GAA.

3.1.2 PM ratios

The variability of the PM fractions was examined at all locations. Strong correlations were observed between $PM_{2.5}$ and PM_{10} ($r = 0.63$) for both sites in GAA. The significant percentage of crustal elements content in $PM_{2.5}$ (see Sect. 3.4) is one for the factors responsible. The $PM_{2.5}/PM_{10}$ ratios for the suburban, urban and natural background sites were 0.37, 0.56 and 0.58 respectively. The smaller ratio at LYK is relevant to the land use characteristics of the surrounding area (mainly unpaved roads and non built land), which favor the suspension of soil particles, as demonstrated by the high nss-Ca^{2+} levels (see Sect. 3.2.3). The $PM_{2.5}/PM_{10}$ ratio observed for central Athens site (GOU) is in agreement with the ratios reported by Chaloulakou et al. (2003, 2005), Sillanpää et al. (2005) and Karageorgos and Rapsomanikis (2007) for measurements conducted at same-type locations.

On the other hand the regression between PM_1 and PM_{10} presented an important degree of scattering (Fig. 2). For instance at FKL the relation between PM_1 and PM_{10} (Koulouri et al., 2008b) revealed the existence of two data subsets, corresponding to non-dust and dust events. The first had a slope of 0.90 manifesting the dominance of pollution particles, while the poorer correlation ($r = 0.49$) depicted the variability of submicron particle sources in the area. The second demonstrated higher PM_{10} levels for the same order of PM_1 values (slope 9.6) as the non-dust case with a significant correlation ($r = 0.89$) related to transported dust.

As in FKL, PM_1/PM_{10} ratios between the two GAA stations revealed also the existence of two data pairs corresponding to dust and non-dust events with PM_1/PM_{10} 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, PM_1 rather than $PM_{2.5}$ monitoring can provide an estimation of the anthropogenic fraction. On that account in the following discussion fine and coarse fractions will correspond to PM_1 and PM_{10-1} respectively.

3.1.3 Seasonal variation of PM fractions

The monthly variations of PM_1, $PM_{2.5}$ and PM_{10} at all sites ($\mu g\,m^{-3}$) are displayed in Fig. 1. To better understand the PM variability a brief presentation of the prevailing meteorology in the studied area is presented. On a yearly basis, more than half (66%) of the air masses arriving in the area originate from the North sector, which covers Central and Eastern Europe as well as part of western Turkey. This northern contribution reaches almost 85% during summer. On the other hand, Sahara dust events are very frequent in the area during spring and autumn contributing up to 25% of the prevailing air masses.

Very high levels of PM_{10} and $PM_{2.5}$ were 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 PM_{10} and $PM_{2.5}$). Note that the dust events were not visible in PM_1.

At all locations, the seasonal variation of PM fractions was examined after separation in warm (April to September) and cold season (October to March). During the warm season the PM_1 ratio between the GAA and background site ranged 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 GAA during the winter (e.g. heating), associated with a more shallow boundary layer can be accounted for the difference during the cold season. On the other hand during the warm season, traffic related emissions were comparably less intense (this is a stable temporal pattern for the GAA) and the increased atmospheric turbulence favored ventilation of the GAA but also long range conditions (see below Sect. 3.2). An example of regional influence on PM_1 levels recorded at all locations is depicted in Fig. 3.

Regarding the coarse fraction (PM_{10-1}) no seasonal trend was observed. Indeed the GOU/FKL ratio varied 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.

3.2 Ionic composition

3.2.1 Levels and size segregated distribution of water soluble ions

As in the case of FKL (Koulouri et al., 2008b), 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 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.

In PM_{10} 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 al., 2006; Karageorgos and Rapsomanikis, 2007). For PM_1 to our knowledge this is the first time that water soluble ions are reported.

The PM_1/PM_{10} ratios for all studied water soluble ions are shown in Fig. 4d. Water-soluble ions (Cl^-, Mg^{2+} and Ca^{2+}) were 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. Nitrate (NO_3^-) presented different behavior at FKL and in GAA. At FKL on average, about 94% of particulate nitrate (NO_3^-) was associated with coarse particles, strongly indicating that it was chemically bounded mainly with alkaline ions (Mamane and Gottlieb, 1992; Pakkanen et al., 1999). The most likely formation pathway for particulate nitrate (NO_3^-) is the reaction of gaseous nitric acid or some other nitrogen compounds with sea salt and mineral dust particles (Metzger et al., 2006). In GAA, a significant portion of NO_3^- (about 30%) was found in fine mode, indicating ammonium nitrate formation (see further Sect. 3.2.3 on NO_3^-).

