Atmos. Chem. Phys. Discuss., 9, C11705–C11715, 2010
www.atmos-chem-phys-discuss.net/9/C11705/2010/

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

Received and published: 25 March 2010

Firstly, we would like to convey our gratitude to the referee for their helpful and encouraging comments on the manuscript. The following will detail our response to the referee's comments.

1. The paper says that it presents evidence to support the framework suggested by Jimenez et al., 2009. This is fair to a certain extent, but really the paper supports the general idea that VOC is oxidised more the further downwind one looks. The paper misses the opportunity to evaluate the time-scales of the conversion from HOA to SVOOA to LV-OOA that would really underpin the Jimenez framework. I think that

such an evaluation is possible from the data, and would make the paper much more useful to the community.

We agree with the referee that the paper supports the general idea of increasing oxidation with distance from source and we will make this more explicit in the paper. The statements regarding our data supporting the framework suggested by Jimenez et al. (2009) refer to the fact that we can link the increasing oxidation to the conversion of OM from predominately SV-OOA to LV-OOA.

In terms of evaluating the time-scales for conversion of Organic Matter (OM) composition, we found that it was unfeasible to include such an analysis due to the highly dense source footprint in Northern Europe which meant that we were sampling a mixture of air mass ages in terms of both their time since emission and atmospheric processing. Furthermore, the nature of the aircraft operations meant that we were unable to sample in very close proximity to a major source and then probe the evolution at a range of distances downwind in the same air mass. As such we would be "missing" the initial stages of oxidation in closest proximity to a major source.

We did highlight the spatial and photochemical evolution of the OM by presenting the longitudinal gradients and relating this evolution to gas phase markers.

We do agree with the referee that the data set could be used to investigate ageing timescales but only if they are used to test a model framework that includes a robust consideration of organic aerosol that incorporates transformation and repartitioning. Such a model activity is underway and will form the basis of a separate publication. This paper provides a detailed overview of the data that frames such a model exercise.

2. The paper makes no attempt to put the AMS results in the context of what is already known in Europe. In particular, the authors find good correlation of OOA with nitrates and sulphates, which at first sight suggests an anthropogenic source. However, these results needs to be compared and contrasted to conclusions from other studies, notably the 14C studies of Gelencser et al. (JGR, 2007), or Szidat al. (e.g. JGR, 2006, ACP,

ACPD

9, C11705–C11715, 2010

2009), Yttri et al.(ACP, 2009), or the PMF studies (e.g. Saarikoski, ACP 2008). These all suggest BSOA as the source of most OM.

Our data does show good correlation between OOA and inorganics, however given the nature of the aircraft operations and the instrumental fit aboard the aircraft, drawing concrete conclusions regarding sources would prove difficult. During most of the aircraft operations we were sampling at distances further downwind of sources and the accumulation mode aerosol sampled by the AMS was predominantly internally mixed. As such, we often observed the chemical components to be well correlated with each other. Furthermore, the instrumental fit of the aircraft was biased towards aerosol-climate studies, thus we did not have the required information on gas-phase organic precursors in order to further investigate the sources of OM.

We will add a discussion of previous literature in polluted environments, namely Europe and the United States, in order to set our measurements in the context of such studies. As the referee notes, previous studies have suggested that OM in Europe contains an elevated biogenic fraction and this is consistent with rural measurements in the United States (e.g. Bench et al., 2007). However, several studies located in more urban locations (particularly in urban plumes) have suggested that anthropogenic VOCs dominate SOA formation (e.g. de Gouw et al., 2005, 2008; Bahreini et al., 2009). A further complication to this picture is that both biogenic VOCs and anthropogenic pollutants/oxidants may play a role in SOA formation (e.g. Weber et al., 2007; Goldstein et al., 2009). However, given the deficiencies in our measurement capability previously discussed, we do not feel able to unequivocally conclude whether the OM is predominantly biogenic or anthropogenic in origin or a mix of both for that matter.

3. The reason for the correlation with sulphates is also interesting to discuss. The spatial distribution of S in the UK for example is very different to that of NOx and VOC (or BVOC). Don't the high time-resolution data allow any conclusions to be drawn concerning whether S is indeed involved in SOA formation or not?)(The recent review of Hallquist et al., ACP 2009 suggests many possible pathways to OM formation. Do

ACPD

9, C11705–C11715, 2010

the current data not give any hints as to sources?)

