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Comment

Interactive comment on “Mass and chemical composition of size-segregated aerosols (PM₁, PM_{2.5}, PM₁₀) over Athens, Greece: local versus regional sources” by C. Theodosi et al.

C. Theodosi et al.

mihalo@chemistry.uoc.gr

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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 dis-

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tant by about 400km (in particular for background coarse particles which may not be distributed homogeneously for such distance).

Answer: To persuade the reviewer on the validity of our hypothesis we compared PM10 levels recorded at Finokalia (FKL) with those measured at a remote suburb area of Athens Thrakomakedones (THR). Thrakomakedones is located at a foothill of Parnitha Mountain, about 550m above sea level and 23 Km from the city center. This site is considered as a background, because of the absence of primary sources affecting PM concentrations (Grivas et al., 2004a). The comparison between THR and FKL revealed significant covariations between the two sites in terms of PM10 during the sampling period. Correlation between monthly mean values gave a slope of 1 with r^2 of 0.6 indicating that FKL can be considered as a background (reference) site for the GAA. Similar climatology between GAA and FKL can account for the observed similarity in PM10 (see below). Differences between THR and FKL exist only during strong dust events occurring few times during the year, with Finokalia values being higher compared to THR, which is expected given the vicinity of FKL to N. Africa. Apart of these extreme dust events coarse mode in FKL is lower compared to GAA, indicating significant contribution for local sources in GAA (wind and road dust). Page 6, Section 3.1.

- 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.

Answer: We follow reviewer's suggestion and air masses back-trajectories have been calculated for all sites both for the sampling period (2005-2006) as well as for a longer period (2002-2006). As it can be seen in figure 2, a very good agreement between GAA and Finokalia in terms of percentage and seasonal distribution of air masses origin occurs. In addition no difference was observed for all sites between the sampling period and 2002-2006 period. Page 6, Section 3.1.

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

Answer: See above comment on the comparison between an Athens urban background site (Thrakomakedones) and Finokalia. Page 6, Section 3.1.

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)

Answer:As suggested by the reviewer the proper tense has been used, abbreviations have been included in the abstract and figures have been labeled.

Specific comments: Abstract : + This abstract could be slightly re-organized. It goes forward and backward between GAA sites and FKL and between each PM_x 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.

Answer:We agree with the reviewer remark and the abstract has been re-organized.

+ Provide information on sampling time & interval (24- h sampling every 3 days). + “Warm season”. Be more specific. Summer months? JJA ? + Organic Carbon may be replaced by Organic matter

Answer:All suggested changes have been performed. Page 1, lines 15, 25-28, 34-35.

+ 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.

Answer:As mentioned before PM₁₀ levels at Finokalia are in agreement with those reported at an urban background site of Athens (figure 3) and discussion above. Page 6, Section 3.1 and Figure 3.

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Introduction: +Few sentences should be reported here to provide more information on EU directives regarding PM_{2.5} (yearly target & limit values for 2015 & 2020) and PM₁₀ (yearly limit value of 40 $\mu\text{g}/\text{m}^3$ & max authorized 24-h mean PM above 50 $\mu\text{g}/\text{m}^3$). 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).

Answer:The requested information has been added in the manuscript. Page 3, lines 55-59, 63-65.

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).

Answer: More information describing the sites has been provided, while for FKL the dataset was already restrained for that specific time period. Page 4, lines 80-98.

2.2 Sampling and analytical techniques + You may add few information on the manufacturers of the PM samplers as well as the flow rate 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. + Please provide few more information on IC such as field blank values (GAA & FKL). Idem for metal analyses + Cut-off diameters are often reported as 50% cut-off. You may add this information here.

Answer: As suggested by the reviewer more information on samplers, frequency of sampling and EU directives have been provided. Page 5, lines 104-108, 109-111, 112-113, respectively.

3.1.1. Levels You may better label it “Atmospheric concentrations” + You may define here which PM10 you use for FKL (VI or SDI ?). + 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. + Values in Table 1 should be reported with number of valid points for each station. First column label should be “Location” + You may recall here that $50\mu\text{g}/\text{m}^3$ is not the annual EU limit value for PM10 but stands for the 24-h EU limit value that should be 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 $50\mu\text{g}/\text{m}^3$ (and show that even with 1 day sampling every 3 days you are already above the maximum of 35 days above $50\mu\text{g}/\text{m}^3$). + Please provide 1 sentence to explicit what is p and provide r2

Answer: We agree with the reviewer remarks and all clarifications needed and changes suggested by the reviewer have been performed. Throughout the manuscript FKL is referred as remote background site. Number of data points have not been included in the suggested Table since they are presented in section Sampling and analytical techniques. Section 3.3.1.

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 of 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 14, page 7665, “between” may be replaced by “at” + line 20, page 7665, “an estimation” may be replaced by “a more accurate estimation”

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Answer:As suggested by the reviewer the appropriate changes have been performed, Page 8, Section 3.2.2.

+ line 10, page 7665, please define what are considered as “dust events” and “non-dust events”. Air masses origin ? Treshold value in Ca²⁺ concentrations ?

Answer:Dust events were identified by air-mass trajectory analysis. In order to address this issue a sentence was added in the manuscript, Page 9, lines 206-207.

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

Answer:As suggested by the reviewer the appropriate changes have been performed in the revised version, Page 9, line 222.

+ line 12, page 7666, the discussion on the higher PM₁ ratio (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).