The mass concentrations of oxalate ($C_2O_4^{2-}$) and non-sea salt sulfate (nss-SO_4^{2-}, estimated using Na^+ as a sea salt tracer) were mainly found in the fine mode (70–75% and 72–88%, respectively in the GAA). For NH_4^+ it is interesting to note the lower values observed in PM_{10} compared to $PM_{2.5}$ and PM_1. This behavior has been also reported by other authors (Querol et al., 2009) and was due to NH_4^+ volatilisation from PM_{10} owing to their alkaline character and ammonium nitrate formation. 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). On the other hand as no intercomparison between the different samplers used was performed, the use of VI impactors at FKL could partly explain the difference observed between this site and the GAA ones for the ammonium PM_1/PM_{10} ratio.

3.2.2 Ionic balance

The ionic balance can be employed to determine potentially missing ionic species. For this purpose, ionic balance was calculated both for the fine and PM_{10} fractions of the aerosol particles for both GAA stations. Plots of total anions equivalents (eq) against total cations equivalents for each size class are presented in Figs. 5a and b. The slope of the regression line for PM_{10} particles indicated a value smaller than unity (slope = 0.3 to 0.5, $r = 0.63$ to 0.77), which may be due to the existence of CO_3^{2-} in this size fraction, which has not been measured using ionic chromatography. 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 PM_{10} and fine fractions, respectively (Figs. 5c and 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 against the anions deficiency (sum cations - sum anions, in equivalents), indicating that CO_3^{2-} was 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 was also found between SO_4^{2-} and the cation deficiency in the fine fraction, indicating possible association of H^+ with SO_4^{2-}. 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), indicating that 27–31% of SO_4^{2-} could be associated with H^+. 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.

3.2.3 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), respectively. In addition these ions followed a very similar spatial distribution pattern in the GAA (Fig. 6). Indeed for the PM_1 fraction, the correlations (r) between LYK and GOU were 0.93 for SO_4^{2-} with slope of 1.1 and 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 ($r = 0.54$). All the above significant correlations with slopes close to 1, indicate high spatial homogeneity for sulfate, nitrate and in a lesser extend for nss-Ca^{2+} within GAA. Local sources of crustal particles at LYK could account for slope smaller than 1 observed for nss-Ca^{2+}.

Below the temporal variability for each of the main ions is presented.

Non-sea-salt sulfate (nss-SO_4^{2-}): nss-SO_4^{2-} presented a prominent peak in winter (only in GAA) and summer (in all sites; Fig. 6a). 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). The secondary maxima of SO_4^{2-} concentration commonly recorded during 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 was a clear decreasing gradient from urban to suburban and to natural sites (5.3, 5.0 and 4.2 $\mu g\,m^{-3}$ in PM_1 for GOU, LYK and FKL, respectively). In addition a clear seasonal variation was observed in the GAA/FKL ratio regarding nss-SO_4^{2-} or ammonium sulfate, as nss-SO_4^{2-} is mainly associated with NH_4^+ at both GAA sites. Indeed during the warm season the GAA/FKL ratio ranged from 1.0–1.1 (when ammonium sulfate is considered) or from 1.1–1.25 in the case of nss-SO_4^{2-}, 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 significantly increased ranging from 1.3 to 1.4–1.5 when ammonium sulfate or nss-SO_4^{2-} were respectively considered. This behavior indicates significant contribution from local anthropogenic sources (combustion of sulfur-rich diesel for domestic heating) within GAA during the cold-season.

Nitrate (NO_3^-): As expected higher contributions of nitrate were found at the urban and suburban sites compared to the background one due to the presence of local sources of NO_x (PM_{10}: 2.7, 2.5 and 1.7 µg m^{-3}; PM_1: 0.8, 0.8 and 0.1 µg m^{-3}, for LYK, GOU and FKL respectively; Figs. 6c and d). In GAA, NO_3^- presented strong seasonal variability in both PM_1 and PM_{10}, with higher values during colder months, which, as in the case of SO_4^{2-}, were likely to originate from local pollution sources and especially vehicular traffic. On the contrary, no clear seasonal trend was observed at FKL. The winter maximum of NO_3^- in GAA, which was more prominent in the fine mode was due to the 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 was 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 GAA yet again a clear seasonal trend was evident for nitrate partitioning with the lowest values in winter (down to 50% in January) due to ammonium nitrate formation.

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 µg m^{-3}, respectively), highlighting as in the case of SO_4^{2-} the important role of long-range transport. On the other hand local anthropogenic sources within GAA dominated during the cold season as for PM_{10}

the GAA/FKL ratio was reaching values up to 2. Similar trend also existed for NO_3^- in 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 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., 2008; 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. 6g). Additional sources of nss-Ca^{2+} in 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 was obtained from all sites (r^2 of 0.67–0.81), 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 was due to regional dust, the remaining part for the GAA could be explained by "local dust", most probably resuspension from traffic. Thus local sources in GAA (mainly dust re-suspension from traffic) 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, when prevailing weather conditions (reduced relative humidity, leading to the drying up of surfaces) favor road dust resuspension (Nicholson and Branson, 1990).

