

Interactive comment on “Quantitative assessment of organosulfates in size-segregated rural fine aerosol” by H. Lukács et al.

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Received and published: 7 May 2008

General Comments

Sulfur-containing organic compounds have been identified in ambient fine aerosol collected from many field campaigns across the United States and Europe using several analytical techniques (such as FTIR and electrospray ionization-mass spectrometry (ESI-MS)). As the authors clearly indicate in their manuscript, recent work has chemically characterized many of these compounds as organosulfates (as well nitrooxy organosulfates) using advanced MS techniques (e.g. ESI tandem MS and ESI-high resolution MS). Even though it has been revealed that many of the organosulfates detected in ambient aerosol form from the oxidation of biogenic volatile organic compounds (BVOCs), such as isoprene, alpha-pinene, and beta-pinene, in the presence

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of acidified sulfate seed aerosol, quantification of these products has been lacking. Quantification of organosulfates has been problematic owing to the fact that authentic standards are not commercially available, as well as the lack of suitable surrogate compounds. Quantification by chromatographic separation coupled to ESI-MS (i.e. LC/ESI-MS) cannot be accomplished until the synthesis of the characterized organosulfates is carefully completed. The lack of quantification has not allowed our research community to determine the overall significance of these compounds to ambient organic aerosol; thus, alternative methods to that of LC/ESI-MS need to be developed and employed. This study presents a significant new contribution to our understanding of organosulfate formation in ambient fine aerosol by estimating the total contribution of organosulfates in ambient aerosol using the combination of ion chromatography (IC) and X-Ray fluorescence (XRF). The estimated concentration of the organosulfates in summer-time fine aerosol in K-pusztá appears to be significant (6-12% of bulk sulfur concentrations). As a result, it is important that this data set be published in ACP, as it is the first attempt made in quantifying the overall contribution of these compounds to ambient fine aerosol. The demonstration of their technique should allow others to estimate the contribution of organosulfates in ambient aerosol collected from other regions of the world. Before publication, the authors should consider addressing the following minor comments below.

Specific Comments/Questions

1.) For quality control purposes, have the authors also considered analyzing filter samples collected from this field site using the same analytical approach (i.e. XRF and IC analyses), and comparing these results to the Al foil samples analyzed in the current study? Does one have to worry about particle bounce/loss with collecting aerosol samples on Al foil?

2.) Section 3.2, Page 6835: In the authors' discussion of possible mechanisms of organosulfate formation in ambient aerosol, they only consider the role of sulfuric acid. Recent work by Surratt et al. (2006, 2007a) and Ng et al. (2008, ACPD) has

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shown that organosulfates and nitrooxy-organosulfates of isoprene can form in the presence of non-acidified sulfate seed aerosol. The latter finding has raised serious questions as to whether acidity generated from sulfuric acid is necessary to generate organosulfates/nitrooxy-organosulfates, or whether it is the total sulfate mass concentration that matters. Additionally, ionic strength of the aerosol could also play a role in organosulfate formation and should not be ruled out. Interestingly, recent work by Surratt et al. (2007a) and Iinuma et al. (2007b) has shown that organosulfates of monoterpenes only form when the sulfate seed aerosol has been acidified by sulfuric acid. From this information described above, the authors may want to provide some word of caution in their description of the possible mechanism.

Details for the reference by Ng et al. (2008) are as follows:

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crouse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), *Atmos. Chem. Phys. Discuss.*, 8, 3163-3226, 2008.

Technical Comments

1.) Page 6827, Line 10: The authors may want to include the reference by Tolocka et al. (2004) in this citation, as this study also observed enhancements in SOA yields from alpha-pinene oxidation in the presence of acidic seed aerosol.

Details for the reference are as follows:

Tolocka, M. P., Jang, M., Ginter, J. M., Cox, F. J., Kamens, R. M., and Johnston, M. V.: Formation of oligomers in secondary organic aerosol, *Environ. Sci. Technol.*, 38(5), 2105-2115, 2004.

2.) Page 6827, Line 13: The authors may want to include the references by Edney et al. (2005), Surratt et al. (2006), and Surratt et al. (2007b) in this citation, as these studies observed enhancements in SOA yields from isoprene oxidation in the presence

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of acidic seed aerosol.

Details for these references are as follows:

Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M.: Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States, *Atmos. Environ.*, 39(29), 5281-5289, 2005.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, *J. Phys. Chem. A*, 110(31), 9665-9690, 2006.

Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41(15), 5363-5369, 2007b.

3.) Page 6827, Lines 25-28: The authors may want to consider the use of the following alternative statement:

"Matrix-assisted laser desorption ionization-MS measurements conducted on smog-chamber aerosol indicated that sulfate diester formation or sulfate ester oligomerization reactions may also be possible (Surratt et al., 2007); however, Iinuma et al. (2007b) provided conclusive mass spectrometric evidence for the presence of sulfate diester formation in beta-pinene SOA (i.e. the esterification of two beta-pinene oxidation products with one sulfuric acid molecule)."

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 6825, 2008.

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