Atmos. Chem. Phys. Discuss., 9, C760–C765, 2009
www.atmos-chem-phys-discuss.net/9/C760/2009/

Atmospheric Chemistry and Physics Discussions

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

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Received and published: 13 May 2009

Reply to comments by: Dr. W. Aas (Referee) waa@nilu.no Received and published: 6 May 2009

We sincerely appreciate the positive comments by Dr. Wenche Aas at helped us to improve the quality of our paper. Following the suggestions of the referee, we have performed the required improvements in the manuscript. Below we attach a summary of how we addressed these changes and some replies to queries.

1. "The paper gives a nice overview of the pollution level of aerosols and its spatial and temporal distribution in the Mediterranean area. I do however miss some more in depth evaluation of the quality and comparability of the data. More specific comments

Chapter 4.1.1 Not specific on the when the average value for Ayia Marina in Cyprus is valid. The annual average of PM10 mass ranges from 28.8 ug/m3 in 2005 to 33.7 in 2006 (EMEP status report 4/2008). Are the data really comparable when different year are used in this study? Depending on the influence of Sahara dust episode there may be relatively large inter annual variations. Some discussions on the variety of the averages are needed to compare the datasets."

Reply: We agree with referee 1 in this comment. Some missing, but important, information is needed in the final version of the manuscript, such as the periods used for the calculation of the mean values. Mean annual PM levels at RB sites across the Mediterranean may vary largely year to year mainly because of the influence of the African dust, as illustrated by Querol et al., 2009. In order to minimize differences on the natural dust contribution due to the lack of temporal coincidence we have included the maximum data coverage for each site in this study. As shown in Table 2, most of the selected monitoring sites have 6-7 years of data. The above recent paper also illustrates the spatial and temporal variation of PM and African net dust across the Mediterranean, showing important inter-annual variations on the net African dust contribution, especially in the closest areas to North Africa; with lower variation of background PM levels throughout the years. This study also shows similar annual contributions and spatial variations of dust to the ones obtained here. We added this text and a Table in the revised manuscript showing the monitoring sites information and sampling periods.

2. "Furthermore, the methodologies for mass measurements are different. TEOM is used at Cyprus and this may underestimate compared to gravimetric method."

Reply: We agree with this important issue. The use of different techniques to measure the PM concentrations may result in differences owing to the particularities of each technique. TEOM and Beta instruments may heat the sample up to 50 °C in order to avoid condensation of water and consequently the overestimation of the PM mass. This may result in the loss of semi-volatile compounds such as the ammonium nitrate. This problem, however, do not affect other PM components such as the mineral dust,

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typically associated to the African dust events. In any case, for the three main sites used to compare PM speciation, the PM levels were measured with the gravimetric method (see new Table inserted). We added text on this question.

3. "Figure 2. Caption is misleading since the diurnal cycle at EMB is not calculated using all the data. The caption should contain all relevant information since many people only look at the figures and don't read the whole manuscript."

We concur with the referee on this comment. The caption is not complete so we have completed it in the revised version as follows: "Figure 2. Mean seasonal daily evolution of PM10, PM2.5 and PM1 levels in the WMB (MSY) and EMB (FKL). Note that the PM 2.5 and PM1 daily levels at FKL has been calculated from the PM1/PM10 and PM2.5/PM10 ratios".

4. "Chapter 4.1.2. When discussing the chemical composition it is necessary to also include some elaboration of the uncertainty. NH4NO3 loss as well as artefact in the EC/OC needs more attention.

4.1. "Are the data from the different sites as well as the other European measurements comparable? There are differences in methodology as well as different artefact problems due to different chemical composition in the atmosphere and different meteorology."