3.3 Metals speciation

Trace metals are emitted in the atmosphere from a variety of sources and subsequently can be used as tracers of specific sources such as Earth's crust, combustion etc. Trace metals were analyzed in PM_{10} samples collected at LYK and GOU and well as in the PM_1 fraction sampled at LYK. The annual average concentrations of all studied metals are presented in Table 2 and Fig. 7a. In general, 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.

The ratios of trace metal concentrations in PM_1 to those in PM_{10} for all studied trace metals are shown in Fig. 7c for LYK where they are compared with those reported for FKL (Koulouri et al., 2008b). The majority of the measured trace levels were 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 were confined in the fine mode indicative of anthropogenic sources. Generally metals distribution in GAA presented similarities that were observed at FKL (Koulouri e al., 2008b).

Figure 7b depicts the ratios of the levels of trace metals in PM_{10} measured in GAA during this work to those reported at FKL. Based on the GAA/FKL ratio metals can be divided in two categories: Those having a ratio below 2 and those above. Ratio lower than 2 or even closer to 1 is calculated for Fe, Mn and Pb and Cr. Long range transport from arid areas of Sahara represented the main source of Fe, Mn and Cr. Trajectory analysis confirmed our assumption since the above trace metals presented the highest values in air masses originating from that area. Pb is also associated with transport from the Southern sector (N. African countries) as they also used it as additive in gasoline.

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 was also confirmed by the lack of correlation between these elements within GAA indicating significant contribution from local rather regional sources.

3.4 Chemical mass closure

Chemical composition was defined by three main classes: Dust, Ionic Mass (IM) and "unidentified", the later accounting mainly for elemental (EC) and organic carbon (OC). IM is the sum of the anions and cations measured. Dust levels have been 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 8 presents monthly source apportionment analysis for PM_{10} fraction for both GAA sites (IM and Dust) in comparison to the PM_{10} mass fraction.

In total crustal elements can account for 36–46% of total 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 dust resuspension due to vehicle circulation. IM, mainly secondary aerosol contribution (nss-SO_4^{2-}, NO_3^- and NH_4^+) showed lower contributions that minimized in winter and sharply increased from winter to summer. On a yearly basis, ionic composition, account for about 32% of the total mass at both GAA sites. On average ionic and crustal mass represent 77% and 78% of the gravimetrically determined mass for PM_{10} samples in LYK and GOU respectively. The unidentified mass might be attributed to aerosol water and OC, EC which was not measured and accounted for the remaining of the PM_{10} mass. This percentage is in agreement with results reported by earlier studies in central Athens. Prosmitis 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 $PM_{2.5}$ and $PM_{10-2.5}$ respectively. Grivas et al. (2008b) calculated the contribution of the sum of POM and EC to $PM_{2.5}$ at 31% for central Athens.

3.4.1 Local vesus 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 PM_1 and PM_{10} fractions. The results are presented in Fig. 9. In this figure two columns are presented for each GAA site for both PM_1 and PM_{10} 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 (mainly resuspension) contributed significantly to the local PM_{10} mass (up to 33% of PM mass). The contribution of IM ranged form around 20% in local PM_{10} to less than 40% in local PM_1). The reduced contribution of IM was somehow expected given the role of long range transport on SO_4^{2-} and in lesser extend on NO_3^- levels in the area. As mentioned before these anions contribute significantly to the measured IM mass.

Carbonaceous material (POM and EC) seemed to be the main contributor of the missing local PM mass (up to 62% in PM_1). Simultaneous OC and EC measurements performed during winter and summer of 2008 in various locations around GAA and at FKL as background site confirmed the above conclusion (Mihalopoulos, unpublished data, 2011).

4 Conclusions

The chemical composition of size-segregated aerosols (PM_1, $PM_{2.5}$ and PM_{10}) was determined at three sites: natural 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 the three regions and to evaluate the role of local versus regional sources.

The EU annual limit value of 40 µg m^{-3} for PM_{10} was exceeded on yearly basis at both urban and suburban sites and frequent exceedances of the 24-h limit value of 50 µg m^{-3}were recorded at all locations.

Simultaneous measurements of PM_1 and PM_{10} can highlight natural contributions, since PM_1 is closely related to anthropogenic aerosol and thus better represent the anthropogenic particle fraction. For air quality monitoring policy our results imply that PM_1 would be a better indicator for fine/anthropogenic aerosols and should be also continuous monitored.

During the warm season the no significant difference in PM_1 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 Ca^{2+} 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.

