**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Mass and chemical composition of size-segregated aerosols (PM$_1$, PM$_{2.5}$, PM$_{10}$) over Athens, Greece: local versus regional sources" *by* C. Theodosi et al.

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This paper aims to better depict PMx (PM1, PM2.5, PM10) concentration levels and chemical composition of Athens (Greece) on an annual perspective and better characterize local aerosol sources by comparison with a regional background site providing similar observations. Local versus regional PM are discussed on a seasonal basis and PMx (PM1, PM2.5, PM10) perspectives providing, for the first time in Athens, preliminary insights on the aerosol contributing to PM pollution in this highly urbanised area.

General comments:

Although this paper provides new and original aerosol chemical datasets, I have the

feeling that a deeper analysis of these datasets could be performed in some sections (see specific comments).

Also, most of the results obtained in this paper rely on the use of Finokalia station as representative of the regional background pollution of Athens. Doing so, the authors estimate a local contribution for GAA (using ratios GAA/FKL). This methodology (Lenschow et al., 2001 ??) is valid only if we assume that PM sources in GAA are the sum of local sources (GAA) + regional sources (Finokalia). This hypothesis is particular strong considering that the 2 sites are distant by about 400km (in particular for background coarse particles which may not be distributed homogeneously for such distance).

- First, a better justification should be provided here. Climatology – similar to Sciare et al., ACP, 2008, for instance - could be performed during the period of the study at the 2 sites (Finokalia & Athens). This will convince the reader that similar air masses influence both sites.

- Second, a better justification should be given in the manuscript to demonstrate that PM concentrations and composition between 1 & 10μm at FKL can be used to depict regional background aerosol sources in GAA.

English may be checked again (incl. the proper use of past/present), abbreviations defined the first time they appear (incl. in the abstract), Figures properly labelled (add "a", "b", . . . for panel figures)

Specific comments:

Abstract :

+ This abstract could be slightly re-organized. It goes forward and backward between GAA sites and FKL and between each PMx fraction making difficult to understand important results of the paper. It could be re-organized like 1) PM levels & composition in GAA, 2) Comparison with FKL. + Provide information on sampling time & interval (24-

h sampling every 3 days). + Reconsider here the comparison on PM10 (between GAA and Finokalia) unless you can provide in the manuscript some evidences that PM10 in GAA is the sum of local (Athens) plus regional (Finokalia) sources. + "Warm season". Be more specific. Summer months? JJA ? + Organic Carbon may be replaced by Organic matter

Introduction:

+ Few sentences should be reported here to provide more information on EU directives regarding PM2.5 (yearly target & limit values for 2015 & 2020) and PM10 (yearly limit value of 40 μg/m3 & max authorized 24-h mean PM above 50μg/m3). Regarding these EU directives a minimum coverage of the year is required (which is more than 1 day of sampling every 3 days). This should be also mention somewhere. + You may also add few information on GAA (like the total population for instance) as well as providing (end of the introduction) few information regarding the time duration of the study (and sampling frequency).

2.1. Sampling site.

+ Although reported in other studies, you may provide here 1 or 2 more sentences to better describe the sites. + For comparison purposes, you may restrain your FKL dataset to the time period (Sep. 2005 – Aug. 2006).

2.2 Sampling and analytical techniques

+ You may add few information on the manufacturers of the PM samplers as well as the flowrate used in these samplers. + You may provide more information on the sampling frequency of FKL filter samplings. Are they performed on a continuous basis? (I guess yes). If so, please mention it. + for the 2 sites, you may also provide information on the gravimetric measurements here. Are they performed following EU directives (50% RH) or not? Instruments, precision, blank values. + Cut-off diameters are often reported as 50% cut-off. You may add this information here. + Please provide few more information

on IC such as field blank values (GAA & FKL). Idem for metal analyses.

3.1.1. Levels

You may better label it "Atmospheric concentrations" + You may define here which PM10 you use for FKL (VI or SDI ?). + Values in Table 1 should be reported with number of valid points for each station. First column label should be "Location" + I feel uncomfortable with the use of "natural" background for FKL. Regarding the large influence of anthropogenic emissions at this station (Sciare et al., 2003), you may better report FKL as a "remote" background site. + You may recall here that 50μg/m3 is not the annual EU limit value for PM10 but stands for the 24-h EU limit value that should used to calculate the number of days of exceedence (above this value). Instead of providing % you may better give a number of days above the 24-h EU limit value of 50μg/m3 (and show that even with 1 day sampling every 3 days you are already above the maximum of 35 days above 50μg/m3). + Please provide 1 sentence to explicit what is p and provide r2