Answer:Discussion proposed by the reviewer has been included in the revised version, while information on the backtrajectory calculation was given in the appropriate section 3.1. Page 10, lines 234-236.

+ 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

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1-year climatology as proposed in the general comments

Answer:A new section was now added in the manuscript immediately after the description of sampling sites presenting climatology of air masses for GAA and FKL during the sampling period (Figure 2), Page 6, Section 3.1.

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).

Answer:All comments have been taken into consideration and all changes have been performed. More specifically, this section has been re-organized, while comparison with other references has been added in Table 2. Page 10-11, Section 3.3.1.

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

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quantities in fine and coarse modes, respectively (& provide references). Doing so, we may better understand why you perform ion balance in PM1 & PM10.

Answer: The reviewer is correct and it has been clarified that hydroxyl and carbonate ions are not analyzed by IC. Page 12, lines 283-284.

+ Previously, you classified PM in fine/coarse fractions in order to better discriminate between crustal & anthropogenic sources. Why do you 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.

Answer: For a uniform presentation of our results, as suggested by the reviewer, Figures 7b and c, now refer to the coarse fraction.

+ line 6, page 7668. Is it really eq ? (why they are not reported as eq/m³) ?

Answer: The reviewer is right it is indeed eq/m³ and it has been corrected throughout the manuscript and Figures.

+ line 9, page 7668. Is it really r ? (or r²) ? Also provide N (number of data points used for the correlation) Answer: It is indeed r. Data points used for the comparison is referred to in section 2.2 line 129.

+ 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. Answer: The comment stands for both sites and that specific comment has been added in the revised version. Moreover a comparison between GAA and FKL as suggested by the reviewer has been performed and added in the manuscript. Page 13, line 302, 309-311.

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

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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⁺).

Answer: Following reviewer's suggestion we expand our interpretation to other tracers such as as Na⁺, nss-K⁺, C2O4²⁻. Page 17, lines 400-408.

+ 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).

Answer: References on sources of sulfur in FKL have been added. Page 14, lines 331-342.

+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 PM_{coarse}/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.

Answer: Size distribution of sulfur was already presented and discussed in figure 4d (now 7d) of the submitted version. There we clearly stated that nss-SO₄ is mainly associated to fine mode with PM₁/PM₁₀ ratio for nss-SO₄ being of 0.8. Page 14, lines 343-352.

+ 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. + line 9, page 7669.

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It is stated first that Ca^{2+} has a very similar spatial distribution over GAA but then, end of the paragraph it is stated that local sources (of Ca^{2+}) 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). A Answer: s suggested by the reviewer the appropriate changes have been performed. Page 13, lines 317-329,

+ 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 SO_2 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 SO_4 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.

Answer: We added the explanation proposed by the reviewer for summer time. For winter given the very good agreement in climatology between GAA and FKL if specific air masses not concerning FKL station existed they should not be very frequent.

+ 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.

Answer: As suggested by the reviewer the appropriate changes have been performed. Page 15, lines 355-356.

+ Line 7, page 7671. You may better refer to Sciare et al. (2005) instead of Sciare et al. (2008) for the use of nss-Ca^{2+} to calculate dust concentrations. Then how do you explain your results at FKL in the perspective of those obtained by Sciare et al. (2005)

Answer: The reviewer's proposition had already been taken into consideration. We had used nss-Ca^{2+} to calculate dust. Although the results for FKL are reasonably good compared to dust estimation using Fe or Mn, in GAA an overestimation in dust contribution was observed using nss-Ca^{2+} .

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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, . . .).

Answer: As suggested by the reviewer the appropriate changes have been performed. At Table 2 data from other works performed in GAA related to trace metals were added. Page 17, line 410, 421, 422.

+ 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.

Answer: Referring to Fe: From Figure 9, it is clear that the majority of Fe exists in the coarse mode (90%) and thus the anthropogenic fraction (assuming that all fine mode is anthropogenic) is minor. As for Cr, in the case of LYK is indeed in the fine mode, and this has been mentioned in the text. (370, 380, 362-363, 374-377), Page 18, line 424.

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

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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.

Answer: Mass closure was performed for both PM10 and PM1 fractions. OM was calculated by removing IM and dust from weighted mass as suggested by the reviewer and compared with the available literature.

+ 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.

Answer: Yes Ca²⁺ was removed from dust calculation.

+ Line 5, page 7673. How your dust calculation compare with the one proposed by Sciare et al. (2005)?

Answer: We have used nss-Ca²⁺ to calculate dust. Although it gives reasonably good results for Finokalia, in GAA largely overestimates dust contribution.

+ 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.

Answer: All references (even that of Sillanpää et al. (2005; 2006) originate from work performed in Athens area.

+ 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” + You state that the unidentified mass could be aerosol water and OC, EC. To which paper do you refer to state that liquid

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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”

Answer: The appropriate changes and the references required have been added. Page 18-19, lines 444-445, 448-449, 462.

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 PM_{coarse} at FKL is representative of GAA background (see general comments).

Answer: The title has been changed and the reviewer’s comment on the role of FKL as a regional background point has been addressed before in the 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 μ g/m³). You may state here that you have already reach this number although you have only documented 1/3 of the year.

Answer: As suggested by the reviewer the appropriate changes have been performed and a new comment about the coverage of our samples (just 1/3 of the year) has been added. Page 20-21, lines 492, 496-499.

+ 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 (high-

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lights instead of highlighting ?)

Answer: The reviewer is correct and the importance of chemical composition measurements for the distinction between natural/anthropogenic sources has been added.

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