

We are very grateful to the reviewer for the constructive suggestions and for the proposed corrections to improve our paper. Here, all the issues raised had been addressed. Accordingly, the manuscript had been modified.

The abstract line: ‘This difference might be explained by the surface tension effects, solution non-ideality, and the partial solubility of constituents or non-dissolved particle matter. However, due to these effects being included in HTDMA-derived calculations, we could not distinguish the specific roles of these effects in creating this gap’ is a little confusing. This first suggests the authors believe that using k from the HTDMA is sufficient to account for these additional properties in explaining the discrepancy between HTDMA and CCN derived k values. On the other hand, the authors recognize in the manuscript that care must be taken when assuming extrapolation of this value to the point of activation is valid. Alternatively it suggests an analysis of the range of values representative of each process has been explored, which is not the case. I presume the text is referring to the implicitly coupled interaction of all effects combined at 90% RH? Ignoring the surface tension effect at 90%, which is generally valid, it would still be useful to assess what values could be prescribed to the remaining effects to achieve closure and then put this in a wider context of expected values.

Response:

Yes, we agree. The statement is unclear. The discrepancy between κ_{HTDMA} and κ_{CCN} is caused by the coupled interaction of all effects. Such discrepancy cannot be explained by using κ derived from the HTDMA measurement. Originally, we intended to report that these effects are subject to the discrepancy and are only indicative of the existence, and not the exact magnitude. In the revised version, “However, due to these effects being included in HTDMA-derived calculations, we could not distinguish the specific roles of these effects in creating this gap” will be removed from the manuscript.

As above-mentioned, the combined effects lead to the discrepancy between κ_{HTDMA} and κ_{CCN} . These effects include the surface tension effects, solution non-ideality, and the partial solubility of constituents or non-dissolved particle matter. Additionally, the referee also addressed the potential effect of organic semi-volatile partitioning on hygroscopicity closure as below. To assess the exact magnitude is not possible on a basis of our dataset and knowledge.

Page 7658, line 15. ‘Because the uncertainty in the estimation of K_{org} decreases with increasing organic fraction (Duplissy et al 2011): : .only data with NH_4NO_3 volume fraction below 10% are considered’. On the contrary, this needs to be put in context of more recent discussions regarding the potential effect of semi-volatile partitioning which the authors already touch upon through a consideration of NH_4NO_3 . The authors refer to empirical studies that show a discrepancy between HTDMA and CCN κ . Recently Topping and McFiggans (2012), in referring to these studies, discussed the potential effect of organic semi-volatile partitioning on hygroscopicity closure. If you use only data that had evidence of organic

fractions larger than 50%, what are the potential impacts of this process? Furthermore, would this then impact on attempting to correlate O:C ratio with κ ? Section 4.4 This needs to include the more recent discussion of semi-volatile loss with regards to closure discrepancies between k-htdma and k-ccn. When the authors discuss non-ideality effects, presumably this relates to the notion that deviations from ideality impact the concentration of water, and not the organic solutes? Can the authors predict what level of deviation would need to account for the measured discrepancy by running a simple Kohler model? How much more 'soluble' organic mass would be needed to corroborate the measured k-CCN values?

Response:

Thanks for the reviewer's information. We read Topping and McFiggans's article, carefully. They made a great progress about the potential effect of organic semi-volatile partitioning on hygroscopicity closure. It was found that accounting for the co-condensation of any number of organic compounds substantially decreases the saturation ratio of water vapour required for droplet activation. This effect is far greater than any other compositional dependence.

We admit that there are a large number of semi-volatile organic species in both particulate and gaseous phases. The partitioning of these organic compounds could significantly impact the closure results in our study according to Topping and McFiggans's study. In the revised manuscript, we will give the discussions from two aspects: the effects of gas-particles portioning on the chemical composition-particle hygroscopicity closure and discrepancy between κ s derived from HTDMA and CCNc.