Chemical speciation data showed that PM in GAA was characterized by relatively constant contribution of ionic mass, 32% of the PM_{10} mass, with SO_4^{2-} and NO_3^- as the dominant ionic species. Crustal material was accounting for almost half of the mass contribution (46%), with maximum during the transition period (spring and autumn). On a yearly basis, ionic and crustal mass represent 77% and 78% of the gravimetrically determined mass for PM_{10} samples in LYK and GOU, respectively. The unidentified mass might be attributed to OC 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 62% in PM1). Dust from local sources (mainly resuspension) contributed significantly to the local PM_{10} mass (up to 33%). The contribution of local IM ranged from around 20% in PM_{10} to less than 40% in PM_1 given the role of regional sources on the measured SO_4^{2-} and NO_3^- levels.

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

Particulate Matter (µg m^{-3})		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

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Table 2. Annual mean concentrations of metals ($\mu g\,m^{-3}$) measured at Lykovrissi (PM_1 and PM_{10}) and Goudi (PM_{10}) from September 2005 to August 2006.

PM ($\mu g\,m^{-3}$)	Lykovrissi		Goudi
	PM_1	PM_{10}	PM_{10}
V	0.025	0.025	0.024
Cr	0.010	0.010	0.011
Fe	0.164	1.304	1.024
Mn	0.006	0.020	0.019
Ni	0.001	0.011	0.011
Cu	0.010	0.032	0.041
Cd	0.001	0.001	0.001
Pb	0.015	0.023	0.016

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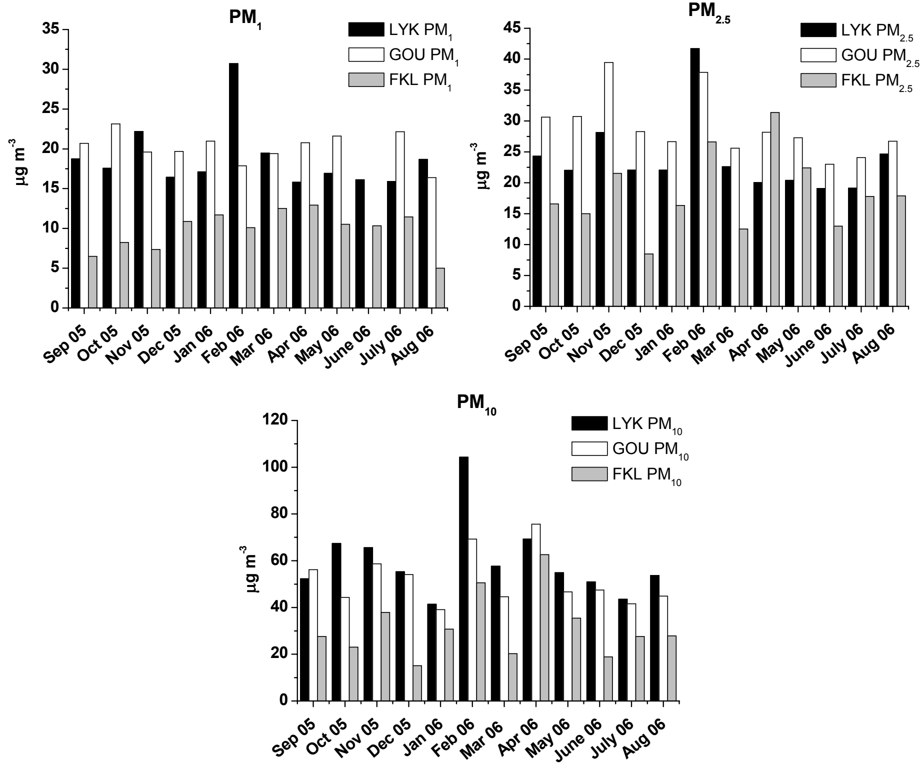

Fig. 1. Temporal variability of size segregated concentrations (µg m^{-3}) **(a)** PM$_1$, **(b)** PM$_{2.5}$ and **(c)** PM$_{10}$ for all three stations: LYK, GOU and FKL.

