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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Airborne measurements of the spatial distribution of aerosol chemical composition across Europe and evolution of the organic fraction" *by* W. T. Morgan et al.

W. T. Morgan et al.

william.morgan@postgrad.manchester.ac.uk

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Firstly, we would like to thank the referee for their comments on the manuscript. The following will detail our response to the referee's comments.

The paper has a double focus: a) It addresses the technicalities of how to derive some conclusions as to the relationship between emission sources and the most important chemical fractions of the aerosols. b) It also tries to communicate the main results - the spatial variability of the sub micron aerosol composition in the boundary layer and the free troposphere over Europe in selected weather situations.

For the broad readership part b) is most important. Here the graphical material is

quite important (Figs 1-4, 6b, (7) and in particular 8 and 9). In particular Figs 2-4 are somewhat frustrating as it is hard to get an overall picture of the total mass and composition of the aerosol at a given location. It is also difficult to get an impression of the height dependence of mass and composition, or its temporal variability. The boxwhiskers' plots provide some insight, but the 3d (or 4d when time is included) picture disappears.

In order to improve the visual impression of the data, we have segregated the data into different zones which encompass regions in Northern Europe and summarised this in Fig. 1. This communicates some of the salient points in terms of the spatial distribution in order to set the latter discussions in context. In the revised manuscript we will remove Figs. 3 and 4 but retain Fig. 2 as this is the most relevant figure to the following discussion. In terms of representing the vertical distribution, we will include an additional figure to present this information and discuss how the vertical distribution changes across Northern Europe based upon our measurements. As mentioned on page 27244, we are preparing a manuscript regarding the vertical distribution of aerosol chemical composition in North-Western Europe for the EUCAARI special issue.

In terms of presenting the temporal variability, this is highly challenging to accomplish as by definition, aircraft operations are transient in their very nature and we did not resample particular locations with the required statistical robustness which would be needed to establish temporal changes at a specific location. Aircraft operations are suited to establishing spatial gradients in either the horizontal or vertical, thus we focussed upon this strength rather than attempting to establish the temporal variability from small snapshots of the air masses encountered. The data from the EUSAAR ground based networks will be used to investigate the temporal behaviour in a subsequent publication.

Part a) of the paper is dealt with mainly in ch 4, which is very hard to follow and which follows and relies on the terminology and methods of Ulbrich et al., 2009. I would think

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very few readers are capable of appreciating the content of chapter 4.

In the revised manuscript we will condense this section to provide a more general overview of the methods/interpretations employed and move some of the heavier technical details into the supplementary material so that it is still accessible to interested readers.

While we appreciate that section 4 is highly technical in places and potentially difficult to follow for readers unfamiliar with Positive Matrix Factorisation (PMF) and its application to AMS datasets, we disagree that few readers are capable of appreciating the content.

Firstly, the AMS community is strongly interactive and papers discussing the AMS (which now exceed 300) are highly cited. Consequently, there is a significant readership that has the required knowledge base to appreciate the content of section 4.

Secondly, this is the first study to apply PMF to an AMS dataset across multiple airborne operations and as such a sufficient level of detail and robustness is required in discussing the technicalities and interpretation of the peculiarities of the solutions presented.

Thirdly, there are important details regarding the interpretation of PMF factors from AMS measurements which need to be communicated. Recently a number of AMS papers have used PMF to investigate the OM component in ambient environments and the results of these are being used outside of the AMS community e.g. for comparison with regional or global aerosol models. Section 4 presents important details which show that the PMF factors retrieved from AMS data represent particular points along a continuum in oxidation and are thus liable to change depending upon the sampling location and proximity to sources and photochemical processing. This paper shows that the real chemical processes act to gradually age and transform the OM from less oxygenated to more oxygenated and from semi volatile to less volatile in a continuous manner. PMF in this context delivers factors that represent different stages in that cycle which best minimise the variability in the data. This is a very important message

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to deliver. The aerosol community should not see that an AMS OOA factor represents a real atmospheric entity but a simplified construct.

The part of the paper that deals with b) above, in a number of places statements are made on how gases and particles evolve chemically with time, and what kind of sources that contribute to the different fractions of the aerosol. The role of biogenic emissions of aerosols or precursors is not discussed much or at all. This is a bit puzzling. Also, in view of the qualitative nature of the discussion, the solidity of statements and conclusions can be questioned. One example (among many): (p 27237-27238) "Once formed, ammonium nitrate exists in a chemical equilibrium with its chemically unreactive gas phase precursors, whereas OOA undergoes complex and continual processing involving repartitioning and oxidation." NH3 and HNO3 can hardly be said to be unreactive, and their concentrations are influenced by dilution and removal (and formation) processes which readjusts the equilibrium continuously. At the same time OOA obviously also is modified through chemical transformation processes, growth and fractionation. The picture can only be understood through model calculations where the most important processes are included.

Referee 1 also noted that there was little discussion regarding the source of OM and we have addressed this point in our response to referee 1.

Regarding the solidity of some of the discussion statements, we will carefully review the manuscript to identify the examples which the referee has identified. The referee correctly points out that that our statement that ammonia and nitric acid are unreactive was incorrect. What we meant to convey is that further oxidation of nitric acid and chemical processing of ammonia do not take place in the atmosphere, rather their transformation is dictated by their chemical equilibrium with ammonium nitrate. In comparison organic aerosol undergoes repartitioning in a similar way but is continually chemically transformed through multiple oxidation steps during its ageing. This statement is a case of poor phrasing on our part and we will rework this in the revised manuscript.

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The abstract contains a last sentence "Such anthropogenically perturbed air masses can significantly perturb regional climate far downwind of major source regions." This is not addressed in the paper, while being stated in the abstract the reader may think the claim is substantiated in the paper. I suggest to remove this sentence.

The referee rightly points out that this paper does not address the climate impacts of the polluted air masses that were sampled. This will be considered in a subsequent publication. We meant to convey that the anthropogenically perturbed air masses significantly perturb the regional aerosol burden and this extends far downwind of the source regions.

The paper is long and difficult to read. I think the authors should reassess ch 4 and shorten it considerably.

The length of the paper is mainly a reflection of the significant detail required in the discussion of the PMF analysis in section 4. As noted previously, we will rework this section in the revised manuscript and concentrate upon the important points raised in this section which require communication.

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