Modifications in the MS:

(1) At the end of section 4.3:

“Except for the aforementioned reasons, the gas-particle partitioning of semi-volatile organic vapors could also produce the potential effect on hygroscopicity closure. Recent study found that allowing the co-equilibration of semi-volatile soluble organic compounds results in significantly increasing the amount of soluble material in the particles, thereby substantially increasing the particle hygroscopicity (Topping and McFiggans, 2012). The co-condensation of semi-volatile components was not considered when predicting particle hygroscopicity using chemical composition on a basis of the ZSR mixing rule. This leads to the discrepancy between measured and predicted particle hygroscopicity parameter. Further, such discrepancy will add to the uncertainty in the calculation of κ_{org} and thereby change the relationship between O:C ratio and particle hygroscopicity.

(2) Adding some texts in section 4.4:

In addition, recent study found that the co-condensation of semi-volatile soluble organic compounds can substantially decrease the saturation ratio of water vapor required for droplet activation by changing the amount of solutes in the liquid droplets during particle growing (Topping and McFiggans, 2012). This co-condensation process is influenced by particle number concentration, available semi-volatile compounds, particle size, and the equilibrium timescale (Topping and McFiggans, 2012). Compared to HTDMA, the circumstance under which particles are detected may be significantly different in CCNc. Therefore, to which extend the co-condensation of semi-volatile soluble compounds impacts the ability of particle taking up water is not the same between two systems. This is one of reasons as to why there is a discrepancy between κ_{HTDMA} and κ_{CCN} .

In figure 7, this study shows a significant difference in the trend of O:C ratio versus kappa as compared with the Jimenez and Duplissy results. For heavily aged aerosol, the differences could be significant could they not? Also, which K do the authors recommend in fitting this function if there is discrepancy between the HTDMA and CCN value? Please adjust the figure caption accordingly. How does this fit in which recent studies suggesting there is no correlation between O:C ration and hygroscopicity (Alfarra et al 2013)? Please include a wider consideration. (Alfarra, M. R., Hamilton, J. F., Wyche, K. P., Good, N., Ward, M. W., Carr, T., Barley, M. H., Monks, P. S., Jenkin, M. E., Lewis, A. C., and McFiggans, G. B.: The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of β -caryophyllene secondary organic aerosol, Atmos. Chem. Phys., 12, 6417-6436, doi:10.5194/acp-12-6417-2012, 2012.)

Response:

Yes, we can draw such conclusion that the differences could be significant for more aged aerosol by linear extrapolation in figure 7. But, extrapolation is subject to greater uncertainty. We would not discuss it in the manuscript.

In the published articles, both κ s derived from HTDMA (Duplissy et al., 2011; Jimenez et al., 2009; Alfarra et al., 2012) and CCNc (Mei et al., 2013; Chang et al., 2010) measurements were used. These studies showed different relationship between O:C and κ_{org} . In Massoli et al.'s study (2010), both HTDMA- and CCNc- derived κ_{org} are taken. Their results showed that the HGF90% varied linearly with O:C, while $\kappa_{\text{org,CCN}}$ mostly followed a nonlinear trend for laboratory generated secondary organic aerosol (SOA) particles. Alfarra et al.'s measurements showed that the increasingly oxidised nature of the aerosol appeared to increase the growth factor only marginally, if at all for β -caryophyllene secondary organic

aerosol (Alfarra et al., 2012). They pointed out these findings might have been influenced by the difference in pre-treatment of the semivolatile-containing particles prior to their measurements. Up to now, no universal equation can be utilized to describe the relationship between O:C and κ_{org} . Regarding particle hygroscopicity related to organic oxidation state, we will include a wider consideration and give more discussions in the revised manuscript.

Modifications in the MS:

In section 4.3.2:

“One should note that both κ s of organics derived from HTDMA (Duplissy et al., 2011; Jimenez et al., 2009; Alfarra et al., 2012) and CCNc (Mei et al., 2013; Chang et al., 2010) measurements were used to correlate to O:C ratio in the literature. Due to the discrepancy between κ_{HTDMA} and κ_{CCNc} (Good et al., 2010; Irwin et al., 2010) (also see section 4.4), the same dataset may produce different relationship between O:C ratio and κ_{org} . In our study, the κ derived from HTDMA measurement is taken considering the better closure of HTDMA and AMS measurements (see section 4.4).