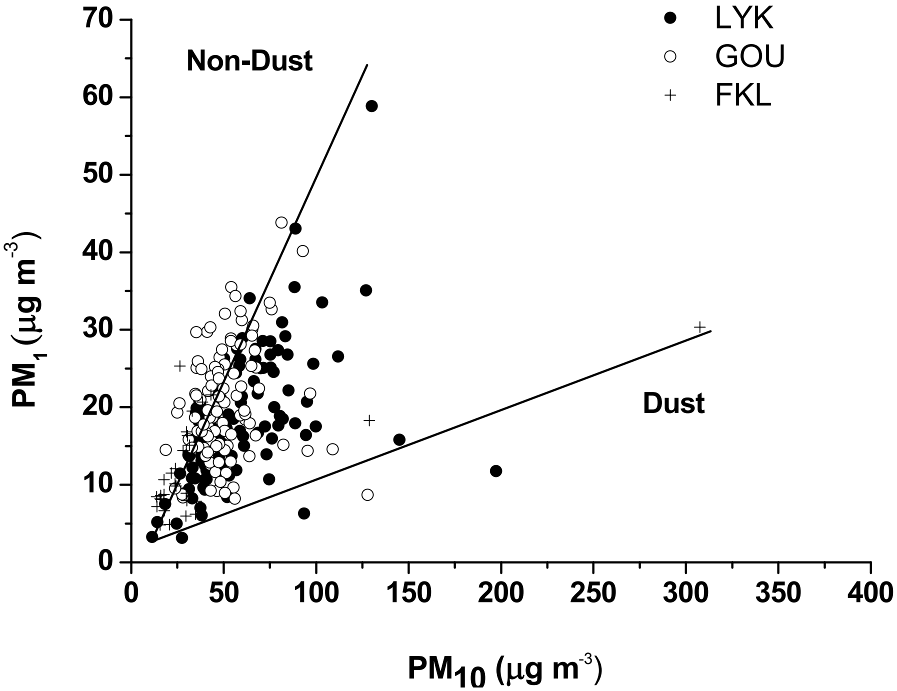

Fig. 2. PM$_1$/PM$_{10}$ ratios for all three stations during dust and non-dust events.

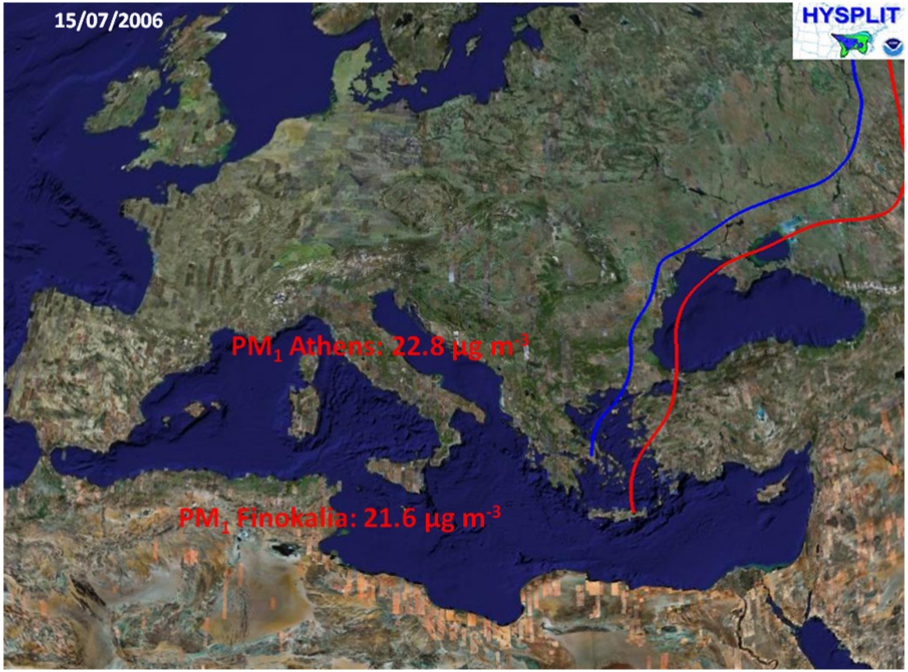

Fig. 3. A characteristic long range transport influence on PM_1 levels in the studied sites.

