

***Interactive comment on* “Source apportionment of fine PM and sub-micron particle number concentrations at a regional background site in the western Mediterranean: a 2.5 yr study” by M. Cusack et al.**

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Authors' response

The authors would like to take this opportunity to thank the editor and reviewers for taking the time to read this publication and for their insightful corrections. We believe the manuscript has benefited greatly from the reviewers comments and corrections.

RC C170: 'Review', Anonymous Referee #1, 19 Feb 2013.

This is a well written paper and for the most part I don't have any major comments. I do
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however have quite a few minor comments which I outline in the following paragraphs:

Thank you for your comments. Please find a point by point response to each of your comments.

Reviewer: General Comment: it appears that, as the authors rightfully point out, the use of PCA yields quite tenuous findings compared to for example the much more robust PMF results. Is the PCA essential in this paper? Could the number concentrations of PM groups be included in the PMF and forgo entirely the PCA analyses? It is difficult to put faith in a statistical tool that for example identifies photochemistry as a source of PM but in it we don't see organic matter! Clearly this needs to be re-thought- see also several comments on the same topic that I make below.

Authors' Response: While the authors understand the reviewer's concerns regarding the PCA analysis, we believe that the paper does benefit from the PCA analysis for various reasons. The authors believe it to be the case that PMF analysis can only include variables of the same parameters, i.e. that it is not suitable to mix PM chemical speciation, particle number concentration, meteorological variables and gaseous concentrations in PMF. Therefore, we used PCA in order to determine the relationship between all these variables as this limitation does not apply. However, the limitations encountered for the PCA analysis would likely still apply to the PMF analysis, i.e. the reduced dataset (when we had simultaneous PM speciation and number concentrations which amounted to 61 cases). We believe that the absence of Organic Matter in the source of particles associated with photochemistry (NPF + G) is also owing to the lack of measurements during the summer as compared to the colder months. As outlined in the section dedicated to PMF analysis, the SOA source during the colder months appears to be dominated by anthropogenic emissions, which is why we only see OC in the Industrial + Traffic + Biomass burning in the PCA analysis (as the data used for the PCA analysis doesn't include summer data). Finally, the PCA analysis also allowed the authors to apply MLRA to the dataset.

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Reviewer: P3920- is the use of 2.1 as the OC multiplier based on the fact that we have a regional background site? Some elaboration is needed here since this is a rather unusually high multiplication factor. Most of the papers that I have seen use factors ranging between 1.2-1.4 for fresh and 1.8 for aged aerosols.

Authors' Response: According to Turpin and Lim (2001), a conversion factor of 1.6 ± 0.2 was suitable for urban areas, whereas 1.9-2.3 was more suitable for aged aerosols and 2.2-2.6 for aerosols originating from biomass burning. Based on these results and considering the regional background status of MSY with some influence of biomass burning emissions, the authors believe that a multiplier of 2.1 is a reasonable correction factor. A study of OC and EC concentrations across various sites within the EMEP network in Europe (Yttri et al., 2007) calculated correction factors for 12 rural background sites in Europe, which ranged from 1.4 to 1.8. However, none of these sites were from southern Europe/the Mediterranean region except for Ispra in Italy, which is located in the heavily polluted Po valley. Considering the prevailing warm weather conditions and intensified solar radiation typical of Mediterranean climates, the rural, forested and mountainous location of MSY, and the impact of biomass burning, we believe a conversion factor of 2.1 to be most suitable.

Reviewer: P3923- what was the basis for grouping PN in these specific size groups listed here?

Authors' Response: We chose the Nucleation mode (N9-30) in order to identify new particle formation, the lower Aitken mode (N30-50) to identify particle growth or transport of growing fresh particles to the site, the upper Aitken (N50-100) to observe if the freshly formed particles are growing to CCN sizes and to investigate emission sources of particles in this size range. Finally, the accumulation mode (N100-825) was simply divided as presented in the article (N100-300, 300-500 and 500-825) after several runs with PCA and was determined to give the most robust results.

Reviewer: P3923- the authors could attempt to do an ion balance, that is determine

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whether the measured ammonium ion is sufficient to neutralize the measured sulphate and nitrate ions in each season. My cursory calculations show that we almost have a fully neutralised aerosol in the sampling site, which isn't surprising. What is surprising, however, is that the nucleation appears to be a significant formation mechanism in that site, as suggested by the authors as well as their PCA analysis- this type of formation requires that the aerosols be quite acidic (see for example "simulating the size distribution and chemical composition of ultrafine particles during nucleation events"-JG Jung, PJ Adams, SN Pandis – Atmospheric Environment, 2006) and many references therein. So how can these two findings be internally consistent?

