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Interactive comment on "Wintertime aerosol chemical composition, volatility, and spatial variability in the greater London area" *by* L. Xu et al.

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The manuscript describes measurements of aerosol chemical composition at two sites in the greater London area. One site was located in a rural location, the other in an urban background location. The manuscript discusses differences in observed concentrations and composition between the two sites. It also evaluates results of measurements at the rural site using an Aerodyne thermodenuder (TD) to derive aerosol volatility and investigate how it depends on the O:C ratio. The manuscript has several weaknesses that need to be addressed prior to final acceptance. The main weakness concerns the treatment of aerosol volatility, which is given most attention in this review.

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Volatility treatment.

The key problem is the use of the (unfortunately) very popular mass fraction remaining (MFR). In this manuscript, and the authors are not alone in this approach, MFR is treated as if being identical in meaning to aerosol volatility. This is not correct. MFR is an extensive parameter, as it explicitly depends on aerosol mass concentration. On the other hand, aerosol volatility (saturation vapor concentration for pure compounds or a mole-fraction-averaged saturation concentration for compound mixtures) is an intensive parameter, which depends only on chemical nature of compounds in a mixture. Substituting one of these parameters for another leads to much confusion in this and many other papers on the subject. For example, this manuscript talks about OOA being less volatile than other OA fractions, which is true, but at a closer examination appears to be not as dramatic as it looks on MFR graphs. By observing an enrichment of OOA at higher temperatures, the authors seem to suggest that all low-volatility material is OOA, but that observation could be, at least partly, explained by the higher initial concentration of OOA (which is lost in the MFR representation). Differences in the initial concentration of OOA could also probably explain why O:C correlation with MFR-based “volatility” do not agree among different studies.

Below, I explain my point by using a back-of-the-envelope analysis. It is very simplistic, but does demonstrate the point. For the actual answers about the observed aerosol volatility, the authors should use kinetic modeling.

Let us begin with the fact that it is very unlikely that the aerosol was equilibrated in the TD used in this study. The characteristic time for aerosol equilibration is (Saleh et al. 2011): $\tau = 1/(2\pi D N_p d_p F(d_p, \alpha))$, in which D is the species diffusion coefficient in the gas phase, N_p is particle number concentration, d_p is the particle size, $F(d_p, \alpha)$ is the Fuchs-Sutugin correction, and α is the accommodation coefficient. Assuming $d_p = 100$ nm and given that the aerosol volume concentration is about 10 μm^3/cm^3, N_p would be of the order of 10^4 cm^{-3}. Making a generous assumption of $\alpha = 1$, the characteristic time is about 30 s. For a 200 nm aerosol, it will be about 2 times longer. It is more likely that α is of the order of 0.1 (Saleh et al., 2012, 2013), in which case the characteristic time will be about 10 times longer. In any case, the residence time of 5 s used in this study is (much) smaller than the characteristic time.

We should note that τ is the e-folding time, so at $t = \tau$ evaporation will proceed only about 30% towards equilibrium. At 5 s used in this study, equilibrium process is far from being completed, being actually just in its initial stages. This means the gas phase remains virtually unsaturated at the end of the TD and one can assume particles to be evaporating in a vapor-free environment. This allows us to make a back of the envelope approximation of saturation vapor concentration at the TD temperature for each of the factors (HOA, SFOA, OOA), see below.

Assuming vapor-free evaporation and making a first-order approximation of a constant particle size and $F = 1$, the change rate of aerosol concentration (C_a) is: $\frac{\mathrm{d}C_a}{\mathrm{d}t} \approx \frac{\overline{C^*}}{\tau}$ in which $\overline{C^*}$ is the mole-fraction-averaged saturation concentration, which for simplicity is assumed constant during evaporation (or one can use it as the evaporation-time-averaged saturation concentration). This can be easily integrated, such that a change in concentration after passage through the TD is: $\Delta C_a \approx \overline{C^*} t_{res}/\tau$, where t_{res} is the residence time in the TD. Please note there are no MFRs in this above equation, only the absolute change in aerosol concentration. However, for our analysis, the key is that ΔC_a for each component is proportional to its $\overline{C^*}$; the other parameters are the same for all the components. In other words, the ratio of ΔC of two compounds is equal to the ratio of their $\overline{C^*}$.

To estimate ΔC_a , we can use the reported MFRs, AND the initial aerosol concentrations ($\Delta C_a = C_{a,0}(1 - MFR)$). By using data from Fig.6 for the initial concentrations and Fig.9 for MFRs, I estimate that $\overline{C^*}$ for OOA is within a factor of 2 of that of the other components. Yes, OOA is less volatile than the other two components, but the difference is less than one volatility bin in the traditional VBS representation (which is a factor of 10 in volatility space). In my opinion, the differences in volatilities between the three classes are minimal. This cannot be deduced from MFR alone, however. This also shows that making statements that OOA is the main contributor to the extremely low volatility compounds is not justified. For example, if there were 4 times more of HOA initially, there could be still a significant amount of HOA left after the TD. My point is that the presented data alone are not sufficient to make any conclusions about the contribution of OOA to the low volatility fraction.