Similarly for the points raised in (2), we do not feel that our data can be used to draw concrete conclusions regarding SOA formation. We were principally operating in high pressure systems, where aerosol removal was diminished and single well defined plumes were not observed. As such we were unable to compare organic aerosol in one plume with that in another. Consequently, we did not speculate upon SOA formation pathways in the manuscript and instead focussed upon its evolution subsequent to formation, an area that the data was far more suited to given the nature of the aircraft operations.

4. There is no discussion or presentation of vertical profiles of OM or OM:PM ratios. Did these change much with height? Over 2-3 km there is a substantial temperature change, which could be expected to affect condensation of SOA - is there any sign of such effects?

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. This will include presentation of vertical information of OM.

However, as both referees have enquired about such information, we will include an additional figure to present this information and discuss how the vertical distribution changes across Northern Europe based upon our measurements.

5. The paper is rather long and heavy to read. This is partly as the authors have erred on the side of providing more information than less (that's okay I think), but some things could be improved to help the reader. Ideas follow.

The length of the paper is mainly a reflection of the significant detail required in the discussion of the PMF analysis in section 4. In the revised manuscript we will condense this section to provide a more general overview of the methods employed and move some of the heavier technical details into the supplementary material so that it is still

ACPD
9, C11705–C11715, 2010

accessible to interested readers.

6. Figs. 2-4 could be usefully condensed into one map, with pies to show the OM, SO4 and NO3 splits. This would give a much faster visual impression of the data. I would also like to see a Table with these numbers (in the Supplementary would do), since figuring out the masses and ratios by eye, and in comparison to the flight paths of Fig. 1 is difficult.

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.

We will also include summary tables in the supplementary material.

7. Tables would also help the discussion in section 3 (p27223–27224). Here I can read that OM is significant in both background and polluted conditions, but I can't see where this statement comes from.

The statement comes from Fig. 2, which shows that OM almost always composes more than 20

This will be more explicitly stated in the revised manuscript.

8. p27229. Lines 25 on. Here the authors use OOA-2, OOA-2 etc. This notation reminds of that used previously by many authors (e.g. Ulbrich et al. 2009). Make it clear the extent to which the notation is consistent across papers, or simply a result of PMF?

As stated on page 27229, we used the OOA-1, OOA-2 nomenclature to signify the level of oxidation (signified by the m/z 44 contribution) for each identified factor which is how the terms were originally introduced by Lanz et al. (2007). We used this terminology to

ACPD
9, C11705–C11715, 2010

discuss the factors prior to assigning each factor to either LV-OOA, SV-OOA or HOA, which was done after the factors were compared with reference mass spectra and external tracers.

We will make this clear in the revised manuscript.

9. p27230, 4.2.1 etc. Data are discussed without any supporting figs or tables for the reader to refer to. Addition of Tables would be best.

We will add this information to the supplementary materials in the form of tables.

10. p27231, similar point here. On lines 7-8 the "slope" is compared against literature, without either this study's slope or the literature values being given. Give both.

These will be added to the main text and figures.

11. p27231, emission ratios cont. 2 papers is a very limited resource when citing emission rates. What about official emission rates of OM, NOx, CO, etc.?

We will add some further emission estimates to the comparison in the revised manuscript.

12. Fig. 1. I found the mix of periods and labels confusing. Each period consists of many days. How do the individual flights shown relate to the full period - did the aircraft follow exactly the same flight path for every day of each period?

The aircraft often flew similar flight paths in each period as the nature of the operations requires that fixed waypoints are used. However, this was not always the case, particularly when operating in the Baltic Sea region and the eastern Atlantic as these were sampled less frequently.

We will make this clearer in the revised manuscript by masking the higher altitude sections so that the focus is upon the lower levels sections of interest to the paper. Furthermore, we will make the distinction between overlapping flight tracks more distinct by offsetting the tracks slightly.

ACPD

9, C11705–C11715, 2010

13. Fig. 4 The caption presumably means Nitrate total mass, not AMS total mass.

The figure caption is correct.

14. Fig. 5a. One usually refers to vertical and horizontal bars or lines, not "sticks and bars". Sticks could be in either direction anyway, so this new notation is only confusing.

This will be revised in order to be consistent with generally accepted nomenclature.

15. Fig. 5b. Why does this figure again use just 2 literature values, and why different from that used above (now Allan, not Lanz). Would you expect these emission values to apply to NW Europe anyway?

