

## ***Interactive comment on “Variability in regional background aerosols within the Mediterranean” by X. Querol et al.***

**X. Querol et al.**

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Interactive comment on “Variability in regional background aerosols within the Mediterranean” by X. Querol et al. Anonymous Referee #3 Received and published: 27 May 2009

This paper discusses aerosol properties across the Mediterranean basin from several multi-year records, namely their concentration, size ranges (PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>), chemical composition, variability in time (daily and seasonal), and relationship with meteorological situations. The topic is very much within the scope of ACP. The paper is very interesting and well-written, and I learned a quite a bit by reading it. I was thankful to have the chance to review paper that compares data across multiple stations over a larger region, as opposed to the more common single-site papers. Also

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the Mediterranean tends to receive less attention in the scientific literature than Central and Northern Europe, so this focus is very welcome. I highly recommend the paper for publication in ACP after a few minor issues are addressed. (I will use the notation 10154-15 for page 10154 line 15 etc.) Answer: Thank you very much for your comments.

Main issues

\* 10159-22-24, here CO<sub>23</sub><sup>-</sup> was divided by 2 to account for possible coarse calcium nitrate and sulfate. This appears unnecessarily inaccurate. Why not do an ion balance on the Calcium? E.g. if 100 nmol/m<sup>3</sup> of coarse Ca are measured along with 20 nmols/m<sup>3</sup> of coarse NO<sub>3</sub> and 10 nmols/m<sup>3</sup> of coarse SO<sub>4</sub>, then the CO<sub>3</sub> necessary for ion balance is 85 nmols/m<sup>3</sup>. (Rather than 50 nmols/m<sup>3</sup> as the authors's rule would estimate) Answer: We calculated the free CO<sub>23</sub><sup>-</sup> according to the output of the ion balance. Ammonium/sulphate excess was obtained, then ammonium nitrate is calculated. The excess sodium/chloride was calculated and balanced with sulphate and nitrate. The remaining sulphate and nitrate excess was then balanced with calcium, and then the Ca excess was considered to be calcium carbonate. The results reduce only around 0.1 micrograms/m<sup>3</sup> the original values, but we changed accordingly text and tables.

\* 10159-25, I assume that the non-measured mass is mostly water, but this should be stated explicitly here for clarity. Answer: We agree with the reviewer and have modified the text according to this suggestion.

\* 10161-16, why were trajectories not initiated at lower altitudes for the FKL (230 m amsl) and ERL (22 m asl) sites? Answer: The model used for the classification of the long range transport episodes (HYSPLIT) does not have enough definition to differentiate these altitudes. We believe that the model reproduce the transport better at higher levels. But in our opinion, the method used is right since we are searching for long range transport of pollutants.

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\* 10162-14, can this trend only be explained by the gradual deposition of dust? It seems that just lower frequency of air transport arriving from the dust sources may be as or more important as a factor in creating the observed concentration gradient. Also dilution of dust-laden air with regional air can also create a gradient, without the need to invoke deposition. Probably all factors play a role and I suggest listing them all here. Answer: We agree with the reviewer's suggestion and have modified the text according to it.

\* 10164-17, here photochemical activity is invoked to explain a peak at 4-6 am GMT. Has the photochemistry started at that time at this site? Perhaps transport may have more to do with this peak? Answer:

The explanation of the 4-6 a.m. peak was not clear in the text, but in any case, as the referee stated, it is not due to photochemical activity. In order to clarify the origin of the diurnal trend at FKL we have modified the text as follows: "In summer two morning peaks are found (Figure 2) at 4–6 h GMT and 8–10 h GMT, the first one coinciding with an increase of NO<sub>x</sub>, and probably attributed to anthropogenic emissions; and the second one associated to an increase in ozone, possibly demonstrating the effect of regional sources of pollution under intense photochemical activity (Gerasopoulos et al., 2005)."

\* 10168-3, the wording 'with a minor relevance' seems too strong here, as the acidity is likely an important factor on preventing the formation of NH<sub>4</sub>NO<sub>3</sub>, which makes the HNO<sub>3</sub> stay in the gas-phase longer and react predominantly with dust. Of course dust has to be present for this to happen, but in the absence of a modeling study to evaluate the importance of the submicron aerosol acidity in the formation of coarse nitrates, I suggest describing this in a more neutral language. Answer: We have clarified this issue in the text, as suggested by the referee. 'The high levels of sulphate in the EMB may deplete the available gas-phase NH<sub>3</sub> so that little ammonium nitrate can form due to the low NH<sub>3</sub> levels. Note that this is consistent with the aerosols in the EMB being acidic and those in the WMB being neutralized by NH<sub>4</sub><sup>+</sup>. This may be the reason for

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the coarse prevalence of nitrate in the EMB, where the interaction of HNO<sub>3</sub> with sea salt and mineral matter may be favoured by the low NH<sub>3</sub> available'.