Reply: We also agree with this comment. Unfortunately, a great variation in sampling (including artefact issues) and analysis protocols for OC and EC may result in difficult inter-comparison of data. This will be not the case in future when more standardised methods will be available. This was added to the text to show the limitations of the inter-comparison. As regards for NH4NO3 , we agree that negative artefact could be important for filter sampling. The formation of coarse and non-volatile NaNO3 at FKL and ERL minimize the seasonal trend at these sites. However, at MSY, the low availability of NaCl, and the high levels of NH3, results in the dominant presence of NH4NO3 throughout the year. High ambient temperatures in summer in this area result in the

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volatilization of this phase in ambient conditions, although a contribution of a negative artefact (volatilization in the filter of the night formed NH4NO3) may also occur. More studies are currently addressed in order to evidence and quantify the possible artefact. 1. A paragraph on this possible artefact is included in the text: It has to be noticed NH4NO3 measurements may suffer negative artefact, mainly in summer due to the high ambient temperatures. This summer artefact may be more important at MSY than at FKL and ERL (where the high proportion of NaNO3 avoids the artefact volatilization). This artefact may result in the volatilization during day time of the ammonium nitrate sampled during the night, because ambient summer temperatures at day time favour the major occurrence of NH3 and HNO3 instead of NH4NO3. 2. As previously stated the influence of possible summer sampling artefacts causing volatilization of NH4NO3 may also exert and influence on the seasonal trend of nitrate in PM.

4.2. For EC/OC it could be valuable to include the data from a complete dataset using same method all over Europe (Yttri et al ACP 2007, 7, 5711-5725). However the conclusion of relatively low OC compared to south and central sites in Europe is still relevant. Same is true for EC. But some comments on why would be interesting. Can it be an artifact or is there some explanation of different emission sources. Somewhat puzzling since Ispra in Northern Italy has very high OC level (7-10 ug from 2003 to 2006 from the EMEP status report 4/2008), but this site is very much influence by the Po area. However the Portuguese site Braganca has a level of 4ug (2002-2003), which is a bit higher than seen in this study. Same is true for Montelibretti in Italy (EMEP PM assessment report)"

Reply: We partially agree with referee in this case. We disagree on the comment that the paper suggested contains data all over Europe, since data from the Mediterranean basin (our study area in this paper) is completely missing. In any case we accepted the comment and we added to the text that the paper by Yttri et al. (2007) using the same procedure for OC/EC analysis all over Europe, with the exception of the Mediterranean Basin, showed that the levels of EC varied in most cases from 0.5 and 1 μgEC/m3, sup-

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porting our conclusion that lower EC levels are recorded in the Mediterranean Basin. Concerning OC levels, Yttri et al. (2007) reported levels of OC ranging in most cases from 2 to 6 μgOC/m3, also relatively higher than the 2-3 μgOC/m3 range measured in our study for the Mediterranean. .We added this in the text.

4.3. "Table 1. Melpitz has also measurements of EC/OC. 2006 data found in EMEP status report 4/ and Birkenes has measurements for both PM10 and PM2.5.

Reply: We added to the table the estimated values of OC and EC from the figure on Melpitz. We did not add PM2.5 from Birkenes because we know already from PM10 that the values are the lowest.

4.4. "And Birkenes is a site in Norway not Finland."

Yes, it was a mistake. We have corrected it in the revised version.

4.5 "The mineral dust data is not always comparable because at several sites this is only sum of Ca and K since Si and Al is not always analyzed. However, one may look at the unaccounted mass to state that the mineral dust is not on the same level as for the sites in this study. Should be separated however so there is no confusion whether one compare the same things."

Reply: Yes we agree on this issue, we added this text: It has to be pointed out that in several studies from the cited Central and Northern Europe the crustal fraction is in many cases indirectly estimated from the determination of a few element, however as shown in Table 1 the levels of the unaccounted mass are similar to those measured in our study. This indicates that the differences in levels of mineral matter are real.

5. "Would be useful to include Italy (e.g with Montelibretti) by Perrino et al in the EMEP PM assessment report, since also this site experience frequent Sahara dust episodes and they use denuder for NO3 and NH4 measurements showing that it can be big loss of NH4NO3 on regular PM filters."

Reply: We agree with the referee in the fact that Montelibretti could be a good site for

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the study of the African dust episodes, but we think that this site is highly influenced by the pollution of Rome, and consequently the amount of anthropogenic aerosols may be very important, not comparable with the main sites selected for this study (FKL, ERL and MSY).

Thanks again for the valuable comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10153, 2009.