The above analysis can also explain the "strange" dependence of MFR-based "volatility" on the O:C ratio, as well as discrepancies with other studies (unless MFR values are converted to more meaningful parameters). I do agree with the authors that distribution of O:C and individual factors over volatility bins needs to be known. But this can be achieved only using kinetic modeling, which has not been done in this study.

Thus, I suggest re-evaluating the data, preferably using a kinetic model to derive a VBS, though it may be difficult given only two temperature points have been measured.

As a side note, even if equilibrium is achieved, MFRs are still meaningless as can be easily demonstrated using a single component aerosol as an example – the same aerosol that has different initial concentrations will have different MFR "volatilities", which is nonsense, of course. One should either derive a VBS or report OA mass loss data together with parameters of the size distribution and the residence time.

Other comments:

p.21181, l.2. Even though the measurement setup at the urban site has been described elsewhere, it would be useful to have its brief description in this manuscript too.

p. 23181, l. 24. Equilibrium does not depend on aerosol volatility (Saleh et al., 2011,2012). The references sited in the text used a wrong criterion for equilibration (Saleh et al., 2011).

p. 23182, 1st paragraph. Equilibration time depends not only on aerosol concentration, but aerosol mean size and the accommodation coefficient (Saleh et al, 2011). Giving

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an equilibration time for an aerosol concentration without specifying the other two parameters is meaningless. As discussed above, it is very unlikely that equilibrium was achieved in the TD.

Section 2.3. Much of the discussion of particle density derivation can be moved to the Supplement. I wonder how size changes upon evaporation affect the comparison between the derived and SMPS volumes. The SMPS measures up to 550 nm, while the optimal window for the AMS is between 100 - 500 nm, with larger sizes still contributing. Thus, a shift in size distribution could affect the intercomparison between different temperatures. I think the authors could also try to get a better insight into the BC density using SP2 and SP-AMS data: if a large fraction of BC particles was coated, the bulk density could be more appropriate.

Fig.S12 shows that the NO+/NO2+ is 10-20% higher than for pure ammonium nitrate. What are the ratio values for organonitrates?

p.23190, l.18: Figure 4 is mentioned before Figure 3.

p.23193, 2nd paragraph. The differences in sulfate concentration are troubling. If the differences in sulfate concentrations are observed mostly due to easterly flow, i.e. during long range transport, one has to wonder where does sulfate go during the transport over 45 km? Since easterly flows are associated with higher concentrations, one has to wonder about the instrument performance. A comparison between the two AMS-type instruments does not provide much insight, as both are essentially similar instruments.

p.23193, 3rd paragraph. A more appropriate formulation would be “contribution of different sources is different” (the only source missing in Delting is cooking).

p.23197, 3rd paragraph. When discussing volatility of rBC coatings (Fig. 11), it would be more appropriate to compare the loss of mass from rBr with the bulk loss of mass.

p.23199 1st paragraph. I cannot exclude the possibility of an external mixture in ambient aerosols and that it could explain some of the “strange” (from the MFR point of view) behavior with respected to the O:C ratio, but this argument does not hold for laboratory studies (such as smog chamber studies), where aerosol is most probably internally mixed. In addition to the issues associated with the use of MFR, O:C ratio's connection to volatility is quite tenuous anyway. Yes, addition of an oxygenated group to a molecule significantly reduces its volatility. On the other hand, taking dicarboxylic acids as an example, volatility decreases 3-4 orders of magnitude from oxalic acid to azelaic acid, while the O:C decreases from 2 to 0.44 thus showing an opposite trend. This demonstrates that using O:C as a surrogate for volatility is always going to be quite problematic unless other parameters (such as the carbon chain length) are taken into account.

References

Saleh, R. and Donahue, N.M. and Robinson, A.L. 2013 Scales for Gas-Particle Partitioning Equilibration of Secondary Organic Aerosol Formed from Alpha-Pinene Ozonolysis, Environmental Science and Technology, 47: 5588-5594

Saleh, R., A. Khlystov, and A. Shihadeh. 2012. Determination of evaporation coefficients of ambient and laboratory-generated semi-volatile organic aerosols from phase equilibration kinetics in a thermodenuder. Aerosol Science and Technology 46:22–30.

Saleh, R., A. Shihadeh, and A. Khlystov. 2011. On transport phenomena and equilibration time scales in thermodenuders. Atmospheric Measurement Techniques 4:571–581.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23173, 2015.

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