This was an error in the text as the figure was changed to use the Allan (2004) reference but the text was not. The Allan (2004) reference is for a study in Manchester and given that the flight in question is thought to sample the outflow from Manchester and the North-West of the UK then yes the emission value would be assumed to be representative. This value has since been updated in Allan et al. (2010) and will be included in the revised manuscript alongside a discussion regarding the applicability of the chosen emission profiles.

16. Fig. 6a. The flight names are so long as labels that it isn't clear which correlation coefficient applies, and the plot is sometimes so messy that the labels can't be read anyway. Use e.g. a cross to indicate where the r2 values are.

The flight names were used to draw attention to those that lie outside of the usual behaviour. We will change the markers to crosses and include a textual label to highlight particular flights of interest.

References

Allan, J.: An Aerosol Mass Spectrometer: Instrument Development, Data Analysis Techniques and Quantitative Atmospheric Particulate Measurements, Phd thesis, University of Manchester, 2004.

ACPD

9, C11705–C11715, 2010

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, Atmospheric Chemistry and Physics, 10, 647–668, 2010.

Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., de Gouw, J. A., DeCarlo, P. F., Jimenez, J. L., Brock, C. A., Neuman, J. A., Ryerson, T. B., Stark, H., Atlas, E., Brioude, J., Fried, A., Holloway, J. S., Peischl, J., Richter, D., Walega, J., Weibring, P., Wollny, A. G., and Fehsenfeld, F. C.: Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, J. Geophys. Res., 114, D00F16, 10.1029/2008JD011493, 2009.

Bench, G., Fallon, S., Schichtel, B., Malm, W., and McDade, C.: Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites, J. Geophys. Res., 112, D10 205, 10.1029/2006JD007708, 2007.

de Gouw, J., Middlebrook, A., Warneke, C., Goldan, P., Kuster, W., Roberts, J., Fehsenfeld, F., Worsnop, D., Canagaratna, M., Pszenny, A., Keene, W., Marchewka, M., Bertman, S., and Bates, T.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, Journal of Geophysical Research-Atmospheres, 110, 10.1029/2004JD005623, 2005.

de Gouw, J. A., Brock, C. A., Atlas, E. L., Bates, T. S., Fehsenfeld, F. C., Goldan, P. D., Holloway, J. S., Kuster, W. C., Lerner, B. M., Matthew, B. M., Middlebrook, A. M., Onasch, T. B., Peltier, R. E., Quinn, P. K., Senff, C. J., Stohl, A., Sullivan, A. P., Trainer, M., Warneke, C., Weber, R. J., and Williams, E. J.: Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes, Journal of Geophysical Research-Atmospheres, 113, D08 301, 10.1029/2007JD009243, 2008.

ACPD

9, C11705–C11715, 2010

Gelencsér, A., May, B., Simpson, D., Sánchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., and Legrand, M.: Source apportionment of PM2.5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin, Journal of Geophysical Research - Atmospheres, 112, 10.1029/2006JD008094, 2007.

Goldstein, A. H., Koven, C. D., Heald, C. L., and Fung, I. Y.: Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States, Proceedings of the National Academy of Sciences, 106, 8835–8840, 2009.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics, 9, 5155–5235, 2009.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525–1529, 10.1126/science.1180353, 2009.

ACPD

9, C11705–C11715, 2010

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prevot, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmospheric Chemistry and Physics, 7, 1503–1522, 2007.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M., and Hillamo, R.: Sources of organic carbon in fine particulate matter in northern European urban air, Atmospheric Chemistry and Physics, 8, 6281–6295, 2008.

Szidat, S., Jenk, T. M., Synal, H.-A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C, J. Geophys. Res., 111, D07 206, 10.1029/2005JD006590, 2006.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.-A., Hallquist, M., Shannigrahi, A. S., Yttri, K. E., Dye, C., and Simpson, D.: Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden, Atmospheric Chemistry and Physics, 9, 1521–1535, 2009.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmospheric Chemistry and Physics, 9, 2891–2918, 2009.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, J. Geophys. Res., 112, D13 302, 10.1029/2007JD008408, 2007.

Yttri, K. E., Dye, C., Braathen, O.-A., Simpson, D., and Steinnes, E.: Carbonaceous aerosols in Norwegian urban areas, Atmospheric Chemistry and Physics, 9, 2007–2020, 2009.

ACPD
9, C11705–C11715, 2010

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27215, 2009.

ACPD

9, C11705–C11715, 2010

Interactive Comment