Figure 7 shows the O:C ratio as a function of κ_{org} . A positive correlation was found ($r^2=0.67$). This agrees with previous studies (e.g. Duplissy et al., 2011; Jimenez et al., 2009), as also displayed in Figure 7. In most previous studies, κ_{org} varied linearly with O:C ratio. Recent measurements performed by Alfarra et al. (2012) showed that the increasingly oxidized nature of the aerosol appeared to increase the growth factor only marginally, if at all for β -caryophyllene secondary organic aerosol. They pointed out these findings might have been influenced by the difference in pre-treatment of the semivolatile-containing particles prior to their measurements.”

Minor comments:

Page 7653, line 4. Which individual species?

Response: These individual species mean the chemical species listed in the table. We modified the texts: “The κ_{CCN} values of those individual species listed in table 1 were reported”

Page 7654, line 9: fraction of what? Mass?

Response: It is mass fraction. We added this word “mass” in this sentence.

Page 7652:, line 15. As well (as the concentration of) ?

[Response:](#) We corrected it.

Page 7656, line 17. ($r^2=0.?$)

[Response:](#) $r^2=0.$ was deleted.

Reference

Alfarra, M. R., Hamilton, J. F., Wyche, K. P., Good, N., Ward, M. W., Carr, T., Barley, M. H., Monks, P. S., Jenkin, M. E., Lewis, A. C., and McFiggans, G. B.: The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of β -caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, **12**, 6417-6436, 10.5194/acp-12-6417-2012, 2012.

Chang, R. Y. W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R., and Abbatt, J. P. D.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: Relationship to degree of aerosol oxidation, *Atmos. Chem. Phys.*, **10**, 5047-5064, 10.5194/acp-10-5047-2010, 2010.

Duplissy, J., DeCarlo, P. F., Dommen, J., Alfarra, M. R., Metzger, A., Barmpadimos, I., Prevot, A. S. H., Weingartner, E., Tritscher, T., Gysel, M., Aiken, A. C., Jimenez, J. L., Canagaratna, M. R., Worsnop, D. R., Collins, D. R., Tomlinson, J., and Baltensperger, U.: Relating hygroscopicity and composition of organic aerosol particulate matter, *Atmos. Chem. Phys.*, **11**, 1155-1165, 10.5194/acp-11-1155-2011, 2011.

Good, N., Topping, D. O., Allan, J. D., Flynn, M., Fuentes, E., Irwin, M., Williams, P. I., Coe, H., and McFiggans, G.: Consistency between parameterisations of aerosol hygroscopicity and ccn activity during the rhamble discovery cruise, *Atmos. Chem. Phys.*, **10**, 3189-3203, 10.5194/acp-10-3189-2010, 2010.

Irwin, M., Good, N., Crosier, J., Choularton, T. W., and McFiggans, G.: Reconciliation of measurements of hygroscopic growth and critical supersaturation of aerosol particles in central germany, *Atmos. Chem. Phys.*, **10**, 11737-11752, 10.5194/acp-10-11737-2010, 2010.

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., Shimojo, 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.

Massoli, P., Lambe, A. T., Ahern, A. T., Williams, L. R., Ehn, M., Mikkilä, J., Canagaratna, M. R., Brune, W. H., Onasch, T. B., Jayne, J. T., Petäjä, T., Kulmala, M., Laaksonen, A., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (soa) particles, *Geophysical Research Letters*, 37, L24801, 10.1029/2010gl045258, 2010.

Mei, F., Hayes, P. L., Ortega, A., Taylor, J. W., Allan, J. D., Gilman, J., Kuster, W., de Gouw, J., Jimenez, J. L., and Wang, J.: Droplet activation properties of organic aerosols observed at an urban site during calnex-la, *Journal of Geophysical Research: Atmospheres*, 118, 2903-2917, 10.1002/jgrd.50285, 2013.

Topping, D. O., and McFiggans, G.: Tight coupling of particle size, number and composition in atmospheric cloud droplet activation, *Atmos. Chem. Phys.*, 12, 3253-3260, 10.5194/acp-12-3253-2012, 2012.