\* 10168-11, 10171-28, 10172-5, 10175-20, these statements about the sources of SOA are too strong since no references are provided on studies of the relative importance of the different SOA sources for this region, and since this is a very controversial topic at present (see e.g. Hallquist et al., ACPD, 2009, <http://www.atmos-chem-physdiscuss.net/9/3555/2009/acpd-9-3555-2009.html>). I suggest that the authors list the possible sources of SOA and suggest that they may all play a role: biogenic VOCs, anthropogenic VOCs, and VOCs emitted by biomass burning. Note that the formation rates for all of them would be enhanced by the more intense summer photochemistry. Also the emission rates of anthropogenic precursors (e.g. gasoline evaporation) increase greatly with high temperatures due to the exponential increase of vapor pressure with temperature, so higher summer emissions are not limited to the biogenic precursors. Answer: We agree with the referee. According to the proposed suggestions we have listed different sources probably contributing to the higher SOA formation in the WMB.

\* Fig 4 for FKL shows significant coarse OM+EC which is not present at MSY, but this is not discussed in the paper. High concentrations of these species in the coarse mode are unusual in my experience, so the possible cause for their presence should be addressed. Answer: We do not have a clear explanation for this coarse OM+EC occurrence, but we highlighted this difference in the text of the reviewed version.

\* For the material in tables 1-4, in my opinion it would be much easier to communicate it with the readers if it was presented in graphical form. The authors are clearly skilled in creating complex figures such as Figure 4, so I strongly suggest that they invest the time to express most of this information in the form of graphics. Most readers are visual and tabular information is more often overlooked. The tables should then be moved to a Supp. Info. section, which is published together with the paper and is then available for readers who want to know the actual numbers (which would be a very small minority

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of the readers in my experience). Answer: The new Table added as a consequence of comment by reviewer 2 was transferred to supplementary information and the location of the sites is shown in Figure 1. The information of the large Table 1 is now converted into Figure 6. The old Table 1 is now Table S.2. in the supplementary information. Tables 3, 4 and 5 are very difficult to be converted into graph information, and then we decided to leave them as tables.

\* The figures are very small, given the amount of detail in them, in the print ACPD version. The authors should make sure that in the ACP version they are reproduced at a large enough size to be able to comfortably read them. Answer: We will be careful when the print proofs will be ready.

Minor items, typos etc.

\* 10154-15, the wording of this sentence is slightly ambiguous / confusing. I think the authors mean to say that both V and Ni are high in the WMB and only V in the EMB, but a reader could think that both elements are only high on the WMB. I suggest re-wording Answer: We changed this sentence to say that both V and Ni levels are high in the Mediterranean Basin, but higher in the EMB.

\* 10155-2, object -> subject Answer: We have modified the text according to the reviewer's suggestion.

\* 10156-8, giving -> given Answer: We have modified the text according to the reviewer's suggestion.

\* 10157-26: not clear to me what you mean with the 'contrast throughout instead of along the year', suggest re-wording Answer: We have modified the text according to the reviewer's suggestion.

\* 10158-23, does the Gerasopoulos article describe only the prevailing local winds, or also the transport paths / back trajectories to FKL? Answer: The article by Gerasopoulos describe both local winds and transport paths to FKL.

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\* 10159-4, corrected with -> scaled to Answer: We have modified the text according to the reviewer's suggestion.

\* 10160-2: the Turpin et al. reference listed is not the one in which OM/OC values are reported. Rather the following paper should be cited: Turpin, B. J.; Lim, H. J. Species contributions to PM<sub>2.5</sub> mass concentrations: Revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* 2001, 35 (1), 602–610. [http://www.informaworld.com/smpp/content\\_content=a713834675\\_db=all\\_order=page](http://www.informaworld.com/smpp/content_content=a713834675_db=all_order=page) Answer: We have changed the reference as the reviewer suggested.