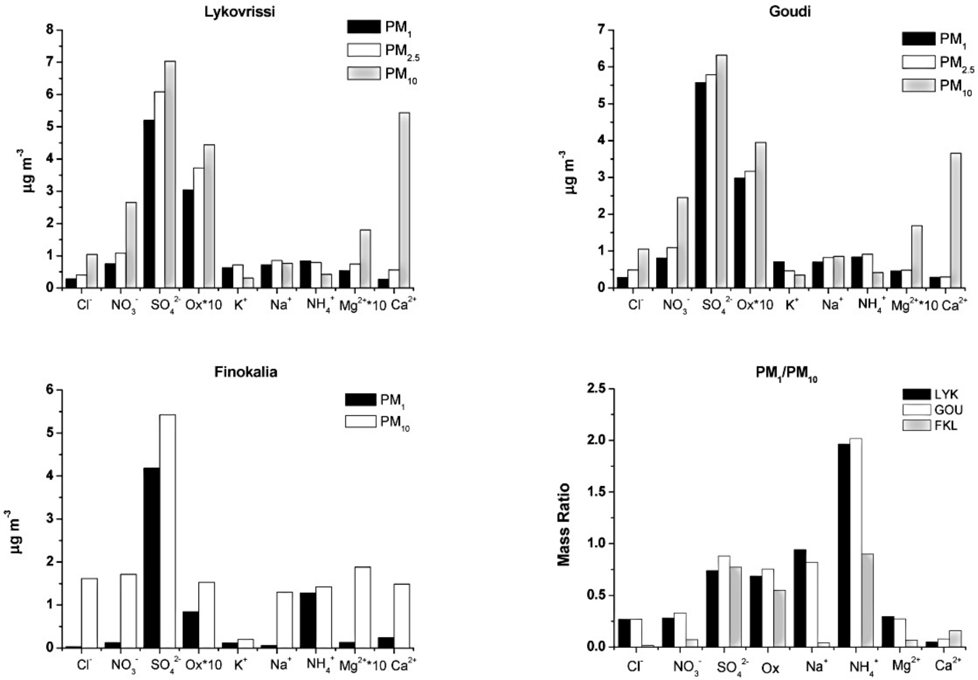

Fig. 4. Annual average concentrations (µg m^{-3}) of various ions for all three stations **(a)** LYK, **(b)** GOU, **(c)** FKL and **(d)** their PM$_1$/PM$_{10}$ mass ratios.

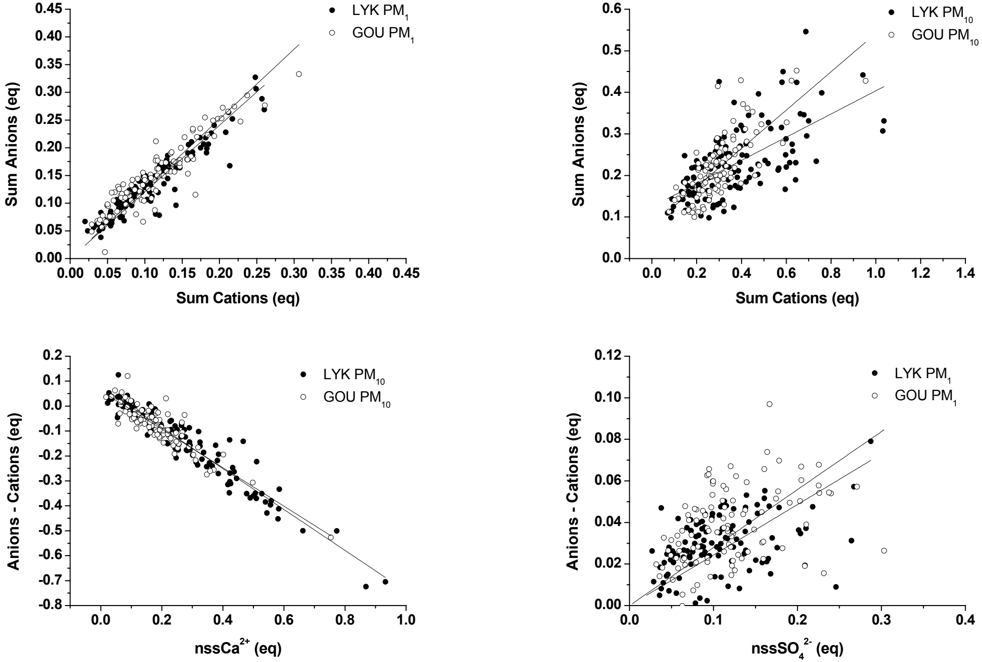

Fig. 5. Ionic balance (equivalents) for both GAA stations for **(a)** fine and **(b)** PM$_{10}$ fractions. Anions deficiency versus nssCa^{2+} in PM$_{10}$ samples **(c)** and nssSO$_4^{2-}$ in PM$_1$ samples **(d)**.