3.1.2. PM ratios

You may better label it "PM comparison between the different sites" + line 20, page 7664, "all" may be replaced by "the 3" + line 21, page 7664, Is it r or r2? Provide N (number of data points). + line 23, page 7664, "for this strong correlation" may be added after "responsible" + line 24, page 7664, "is relevant to" may be replaced by "can be related to" + line 1, page 7665, "suspension of soil" may be better replaced by "re-suspension of local soil" + line 2, page 7665, "the" between "for" and "central" + line 3, page 7665, along with references numbers should be given for the PM2.5/PM10 ratios + line 6, page 7665, "plot" may be also appropriate instead of "regression" + line 9, page 7665, "manifesting" may be replaced by "suggesting" + line 10, page 7665, please define what are considered as "dust events" and "non-dust events". Air masses origin ? Treshold value in Ca2+ concentrations ? + line 14, page 7665, "between" may be replaced by "at" + line 20, page 7665, "an estimation" may be replaced by "a more

accurate estimation"

3.1.3 Seasonal variation of PM fractions

+ line 23, page 7665, "monthly variations" may be replaced by "monthly mean variations" + line 23, page 7665, "μgm-3" can be removed + line 27, page 7665, All the discussion on the climatology should be moved in a dedicated section (after the sampling site description for instance), together with the 1-year climatology as proposed in the general comments + line 12, page 7666, the discussion on the higher PM1 ratios (between GAA sites and FKL) may have to be completed and partly reconsidered. Does heating really contribute to these higher ratios during winter? Do you have data or references to prove this assumption? You did not consider other possible sources here like ammonium nitrate (which is only observed at GAA sites). Differences in air masses origin may also be proposed. For instance, Gerasopoulos et al. (ACP, 2011) found that the "Po Valley anthropogenic hotspot" may significantly contribute to AOD levels above Athens during the winter period. + line 18, page 7666. The discussion on Figure 3 is completely missing here. Please comment this Figure and provide more information on backtrajectory calculation (Hysplit references and so).

3.2.1. Levels and size-segregated distribution of water-soluble ions.

+ It would be useful for the reader to see how much representative are the FKL datasets during the studied period. Any references that could be provided to see that the ionic concentrations are close to those observed the previous years with other types of samplers? (see for instance Sciare et al., ACP, 2008). + For clarity purpose, this section may be re-organised as 1) presentation of mean concentrations of ions at the 3 different sites, 2) comparison of PM1/PM10 ratios. + lines 1-4, page 7667. The discussion on Figure 4a, 4b, and 4c is completely missing here. + lines 5-8, page 7667. Along with the references, the authors should provide numbers + line 10, page 7667. "extensively" may be replaced by "mainly" + lines 12, 13, 16, 19, page 7667. You can remove (NO3-) + line 12, page 7667. Be more specific and label the 2 different sources (sea

salt and dust) + lines 18-19, page 7667. This statement (ammonium nitrate) may be valid mainly for the winter period. If so, specify it. + line 18, page 7667. "the" may be added between "in" and "fine mode" + line 24, page 7667. It may be more NH3 (gas phase ammonia) volatilisation rather than NH4+ volatilisation + The last sentence of this section is not clear enough. You may better explain why VI should be less affected by this NH3 volatilisation artefact (i.e. no basic material impacted onto the filter matrix that may react with ammonium).

3.2.2. ionic balance

+ lines 4-5, page 7668. Be more specific and explain here that hydroxyl and carbonate ions are not analysed by IC but can be observed in rather large quantities in fine and coarse modes, respectively (& provide references). Doing so, we may better understand why you perform ion balance in PM1 & PM10. + Previously, you classified PM in fine/coarse fractions in order to better discriminate between crustal & anthropogenic sources. Why you do not use these 2 fractions to investigate the ion balance at your different sites? Instead, you use PM10 which contain a significant amount of anthropogenic (acidic) PM1. + line 6, page 7668. Is it really eq ? (why they are not reported as eq/m3) ? + line 9, page 7668. Is it really r ? (or r2) ? Also provide N (number of data points used for the correlation) + lines 22-26, page 7668. Please specify for which site this statement stands for (yearly round acidic species in the fine mode). For the GAA sites, you may also take into account ammonium nitrate. It may be also interesting to compare the acidification of PM1 between GAA sites and FKL.

3.2.3. Temporal variability of the main ionic species.

+ Why did you choose to restrain your interpretation to the 3 major ions when you have other tracers (such as Na+, nss-K+, C2O42-) to investigate the contribution of sea salt of biomass wood burning? A small paragraph should be added here to compare the monthly mean concentration of these species at the 3 sites. Since one of the objective of this paper is to better identify the contribution of natural sources in PM10 (which