\* 10160-2, a recent paper that also reports measurements of OM/OC ratios with a different technique from that of Turpin and Lim but that arrives at almost the same values is Aiken et al. (*ES&T* 2008, <http://pubs.acs.org/doi/abs/10.1021/es703009q>). I suggest citing this reference as well so that there is broader support for the values chosen. Answer: We have added the reference that the reviewer suggested.

\* 10160-7, the Greek letter beta should be used here Answer: We have modified the text according to the reviewer's suggestion.

\* 10162-4, I suggest referring to Figure 1 at this point, otherwise the reader may miss the connection with this discussion. Answer: We have modified the text according to the reviewer's suggestion.

\* 10162-7, not sure what is meant by '2-day in average samplings' Answer: We have clarified the sentence: 48-hour means.

\* 10162-16, please provide the concentrations measured at the Spanish EMEP stations Answer: We have modified the text according to the reviewer's suggestion. 'The same gradient holds in the WMB when comparing PM<sub>10</sub> levels measured at MSY with those recorded at Spanish EMEP stations, from 13 μg PM<sub>10</sub>/m<sup>3</sup> in the NW to 22 μg PM<sub>10</sub>/m<sup>3</sup> in the SE (Pérez et al., 2008).'

\* 10166-15, show -> shows Answer: We have modified the text according to the re-

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viewer's suggestion.

\* 10166-20, pls give both PM10 and PM2.5 when removing the 6 major dust events, otherwise this sentence is confusing Answer: We have added a PM10 value according to the reviewer's suggestion (10 and 0.8)

\* 10167, as later discussed -> as discussed later Answer: We have modified the text according to the reviewer's suggestion.

\* 10168-21, shore-line -> shoreline Answer: We have modified the text according to the reviewer's suggestion.

\* 10168-24, suggest inserting 'in the Mediterranean' after 'coastal areas' for clarity, since Atlantic sites are mentioned next Answer: We have modified the text according to the reviewer's suggestion.

\* 10169-26 and also 10171-3, remove 'the' before 'ammonium nitrate' Answer: We have modified the text according to the reviewer's suggestion.

\* 10170-4, not clear why there is a reference to Fig 5 here Answer: It was a mistake. We have changed the reference to Fig 4.

\* 10170-9, in the coarse mode -> to the coarse mode Answer: We have modified the text according to the reviewer's suggestion.

\* 10172-4, rate -> ratio Answer: We have modified the text according to the reviewer's suggestion

\* 10172-8, suggest inserting 'markedly' after 'change', since the correlation coefficient does change some between the seasons Answer: We have modified the text according to the reviewer's suggestion

\* 10172-14, the wording 'agricultural waste, and burning' is unclear. I assume the authors mean 'agricultural waste burning'? Answer: We have changed the text by: long-range transport of agricultural waste burning and biomass burning emissions

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\* Some references that support the lack of significant of OC content in Saharan dust, and which could be cited here are: Formenti, P., M. O. Andreae, L. Lange, G. Roberts, J. Cafmeyer, I. Rajta, W. Maenhaut, B. N. Holben, P. Artaxo, and J. Lelieveld, Saharan dust in Brazil and Suriname during the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) – Cooperative LBA Regional Experiment (CLAIRE) in March 1998, *J. Geophys. Res.*, 106, 14919- 14934, 2001. Mayol-Bracero, O. L., Santos-Figueroa, G, Morales, F, Colon, L, Carbonaceous Aerosols in African Dust Over the Caribbean, *EOS Trans. AGU, Fall Meeting Supp.*, Abstract A11C-0122, 2008. Answer: We have added the references proposed by the referee and changed the text to introduce them. 'During these episodes, the contribution of carbonaceous aerosols is at the lowest for all sites, which is supported by the low OC contributions found in Saharan dust in other studies (Formenti et al., 2001; Mayol-Barcelo et al., 2008).'

\* 10173-3, associated to -> associated with Answer: We have modified the text according to the reviewer's suggestion

\* 10173-25, pls define WAE in the text Answer: We have modified the text according to the reviewer's suggestion

\* 10175-12-18, this explanation about the depletion of NH3 is clearer and more detailed than the one earlier in the paper, I suggest using the same wording in both locations. Answer: We have modified the text according to the reviewer's suggestion

\* 10176-20, it is not clear to me how this study shows that the Mediterranean 'is vulnerable to climate destabilization' Answer: We agree with the reviewer's comment and we have modified the text as follows: 'This study clearly demonstrates that the significant and complicated phenomenology of aerosols across the Mediterranean may play an important role on climate forcing.'

End of report