

## ***Interactive comment on “Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions” by O. Vesna et al.***

**O. Vesna et al.**

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We would like to thank C. Chan for his valuable comments.

We will be happy to include the results from his newest studies in the revised version of our manuscript. It seems that for oleic acid, the mass growth factors observed by Lee and Chan (2007a) of 2-3% are consistent with the diameter growth factors reported in our study around 2%). We also note that while the ozone concentration in our study was about a factor of 8 higher, the integrated exposure in our experiment ( $6.4\text{e-}4$  atm s) was 22 times lower than in the Lee and Chan (2007a) study ( $1.4\text{e-}2$  atm s). As we note in our manuscript, we have not observed a significant change within uncertainty at lower concentrations (this meant down to 0.5ppb, we will mention this in the revised version). Also Lee and Chan find no significant changes in the product chemistry (at least from the Raman signatures), when the ozone concentration was increased to

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10ppm. As discussed in the manuscript, the more substantial changes in water uptake observed in the studies by Hung (2005) and Asad (2004) were observed under orders of magnitude higher ozone concentration and exposure (0.5 atm s and 0.1-1 atm s, respectively), where second order chemical effects may indeed have played a role. In the revised version, we will make sure that this difference will be clearly emphasised.

Given the similarities in hygroscopic growth observed for oleic acid ozonolysis products between our and the Lee and Chan (2007b) experiments, it is indeed surprising that we have observed much smaller growth factors at dry conditions and higher ozone concentration, though lower total exposure, for the polyunsaturated compound arachidonic acid. Several aspects may come into play here. The first might be that the autoxidation mechanism (see below) might lead to more hygroscopic products under dry conditions over longer time scales. It is not clear how fast ozone and water molecules can enter the particles. While in our experiments only an outer layer may have reacted, in the long term experiments, the whole particle bulk may contribute to products. In our HTDMA experiments, about one minute is allowed for equilibration of the particle with the higher humidity, which is much shorter than in the electrodynamic balance experiments. This would indicate that we may not have probed all available hygroscopic compounds under dry conditions. Under humid conditions, the continuous swelling of the particles by water may open the path for water accessing their interior. We will add this discussion to the presentation of our results for dry conditions on p15658.

As pointed out in the Lee and Chan (2007b) study, the autoxidation mechanism could be important at lower ozone levels (200-250 ppb). They could not observe any evidence at high ozone concentrations (10 ppm). For oleic acid (the monounsaturated compound), they did not find any evidence for this mechanism even at low concentrations. Our experiments with arachidonic acid were performed at small reaction times between 0.5 ppm and 2 ppm, i.e., in between the two limits above, and we observed a roughly linear increase of the hygroscopic growth factor with the ozone concentration. It is likely that the autoxidation mechanism contributes to the degradation mechanism,

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even though we were probably not sensitive to it within our short time scales, and it would remain entirely open what the role of water could be in that process. We will include this possibility in the discussion of the mechanism on p 15659.

Asad, A., et al. (2004), Enhanced uptake of water by oxidatively processed oleic acid, *Atmos. Chem. Phys.*, 4, 2083-2089.

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Lee A.K.Y. and Chan C.K. (2007b), Heterogeneous reactions of linoleic acid and linolenic acid particles with ozone: Reaction pathways and changes in particle mass, hygroscopicity, and morphology, *J. Phys. Chem. A*, 111, 6285-6295.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 7, 15651, 2007.

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