may be removed for the data reporting to EU), it seems legitimate to evaluate also the contribution of sea salts (and validate the use of Na+ to trace this source from the correlation between Na+ and Mg2+). + Again this paragraph is starting from the comparison between the 3 different sites and then moves to the discussion of the dataset for each site. It may re-arranged as 1) datasets for each site, 2) comparison between the different sites. + The statement of sources of NO3, SO4, Ca may have to be better explained. Sources of SO4 in the E. Mediterranean are mainly natural (DMS oxidation product) and anthropogenic (SO2 from fossil fuel). Please provide references (several papers have addressed this issue at FKL). + line 9, page 7669. It is stated first that Ca2+ has a very similar spatial distribution over GAA but then, end of the paragraph it is stated that local sources (of Ca2+) can explain the discrepancy between LYK and GOU. Please correct accordingly. Please also add few sentences here to comment Fig. 6 (which is not commented at all). + lines 19-24, page 7669. Don't forget also that during summer you have much more air masses originating from Central/Eastern Europe which may bring higher levels of SO2 than the rest of the wind sectors. The explanation for the winter peak is not clear. Please re-write this part. Keep also in mind that the winter peak of SO4 at GAA may not be only explained by atmospheric processes but also from specific air masses (Po Valley ?) which may not concern the FKL station. + Line 1, page 7670. You state that SO4 is mainly in the form of Ammonium Sulfate. This is a strong statement which can be verified investigating the PMcoarse/PM10 ratio for SO4. What this ratio is telling us ? Also don't forget that ammonium cannot be used in conjunction with SO4 at GAA due to the presence of ammonium nitrate the winter months. + Line 10, page 7670. The vicinity of the traffic source is not the only reason that can be proposed to explain the presence of ammonium nitrate in GAA. You may have also some favourable thermodynamic conditions to produce ammonium nitrate. + Line 7, page 7671. You may better refer to Sciare et al. (2005) instead of Sciare et al. (2008) for the use of nss-Ca2+ to calculate dust concentrations. Then how do you explain your results at FKL in the perspective of those obtained by Sciare et al. (2005)

3.3 Metal speciations

Could be re-labelled as Atmospheric concentration of trace metals + The first part of this section could be moved in section 2 (experimental). + Lines 26-28, page 7671. Again you state a good agreement between your datasets and others (reference), but no datasets are presented and compared. Please provide numbers (from references) so that the reader can be convinced that your dataset is really in good agreement with literature data. + Line 5, page 7672. First sentence could be re-write as " The PM1/PM10 ratio of trace metal concentrations are shown in Fig. 7c." + Line 7, page 7671. Should be "trace metals" instead of "trace levels". Also you have not provided in this paper information regarding the trace metal datasets published by Koulouri et al. (2008b). Two or three sentences could be added in this paper (experimental section) to provide this information (sampling step, period of the study, instrumental settings, . . .). + You mention that Fe is of crustal origin, but I have in my mind many papers that have stated that Fe in the fine mode is more anthropogenic. Please take this into account in your data analysis. + Line 16, page 7672. "arid areas" of Sahara may be removed. Sahara is already a very arid. You state also here that Fe and Cr are of crustal origin but you have shown that they are mainly located in the fine mode. This is not consistent of dust being mainly located in the coarse mode. Should be corrected.

3.4. Chemical mass closure

+ You present here a mass closure only on PM10 samples. Why you did not do the same for PM1? You could for instance hypothesize that most of C aerosols are located in PM1. Doing so an estimate of [C] (i.e. EC+OM) could be obtained as [PM1]-[IM in PM1]-[dust in PM1] and reinject in the PM10 mass closure study the authors have discussed. + You have previously integrated Ca2+ in the ionic mass (IM). Now, I believe that you have removed it (since it is included in the dust fraction). If so, please state clearly. + Line 5, page 7673. How your dust calculation compare with the one proposed by Sciare et al. (2005) ? + Line 8, page 7673. A chemical mass closure is not a source apportionment analysis. Please correct accordingly. + Line 13, page 7673. When is the transition period? (period of the year ?). + Line 18, page 7673. Should be "ionic mass

plus crustal mass" instead of "ionic composition and crustal mass" + End of this section you compare your remaining mass (supposed to be C aerosols) with references which, for some of them, have not been performed in Athens. Since I suspect that chemical composition of PM2.5 in Athens to be rather different compared to other EU cities (i.e. more dust, more sulfate, possibly less ammonium nitrate), it is hard to use the datasets from these EU cities to validate the PM10 missing mass in Athens. + You state that the unidentified mass could be aerosol water and OC, EC. To which paper do you refer to state that liquid aerosol may still exist on the filter matrix (assuming that you have weighed your filter samples at RH below 40%) ? Should be "OM" instead of "OC"

3.4.1. Local versus regional contribution to PM mass There is not 3.4.2. Then you can assign this section to 3.5. + In this section you assume that PM10 at FKL can be used as a regional background point to estimate the contribution of PM10 from GAA. This is valid only if you have demonstrated that PMcoarse at FKL is representative of GAA background (see general comments).

4. Conclusions + Line 20, page 7674, Please remove "natural" before background + Line 23, page 7674. "in the three regions" may be replaced by "GAA" since the focus is made on Athens (and not FKL). + Lines 24-26, page 7674. This is a strong statement. You should state that your dataset only covers 1/3 of the year. For that reason, it can only serve as an indicator for PM10 annual concentration in GAA. On the other hand, you can use your dataset to investigate – for only 1/3 of the year – the number of exceedence days (above $50\mu g/m3$). You may state here that you have already reach this number although you have only documented 1/3 of the year. + Lines 1-5, page 7675. You state that PM1 should be monitored to estimate the anthropogenic fraction of PM. This is true. But you may also mention that PM chemical information is more suitable (than PM mass measurements) to investigate the natural/anthropogenic sources in GAA. + Line 7, page 7675. Check the sentence (highlights instead of highlighting ?)

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