Authors' Response: The reviewer makes a fair point here and unfortunately the authors believe that this is a limitation of the analysis owing to the 24 hr sampling. Real time measurements of ion concentrations would reveal the true acidity of the particles at any point in time, specifically when a new particle formation event occurs. Since these events occur over a relatively short period of time (a few hours), the necessary acidity of the particles is not completely reflected in the 24 hr samples. However, the authors have completed an ion balance, please see the figure 1 attached. Thus, as is evidenced by the figure, the aerosol is not always neutralised (based on 24 hr sampling), and the aerosols can be quite acidic at the site.

Reviewer: P3929- the monthly variations here are far more informative than the daily variations, which almost misleadingly show that there is little day to day variation. I would propose breaking the daily variation plots into two different seasons, one in winter and one in summer, and redoing the analysis. I bet that an entirely different picture would emerge.

Authors' Response: While the authors agree that the daily variations are not extremely large, we do believe that the variation does reflect the variation one might expect each of the sources to undergo. For example, it is evident that traffic + biomass burning, nitrate, industrial and fuel oil combustion sources all undergo an increasing trend during the week with an (admittedly small) decrease at weekends. While this finding may not

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be groundbreaking, the authors do believe that it helps to confirm that the sources have been identified correctly. The average concentrations for each day from which the daily variation has been calculated are on average about 27 values for each day. Unfortunately, by dividing the daily cycles by season as suggested by the reviewer, the averages for summer and winter would be reduced to 14 values. Thus, the daily variation is strongly affected by outlier values and the credibility of the daily variations is compromised owing to the reduced dataset. The authors have changed the graph of the daily variations in order to make the variations of each source more visible, which is shown in Figure 2 attached.

Reviewer: P3932- statement on L 8 about the lack of SOA in the PCA analysis – see also my general comment; wouldn't this observation seriously compromise the integrity of the PCA analysis and its validity?

Authors' Response: We do agree that it is unfortunate that SOA is not identified as a source by PCA, but this is most likely due to the lack of simultaneous measurements of particle number size distribution and chemical speciation during the summer months. For the PMF analysis, 2.5 years of data allowed for identification of SOA separately from the traffic + biomass source. However, as suggested in the discussion of PMF, the sources of SOA in winter are more influenced by anthropogenic emissions during the colder months (during episodes of winter pollution). For this reason, OC is present only in the Industrial + Traffic + Biomass burning in the PCA analysis. We would hope that a lengthened data set for PCA analysis (such as 2.5 years similar to the PMF analysis) would allow for the identification of SOA as a source of particles, but for the purposes of this article this is unfortunately not available.

Reviewer: Table 2- traffic and industrial source contribute to PN>100 nm but not to PN smaller than that size? So no contributions to ultrafine PN? Recognising that this is a remote site and there is considerable aerosol aging prior to reaching the area, the notion that we have contribution from combustion sources that leaves out the ultra-fine mode is quite problematic. This is clearly impossible and again reinforces major

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concerns about the integrity of the PCA analysis.

Authors' Response: Table 2 gives the most important (that is, the highest) factor loadings for each component in that source. Although not shown, this source gave a factor loading of 0.50 for particles N50-100, which by comparison to the other factor loadings is not quite as high, but is not negligible either. This is reflected in Figure 10 where the mean contribution of each source to the mean particle number concentration is shown (as determined by Multilinear Regression Analysis). As shown in Figure 10, the industrial + traffic + biomass burning is the second most important source for particles > 100 nm. That is, for N30-50, this source contributes around 8% and for N50-100 around 21% of the total particle number concentration in these ranges.

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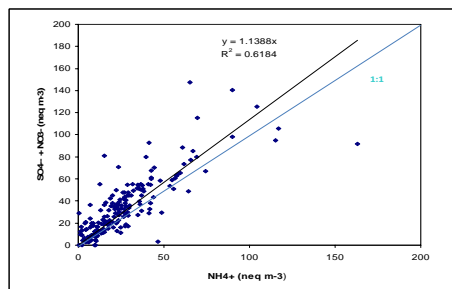
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Fig. 1.

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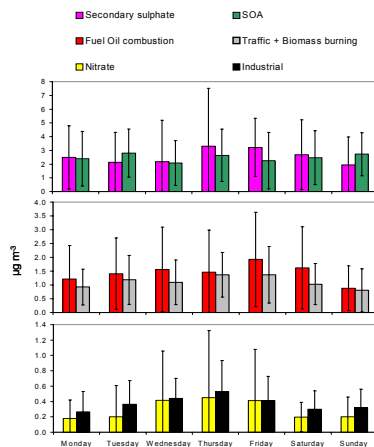
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Fig. 2.

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