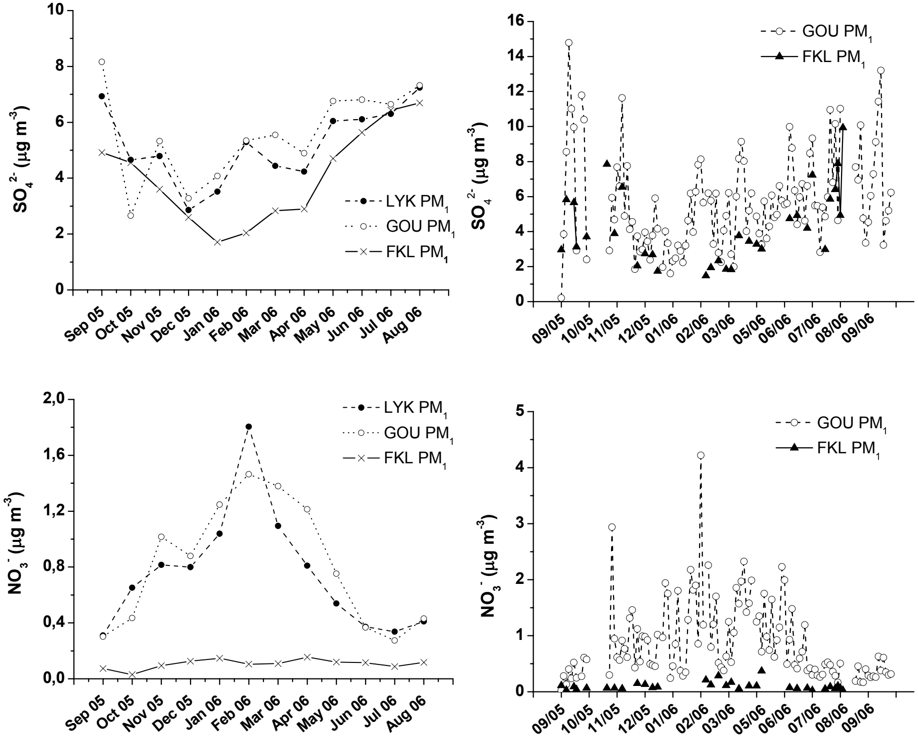

Fig. 6. Seasonal (**a, c, e** and **g**) and daily (**b, d, f** and **h**) variations (µg m^{-3}) for SO_4^{2-}, NO_3^- and Ca^{2+} in PM_1 and for NO_3^- in PM_{10} samples.

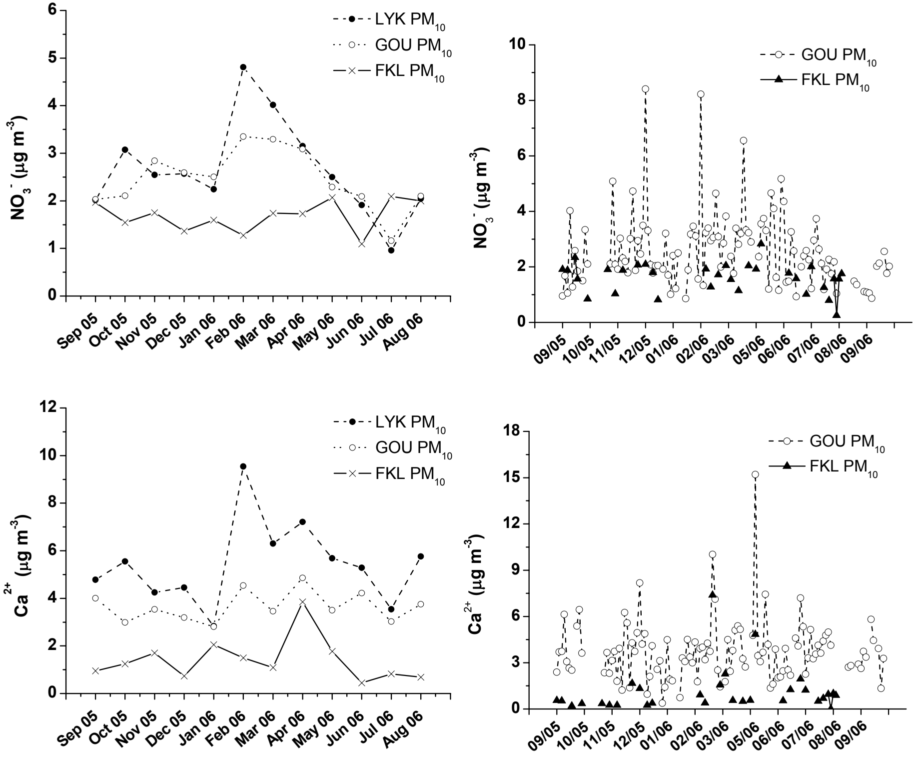

Fig. 6. Continued.

