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Interactive comment on "Volatility of secondary organic aerosol during OH radical induced ageing" *by* K. Salo et al.

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SOA gold rush and cycles of oblivion & rediscovery

The discussion paper by Salo et al. 2011 presents interesting measurement results on the properties of secondary organic aerosol (SOA) formed and aged in chamber experiments. I appreciate the authors' scientific work, and I regard the presented results as a valuable contribution to atmospheric research.

After reading this and other recently published manuscripts, however, I have the impression that relatively little effort seems to go into the synthesis and integration of the available scientific information. While the cycles of oblivion and rediscovery in science usually extend over decades, the current gold rush of SOA research appears to trigger

a neglect of earlier studies already after a few years or even months. With "gold rush" I mean the publication of about one new SOA paper every day (ISI Web of Science), and with "neglect of earlier studies" I mean that publications with similar or contrary conclusions are not mentioned or discussed, even though they sometimes have the same co-authors. Unfortunately, this lack of coherence seems to propagate like a domino effect. At least for non-specialists, but probably also for specialists, the rapid accumulation of information without cross-referencing and discussion tends to dilute rather than generate scientific knowledge and understanding.

Under this impression I would like to contribute a few comments and suggestions to the review and discussion of this study. If I had enough time, I would like to contribute similar comments and suggestions also to other recent SOA studies. Due to limited working capacities, however, I can only take the present study as an example. I hope that the authors will find my specific comments and suggestions constructive and useful, and that other colleagues will take the general aspects of this interactive comment into consideration.

The scientific conclusions of the discussion paper by Salo et al. (2011) address the long-standing question if and to which degree chemical reactions in the gas phase and in the condensed phase contribute to the chemical aging of atmospheric SOA. Quote: "A major conclusion from the work is that the OH induced ageing can be attributed to gas phase oxidation of products produced in the primary SOA formation process and that there was no indication on significant bulk or surface reactions. The presented results, thus, strongly emphasise the importance of gas phase oxidation of semi- or intermediate-volatile organic compounds (SVOC and IVOC) for atmospheric aerosol ageing processing." … "In order for pronounced OH ageing to occur the SVOC or IVOC must be found in the gas phase, i.e. the ageing is due to OH oxidation in the gas phase."

With regard to these general conclusions, I would like to raise the following specific comments and suggestions:

1) It would seem worthwhile to discuss why earlier studies using similar or alternative methods had come to different conclusions. For example, Kalberer et al. (2004) are cited to support the robustness of the applied VTDMA method, but their conclusions about substantial reaction in the particle phase are not mentioned (oligomerization; Hallquist et al., 2009; Jimenez et al., 2009; and references therein). In a review of organic aerosol aging, Rudich et al. 2006 stated that "Speciated ambient measurements thus suggest a major role for OH heterogeneous chemistry and leave open the possible oxidation of unsaturated markers by ozone." McNeill et al. (2008) stated that their studies "provide support for the ideas that oxidative aging of aliphatic organic aerosol is a source of small oxidized volatile organic compounds (OVOCs), and that OH oxidation may initiate secondary condensed-phase reactions." Chen et al. 2011 also investigated SOA formation and aging and concluded that "the measurement-model gap was small for particle mass yield but significant for particle-average elemental composition. The implication is that a key chemical pathway is missing from the chemical mechanism. The data can be explained by the particle-phase homolytic decomposition of organic hydroperoxides and subsequent alkyl-radical-promoted oligomerization." The conclusions of these studies indicate that heterogeneous and condensed phase reactions may be important for OH-induced aging of organic aerosol, but these earlier studies are not mentioned and discussed in the present study which suggests more or less the opposite. George and Abbatt (2010) are cited, but their specific statements about the relative importance of gas-phase chemistry and heterogeneous oxidation (pp. 719-720) and their general conclusion "that OH heterogeneous oxidation of typical SOA needs to be considered as an atmospheric organic aerosol aging mechanism, most likely of higher relative importance away from VOC source regions, where other aging mechanisms are less dominant" are not addressed.

2) It would seem worthwhile to consider related earlier studies with complementary methods and similar findings. For example, Zhang et al. (2010) had found a close correlation of methylbutanetricarboxylic acid (MBTCA) in atmospheric aerosol samples with ambient temperature and OH radical concentrations from atmospheric model calculations. These observations are in line with the laboratory results of the present study and support their atmospheric relevance. In view of the contradictory conclusions of laboratory and chamber studies outlined above, it appears important to use the results of atmospheric field and model studies for orientation. Care should be taken, though, not to over-interpret gas phase reactions of individual compounds as evidence that heterogeneous reactions and multiphase chemistry would play no significant role in the atmospheric transformation of organic aerosols.

The studies cited above are only a few examples out of numerous earlier studies that seem relevant but are not addressed in this and other recent SOA studies. I would like to encourage the authors of this study and the SOA community at large to build on and discuss rather than neglect the large amount of pre-existing information and publications in the scientific literature. Continuous synthesis and integration of available knowledge appear at least as important for scientific progress as the production of new results.

References:

Chen, Q., Liu, Y., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-Phase Chemistry of Secondary Organic Material: Modeled Compared to Measured O:C and H:C Elemental Ratios Provide Constraints, Environ. Sci. Technol., 45, 4763-4770, 2011.

George, I. J. and Abbatt, J. P. D.: Chemical evolution of secondary organic aerosol from OH-initiated heterogeneous oxidation, Atmos. Chem. Phys., 10, 5551-5563, 2010.

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, Th. 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, Atmos. Chem. Phys., 9, 5155-5236, 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., Dunlea, E. 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, 2009.

Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of polymers as major components of atmospheric organic aerosols, Science, 303, 1659–1662, 2004.

McNeill, V. F., Yatavelli, R. L. N., Thornton, J. A., Stipe, C. B., and Landgrebe, O.: Heterogeneous OH oxidation of palmitic acid in single component and internally mixed aerosol particles: vaporization and the role of particle phase, Atmos. Chem. Phys., 8, 5465-5476, 2008.

Rudich, Y., Donahue, N. M., Mentel, T. F: Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies, Annu. Rev. Phys. Chem., 58, 321–352, 2007.

Salo, K., Hallquist, M., Jonsson, Å. M., Saathoff, H., Naumann, K.-H., Spindler, C., Tillmann, R., Fuchs, H., Bohn, B., Rubach, F., Mentel, Th. F., Müller, L., Reinnig, M., Hoffmann, T., and Donahue, N. M.: Volatility of secondary organic aerosol during OH radical induced ageing, Atmos. Chem. Phys. Discuss., 11, 19507-19543, 2011.

Zhang, Y. Y., Müller, L., Winterhalter, R., Moortgat, G. K., Hoffmann, T., and Pöschl, U.: Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter, Atmos. Chem. Phys., 10, 7859-7873, 2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 19507, 2011.