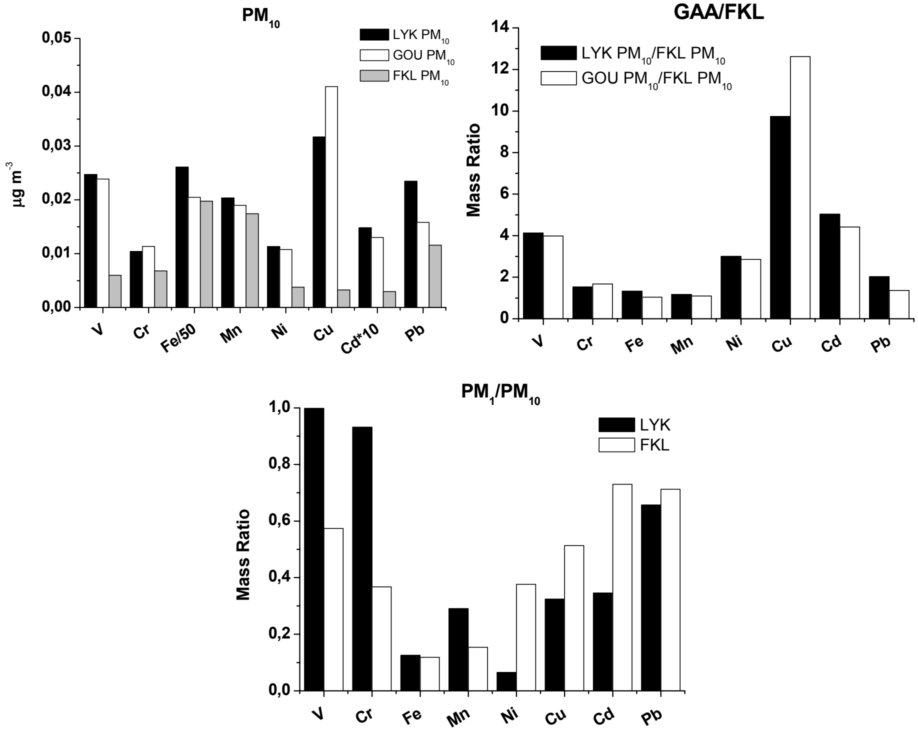

Fig. 7. Annual average concentrations (μg m^{-3}) of the studied metals for the three stations **(a)** in PM$_{10}$, **(b)** GAA/FKL mass ratio and **(c)** PM$_1$/PM$_{10}$ mass ratio.

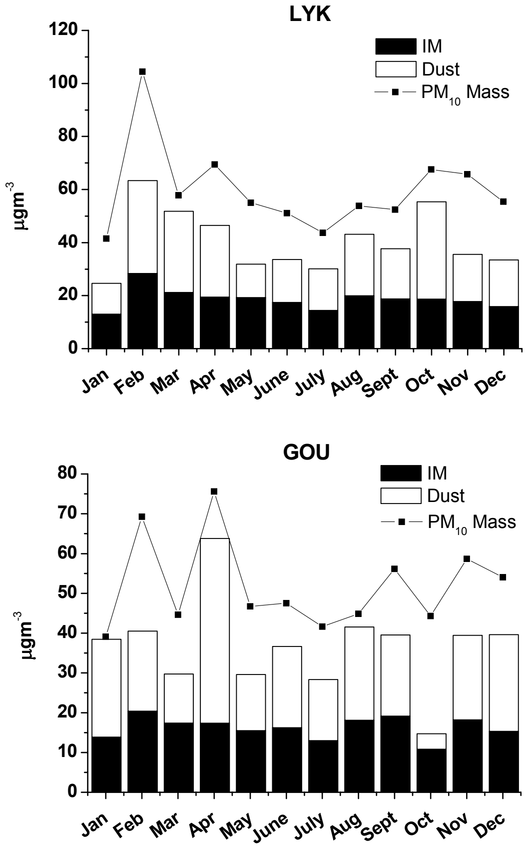

Fig. 8. Mass Closure (Ionic Mass and Dust) versus measured PM_{10}: **(a)** LYK and **(b)** GOU.

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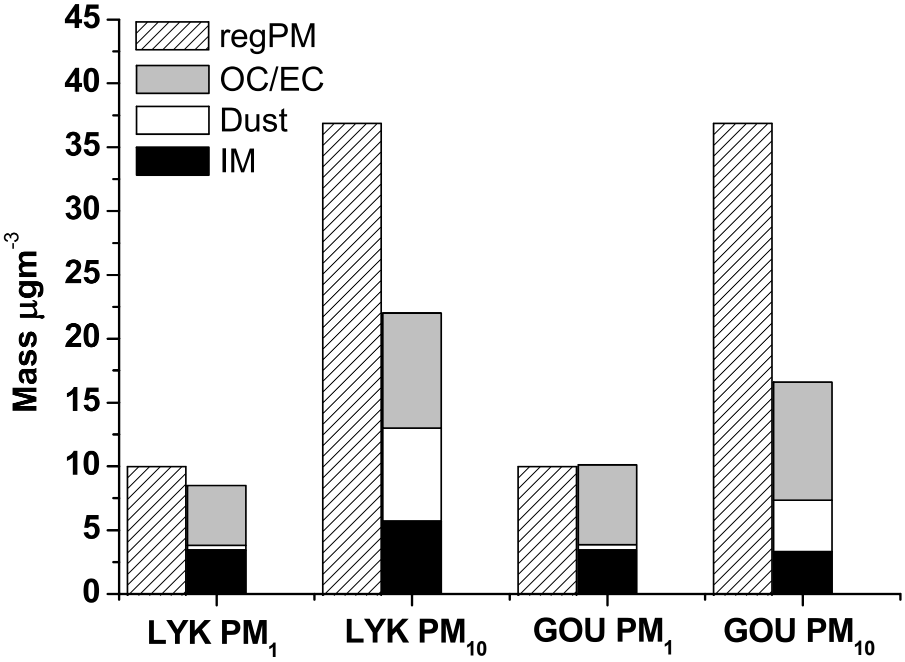

Fig. 9. Relative contribution of regional and local sources to PM levels in GAA. Regional PM (regPM) corresponds to PM measurements at FKL.